# INVESTIGATION ON THE CONVERSION OF BUTYRIC ACID AS AN INTERMEDIATE FROM BIOMASS INTO PROPYLENE WITH ZEOLITE

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## *Abstract*

To establish a new production route of biomass-derived propylene, the catalytic conversion of butyric acid which can be obtained by the acid fermentation of molasses was investigated with zeolites, ZSM-5, SAPO-11and SAPO-34. Using SAPO-11 as the catalyst, butyric acid is converted to propylene at high yields. The yield for propylene was at the maximum value of 58.8 C% at 723 K, with the ratio of propylene to gaseous hydrocarbon products increased up to 90.4 C%.

Keywords: butyric acid, propylene, catalytic conversion, zeolite, SAPO-11

## 1. Introduction

Chemical raw materials such as benzene, toluene, xylene (so-called BTX) and propylene have been produced from the fossil fuels such as petroleum oil [1]. However, it is said that consuming the fossil resources causes climate change due to the increase of carbon dioxide concentration in the atmosphere. Furthermore, there is a limit in the future in supplying the fossil fuel for the growing demand. Therefore, the significance of utilizing inedible biomass as renewable resources for the chemical raw material is increasing [2, 3].

Especially, propylene is one of the most important chemical raw materials and has been produced with ethylene by the thermal cracking of naphtha [4, 5]. Recently, the availability of shale gas has increased and the olefin production method is changing from naphtha cracking to ethane cracking where propylene is not produced [6]. As a result, the demand-supply balance of propylene is changing and new production routes are being sought [7-9]. Considering carbon dioxide problem, it is thought important to establish a route from biomass to propylene.

In this study, the conversion of butyric acid, which can be obtained by the acid fermentation of molasses, is investigated for establishing a new production route of biomass-derived propylene. In order to obtain a high carbon yield of propylene, reactivity of various zeolites as catalyst and optimum reaction condition were investigated for the catalytic conversion of butyric acid.

## 2. Experimental

### 2.1 Catalyst and feed material

As the zeolite catalyst, ZSM-5 (proton type) with Si/Al=27 was used in the form of pellet, and SAPO-11 and SAPO-34 (Si:P:Al=0.13: 10.89:1), with pore size 0.63×0.39 nm and 0.38×0.38 nm, respectively, in the form of powder.

As feed material, the butyric acid with 98 % purity was used.

### 2.2 Reaction apparatus

Fig. 1 shows the schematic diagram of the reaction apparatus used in this work. A fixed bed reactor made of SUS-316 tube with 8mm inner diameter and 500 mm length was used and installed in an electric furnace. A specific amount of catalysts were packed in the reaction zone and fixed by some silica wool. At the top and bottom of the furnace, the thermal insulation blocks were installed to keep the temperature of reaction zone constant.

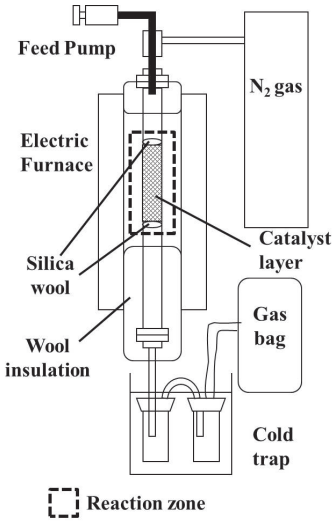


**Figure 1.** Reaction apparatus

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Feed material was supplied to the top of the reactor by a syringe pump and mixed with nitrogen carrier gas. At the outlet of reactor, the two cold traps submerged in the water bath were connected to recover the product oils and unconverted feed material. The carrier gas containing product gas was collected by a gas bag. Table1 shows the operating conditions of the reaction apparatus.

**Table1.** Operating conditions of the reaction apparatus

| Catalyst | ZSM-5 | SAPO-34 | SAPO-11 | | | |
|---|---|---|---|---|---|---|
| Material | butyric acid (aq) | | | | | |
| Concentration [wt%] | 49 | | | | | |
| Carrier gas | nitrogen | | | | | |
| Flow rate [mL/min] | 30 | | | | | |
| Reaction time [h] | 1 | | | | | |
| Reaction temperature [K] | 723 | 723 | 623 | 673 | 723 | 773 |
| Catalyst amount [g] | 1.36 | 2.39 | 1.36 | 0.81 | 0.67 | 2.39 |
| Feed amount [g] | 1.57 | 2.83 | 1.56 | 0.98 | 0.46 | 2.83 |
| Catalyst/Feed-oil [g/g] | 0.86 | 0.85 | 0.83 | 0.83 | 1.45 | 0.85 |
| Contact time [s] | 1.31 | 1.75 | 1.32 | 0.87 | 0.87 | 1.03 |

