INVESTIGATION OF THE PRODUCTION OF GASOLINE BLENDING COMPONENT FREE OF SULFUR

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Abstract. *High octane number and practically sulfur-free isomerates are essential to meet the specifications of modern ultra low sulfur engine gasoline. Therefore, the aim of the study was to investigate the isomerization and desulfurization of sulfur containing n-hexane fractions in one step and in two steps. The experiments were carried out over Pt/H-mordenite catalysts of 0.3-0.75% platinum content with n-hexane fractions containing sulfur in four different concentrations (<1, 23, 47, 76 ppm). During the experiments carried out in one step and applying favourable process conditions sulfur content of the feeds was reduced significantly, while the degree of isomerization decreased only slightly compared to the results obtained with practically sulfur-free feed. The best results were gained with H-mordenite catalyst of 0.4-0.5% platinum content.*

Key words: *clean gasoline, octane number, simultaneous isomerization and desulfurization, Pt/H-mordenite catalyst*

Introduction

During the past decade the quality requirements of engine gasoline were significantly increased (Table 1) [1-5]. Reduction of sulfur content contributes to the direct decrease of pollution and enables the application of advanced aftertreatment catalysts of low sulfur resistance which contributes to the reduction of total emission, too.

Table 1. Change of EU gasoline specifications

Properties	1993	1999	2005	2009
Density, kg/m^3	720-780	720-770	720-770	720-770
Sulphur content (max), ppm	500	150	50 (10)	10
Aromatic content (max), V/V%	-	42	35	35
Benzene content (max), V/V%	5	1	1	1
Olefin content (max), V/V%	-	18	18	18(?)
Reid vapour pressure, kPa	40-70	45-60	45-60	45-60
Distilled to 100°C (min), V/V%	42-65	46-71	46-71	46-71
Distilled to 150°C (min), V/V%	-	75	75	75

The reasons of these changes were the growing regulations for environmental protection concerning production, storage and use of engine gasoline [1-3]. In addition to this, the worldwide increase of vehicles, too, generated an increased quantity demand. The main requirements of modern (reformulated) engine gasoline are the following:

- high research and motor octane number,
- uniform octane level distribution,
- containing no lead additives,
- low benzene content (<0,5-1,0 % (V/V)),
- reduced aromatics level (<35 %(V/V)),
- low sulfur content (<50, <30, <10 ppm),
- reduced olefin content,
- proper shape of ASMT curve,
- low vapor pressure,
- optimal oxygen content,
- optimal level of additives,
- compatibility with engine oils,
- acceptable cost,
- easy and safe handling,
- formation of combustion products being less harmful to the environment and living creatures during their use.

Accordingly the demand on high octane number and non-aromatic blending components of low sulfur content (<50-10 ppm) has to be satisfied. The most favourable blending components are isoparaffins and naphthenes, e.g. isomerates (Table 2).

Table 2. Main properties of C_5/C_6 iso-, normal- and cycloparaffins

Hydrocarbon	Properties Boiling point, °C	Density, g/cm^3 (15,6°C)	Vapor pressure (RVP) kPa	Octane number research RON-0*	 motor MON-0*
2-methyl-butane	28.0	0.6284	131.8	92.3	90.3
n-pentane	36.1	0.6312	95.3	61.7	61.9
cyclopentane	29.0	0.7505	63.9	101.0	84.9
2,2-dimethyl-butane	49.7	0.6540	63.6	91.8	93.4
2,3-dimethyl-butane	58.0	0.6664	47.7	103.5	94.3
2-methyl-pentane	60.2	0.6579	43.6	73.4	73.5
3-methyl-pentane	63.2	0.6690	39.4	74.5	74.3
n-hexane	69.0	0.6640	32.0	24.8	26.0
methyl-cyclopentane	71.8	0.7535	29.1	91.3	80.0
cyclohexane	80.8	0.7834	21.0	84.0	77.0
			20.7		
2,2-dimethyl-pentane	79.2	0.6783	23.5	92.8	95.6
2,4-dimethyl-pentane	80.5	0.6772	21.2	83.1	83.8
2,2,3-trimethyl-butane	80.9	0.6945	21.7	112.1	101.3
3,3-dimethyl-pentane	86.1	0.6977	17.9	80.8	86.6
2,3-dimethyl-pentane	89.8	0.6994	15.1	91.1	88.5
2-methyl-hexane	90.0	0.6830	14.6	42.4	46.4
3-methyl-hexane	91.8	0.6915	13.7	52.0	55.0
3-ethyl-pentane	93.5	0.7026	12.9	65.0	69.3
n-heptane	98.4	0.6882	10.4	0.0	0.0

