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# Investigation of Isomerisation of Light Naphtha Fractions

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In our experimental work the transformability of C6 cycloparaffin components containing typically hydrocarbon mixtures with high n-paraffin and/or cycloparaffin concentration as well as industrial like light naphtha fractions convertible and the kinetic investigation of individual “key” hydrocarbons effect among and on each other in binary mixtures – applying parameters similar to industrial conditions – and also the further applicability of the results were studied.
Experiments were carried out on Pt/sulfated-zirconia catalyst at 150-200 °C temperature, 12-30 bar total pressure, 1:1-2:1 $H_2$-hydrocarbon molar ratio, 1.0-4.0 $h^{-1}$ liquid hourly space velocity in the laboratory scale reactor system for the kinetic investigation of individual hydrocarbons and binary mixtures. The reaction rate, reaction order and apparent activation energies of the individual hydrocarbons were studied as well as in its binary mixtures the change of the individual hydrocarbons reaction rate and the apparent activation energies. Isomerization of individual cycloparaffins and cycloparaffin rich light naphtha fraction was also studied.

## 1. Introduction

The quality requirements of modern engine gasoline have become stricter globally. These specifications simultaneously with the automotive developments contribute to the cleaner environment. In the new millennium the accomplished refinery investments with the stepwise reduction of the aromatic and sulphur content of naphtha fractions the octane yield decreased furthermore the octane number distribution of naphtha fractions/gasoline pool deteriorated versus the boiling range against increasing octane number requirements of the Otto-engines and other spark ignition drives (higher compression ratio→higher octane number requirement→higher efficiency and specific power→lower $CO_2$ and exhaust gas emission (Szoboszlai and Hancsók, 2011). But there was the opposite effect: the application of high octane number and oxygen containing blending components (alcohols, ethers) in engine gasoline. However these components change differently the physical and application properties of the gasoline depending on its blending concentration. So a renewable refinery structure and new focus contain the light naphtha isomerization and its possible feeds and favourable products.

## 2. Experimental

The main goal of our experimental work with different volatility C6 individual hydrocarbons and their different composition binary mixtures was the study of skeletal isomerization. The effect of the individual hydrocarbons on each other’s conversion/isomerization and the kinetic study of their isomerization in a large scale laboratory catalytic system on a stable activity catalyst were investigated. The isomerization of individual C6 cycloparaffins and different cycloparaffin containing light naphtha fractions (on stable activity catalyst) in approximately 800 h was also investigated. The reason for this

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was that the published results are rare or less discussed about the investigated catalyst and feedstock correlations and with the industrial conditions and systematically chosen parameter combinations. The investigation of detailed hydroisomerization of binary and multicomponent mixtures can significantly contribute to the understanding of the multicomponent sources, like higher boiling point hydrocarbons than n-hexane containing feedstocks isomerization results and through these to more effective/economical and safety conversion.

### 2.1 Apparatus

The experiments were carried out in 100 $cm^3$ free volume, vertical, high pressure, tubular reactor containing apparatus (Hancsók et al., 2007). This apparatus contains all the equipment which can be found in an industrial isomerization unit. The experimental apparatus also contains a gas preparation and regulator unit and a directly connected on-line gas chromatograph.

### 2.2 Catalyst

The applied catalyst was 0.42 % platinum containing sulphated-zirconia. The main properties of the catalyst are shown in Table 1.

*Table 1: Main properties of the applied $Pt/SO_4^{2-}/ZrO_2$ catalyst*

| Properties | Values |
|---|---|
| Pt-content, % | 0.42 |
| Pt-dispersion, % | 69 |
| Total acidity, mmol$NH_3$/g | 0.56 |
| BET surface, $m^2$/g | 130 |
| Microporosus surface, $m^2$/g | 12.2 |
| Micropore volume $cm^3$/g | 0.0045 |
| Mezopore volume, $cm^3$/g | 0.2874 |
| Mezo-/micropore volume ratio | 63.9 |
| Avarage pore size, nm(Å) | 8.5(85) |

*Table 2: Main properties of the applied hexane fractions*

| | Properties | Feeds | | | |
|---|---|---|---|---|---|
| | | "A" | "B" | "C" | "D" |
| Composition % | $\Sigma C_{5-}$ | <0.05 | <0.05 | <0.05 | <0.05 |
| | 2,2-DMB | <0.05 | <0.05 | <0.05 | <0.05 |
| | 2,3-DMB | <0.05 | <0.05 | <0.05 | <0.05 |
| | 2-MP | 0.54 | 0.9 | 0.65 | 0.95 |
| | 3-MP | 2.52 | 1.95 | 1.73 | 1.19 |
| | n-$C_6$ | 68.71 | 85.55 | 70.77 | 47.40 |
| | Me-c-$C_5$/MCP | 13.92 | <0.05 | <0.05 | <0.05 |
| | Benzene | <0.05 | <0.05 | <0.05 | <0.05 |
| | c-$C_6$/CH | 14.32 | 11.23 | 25.44 | 50.38 |
| | $C_{7+}$ | <0.05 | <0.05 | <0.05 | <0.05 |
| | Sulphur content, mg/kg | <1 | <1 | <1 | <1 |
| | RON | 47.4 | 37.4 | 44.2 | 56.6 |
| | MON | 44.4 | 35.9 | 41.9 | 52.9 |

