Reactivity of several olefins in the HDS of full boiling range FCC gasoline over PtPd/USY

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1. Summary

Reactivity of C_4-C_6 olefins during the selective HDS of a full boiling range FCC gasoline over PtPd/USY catalyst was studied under various process conditions. Effect of the structure and carbon number of olefins on their conversion is discussed. It was found that the rate of hydrogenation decreases with the carbon number of linear olefins. Terminal olefins are readily converted to internal olefins by double bond shift to approach the equilibrium composition of olefin isomers.

Keywords: HDS, FCC gasoline, olefin hydrogenation, PtPd/USY

2. Extended Abstract

2.1. Introduction

Desulphurization of FCC gasoline is a key process in refineries for blending gasoline of ultra low sulphur content (<10 mg/kg). Hydrodesulphurization (HDS) of highly olefinic cracked naphtha fractions on conventional $CoMo/Al_2O_3$ catalysts results in significant olefin saturation and high H_2 consumption, making this process unsuitable for cracked naphtha upgrading. Quite a number of new catalyst have been developed, which are suitable for the desulphurization of cracked naphthas with minimized olefin saturation (Song, 2003; Brunet et al., 2005). The dissimilar reactivity of various olefins can have a significant effect on the octane number of the products, because the difference in the RON or MON between a certain olefin and its saturated paraffin derivative can greatly depend on its structure and carbon number (Table 1.). Therefore, the differences in the reactivity of various olefins contained in the FCC gasoline can significantly influence the research and motor octane number of the final product.

Table 1. Difference between the average RON or MON of various olefin groups and their paraffin derivatives

Olefins	Paraffins	ΔRON	ΔMON
n-pentenes	*n*-pentane	26.0	13.8
n-hexenes	*n*-hexane	62.9	48.8
n-heptenes	*n*-heptane	72.6	66.3
methyl-butenes	methyl-butane	4.7	-9.4
methyl-pentenes	methyl-pentanes	23.7	9.0
methyl-hexenes	methyl-hexanes	41.3	26.2
dimethyl-butenes	dimethyl-butanes	-4.9	-12.5
dimethyl-pentenes	dimethyl-pentanes	7.9	-5.2
dimethyl-hexenes	dimethyl-hexanes	23.4	2.5

ΔRON: average RON of an olefin group minus average RON of a paraffin group

Hydrogenation rate of individual olefin compounds and their mixtures was studied very early. Lebedev and coworkers (1924) studied the hydrogenation rate of olefins with various structure and carbon number as early as 1924. They stated that the hydrogenation rate decreases with the number of substituents on the double bond. This phenomenon, known as Lebedev's rule, was later expanded to cycloolefins. Lebedev's rule was based on the liquid phase hydrogenation of olefin couples at a temperature of 20°C. The reaction rate of the double bond shift is very low at this temperature; e.g. during the treatment of hexene over Pt/Al_2O_3 the hydrogenation of the double bond is 30 times higher than the double bond migration (Maurel, 1967). In case of gas phase reactions at higher temperature, however, extensive double bond isomerization takes place so it is difficult to compare the hydrogenation rate of the olefin isomers (Dibeler, 1951). Hydrogenation, *cis-trans* isomerization and double-bond migration are simultaneous reactions. In case of a defined olefin the relative rates of hydrogenation, double-bond shift and *cis-trans* isomerization greatly depends on the applied catalyst and reaction temperature. Based on their olefin isomerization activity Bond and Wells (1954) provided the following categorization of metal catalysts:

$$Ni, Pd, Fe > Ru, Rh, Os > Pt, Ir$$
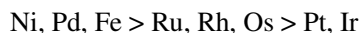
However, less information is available in the literature about reactivity differences between different olefins contained in cracked naphtha matrix under hydrodesulphurization conditions. In a recent study, Toba et al. (2007) found that the conversion of *trans*-olefins is lower that those of *cis*-olefins and the conversion of internal olefins is lower than those of terminal olefins during the HDS of FCC gasoline over sulphided $CoMo/Al_2O_3$. They suggested that the lower conversion of *trans*-olefins and internal olefins is caused by their lower hydrogenation rate because of the steric hindrance of the double bond.

The aim of this study was to try to clarify the behaviour of olefins in the hydrodesulphurization of a full boiling range FCC gasoline. In our previous works we showed that PtPd/USY catalyst is able to selectively desulphurize FCC gasoline fractions containing 50-150 mg/kg sulphur due to the selective poisoning of the hydrogenation active sites (Hancsók et al. 2002 & 2007). The same PtPd/USY was used in this study, too.