*Octane number without octane increasing additive

The possibilities for producing isoparaffins in the boiling range of gasoline are:

- separation from gasoline fractions,
- alkylation of C_3-C_5 olefins with isobutane,
- dimerization of isobutene followed by hydrogenation,
- isomerization of n-paraffins.

Isoparaffins can be produced most economically by isomerization of n-paraffin fractions. Refiners in the European Union are allocating the greatest portion of their investment budget for the revamps of existing isomerization plants and for installation of new ones (Figure 1) [6]. Reasons of this are the excellent properties of the light isoparaffins.

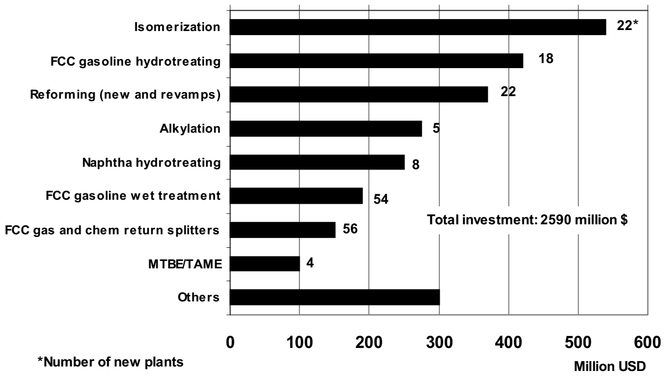


Figure 1. EU-15 investment costs and number of new plants for producing gasoline of <10 ppm sulfur in gasoline

Sulfur content of engine gasoline has to be decreased below 50 and 10 ppm in the future. To meet these requirements the sulfur content of individual gasoline blending components, e.g. isomerates has to be decreased below these values. Sulfur concentration of the fractions rich in n-paraffins used for the production of isomerates varies between 60 to 150 ppm, depending on their origin.

In terms of these, main objective of the research work was investigation of the possibility of producing practically sulfur-free isomerates (isohexane fractions). Possibility of isomerization and desulfurization of sulphur containing n-hexane fractions was investigated in one step and in two steps (Figure 2) on Pt/H-mordenite catalysts of new generation, having various compositions.

Experimental

The main objective of the authors at the present work was to select a catalyst appropriate for hydrodesulfurization and skeletal isomerization of n-hexane fractions in one step.

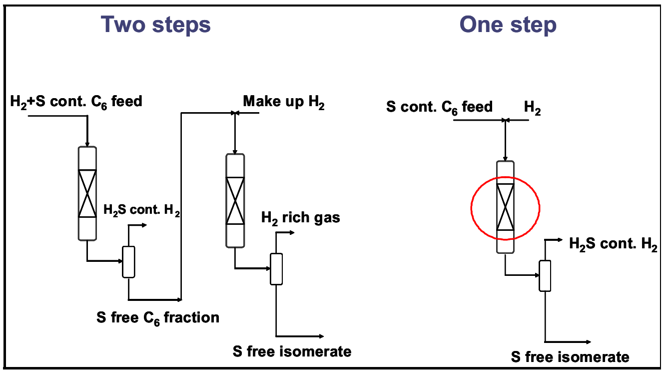


Figure 2. Simplified scheme of desulfurization and isomerization in one step and in two steps

Test apparatus. The desulfurization and isomerization experiments were carried out in a test apparatus containing a tubular flow reactor (volume of catalyst: 80 cm^3) free of back-mixing and all the major equipments and accessories like in commercial scale desulfurization and isomerization plants, respectively [7].