### 2.3 Feedstocks, materials

The (loaded) catalyst volume in the reactor was 60 $cm^3$, the free volume of the reactor was loaded with inert, ceramic Raschig rings. Analytical grade (99.5%, sulphur free) n-hexane, cyclohexane, methylcyclopentane was used as feedstock for the kinetic studies and measurements. Moreover, we investigated the isomerization of industrial like fractions with different cycloparaffin content. The continuous demoisturizing of the sulphur free feedstocks with Linde 4A molecular sieve was ensured.

### 2.4 Analytical and calculation methods

Standard test methods were applied. The platinum content of the catalyst was determined according to UOP-274. BET surface and acidity of the catalysts by $NH_3$ chemisorptions while pore volume and pore size distribution was determined by mercury penetration. Feedstock and product composition was determined according to ASTM D5134. The total sulphur and moisture content of the feedstock was periodically checked and determined according to EN ISO 20846:2003 and MSZ EN ISO 12937:2001.

### 2.5 Process parameters

The catalyst was dried and activated before the measurements. Each point of the experiments and measurements were carried out on stable/constant activity catalysts (on the actual adjusted reaction conditions) confirmed by multiple sampling (4-6 times). Based on the preliminary results the series of experiments were carried out in 150-200 °C temperature range, 12-30 bar total pressure, 1.0-4.0 $h^{-1}$

liquid hourly space velocity and 1.0:1.0-2.0:1.0 $H_2$-hydrocarbon molar ratio. Under the kinetic studies we tried to find those reaction parameters where there were no side reactions or their rate and selectivity were not significant compared to the main isomerization reaction (150-170 °C) of the investigated hydrocarbons and product inhibition did not occur.

## 3. Results and discussion

In case of low temperature the conversion isotherms showed as a function of space times resulted lines, but at higher temperatures and high conversion rates they resulted curves. The n-C6 and cyclohexane apparent activation energy values were determined from the total conversion by the temperature dependence of the reaction rate (Table 4). These values correlated well with the published values, which were determined with partly different catalytic systems (Holló et al., 2002). In case of n-hexane and cyclohexane we determined the space time and the partial pressure of hydrocarbon dependence on the conversion/reaction rate; in addition we investigated the reaction rate of the hydrocarbon function of the hydrogen partial pressure. The alkane conversion rate was also investigated respectively determined in 2-10 bar alkane partial pressure range with constant hydrogen partial pressure (10 bar) as well as in 5-20 bar hydrogen partial pressure range with constant alkane pressure (10 bar). The reaction temperature was 150-160 °C. The logarithmic values represented a linear relationship. The slopes of the lines gave the reaction orders of the variable pressure component. The reaction orders including the alkanes and hydrogen were determined (Table 3.). The n-hexane and cyclohexane conversion was increased as a function of their partial pressure at constant hydrogen partial pressure, temperature and contact/residence time (Figure 1.). The slopes of the lines indicated that the reaction order in these reaction conditions was between 0 and 1. The exact determination of the reaction rate of hydrocarbons in the logarithmic reaction rate as a function of the logarithmic partial pressure is shown in Figure 2. The slopes of the lines and so the reaction orders in case of n-hexane and cyclohexane was 0.34 and 0.24 respectively. Increasing the hydrogen partial pressure clearly inhibits the reaction rate of isomerization. Based on the slopes of the lines (Figure 3.) the reaction orders were -0.66 and -0.40 respectively. Based on the experimental results and the derived values we concluded that the investigated hydrocarbon partial pressure increased, while the hydrogen partial pressure decreased the reaction rate of isomerization.

*Table 3: Conversion (reactions) of n-hexane and cyclohexane on Pt/$SO_4^{2-}$/$ZrO_2$ catalyst (Temperature: 150°C, hydrocarbon partial pressure 10 bar; hydrogen partial pressure10 bar)*

| Description | n-$C_6$ | c-$C_6$ |
|---|---|---|
| Space time, W/F ($10^5 g_{cat}$.s/mol) | 3.55 | 3.21 |
| Total conversion, % | 5.7 | 22.7 |
| Isomerization selectivity, % | 100 | 99.5 |
| Ring opening selectivity, % | - | 0.4 |
| Cracking selectivity, % | 0.0 | 0.1 |

From the n-hexane and cyclohexane the latter was a more reactive component in similar reaction conditions (e.g. 150 °C see Table 3.). It was isomerised to methylcyclopentane primarily. Especially the n-hexane was isomerised to C6 monobranched isoalkanes; very small amounts of 7 or 8 carbon number cyclic hydrocarbons (dimethyl-cyclopentanes and methyl- and dimethyl-cyclohexanes) also formed.