2.2. Experimental

2.2.1. Apparatus

The tests were carried out in a pilot scale HDS unit. The effective volume of the fix-bed HDS reactor is 100 cm^3. The test system contained all the equipments and devices, which are applied in full-scale commercial gasoline HDS units. The tests were carried out in continuous operation. The following process conditions were applied: temperature: 220-280°C; LHSV: 1.0-3.0; H$_2$/HC ratio: 300 Nm^3/m^3.

2.2.2. Feedstock

Full boiling range FCC gasoline of 66 mg/kg sulphur content was used as a feedstock of the HDS tests. Its main properties are detailed in Table 2. Concentration of several C$_5$ and C$_6$ olefins as well as cycloolefins contained in the full range FCC gasoline are given in Table 3. The feed contains more kind of olefins that it is listed in Table 3 but the concentration of the remaining oelfins is very low.

Table 2. Main characteristics of the FCC gasoline feed

Characteristics	Data
Density, g/cm^3	0.7423
Sulphur content, mg/kg	66
Nitrogen content, mg/kg	20
Research octane number	93.4
Motor octane number	81.7
Hydrocarbon composition, wt%	
n-paraffins	4.0
i-paraffins	31.8
olefins	24.9
naphthenes	7.6
aromatics	31.7
Distillation (ASTM D86)	
IBP	36
10 v/v%	54
30 v/v%	65
50 v/v%	92
70 v/v%	136
90 v/v%	180
95 v/v%	195
FBP	205

2.2.3. Catalyst

A PtPd/USY zeolite catalyst was used. The properties of the catalyst are given in Table 4. Before feeding the gasoline into the reactor, the catalyst was dried in nitrogen flow at 400 °C for 10 hours and then treated in hydrogen flow at 300 °C for 15 hours. After the activation procedure, the catalyst bed was cooled to 230°C and the feed was introduced into the reactor.

Table 3. Concentration of several olefins contained in the FCC gasoline

Olefin compounds	Conc., wt%	Olefin compounds	Conc., wt%
Butenes		*t*-2-hexene	0.75
1-butene	0.07	*c*-3-hexene	0.37
t-2-butene	0.24	*t*-3-hexene	0.12
c-2-butene	0.32	2-methyl-1-pentene	0.89
Pentenes		2-methyl-2-pentene	0.94
1-pentene	0.85	3-methyl-1-pentene	0.21
c-2-pentene	1.22	3-metil-*c*-2-pentene	0.95
t-2-pentene	2.16	3-methyl-*t*-2-pentene	0.68
2-methyl-1-butene	2.04	4-methyl-1-pentene	0.13
2-methyl-2-butene	3.68	*Cyclopentenes*	
3-methyl-1-butene	0.38	cyclopentene	0.35
Hexenes		1-methyl-cyclopentene	0.72
c-2-hexene	0.42	3-methyl-cyclopentene	0.12

Table 4. Characteristics of the catalyst

Properties	Data
Composition, %	
palladium content	0.45
platinum content	0.15
Y-zeolite and binder	remaining
Physical properties	
loading density, g/cm^3	0.5
crush strength, N/mm	6.2
BET surface area, m^2/g	650

2.2.4. Methods

Total hydrocarbon composition of the feedstock and liquid products were determined by gas chromatography according to a modified version of NF M07-086 method. Sulphur contents were measured according to ISO 20846 standard (Multi EA 3100 analyzer).

