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Development of New Isomerization Process for Petrochemical By-products

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Abstract

The catalyst and process for Isomerization of petrochemical by-product suitable for clean gasoline production are introduced. $Pt/SO_4^{2-}/ZrO_2$ catalyst indicates higher isomerization activity at lower temperature than Pt-zeolite catalyst and can obtain the product oil with a high octane number in high yield. Although Petrochemical raffinate(PC-raffinate) as a by-product of the ethylene-cracker at petrochemical is the same fraction as the light-naphtha, it is not suitable for ordinary isomerization process because of much moisture and heptane compounds,

In this research, we examined the effect of moisture and heptane content, and developed the new isomerization process with $Pt/SO_4^{2-}/ZrO_2$ catalyst for PC-raffinate. In the commercial operation of an actual isomerization unit, it was confirmed that the isomerization product was stably obtained and the octane number of the PC-raffinate was improved by 11.

1. Introduction

Isomerization of normal paraffin to isoparaffin is considered important petroleum reaction for the production of clean gasoline to improve the research octane number (RON) [1)]. Sulfated zirconia (SO_4^{2-}/ZrO_2) catalyst has been well known as a super solid-acid catalyst that can certainly isomerize normal paraffin to isoparaffin[2)]. Especially, Pt-promoted SO_4^{2-}/ZrO_2 ($Pt/SO_4^{2-}/ZrO_2$) catalyst shows high activity for isomerization of light-naphtha obtained by the crude oil distillation at lower temperature[3)]. Therefore, light-naphtha isomerization with $Pt/SO_4^{2-}/ZrO_2$ catalyst has been applied for one of the important technologies for RON improvement in oil refining[4)].

By the way, Petrochemical raffinate (PC-raffinate) which is a by-product from the ethylene-cracker in petrochemical process has been focused from a point of view to operate efficiently petroleum refinery through the collaboration with petrochemical[5)].

Although the fraction of PC-raffinate is similar to that of gasoline, low RON of PC-raffinate is a problem in terms of using as a gasoline blend-stock. Therefore, the isomerization of PC-raffinate including normal paraffin with a high content is very effective for the production of high octane gasoline. But, it is difficult to isomerize PC-raffinate through the ordinary isomerization process because of much moisture and heptane compounds comparison with the light-naphtha.

In this paper, the effect of moisture and heptane content in the isomerization reaction are described, and the development of the new isomerization process with $Pt/SO_4^{2-}/ZrO_2$ catalyst for PC-raffinate is introduced. Furthermore, we report the operation results of the new isomerization process are presented.

2. Formation of PC-raffinate

In the petrochemical process, ethylene and propylene has been produced through the naphtha cracker unit from the light-naphtha derived from oil refining, then the cracked gasoline has been also obtained simultaneously. The cracked gasoline is introduced to the aroma extractor unit to remove BTX. PC-raffinate is still remained as a by-product after extraction of BTX from cracked gasoline (Figure 1). Table 1 shows the properties of PC-raffinate and light-naphtha. Because of high content of moisture and heptane compounds in addition to low RON, it is difficult to use PC-raffinate as not only a gasoline blend-stock but also a feedstock for conventional isomerization unit to improve RON. Therefore, we have to pave the way for the new isomerization technology for PC-raffinate.

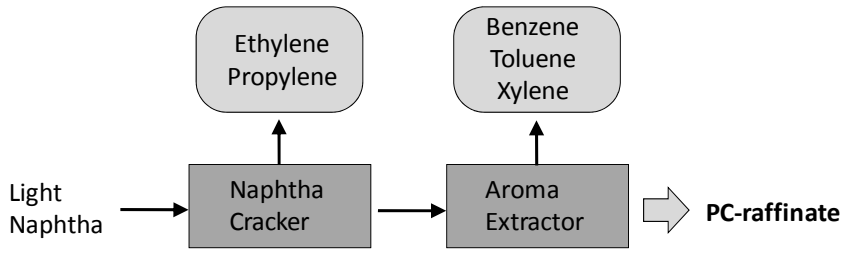


Figure 1 Formation of PC-raffinate.

