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Investigation of benzene and cycloparaffin containing hexane fractions skeletal isomerization on Pt/sulphated metal-oxide catalyst

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The most valuable components of gasoline are iso- and cycloparaffins, because their utilization leads to lower environmental and human biological risk, than aromatic and olefin hydrocarbons. Light naphtha fractions (C_5-C_7) of different type crudes contain different amount of benzene and cycloparaffins. In most case their separation is not economical, thus the quality improvement (desulphurization, benzene saturation, isomerization) of these components has to be carried out with the others. In case of high benzene concentration "two step process" (benzene saturation and isomerization) is recommended. Benzene and cycloparaffins can significantly modify the isomerization mechanism. Hence the aims of our experiments were to investigate the isomerization of binary and multicomponent feeds on Pt/sulphated metal-oxid ($Pt/SO_4^{2-}/MO_x$) in a large scale reactor system. During the experiments we studied the isomerization of binary and multicomponent mixtures and how they influenced each other's isomerization.
The process parameters were: 160-200 °C; 20-30 bar; LHSV:1.0-4.0 h^{-1} and H_2/hydrocarbon molar ratio 1.0:1.0-2.0:1.0. We concluded that the enhanced benzene and cycloparaffin concentration has disadvantageous effects on isomerization efficient, even the optimal process parameters were different at the investigated range depending on the applied feed. The stability and long term application of the investigated catalyst was confirmed.

1. Introduction

The requirements of engine gasolines are getting more and more stringent all over the world [Dixon-Decleve and Ward, 2007, Hancsók et al., 2008, Weyda and Köhler, 2003]. The demand for isoparaffin fractions is increasing constantly. They have low sulfur content and they are free from aromatics and olefins; besides, they have high octane number of low sensitivity and comprises of clean burning compounds [Hancsók et al., 2008, Weyda and Köhler, 2003]. The isomerization of light naphtha has the potential to satisfy these quality and quantity requirements. Therefore, isoparaffins and naphthenes are the most favourable gasoline blending components among the groups of hydrocarbon compounds. Availability of naphthenes is strongly limited in gasolines. Its

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amount mostly depends on the Nelson Index of the refineries and on the type and origin of the crude. Thus special process configurations and catalysts are to be applied ensuring saturation of benzene and skeletal isomerization of normal and cycloparaffins. The real, beneficial and energy efficient solution would be saturation of benzene and isomerization of normal and cycloparaffins in one processing step on the same catalyst [Hancsók et al., 2008, 2005, 1999]. Parallel to the isomerization reactions benzene hydrogenation to cyclohexane and its isomerisation to methyl-cyclopentane or even in ring opening reactions producing paraffin components can take place [Takemi and Hiromi, 2005]. Additionally, on highly acidic catalysts in case of similar carbon number the energy of adsorption of aromatic and naphthenic components is significantly higher than that of paraffin components. Their stronger adsorption to the active sites of the catalysts leads to the decrease of the skeletal isomerization of normal and monobranched paraffins. Articles have not been published with complete results about expediently enhanced benzene and cyclparaffin containing hexane fractions isomerization, and how they influenced each other's conversion. The focus of our investigation was to study isomerization and saturation of relatively high benzene and cycloparaffin containing hexane fraction, thus causing high octane number increment in one step. We investigated how the concentration of benzene and cycloparaffin concentration of the feed influences the successability of isomerization (reactions), and the yield and quality of the products versus applied process parameters on Pt/sulphated metal-oxide. The process parameters were: 160-200 °C; 20-30 bar; LHSV: 1.0-4.0 h^{-1} and H_2/hydrocarbon molar ratio 1.0:1.0-2.0:1.0. Within this range of parameters the values ensuring optimum composition were determined for all feeds having different benzene and cyloparaffin content.

2. Experimental

The objective of our research work was the isomerization of different benzene or cycloparaffin containing n-hexane fractions in a large scale reactor system in one step [Hancsók et al. 2008, 2005, 1999]. The long term experiments were carried out in continuous operation on Pt/sulfated metal-oxide catalyst having stable activity.