In case of n-hexane the presence of propane from the formed cracking products had the highest concentration, because this component mainly formed in the cracking reactions of isohexanes. However, in cyclohexane conversion the isobutene was the main cracking product, which can be formed from a C12 intermediate product, because the ethane quantity and molar ratio compared to isobutane is much lower. We previously mentioned that in the topic of isomerization of binary mixtures relatively few data are available on this type of catalyst in the scientific literature. Therefore our further aim was to study and detect n-hexane/cyclohexane mixtures on a Pt/sulphated-zirconia catalyst. The aim was to investigate the isomerization of one component, and how it affects the isomerization of the other component in binary mixtures compared to the previously determined kinetic data and results of individual hydrocarbons. Over the kinetic investigation the objective was to study the transformability of light naphtha fractions with different composition as well as on the basis of our kinetic results compared to the results of what correlations are shown on high conversions results.

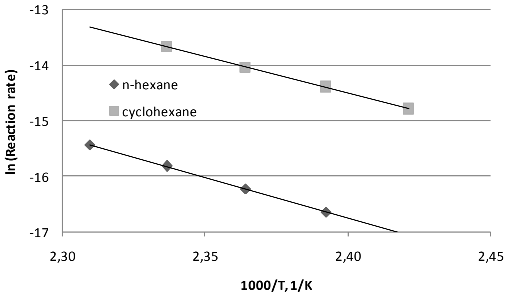

*Figure 1: Reaction rate of n-hexane and cyclohexane versus temperature (Arrhenius plot) (P: 20 bar, $H_2$/HC molar ratio: 1.0)*

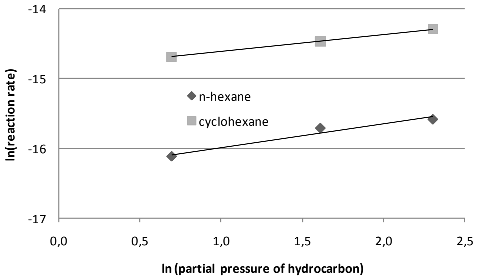

*Figure 2: Reaction rate of n-hexane and cyclohexane versus partial pressure (P: 12-20 bar, $p_{CH}$: 2-10 bar, $p_{H2}$: áll., 10 bar, W/$F_{CH}$: Table 3, T: 150°C)*

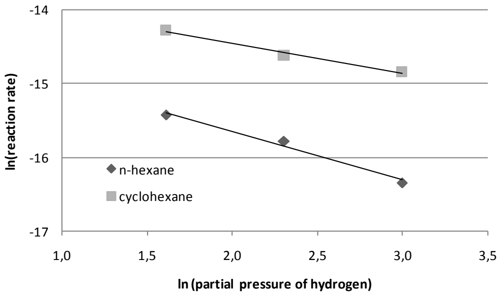

*Figure 3: Reaction rate of n-hexane and cyclohexane versus hydrogen partial pressure (P: 15-30 bar, $p_{CH}$: áll. 10bar, $p_{H2}$: 5-20 bar, W/$F_{CH}$: Table 3., T: 150°C)*

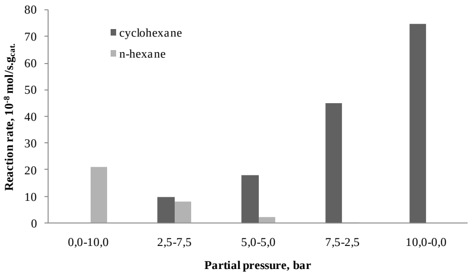

*Figure 4: Change of reaction rates in different composition n-hexane/cyclohexan biner mixtures (T: 150°C, Hydrogen pressure = 10 bar)*

*Table 4: Kinetic parameters of hydroisomerization of n-hexane and cyclohexane*

| Description | n-$C_6$ | c-$C_6$ |
|---|---|---|
| Apparent activation energy, experimentally determined, kJ/mol | 122 | 113 |
| Apparent activation energy, (Holló et al., 2002), kJ/mol | 120, 121 | 100-148 |
| Reaction order of alkane | 0.34 | 0.24 |
| Reaction order of hydrogen | -0.66 | -0.40 |

We concluded that in the binary mixture the individual component's conversion rate was lower than in itself. The determined reaction rates in case of both components decreased the other with increasing the concentrations. The isomerization rate of higher volatility (lower boiling point) components was decreased by the lower volatility (higher boiling point) at a higher rate than inversely. For the confirmation of the abovementioned we systematically investigated the individual component's partial pressure effect in binary mixtures. During this we changed the partial pressures of the individual components in binary mixtures. At 150 °C temperature and 10 bar $H_2$ partial pressure the results clearly confirmed that the higher adsorption ability component (cyclohexane) reaction rate reducing effect is higher on the lower adsorption component (n-hexane) (Figure 4.).