2.3. Results and discussion

The results showed that the rate of olefin hydrogenation under the conditions of gasoline HDS over PtPd/USY catalyst decreases with the carbon number of the olefin. This is favourable from the point of view of octane number, since the loss of RON caused by hydrogenation increases with the carbon number of the olefin (see Table 1.). Hydrogenation of *n*-pentenes is significantly faster than those of methyl butenes and the conversion of *n*-hexenes is also higher than those of methyl pentenes. (Figure 2). These findings are in accordance with Lebedev's rule. This is also advantageous as the octane number loss during the hydrogenation of a methyl alkene is lower compared to that than occurring in the *n*-alkene to *n*-alkane reaction.
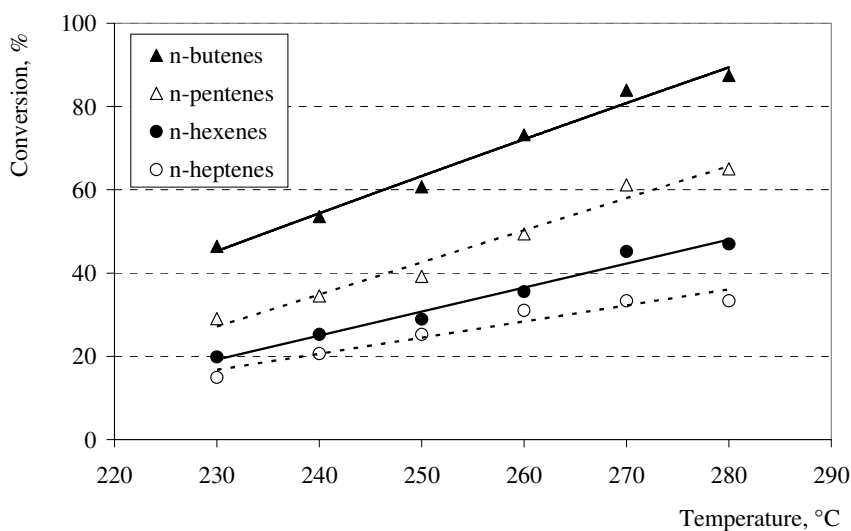
Figure 1. Conversion of *n*-alkenes as a function of reaction temperature
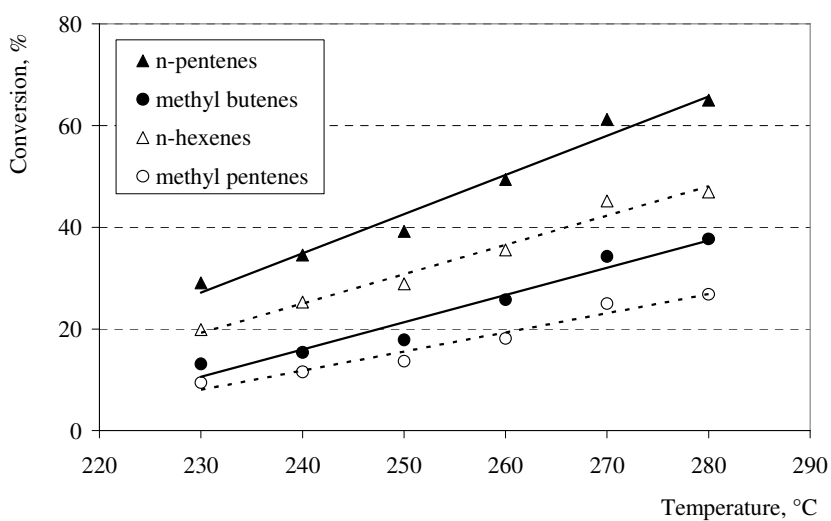(P= 30 bar; LHSV=1.0; H_2/HC=300 Nm^3/m^3)

Figure 2. Conversion of *n*-alkenes and methyl alkenes as a function of reaction
temperature (P= 30 bar; LHSV=1.0; H_2/HC=300 Nm^3/m^3)

The results also showed that double-bond migration took place during the HDS of the
FCC gasoline feed, because the conversion of certain olefins (e.g. 2-methyl-2-butene)
was negative, indicating that more of these olefins formed from other olefin isomers
than they were consumed in their saturation to paraffins (Figure 3.).
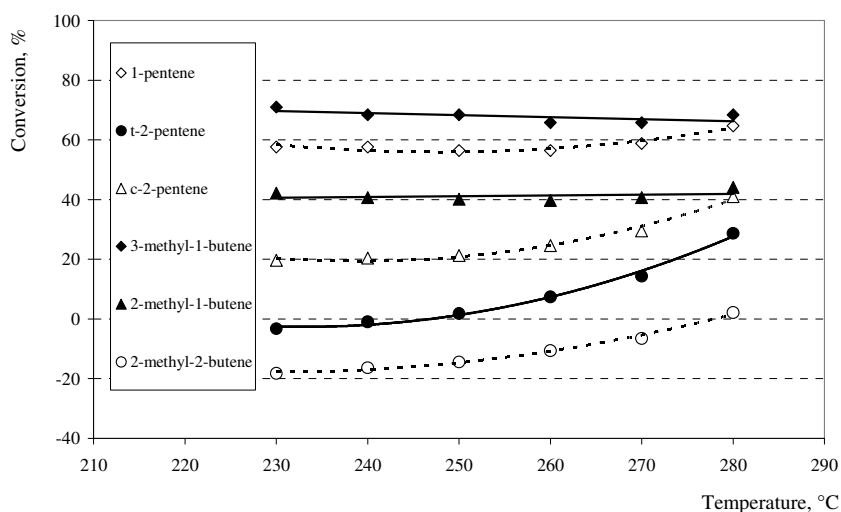
Figure 3. Conversion of C$_5$ alkenes as a function of reaction temperature
(P= 30 bar; LHSV=3.0; H$_2$/HC=300 Nm^3/m^3)

