Production of isoprene by pyrolysis of algae-producing oil derived from squalene

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Abstract:

We examined thermal decomposition on squalene under atmospheric pressure. The conversion and product species were significantly changed at 470 °C, where C_5 and C_{10} were mainly obtained at 470 °C～500 °C. The 80% of C_5 was identified as isoprene. Next, we examined the influence of the linear velocity on thermal decomposition reaction of squalene. C_5 and C_{10} yield decreased with increasing in the linear verbosity. These results strongly suggested that decomposition reaction of the squalene (C_{30}) progresses sequentially. The reaction mechanism can be explained by the effect of the stable allyl radical intermediate.

Keywords: Squalene, Isoprene, Pyrolysis

1. Introduction

Today, the importance of chemicals produced from biomass is increasing to overcome depletion of petroleum resources and global warming [1-3]. Currently many chemicals are produced from edible biomass resource such as vegetable oil and sugars [4,5]. On the other hand, algal biomass is highly promising resource because of their high biomass productivity and no competition of algal cultivation with food production. Squalene ($C_{30}H_{50}$), a kind of microalgae oil can be taken from microalgae, has the isoprene-frame with many branches and double bonds. Isoprene (C_5H_8) is known as a useful chemical raw material. The objective of this study is the selective production of isoprene from squalene at mild reaction conditions. We have thus set up a flow-type reactor and examined thermal decomposition on squalene under atmospheric pressure.

2. Experimental

The reactions were carried out at atmospheric pressure in a fixed-bed, continuous-flow reactor equipped with a quartz tube using 2.0 g of quartz sand. A squalene was pumped into the vaporizer maintained at 290 °C at a rate of 0.015 ml/min and driven through the quartz sand by nitrogen at a flow rate of 34.3 ml/min. The molar ratio of squalene to N_2 was 1:49. We changed two parameters (temperature and liner velocity) .and W / F = 0.89 g h/ml, The reaction is carried out for 8 h. The products gas is analyzed by two online gas chromatographies (Shimadzu GC-2014) with FID detectors equipped with Rt-Alumina bond column and Ultra alloy column. The qualitative analysis of products was performed with GC-MS (Shimadzu ultra-2020) by EI and CI modes. The conversion, selectivity, carbon balance, yield, and unquantifiable products were calculated based on the carbon number.

3. Results and discussion

In thermal decomposition, conversion of squalene was significantly increased at 470 °C as shown in Figure 1. The thermal decomposition products consisted of a multiple of C_5 (C_5, C_{10}, C_{15}, C_{20}, and C_{25}). The conversion of squalene reached approximately 100% at 470 °C, where C_5 and C_{10} were mainly products, indicating that thermal decomposition reaction of higher carbon number components (> C15) proceeded by high reaction temperature. As for the product of C_5, isoprene and 2-methyl-2-butene were confirmed as pyrolyzate. The selectivity of the thermal decomposition reaction to isoprene from squalene at 470 °C was approximately 60%.

Next, we examined the influence of the linear velocity on thermal decomposition reaction of squalene. The results summarized in Table 1. We found that the C_5 and C_{10} yield decreased with increasing in the

linear verbosity. In contrast, production rate of C_{20} and C_{25} increases with increase in the linear verbosity. These results strongly suggested that decomposition reaction of the squalene (C_{30}) progresses sequentially as $C_{30} \rightarrow C_{25} \rightarrow C_{20} \rightarrow C_{15} \rightarrow C_{10} \rightarrow C_5$. The reaction mechanism can be explained by the effect of the stable allyl radical intermediate.

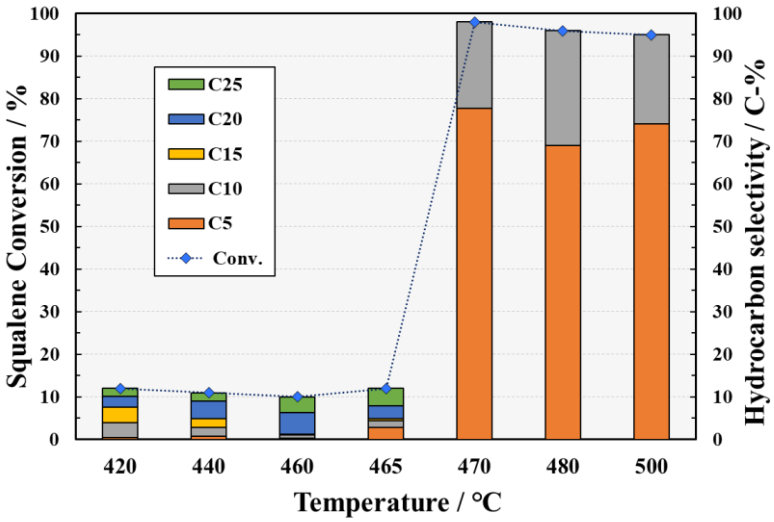

Figure 1. The thermal decomposition reaction activity of squalene as a function of reaction temperature Liner velocity : 13.7 cc/min, Reaction pressure : 0.1 MPa. Squalene : N_2 = 1:49.

Table 1. The thermal decomposition reaction activity of squalene as a function of liner velocity

Line./m·h·r^{-1}	Conv./%	Product Species/C-%					
		C_1~C_4	C_5	C_{10}	C_{15}	C_{20}	C_{25}
13.7	**98**	**-**	**79**	**21**	**-**	**-**	**-**
16.4	**25**	**-**	**3**	**19**	**28**	**19**	**31**
20.5	**24**	**-**	**2**	**12**	**15**	**31**	**40**

Reaction temperature : 470 °C, Reaction pressure : 0.1 MPa. Squalene : N_2 = 1:49.

4. Conclusions

We obtained isoprene from squalene selectively. The conversion and product species were significantly changed at 470 °C, where C_5 and C_{10} were mainly obtained at 470 °C～500 °C. The selectivity of the thermal decomposition reaction to isoprene from squalene at 470 °C was approximately 60%. From the liner velocity dependence at 470 °C, $C_{30}H_{50}$ was suggested to decompose as $C_{30}H_{50} \rightarrow 5C_5H_8 + C_5H_{10}$. This research is first evidence for isoprene production by chemical transformation from squalene.

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