2.1 Apparatus

The isomerization experiments were carried out in an apparatus containing a tubular flow reactor (volume of the reactor: 200 cm^3) free of back-mixing and all the major equipments and accessories like in commercial scale isomerization plants. The reactor system has a gas pretreatment and controller system and an on-line gas chromatograph.

2.2 Feeds, materials

Feeds were analytical grade n-hexanes with different benzene (0.0-4.2%) and cycloparaffin (cyclohexane and methyl-cyclopentane) (0.0-50.4%) concentration. Linde 4A molecular sieve and blue silica gel was used as drying agents.

2.3 Test and calculation methods

The hydrocarbon compositions of the feeds and products were determined according to ASTM D 5134-98 standard, while the total sulphur and water content was measured according to EN ISO 20846:2003 and MSZ EN ISO 12937:2001. Octane numbers of feeds and products were calculated from GC datas.

From the great number of the results only the most important characteristics of those few products will be presented which were gained at favorable process conditions. Results were gained over catalyst of stable activity. In order to evaluate the efficiency of the isomerization the DATEC values (Data of the Approach to the Thermodynamic Equilibrium Concentration) were calculated according to equation (1). These values were calculated for 2,2-dimethyl butane, because the rate of formation of this compound is the lowest among hexane isomers.

$$DATEC_{2,2-DMB,T} = \frac{C_{2,2-DMB}}{C_{2,2-DMB;eq,T}} 100 \qquad (1)$$

Where:

$DATEC_{2,2\text{-}DMB,T}$: DATEC values calculated for 2,2-dimethyl butane at temperature T
$C_{2,2\text{-}DMB}$: concentration of 2,2-DMB in the C_6 alkane fraction
$C_{2,2\text{-}DMB;eq,T}$: thermodynamic equilibrium concentration of 2,2-DMB at temperature T

2.4 Operating conditions

Operating conditions of the tests carried out over catalyst reaching their steady-state activity at (<200 °C) temperatures. On the basis of preliminary experiments the cycloparaffin and benzene containing n-hexane fractions were investigated at temperatures of 160-200°C, total pressures of 20-30 bar, hydrogen to hydrocarbon (HC) molar ratios of 1.0:1.0-2.0:1.0 and liquid hourly space velocities (LHSV) of 1.0-4.0 h^{-1}. Within these ranges of parameters the values ensuring highest iso-, and cycloparaffin and very low benzene contents in the products were determined for different cycloparaffin and benzene contents in the feeds.

3. Results and discussion

Benzene and cycloparaffins significantly modified the isomerization mechanism. Parallel to the isomerization reactions benzene hydrogenation to cyclohexane and its isomerisation to methyl-cyclopentane or even ring opening reactions producing paraffin components can take place. Their stronger adsorption to the active sites of the catalyst leads to the decrease of the skeletal isomerization of normal and monobranched paraffins. Yield of liquid products increased with benzene content of the feeds, because benzene inhibits hydrocracking reactions. Benzene content of the products was less than 0.05% in every case, independently of its initial concentration (up to 4.2%) (Table 1.). Adsorption of benzene and cycloparaffins also inhibits the isomerization and this is the most significant for the slowest isomerization reaction. i.e. the formation of 2,2-dimethyl butane. Octane numbers of the products are high, compared to those of the feeds. The increase of octane number was very significant, approximately 19-32 units (liquid product-feed). In case of benzene containing hexane feed we concluded that the effect of octane number decrement of benzene in the investigated range was compensated on the one hand by inhibiting the isomerisation reactions (by its strong adsorption on platinum and by the partial cover of acidic sites) and on the other hand by the formation of cyclohexane from benzene (and its further isomerization to methyl-cyclopentane).