Table 1 Properties of PC-raffinate and Light-naphtha

			PC-Raffinate	Light-naphtha*
Density@15C		[g/cm^3]	0.6801	0.6588
Sulfur		[massppm]	< 1	< 1
Nitrogen		[massppm]	< 1	< 1
Moisture		[massppm]	52	< 10
RON			55.9	64.7
Distribution	10%	[℃]	72.5	42.5
	50%	[℃]	76.0	53.0
	90%	[℃]	85.0	72.5
	95%	[℃]	88.0	78.0
Cyclic compounds		[mass%]	19.3	11.2
Carbon Distribution				
	C_1-C_4	[mass%]	0.0	3.3
	C_5	[mass%]	3.2	43.0
	C_6	[mass%]	51.9	45.2
	C_7	[mass%]	44.0	8.4
	C_8	[mass%]	0.9	0.1

*After hydrodesulfurization

3. Isomerization reaction of hexane

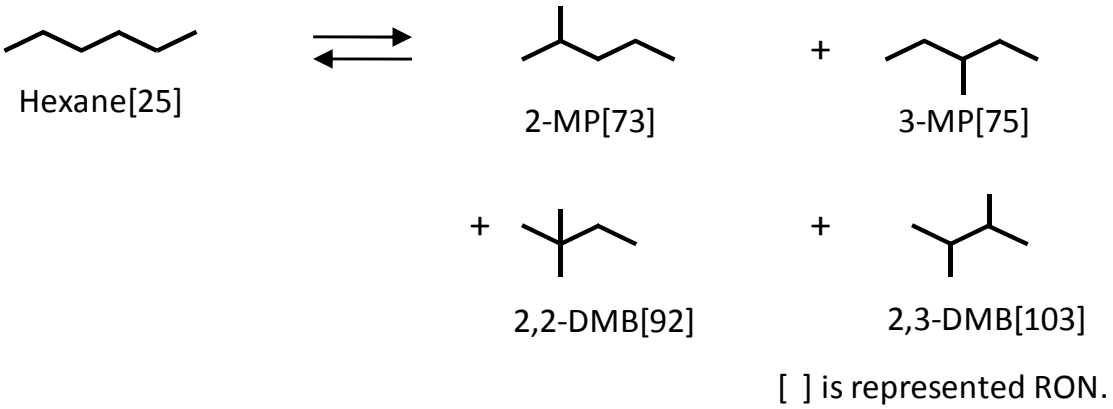
The main components of PC-raffinate are C6 and C7 fraction, especially low RON fractions with a straight chain structure are contained. If hexane is isomerized into mono-branched hexane or di-branched hexane, the effect of octane increment should be obtained. Scheme 1 indicates the skeletal isomerization reaction of hexane. Although n-hexane have only 25 RON, mono-branched hexane such as 2-methylpentane (2MP) or 3-methylpentane (3MP) has from 73 to 75 RON. Furthermore, di-branched hexane such as 2, 2-dimetylbutane (2,2-DMB) and 2,3-dimetylbutane(2,3-DMB) has high RON in the range of 92 to 103.

The dominant parameter of this isomerization reaction depends on the catalyst type, the content of moisture and the content of heptane fraction. We have researched the infuluences of these dominant parameter. 2,2-DMB ratio and C5 heavier fraction are used as a index for isomerization activity and yield respectively.

・ Isomerization activity; 22-DMB ratio (mass %)

= 22-DMB/(all C6 compounds) * 100

- Yield; C5 heavier fraction (mass %) = 100-(C1+C2+C3+C4)



Scheme 1 Skeletal isomerization of hexane.