### 2.3 Analysis of the product

The recovered oil in the cold traps was analyzed by gas chromatograph (GC) (Hewlett-Packard 6890) with a FID detector and a DB-1 capillary column (60m) and/or another GC (Hewlett-Packard 7890) with a MS detector. The gaseous products were analyzed by GC (Shimadzu GC-8A) with a TCD detector fitted with Molecular Sieve 13X, Porapak-Q packed column or VZ-10 packed column and FID detector with Shimalite mesh, respectively. The yield (Y) is defined as

$$Y_i = (C_i/C_0) \times 100 \quad (1)$$

where $C_i$ and $C_0$ are the mass of carbon in the compound i in the product and the feed, respectively. The conversion ($X$) is defined as

$$X = (1\text{-}v/v_0) \times 100 \quad (2)$$

where $v$ and $v_0$ are molar quantity of butyric acid in the product and the feed, respectively. The selectivity (Si) is defined as

$$S_i = (C_i/\Sigma C_i) \times 100 \quad (3)$$

where $\Sigma C_i$ is the mass of carbon in all the compounds of the reaction product.

## 3. Results and Discussion

### 3.1 Chemical reactivity of zeolites

Fig. 2 shows the catalytic conversion of butyric acid with ZSM-5, SAPO-11 and SAPO-34 at 723 K. The yield for aromatics was about 21.9 C% with ZSM-5, larger than SAPO-11 and SAPO-34, most of which is BTX. The conversion of butyric acid with SAPO-34 was about by 30 C% less than SAPO-11. The yield for hydrocarbon gas, CO and $CO_2$ with ZSM-5 was about the same as SAPO-11, most of CO and $CO_2$ being CO. More than 10 C% of coke was formed with SAPO-34, especially the selectivity for coke with SAPO-34 became much larger than SAPO-11 and ZSM-5.

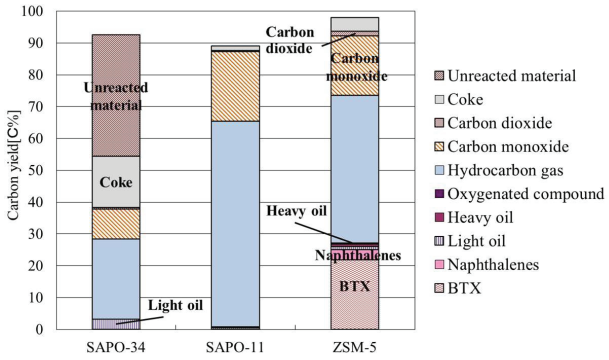


**Figure 2.** Catalytic conversion of butyric acid with ZSM-5, SAPO-11 and SAPO-34 at 723 K

Fig. 3 shows the composition of hydrocarbon gas in the conversion of butyric acid at 723 K. The main products were C3 and C4, i. e., propylene, propane, butene and butane. More olefins were obtained when SAPO-11 and SAPO-34 were used. The ratio of propylene to gaseous hydrocarbon products with SAPO-11 is 90.4 C%, the highest among these zeolites.

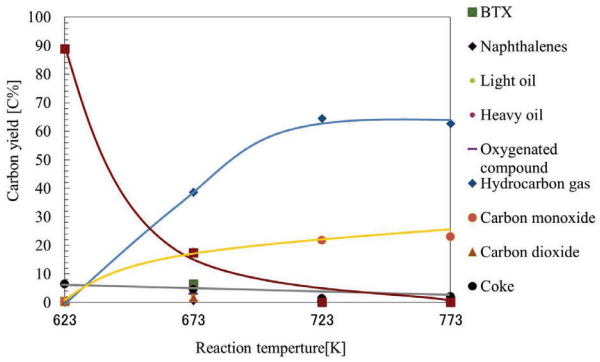


**Figure 3.** Composition of hydrocarbon gas in the conversion of butyric acid at 723 K.

From the above-mentioned results of chemical reactivity, the following reaction pathway can be proposed. First, propylene is formed by the removal of carbon monoxide and the dehydration from a butyric acid molecule. Next, naphthenic hydrocarbons are generated by the cyclization of di-/tri-merized propylene. Then, the hydrogen transfer from the naphthenic hydrocarbons to propylene occurs so that the naphthenic hydrocarbons are converted to BTX while propylene is converted to propane.