Table1: Summary of the most important results in case of benzene containing feeds

Main properties	**Benzene content of the feeds, %**								
	0.0	**0.29**		**0.56**		**1.20**		**2.14**	**4.12**
Process parameters									
Temperature, °C	195	195	200	195	200	195	200	195	195
LHSV, h^{-1}	3.0	2.0	4.0	2.0	3.0	2.0	3.0	2.0	2.0
Properties of the products									
Gas yield, %	6.9	6.6	6.7	3.9	2.9	3.5	3.1	3.5	3.6
Isobutane content of gas phase, %	38.2	48.9	42.4	34.2	40.7	37.6	41.2	45.5	68.5
Liquid yield, %	93.1	93.4	93.3	96.1	97.1	96.5	96.9	96.5	96.4
DATEC$_{2,2\text{-DMB}}$, %	79.1	18.7	12.4	8.0	6.3	7.0	6.0	6.8	5.6
RON	72.3	59.1	55.3	50.9	47.5	49.3	46.4	48.3	48.8
MON	72.6	58.7	55.1	50.8	47.6	49.3	46.6	48.3	48.7
ΔRON(Liquid product-feed)	40.0	32.3	28.6	23.9	20.6	22.1	19.2	20.3	19.0
ΔMON(Liquid product-feed)	41.3	30.9	27.3	22.8	19.6	21.1	18.3	19.5	18.3
Iso- and cycloparaffin yield, %	68.9	62.0	55.6	47.7	41.6	44.9	39.7	42.8	40.1
RON 100% efficiency of n-C$_6$ separation	82.8	80.5	80.0	79.6	79.4	79.4	79.4	79.6	80.1
MON 100% efficiency of n-C$_6$ separation	83.5	79.3	78.7	78.1	78.0	77.9	77.9	78.0	78.1

It was found that by increasing the benzene content of the feed from 0.0 to 4.2% the increment of RON decreases gradually. This is the result of two opposite effects:

- Proportionally less isoparaffin hydrocarbons are formed from n-hexane present in the benzene containing feed, since the isomerization is inhibited by the presence of benzene.
- Octane numbers of the mixtures of cyclohexane (formed from benzene) and methyl cyclopentane are higher than those of isoparaffin mixtures at the investigated reaction temperature. On the other hand the gained results in case of isomerization of benzene containing feeds show that saturation of benzene to cyclohexane then its isomerization to methyl-cyclopentane in equilibrium reaction is beneficial, but the ring open is undesirable, because the octane number of formed paraffin mixture is lower than that of the mixture of cycloparaffins at given temperature. The yield of the mixture of iso- and cycloparaffins obtained after separating n-paraffins with 100% efficiency was relatively high (~40-80%) (Table 1., 2.). These yields decrease with the benzene/cycloparaffin content of the feed. Benzene reduces the rate of isomerization to some extent but it is hydrogenated simultaneously to cyclohexane which isomerizes to methyl cyclopentane having high octane number. The RON of the mixtures of iso- and cycloparaffins are nearly the same for all products (79.4-82.5) and ΔRON~18-32. The most important results are summarized in Table 1. and 2. Under the experiments we observed that the quantity of the methyl-cyclopentane (MCP) over the equilibrium concentration is ineffectual because it isomerizes (in equilibrium reaction) to cyclohexane (CH) and decyclize to lower octane number hexane isomers (methyl-pentanes and n-hexane). On the other hand high amount of cycloparaffin decreases the conversion of n-hexane and methyl-pentanes, because they sorbe to active site of the catalyst and inhibit the formation of multibranched paraffins.

Table2: Summary of the most important results in case of cycloparaffin containing feeds