4. PC-raffinate isomerization

4-1. Effect of catalyst type

$Pt/SO_4^{2-}/ZrO_2$ and Pt-zeolite were used for isomerization reaction of PC-raffinate to figure out the effect of catalyst type. L-RFT prepared through the removal of heptane fraction by the distillation from PC-raffinate described in Table 1, was used as the reactant of the isomerization reaction. These experimental were carried out in a fixed-bed reactor under the following conditions: reaction temperature of 140 - 300C, hydrogen pressure of 3.1MPa, LHSV of $1.5h^{-1}$ and a hydrogen to hydrocarbon molar ratio of 2.0mol/mol.

Figure 2 shows the relationship between reaction temperature and isomerization activity. Although the isomerization reaction over Pt-zeolite catalyst did not take place under 250℃, $Pt/SO_4^{2-}/ZrO_2$ catalyst showed high isomerization activity around 200℃ (Figure 2(a)). In terms of chemical equilibrium, this reason is suitable for low temperature[6]. Furthermore, the yield of C5 heavier fraction for $Pt/SO_4^{2-}/ZrO_2$ catalyst is higher than that for Pt-zeolite because the lower reaction temperature which is available for $Pt/SO_4^{2-}/ZrO_2$ catalyst inhibited the cracking of the heptane fraction.

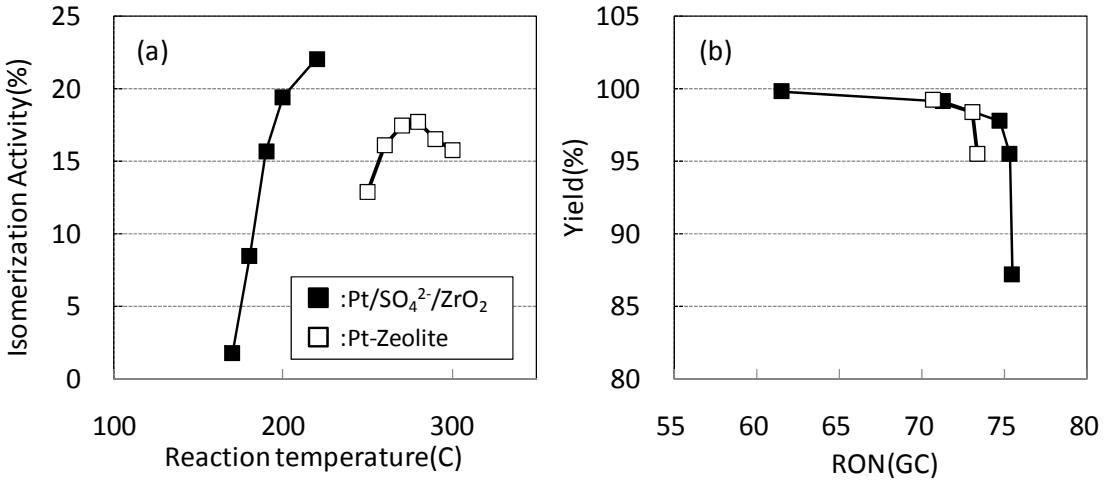


Figure 2 Effect of isomerization catalyst, (a)Relationship between reaction temperature and isomerization activity, (b)Relationship between RON(GC) and yield; reaction temperature=140 - 300C, hydrogen pressure=3.1MPa, LHSV=1.5h^{-1} and H_2/hydrocarbon molar ratio=2.0mol/mol.

4-2. Effect of moisture

The influence of moisture for the L-RFT isomerization with the $Pt/SO_4^{2-}/ZrO_2$ catalyst was examined. Isomerization reactions were carried out under the same conditions as 4-1. If the moisture was absence in the reactant, both the isomerization activity at the same reaction temperature and the yield at the same RON were improved(Figure 3).