Catalysts. The desulfurization tests were carried out with the use of a commercial Co-Mo/Al_2O_3 catalyst. Pt/H-mordenite catalysts of various platinum concentration (0.3-0.75%) on various supports (H-mordenite of different Si/Al ratios) being active at medium temperatures (240-270°C) were applied in the two step desulfurization and isomerization experiments and in isomerization stage of the two step process. Catalysts were dried and activated under suitable conditions before running of the tests [8,9].

Feeds. The feeds (Table 3) consisted of n-hexane, iso-hexanes having sulfur content of <1-76 ppm. They were hydrocarbon mixtures of product streams from the Danube Refinery of MOL (Hungarian Oil and Gas Plc.) , as well as individual compounds. Properties of the feeds were the same, except sulfur content which was as follows: <1ppm (feed "A"); 23 ppm (feed "B"); 47 ppm (feed "C"); 76 ppm (feed "D").

Test and calculation methods. Hydrocarbon compositions of the feeds and products were determined according to ASTM D 5143-98 standard, while total sulfur content was measured according to ASTM D 4045. Platinum content of the catalysts was determined according to UOP-274 standard. Octane number of the feeds and products were calculated from their hydrocarbon compositions and blending octane numbers of the individual components.

Table 3. Main properties of the feeds

Properties	Values
Hydrocarbon composition, %	
n-Pentane	<0.05
2,2-Dimethylbutane	<0.05
2,3-Dimethylbutane	0.1
2-Methyl-pentane	0.35
3-Methyl-pentane	0.4
n-Hexane	98.6
Methyl-c-pentane	0.4
c-Hexane	<0.05
Sulfur content*, ppm	<1-76
Water content, ppm	20
Research octane number (RON)	31.7
Motor octane number (MON)	30.7

*<1 ppm; 23 ppm; 47 ppm; 76 ppm

Results and Discussion

From the large number of results only the most important characteristics of those few products are presented which were gained at process conditions found to be favourable. The results were obtained with catalysts of stable activity. Repeatability of the experiments was higher than 95% summing the errors of technological measurements and analytical methods.

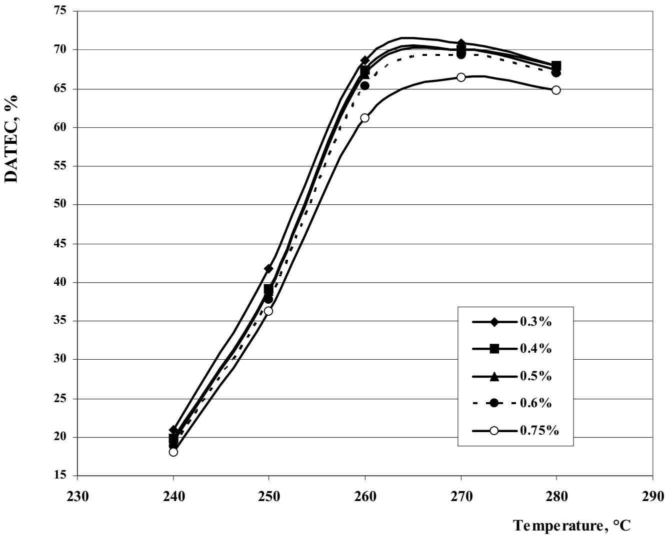
Results of desulfurization and isomerization experiments in one step over Pt/zeolite catalysts of new generation. On the basis of preliminary experiments the sulfur containing n-hexane fractions (Table 3) were investigated on catalysts of various content (0,3-0,75) at temperatures of 200-280°C, total pressure of 30-40 bar, hydrogen to hydrocarbon mole ratio of 1:1-2:1 and liquid hourly space velocity of 0.8-3.0 h^{-1}. Within these ranges of parameters the values ensuring highest content of iso-hexanes, lowest sulfur content and highest octane number of the products were determined for all catalysts and for the feeds having different sulfur contents. From the numerous data only the results obtained at temperatures of 240-280°C and 1.5 h^{-1} space velocity, 30 bar pressure and 2:1 hydrogen/hydrocarbon mole ratio were selected for presentation in detail, because these process parameters were found during the preliminary experiments to be some of the most favourable for the applied catalysts and feedstocks within the investigated temperature range. The results obtained with the catalysts, most suitable for the one step isomerization and desulfurization of n-hexane fractions of different sulfur content will be discussed in detail.