Main properties	**Cyclohexane and (Methyl-cyclopentane) content of the feeds, %**						
	0.00	**11.23**		**14.32 (13.92)**	**25.44**		**50.38**
Process parameters							
Temperature, °C	195	190	195	190	180	190	180
LHSV, h^{-1}	3.0	4.0	4.0	1.0	1.0	4.0	1.0
Properties of the products							
Gas yield, %	6.9	7.3	6.8	5.3	7.6	7.2	7.7
Isobutane content of gas phase, %	38.2	68.4	63.6	46.2	71.9	71.1	74.2
Liquid yield, %	93.1	92.7	93.2	94.7	92.4	92.8	92.3
$\text{DATEC}_{2,2\text{-DMB}}$, %	79.1	18.5	20.1	18.2	26.8	19.0	13.7
RON	72.3	61.8	66.7	67.4	70.4	66.3	79.5
MON	72.6	61.0	66.2	66.1	68.8	64.9	75.0
ΔRON(Liquid product-feed)	40.0	24.4	29.3	20.0	26.2	22.1	22.9
ΔMON(Liquid product-feed)	41.3	25.1	30.3	21.7	26.9	23.0	22.1
Iso- and cycloparaffin yield, %	68.9	55.4	65.2	66.6	69.2	62.9	79.9
RON 100% efficiency of n-C_6 separation	82.8	82.7	82.1	83.0	84.0	83.4	86.3
MON 100% efficiency of n-C_6 separation	83.5	82.1	81.7	81.6	82.1	81.8	81.4

So the cycloparaffins cause lower isoparaffin concentration and octane number, though the MCP (RVP: 29.1 kPa; RON:91.3) and CH (RVP:21.0 kPa; RON:84.0) are good gasoline blending components. The investigated $Pt/SO_4^{2-}/MO_x$ catalyst may be applied for the isomerization of relatively high benzene/cycloparaffin containing light naphtha fractions, though the concentration of MCP of the feed have to be kept low, because it is good blending component, and it is a disadvantageous component during the isomerization, because it causes lower octane number products and octane pool.

4. Conclusions

The investigated catalyst proved to be suitable for simultaneous saturation of benzene and isomerization of cycloparaffin containing light naphtha. Thus, a single-step process was successful for isomerization of n-hexane fractions containing benzene and/or cycloparaffin compounds. Process conditions were optimized considering the reaction rates, thermodynamic limitations and economic point of view. Benzene and cycloparaffin content in the feed reduced the rate of the isomerization of n-hexane. In case of benzene containing hexane feed we concluded that the effect of octane number decrement of benzene in the investigated range was compensated on the one hand by inhibiting the isomerisation reactions (by its strong adsorption on platinum and by the partial cover of acidic sites) and on the other hand by the formation of cyclohexane from benzene (and its further isomerization to methyl-cyclopentane). It is due to the fact that the octane number of C_6 cycloparaffin mixture is higher than that of the n-hexane and that of the mixture of n-hexane isomers (because n-hexane would have been present in spite of benzene). On the other hand the gained results in case of isomerization of benzene containing feeds show that saturation of benzene to cyclohexane then its isomerization to methyl-cyclopentane in equilibrium reaction is beneficial, but the ring open is undesirable, because the octane number of formed paraffin mixture is lower than the mixture of cycloparaffins at given temperature.

However, saturation of benzene proceeded with a significantly higher rate than isomerization. Under the selected reaction conditions saturation of benzene to cyclohexane proceeded completely, and isomerization of cyclohexane to high octane number methyl cyclopentane took place within the thermodynamic limitation but ring opening was avoided. Octane number of the products increased with more than 18-32 units, compared to those of the feeds. The results suggest that the catalyst seem to be suitable for hydrogenation of benzene and izomerization cycloparaffin containing n-hexane feeds in one step. The benzene-free products of low sulphur content (<10 ppm) are excellent gasoline blending components. Based on previous results we discovered that it is useful to determine the ratio of cyclohexane/methyl-cyclopentane in the feed in order that the concentration of cyclohexane (originally fed and the formed from benzene) is higher than the equilibrium concentration in the reaction mixture. In consequence part of cyclohexane (octane number: 86) isomerizes to higher octane number (91) methyl-cyclopentane. The measured and gained results may help to understand the isomerization results of mixed feeds containing several hydrocarbons of higher boiling point than n-hexane (e.g.: methyl-cyclopentane, cyclohexane, benzene or heptanes). Furthermore, these results can also contribute to develop more suitable catalysts.

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