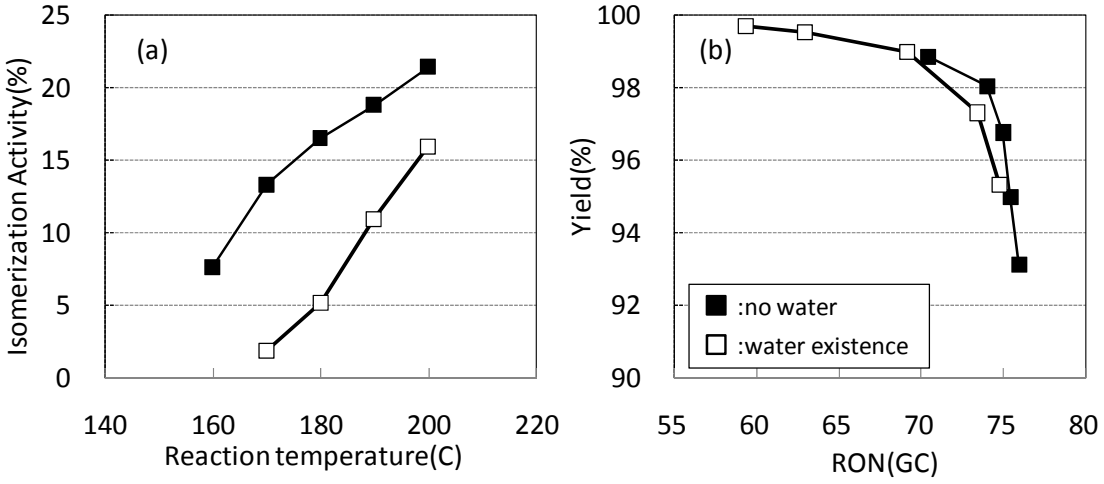


Figure 3 Effect of water existence; (a)Relationship between reaction temperature and isomerization activity, (b)Relationship between RON(GC) and yield; reaction temperature=160 - 200C, hydrogen pressure=3.1MPa, LHSV=1.5h^{-1} and H_2/hydrocarbon molar ratio=2.0mol/mol.

It is thought that the H2O molecules obstruct the isomerization of hydrocarbon such as hexane because it easily adsorbs onto the strong acid aites on the $Pt/SO_4^{2-}/ZrO_2$ catalyst.The PC-raffinate has high moisture content by way of the aroma extractor process using sulforane, therefore it is necessary to equip the new isomerization process for PC-raffinate with the water removal process.

4-3. Effect of heptane fraction

Following to moisture, the influence of heptane fraction for the L-RFT isomerization with the $Pt/SO_4^{2-}/ZrO_2$ catalyst was examined. Isomerization reactions were carried out under the same conditions as 4-1 and the moisture of L-RFT was removed by molecular sieve 5A previously. The isomerization activity increased according to the rise of the reaction temperature, the high heptane content lead to the decline of the isomerization activity(Figure 4(a)). Moreover, in the case of the high content of heptane fraction, isomerization yield decreased because of the conversion to propane and butane compounds(Figure 4(b)). The long carbon chain such as heptane fraction is easy to be cracked, then it is necessary to controll the content of heptane fraction for the new isomerization process for PC-raffinate[7].