The results show that both isomerization and hydrodesulfurization took place, but to different degree, depending on platinum content as well as on other characteristics of thecatalysts, on sulfur content of the feeds and on process parameters.

As examples, Figures 3-6 show the changes of the concentration of 2,2-dimethyl-butane (2,2-DMB) as a function of temperature.

In order to characterize isomerization activity of the catalysts, yield data of 2,2-DMB out of the isomers formed from n-hexane were selected, because our experiences show that the rate of formation of this particular component is the lowest, and concentrations of other isomers in the product approach the relevant equilibrium concentrations in substantially higher degree. Besides, change of TEC data (thermodynamical equilibrium concentration) as a function of temperature is nearly exponential. Thus the changes are well traceable and valuable.

Based on the shape of the curves it was stated that the yield of 2,2-DMB increased nearly linearly in the range of 240-260°C and above this the incline of increase was lower. The reason of



Firure 3. Degree of the approach of thermodynamical equilibrium concentration (DATEC) of 2,2-dimethylbutane as a function of temperature (Sulfur in feed:<1 ppm)

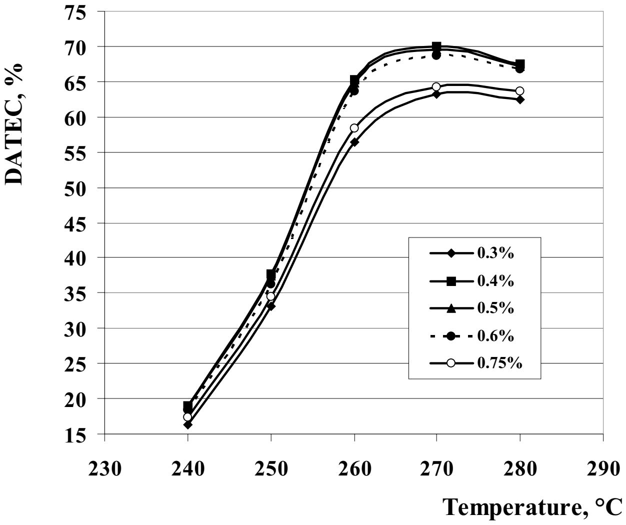


Figure 4. Degree of the approach of thermodynamical equilibrium concentration (DATEC) of 2,2-dimethylbutane as a function of temperature (Sulfur in feed: 23 ppm)

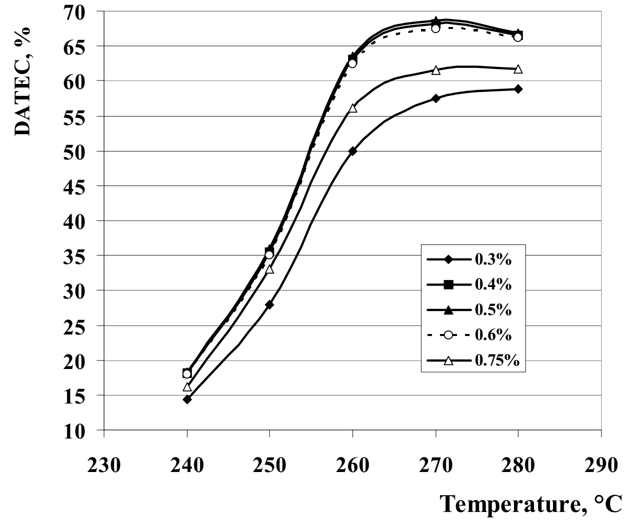


Figure 5. Degree of the approach of thermodynamical equilibrium concentration (DATEC) of 2,2-dimethylbutane as a function of temperature (Sulfur in feed: 47 ppm)