Therefore, when ZSM-5 is used as a catalyst, the hydrogen transfer reactivity would mainly convert butyric acid to naphthenic hydrocarbons and finally to BTX and propane. As for SAPO-11, the di-/tri-merization of propylene and hydrogen transfer are restricted

because of the weak acid strength [10], resulting in the rapid increase in the yield of propylene. On the other hand, much more amount of coke with SAPO-34 may be attributed to the smaller pore size, which result in the outer surface of catalyst covered with the generated coke and gradual decrease in catalytic activity with time on stream.

### 3.2 Reaction temperature

The optimum conditions of catalytic reaction with SAPO-11, which might be suitable for the conversion of butyric acid to propylene, were investigated. Fig. 4 shows the effect of reaction temperature on the catalytic conversion of butyric acid with SAPO-11. The conversion at 623 K is very small which means the drastic decrease in the catalytic activity with the decrease in temperature. The conversion is increasing with temperature, from 8.4 C% at 623 K to 79.2 C% at 673 K and can attain 100 C% at 773 K. The yield for aromatics increased from 623 K to 723 K, but then decreased with increasing temperature from 723 K to 773 K and became almost equal to zero. The yield for CO and $CO_2$ increased with temperature and became almost constant between 723 K and 773 K. The formation of coke decreased with the increase in temperature and became a constant value from 723 K to 773 K.

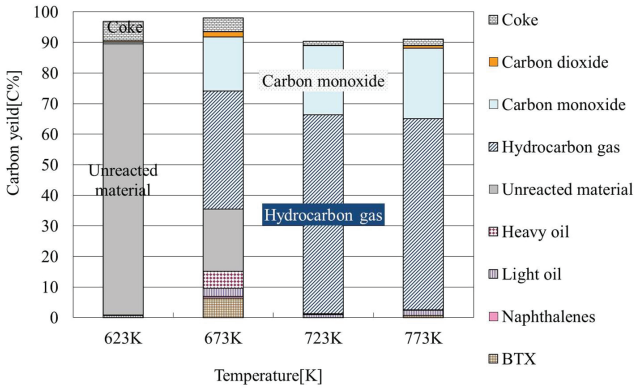


**Figure 4.** Effect of reaction temperature on the catalytic conversion of butyric acid with SAPO-11

Fig. 5 shows the effect of reaction temperature on the composition of hydrocarbon gas in the conversion of butyric acid. The yield for propylene was the maximum value 58.8 C% at 723 K. At lower temperatures, the low yield for propylene is due to the lower conversion of butyric acid. On the other hand, acceleration of the thermal decomposition as well as the di-/tri-merization of propylene and hydrogen transfer resulted in low yield to propylene at higher temperatures.

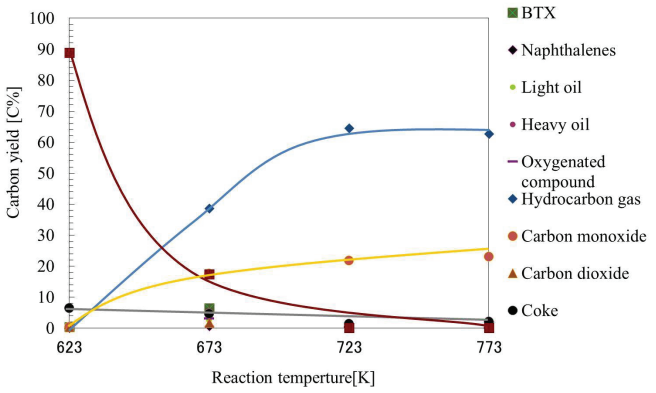


**Figure 5.** Effect of reaction temperature on the composition of hydrocarbon gas in the conversion of butyric acid

Above all, it is concluded that the conversion of butyric acid to propylene with SAPO-11 could achieve the maximum yield and selectivity at 723 K.

## 4. Conclusions

The conversion of butyric acid was investigated to establish a new production route for biomass-derived propylene.

(1) By the catalytic conversion with ZSM-5, SAPO-11 and SAPO-34 at 723 K, it was found that the hydrogen transfer reactivity with ZSM-5 would mainly convert butyric acid to naphthenic hydrocarbons and finally to BTX and propane, and that the di-/tri-merization of propylene and hydrogen transfer are restricted with SAPO-11 because of the weak acid strength, resulting in the rapid increase in the yield of propylene.

(2) The lower conversion of butyric acid and much more amount of coke with SAPO-34 may be attributed to the smaller pore size.

(3) The conversion of butyric acid to propylene with SAPO-11 can achieve the maximum yield of 58.8 C% and the ratio of propylene to gaseous hydrocarbon products of 90.4 C% at 723 K.

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