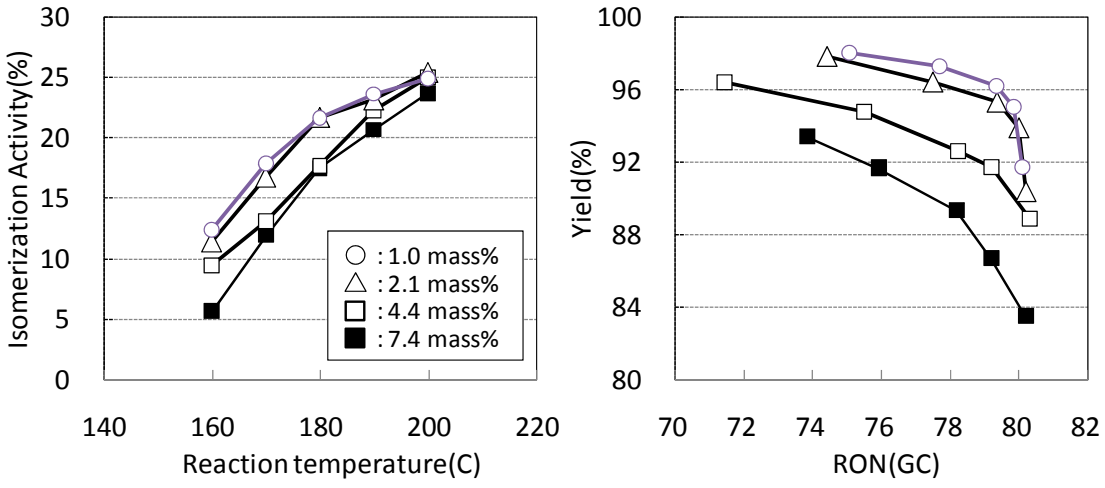


Figure 4 Effect of heptane fraction, (a)Relationship between reaction temperature and isomerization activity, (b)Relationship between RON(GC) and yield; reaction temperature=160 - 200C, hydrogen pressure=3.1MPa, LHSV=$1.5h^{-1}$ and H_2/hydrocarbon molar ratio=2.0mol/mol.

5. Results of commercial operation

5-1. New isomerization process for PC-raffinate

The new isomerization process for PC-raffinate has been developed based on the influences of moisture and heptane fraction content. Figure 5 shows the process flow diagram of the new isomerization process for PC-raffinate. The fractionator to control the content of heptane fraction and the water stripper to remove the moisture were equipped to this process. The chemical property of the reactant for the isomerization reaction was controlled strictly by arranging these incidental facilities. Figure 6 shows the trends of the reaction temperature and the yield in commercial operation for new isomerization process. Commercial operation has been carried out under the operation as the isomerization activity constant (2,2-DMB ratio(%)=16.5%) and the isomerization activity has been adjusted by changing the reaction temperature. When the specification of the reactant was controlled strictly in commercial operation, both the ratio of isomer and the yield of product could be almost kept constant and stable operation could be carried out.

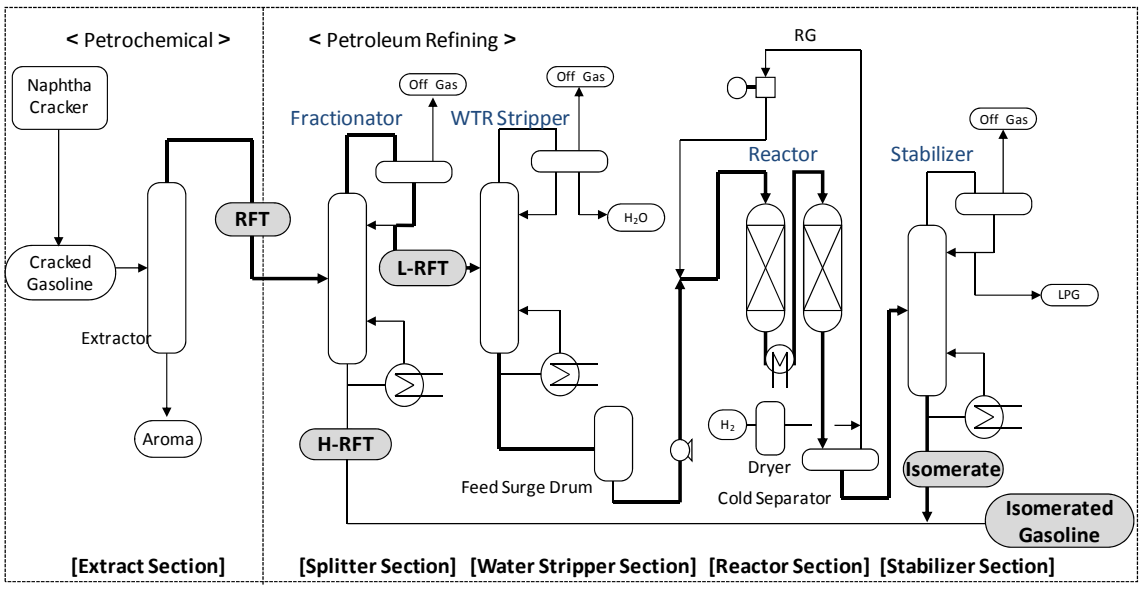


Figure 5 Flow diagram of new isomerization process for PC-raffinate.