After hydrogenation, the composition of *n*-pentenes in the product does not seem to depend on the contact time; it remains almost constant (11 wt% 1-pentene; 28 wt% *cis*-2-pentene and 61 wt% *trans*-2-pentene) while their hydrogenation clearly increases (Figure 4). Similarly, this is also true for the methyl butenes (Figure 5).
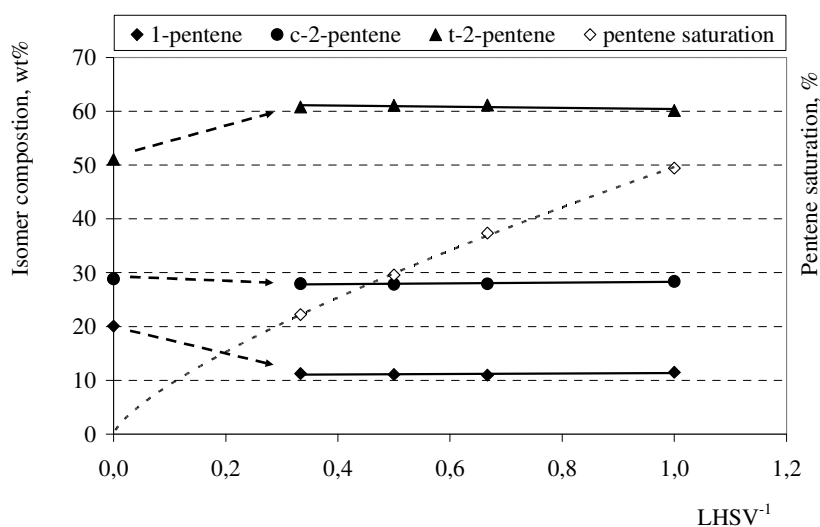

Figure 4. Isomer composition of *n*-pentenes and their saturation
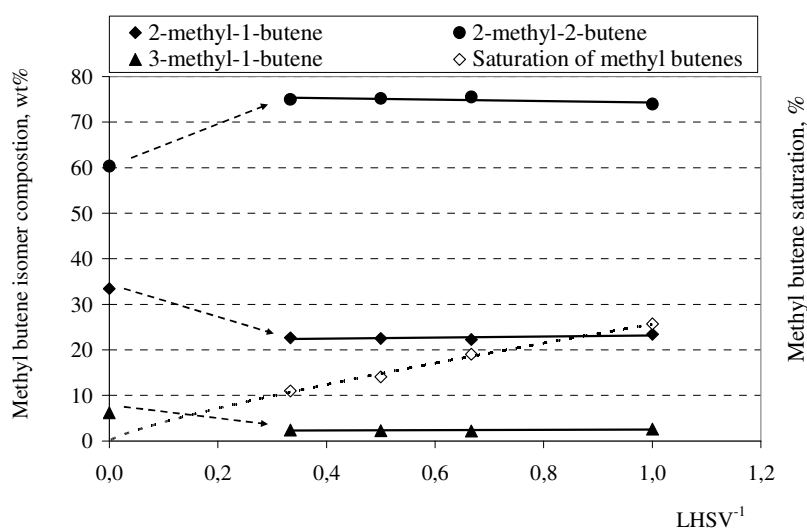(P= 30 bar; T=260°C; H$_2$/HC=300 Nm^3/m^3)

Figure 5. Isomer composition of methyl butenes and their saturation
(P= 30 bar; T=260°C; H_2/HC=300 Nm^3/m^3)