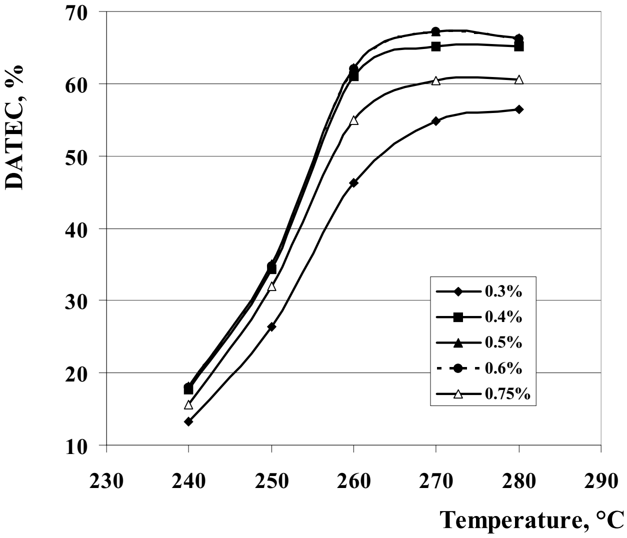


Figure 6. Degree of the approach of thermodynamical equilibrium concentration (DATEC) of 2,2-dimethylbutane as a function of temperature (Sulfur in feed: 76 ppm)

the decrease of yield above 270°C is partly that equilibrium concentration of 2,2-DMB is lower at higher temperatures partly hydrocracking of 2,2-DMB, formed under the heterogeneous catalytic circumstances is faster than that of other isohexanes and n-hexane.

The curve of yield is nearly linear in the temperature range of 200-260°C but above 260°C it is beginning to decrease exponentially. This statement is relevant, because decrements of 2,2-DMB concentration in the n-C_6 fraction are higher than those of the thermodynamical equilibrium concentrations at the individual temperatures. Besides, increments of the concentration of single branched isomers and n-hexane are nearly equal to the decrement of thermodynamical equilibrium concentrations. These arose from the higher equilibrium concentrations at increasing temperatures. (Change of the equilibrium concentration of 2,3-DMB in the investigated temperature range was so low that it was practically negligible.) Thus the selectivity of catalysts remained high at higher temperatures in case of single branched isomers and 2,3-DMB at higher temperature, but selectivity of 2,2-DMB decreased.

The reason of the mentioned change of opposite direction of n-hexane and different C_6-isoparaffins as a result of increasing temperature is that the net reaction heat of isomerization is exoterm. However, the reaction heat is different in case of individual C_6-isoparaffins at the investigated temperature range. Moreover, higher temperature is favourable to the formation of single branched isomers! Highest 2,2-DMB yields (and the highest C_6-isoparaffin yields considering the previous statements) were obtained at 260-270°C in the isomerization of all feeds:

- in case of feed containing <1ppm sulfur over catalyst of 0.3% platinum content
- in case of feed containing 23 ppm sulfur over catalyst of 0.4% platinum content
- in case of feed containing 47 ppm sulfur over catalyst of 0.5% platinum content and
- in case of feed containing 76 ppm sulfur over catalyst of 0.5% platinum content.

Figure 7 (catalyst of 0.4% platinum content, LHSV: 1.5 h^{-1}, pressure: 30 bar, H_2/HC= 2:1 molar ratio) shows for example the amount of C_1-C_4 hydrocarbons formed in secondary side reactions such as hydrocracking as a function of sulfur content of the feeds. Extent of hydrocracking increased with temperature. Therefore, a strong metal function prevails since higher sulfur content of the n-hexane fractions reduces formation of C_1-C_4 hydrocarbons caused by hydrocracking.

Table 4 contains the changes of the yields of liquid products. Yield data of the products obtained at 280°C are not presented, because the values of these were below 60% even in case of 3.0 h^{-1} LHSV. (Thus these results are not important from industrial point of view.)

During the isomerization of n-hexane hydrodesulfurization of several sulfur compounds took simultaneously place with high conversion (for example Figure 8 in case of feed containing 76 ppm sulfur) and high selectivity (Figure 7).

