Production of cellulose-derived olefins and applicability to gasoline

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Abstract: Our present study proposes a gasoline-boiling-range olefin production process, which combines hexanol production from cellulose using Ir-ReO_x/SiO_2, and hexene production from the hexanol using dehydration catalyst (H-ZSM-5). Based on the properties of the hexene mixture obtained by the dehydration of the hexanol mixture with the same composition ratio as those produced from cellulose and the gasoline JIS (Japanese Industrial Standards) specification, it is found that about 22 vol.% and 7 vol.% of the hexene mixture could be blended into gasoline in summer and winter, respectively. Therefore, the hexene mixture obtained from cellulose through our process is a potential biofuel.

Keywords: Biofuel, Cellulose-derived olefin, Dehydration

1. Introduction

Liquid biofuels can play an important role in low-carbon societies by replacing petroleum-derived fuels. In order to supply low-carbon biofuel without producing food-energy competition, cellulose has been considered an attractive source of energy.

In producing hydrocarbons from cellulose, removal of all the oxygen in the molecules is necessary, in which it is considered that hydrogenolysis of C-O bonds and dehydration become important. Ir-ReO_x/SiO_2 catalyst has high activities of C-O bonds cleavage in glycerol and erythritol, while having very low activities of C-C bonds cleavage in them[1-2].

Our previous study[3] found that hexanols could be obtained in relatively high yield of 60%-C in depolymerizing cellulose by mechanocatalysis with the aid of H_2SO_4, and then reacting the cellulose with hydrogen over Ir-ReO_x/SiO_2. The molar ratio of 1-, 2-, and 3-hexanol produced was 1:27:71. The present study investigated the compositions and properties of the hexene mixture obtained by dehydrating the hexanol mixture with the same composition ratio as those produced from cellulose by the above mentioned reaction as well as the applicability of the hexene mixture blending into gasoline.

2. Experimental

The dehydration reactions of the hexanol mixture (1.0 g, 1-hexanol: Sigma-Aldrich, 2-hexanol: Tokyo Chemical Industry, 3-hexanol: Tokyo Chemical Industry) to the hexene mixture over H-ZSM-5 (0.2 g, Si/Al_2 = 90, Süd-Chemie) in *n*-tridecane solvent (10 g, Tokyo Chemical Industry) under 0.6 MPa of N_2 at r.t. were conducted in an autoclave (100 ml). The autoclave was heated to 180 ^oC, and it was immediately cooled with an ice water bath when it reached to 180 ^oC.

The applicability of the hexene mixture to gasoline was evaluated by estimating the maximum allowable amount of the hexene mixture to be blended into gasoline, *i.e.*, the gasoline properties of 6 and 15 vol. % splash blends of the hexene mixture into a commercial gasoline (Density at 15 ^oC: 0.7269 g/cm^3, Reid Vapor Pressure (RVP): 74.8 kPa, Research Octane Number (RON): 90.8, 50% distillation temperature (T50): 83.5 ^oC) were compared with corresponding JIS specifications and the maximum allowable amount of hexene mixture was estimated.

3. Results and discussion

The dehydration reactions of the hexanol mixture gave 3.3%-C of 1-hexene, 55.6%-C of 2-hexene, 20.9%-C of 3-hexene, and 10.2%-C of hexene structural isomers (including 2-methyl-2-pentene, 3-methyl-

2-pentene, 2-methyl-1-pentene, and 4-methyl-2-pentene) with some dimers, which were not quantified. Assuming that those dimers will be removed by distillation in a commercial plant, from the three main products, *i.e.*, 1-, 2-, and 3-hexene, the hexene mixture was prepared by blending those at the same ratio as mentioned above. The properties of the hexene mixture are shown in Table 1. The density, RVP, and RON of the hexene mixture satisfied those specifications, no matter how much the hexene mixture were blended into gasoline. On the other hand, T50 can regulate the maximum allowable blend of the hexene mixture into gasoline. Because the higher blends of the hexene mixture can lower the T50 below the specification (min. 75 °C) due to the fact that the boiling points of each hexene are lower than the specification.

Table 1. Comparison between properties of hexene mixture and gasoline JIS specifications.

	Gasoline JIS Specifications	Properties of Hexene Mixture
Density (15 °C)/g ml^{-1}	< 0.783	0.671
RVP (37.8 °C)/kPa	< 65 (Summer) < 93 (Winter)	35.6
RON	> 89.0	92.0
T50/ °C	75~110	1-hexene*: 63 2-hexene*: 68~70 3-hexene*: 67

* The boiling points of each hexene are shown.

Figure 1 shows a plot of T50 against the blend rate of the hexene mixture into the commercial gasoline. A good liner correlation (solid line) between blend rate and T50 can be obtained. The winter gasoline with the higher RVP specification (see Table 1) allows more high RVP components with low boiling points like butane to be blended into gasoline. Hence, T50s in summer and winter in the Japanese market are different. So, we estimated the maximum allowable blends of the hexene mixture in summer and winter. The average T50s in summer and winter are 83.3 °C and 78.4 °C, respectively. For the winter gasoline, the maximum allowable blend of the hexene mixture was estimated to be about 7 vol.% by parallelly shifting the correlation line at 78.4 °C on the T50 axis and reading the hexene mixture blend vol.% at an intersection between the shifted correlation line (Dotted line) and the T50 = 76 line (although the minimum T50 specification is 75 °C, we assumed 1 °C of the allowance to the specification). In the same way, the maximum allowable blend of the hexene mixture in summer gasoline was estimated to be about 22 vol.%.

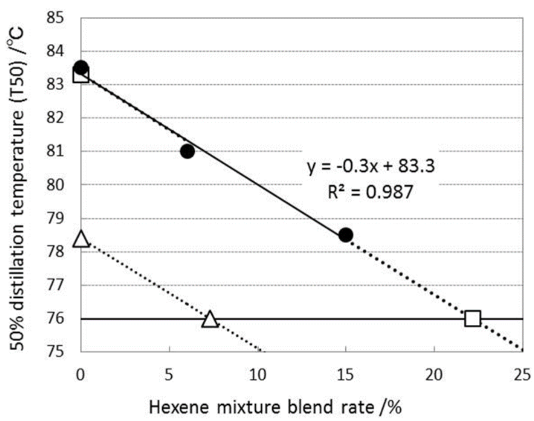

Figure 1. Estimation of maximum allowable blend rate in summer and winter.
Solid Line: relationship between hexene mixture and T50 (Approximation). Dotted lines: estimations of T50 in hexene mixture blends. ●: experimental result, □: average T50 in summer gasoline, △: average T50 in winter gasoline.

4. Conclusions

Based on the properties of the hexene mixture obtained by dehydration of the hexanol mixture with the same composition ratio as those produced from cellulose and the gasoline JIS specification, it is found that about 22 vol.% and 7 vol.% of the hexene mixture could be blended into gasoline in summer and winter, respectively.

References

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