Composition of *n*-pentene isomers is almost practically constant as function of the temperature in the investigated range of 230-280°C (Figure 6). Concentration of *trans*-2-pentene slightly decreases with temperature while those of 1-pentene and *cis*-2-pentene slightly increase, that can be explained with the thermodynamic equilibrium concentrations of these isomers, since higher temperature favours the formation of *trans*-2-pentene. Similarly in case of methyl butenes, the concentration of 2-methyl-2-butene slowly decreases with temperature and those of 2-methyl-1-butene and 3-methyl-1-butene slowly increase (Figure 7).
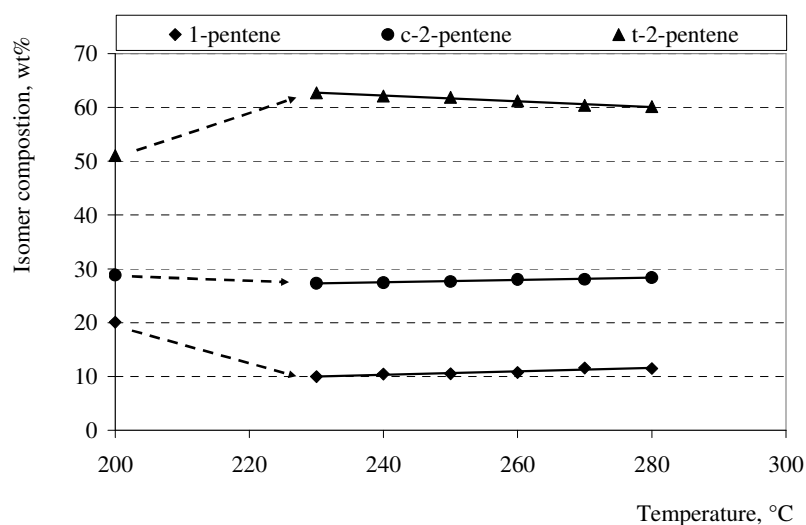

Figure 6. Isomer composition of pentenes as a function of temperature
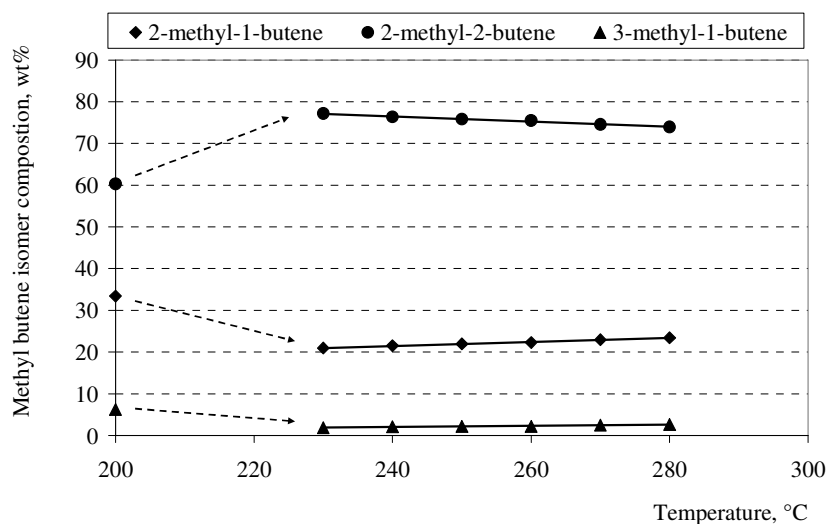(P= 30 bar; T=260°C; H_2/HC=300 Nm^3/m^3)

Figure 7. Isomer composition of methyl butenes as a function of temperature
(P= 30 bar; T=260°C; H_2/HC=300 Nm^3/m^3)

In the cracked HDS, the terminal olefins are readily converted to internal ones until they reach the equilibrium concentration.

3. Conclusions

Our findings suggest that under gasoline HDS conditions the rate of double-bond shift is much higher compared to that of hydrogenation, leading to a near-equilibrium composition of olefins that are taking part in double-bond shift reactions. Consequently, the different conversion of olefin compounds can be attributed to double-bond isomerization instead of the different hydrogenation rates of various olefin isomers. The double-bond migration is advantageous from the aspect of product octane number, since internal olefins have generally higher octane numbers that terminal olefins

References

Brunet, S., Mey, D., Pérot, G., Bouchy, C. and Diehl, F., (2005), *Appl. Catal. A*, 278, 143-172.

Dibeler, V.H. and Taylor, T.I. (1951) *J. Phys. Chem., Ithaca*, 55, 1036.

Hancsók, J., Magyar, Sz. and Lengyel, A. (2002) *Hung. J. Ind. Chem.*, 30, 299-303.

Hancsók, J., Magyar, Sz., Juhász, K. and Kalló, D., (2007) *Top. Cat.,* DOI: 10.1007/s11244-007-0267-y (in press)

Lebedev, S.V., Koblianskii, G.G. and Yakubchik, A.O. (1924) *Zh. Russk. Fiz.-khim. Obstich*, 56, 265.

Maurel, R. (1967) in "La catalyse au laboratorie et dans l'industrie." (B. Claudel ed.), Masson, Paris, 203.

Song, C., (2003) *Catalysis Today*, 86, 211-263.

Toba, M., Miki, Y., Matsui, T., Harada, M. and Yoshimura, Y., (2007) *Appl. Catal. B.*, 70, 542.