Fan shaped curves were obtained when the effect of platinum content of catalysts and of temperature were investigated for all n-hexane fractions having both low and high sulfur contents. Isomerates of lowest sulfur content (ca. 1-5 ppm) were produced at temperatures of 250-280°C on the catalyst having the highest platinum content. This means that strong metal

Table 4. Changes of the yields of liquid products

Property	Sulfur content of feed, ppm							
	<1		23		47		76	
Temperature, °C	240	270	240	270	240	270	240	270
Pt content of catalysts, %	0.3		0.4		0.4		0.5	
Yield of liquid products, %	99.4	91.9	99.5	94.2	99.5	95.1	99.6	96.4

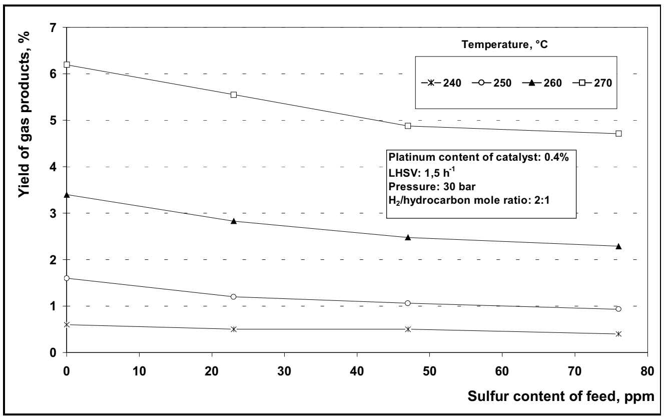


Figure 7. Changes of the yield of gas products (C_{4-}) vs. sulfur content of feeds

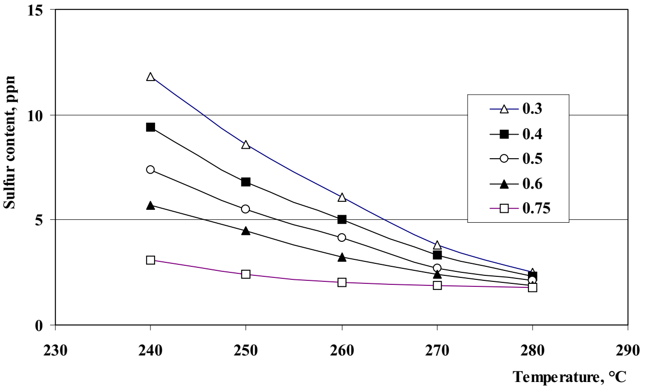


Figure 8. Changes of sulfur content in products as a function of temperature over catalysts of various platinum contents (Sulfur in feed: 76 ppm)

function prevails in deep desulfurization. Regarding the degree of desulfurization, similar tendencies were obtained with feeds of other sulfur content, too.

Summarizing the previously detailed evaluation we concluded that among the tested catalysts best results can be obtained with H-mordenite of 0.4-0.5% platinum content, considering isomerization, desulfurization and undesired hydrocracking of n-hexane feeds as a function of sulfur content of the feed.

In case of catalysts found to be favourable the relative low biases of DATEC values and the cost of the catalyst fundamentally depends on the platinum content, too, considering that catalysts containing 0.4 % platinum are the most appropriate for one step desulfurization and isomerization of n-hexane fractions containing less than ca. 76 ppm sulfur.

At the favourable combination of process parameters (260 and 270°C; 1.5 h^{-1} liquid hourly space velocity; 30 bar pressure; 2:1 hydrogen/hydrocarbon mole ratio) the exact properties of the products obtained on the mentioned catalyst (0.4% Pt content) are in table 5.

Table 5. Properties of the products (260 and 270°C, 30 bar, LHSV 1,5 h^{-1} and H_2/HC molar ratio=2, catalyst of 0.4%platinum content)

Characteristics of products	Sulfur content of feed, ppm							
	<1		23		47		76	
	Hõmérséklet, °C							
	260	270	260	270	260	270	260	270
Yield of liquid products (C_{5+}), %	96.6	93.8	97.2	94.4	97.5	95.1	97.8	95.3
DATEC of 2.2-DMB,%	67.4	70.1	65.3	69.6	63.0	68.2	61.0	65.5
Sulfur content, ppm	<1	<1	2	1	3	2	5	3.5

Using these feeds and changing the pressure from 30 to 40 bar there was no significant difference between the extent of desulfurization and isomerization.