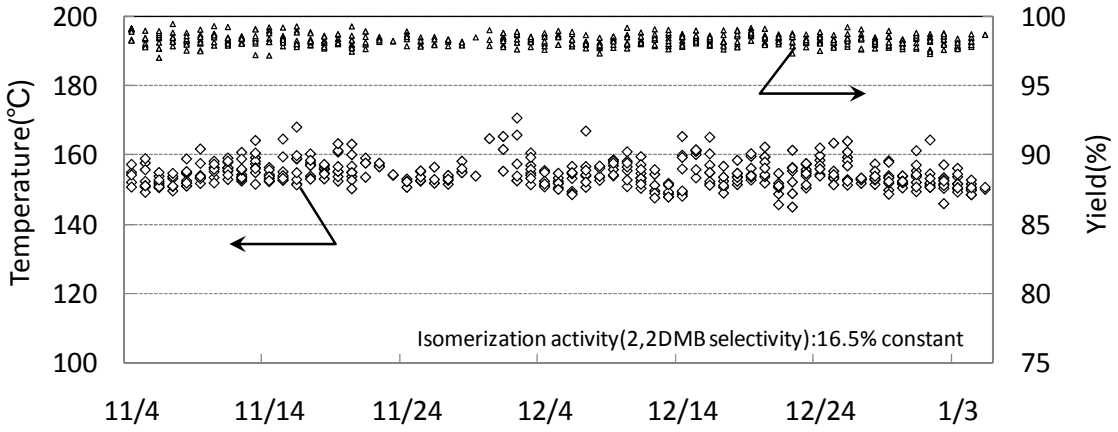


Figure 6 Result of commercial operation on new isomerization unit; Isomerization activity(2,2DMB selectivity)=16.5% constant.

5-2. Properties of isomerated gasoline

Table 2 shows the properties of PC-raffinate and isomerated gasoline obtained from the commercial operation. Isomerated gasoline is the mixture of the isomerization product and the heavy raffinate (H-RFT) that is removed L-RFT by fractionator. RON of isomerated gasoline indicated 71 while the RON of PC-raffinate showed only 60 and thus it is confirmed that the octane increment by the new isomerization process is 11. Furthermore, distillation of isomerated gasoline was the same as that of PC-raffinate and it has been found that the isomerization of the PC raffinate influences only the octane increment. It is thought that the isomerated gasoline obtained from this new isomerization process is very useful because it does not contain any sulfur and nitrogen compounds[8)].

Table 2 Properties of PC-raffinate and Isomerated gasoline

	PC-raffinate	Isomerated gasoline (product + H-RFT)
GC-RON	60.0	71.2
Density, g/cm3	0.696	0.693
Vapor Pressure, kPa	35.0	47.5
Nitrogen, massppm	<1	<1
Sulfur, massppm	<1	<1
T.B.P I.B.P, C	66.5	50.5
T.B.P 50%, C	74.0	72.0
T.B.P 95%, C	91.0	110.0

6. Conclusion

The new isomerization process for PC-raffinate was developed. The new isomerization process uses the $Pt/SO_4^{2-}/ZrO_2$ catalyst that indicated the high activity at lower temperature, and this process has been controlled about the moisture content and heptane fraction that decrease the isomerization activity. In the commercial operation, it was confirmed that the stable isomerization activity was obtained and 11 octane increments was achieved.

Acknowledgements

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