Processing feeds of higher sulfur content the difference of the research octane numbers of the product and feed (ΔRON) decreased, using the mentioned catalyst and process parameters (Figure 9).

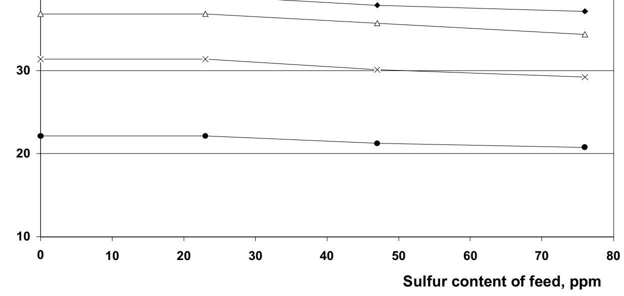


Figure 9. Change of the increase of product octane number (DRON) as a function of sulfur content of feed

The use of n-hexane fractions of 40-80 ppm sulfur content is typical in the refineries, applying liquid hourly space velocity (LHSV) of ca. 1.5 h^{-1} being also acceptable in industrial practice. ΔRON was approximately 34-36 units which is a remarkable octane gain. Assuming 98% separation of n-paraffins from isomerates, research octane number (RON) of the isoparaffin fraction is about 81.2-81.5, which can considered as excellent isomerization of n-hexane fractions (RON of the investigated n-hexane fractions was ca. 32). The motor octane number of the products is also excellent: between 33.8-34.9.

Results of desulfurization and isomerization experiments in two steps. During the desulfurization of fractions rich in n-hexane on the conventional CoMo/Al_2O_3 catalyst under relatively mild experimental conditions (temperature: 310-315°C; total pressure: 30-40 bar; LHSV: 2.5-4.0 h^{-1}; hydrogen/hydrocarbon ratio: 100-150 m^3/m^3) products containing less than 1 ppm sulfur can be obtained. During the isomerization of such a practically sulfur-free n-hexane fraction over catalysts of new generation (0.4-0.5% Pt content on H-mordenite) and under favourable process conditions (T: 260°C; LHSV: 1.5 h^{-1}), conversion of n-hexane to iso-hexanes increased by 1.2-6.7% (yield of isohexanes), while the DATEC values of 2,2-dimethylbutane increased from ca. 59-65% to 66.8-67.4%. In addition to this, the RON values of the isoparaffin products were only by ca. 0.1-1 points higher, depending on the sulfur content of the feeds (see Figures 3-9). The reason of these facts is that for lack of sulfur compounds hydrogenation-dehydrogenation reactions take place undisturbed on the metal sites of catalysts, thus these do not have negative effects on the reaction rate of isomerization. However, on the catalysts of new generation (0.4-0.5% Pt content) in case of feeds having the same sulfur content, applying the favourable process conditions, the attained results in respect of desulfurization and isomerization are better than those obtained on the conventional Pt/zeolite catalyst.

Conclusion

Pt/H-mordenite catalysts having appropriate composition and characteristics could be selected which were able to carry out isomerization and desulfurization of sulfur containing (up to ca. 100 ppm) n-hexane fractions in one step under well-chosen process conditions. An explanation for the high sulfur tolerance of the investigated catalysts might be that the acid sites of zeolite reduce the electron density of the supported platinum metal. Thereby the bonding strength between the platinum metal and sulfur is weakened. Among the tested catalysts the best results could be obtained with H-mordenite of 0.4-0.5% platinum content. Octane numbers of the gained products having sulfur content less than 10 ppm are slightly lower (ΔRON~<0.2-0.5) than those of the isomerates produced in two steps (desulfurization followed by separation and isomerization), concerning the effect of the different LHSVs. However, the investment cost of the previous solution is significantly lower, but the investment cost of the two step process can be lower, if the refinery has surplus capacities of desulfurization and distillation. Selection of the process from these two solutions can only be made with regard to the special possibilities of each refinery: for example capacity, available feeds and financial potential of the refinery. These isohexane fractions together with other usual blending components makes possible to blend engine gasoline of lower sulfur and benzene content, as well as increased isoparaffin content.

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