*Table 5: Apparent activation energies of n-hexane and cyclohexane in different composition binary mixtures in hydroisomerization reaction (P: 20 bar, $pH_2$: 10 bar, T: 150-165°C)*

| n-Hexane content, % | 0.0 | 49.4 | 74.5 | 88.6 | 99.8 |
|---|---|---|---|---|---|
| Cycohexane content, % | 99.8 | 50.4 | 25.4 | 11.2 | 0.0 |
| $E_{a,n\text{-hexane}}$, kJ/mol | - | 133 | 128 | 123 | 122 |
| $E_{a,cyclohexane}$, kJ/mol | 113 | 123 | 129 | 136 | - |

So the stronger adsorption component reaction rate was dominant thereby the conversion was also higher. In case of the binary mixtures based on the experimental results gained from several temperatures the represented reaction rates and further the slopes of the lines determined the apparent activation energies (similarly as on Figure 1.) of the components in the different composition binary mixtures (Table 5.). Based on these results we concluded that the presence one of the components increased the apparent activation energies of the other component. If one of the components was in a higher concentration the increment of the activation energy of the other component was higher because for the active sites of the catalyst the reaction components are competitive with each other in the binary mixtures. Therefore apparently it reduced the number of active sites so deteriorated the catalyst activity for the particular component.

Through the isomerization experiments of the individual C6 cycloparaffins and their 50-50 % mixture we observed that with the rising of the temperature the gas product yield exponentially increased, it reached 10-12 % at 195-200 °C, 20 bar total pressure and 3.0 $h^{-1}$ LHSV. We analyzed the gas composition and we concluded that at any measuring point the isobutene content was dominant and its quantity was about 70-85%, while a significant amount of propane, n-butane and isopentane was presented. Based on these results we concluded that the skeletal isomerization of the cycloparaffins was bimolecular so it took place through the C12 intermediate, and a high quantity of isobutene can be formed in the cracking reaction of this molecule. We analyzed the liquid product composition and we concluded that at low reaction temperatures (160-180 °C) more MCP was converted to cyclohexane than inversely, but the concentration of the formed hexane isomers was higher in case of MCP feedstock. The rising of the temperature and the increase of the residence time increased the quantity of hexane isomers in the liquid products, but their quantity was not too significant in case of the most strict parameter combinations, it was about 5.5-6.0 %. Among the hexane isomers firstly the n-hexane was identified in case of the isomerization of MCP, after that, interestingly, in case of the isomerization of cyclohexane the first open chain molecule was the 2-MP, when in the product mixture the degree approach of the thermodynamic equilibrium concentration of MCP was about 65-75% that was supposedly formed from the ring opening of MCP. Later, with stricter parameters, after the n-hexane and 2-MP the 3-MP also appeared in the product mixture, even at 195-200 °C temperature, these mono branched isomers were further isomerized to 2,3-DMB, but 2.2-DMB was analyzed in none of the samples. The ratio of 2-MP/3-MP at 190-200 °C changed between 1.95 and 2.05 independently from the other applied parameters. Our further investigations with different cycloparaffin containing hexane fractions ("A"-"D") also concluded that the yields of the gas product significantly increased due to the stricter parameters but in 190 - 200 °C temperature range they were very high, between 12-25 %. The higher cyclohexane content in case of "B"-"D" feedstocks made this value higher, while feeding the "A" feedstock in nearly equilibrium concentration the values were much lower, 5.5 - 12.0 %. Based on these results not only their concentration and higher adsorption ability but the concentration ratios of MCP and CH as well as the different reaction mechanisms affected the composition of the produced mixture in this catalytic system. In case of comparing "A" and "C" feedstocks the yields and compositions of the gas products, clearly more gas products formed from the "C" feedstock and its isobutene concentration was higher. We analyzed the liquid product composition and we concluded that with stricter parameters the isoparaffins concentration increased, but the cycloparaffin concentrations were decreased. At 160 °C we observed that in case of every feedstock the cycloparaffin concentration significantly decreased (20-40 %), and with the reduction of the LHSV-s the ratio of decrement was lower. We clearly observed that in case of the isomerization of every feedstock the n-hexane concentration was significantly higher. That increment comparable the cyclohexane quantity decrement in the liquid products suggested that the cyclohexane ring opening is significant at this temperature, while the concentration of MCP in the liquid product was about 1-3 %. At high temperatures (190 - 200 °C) the quantity of cycloparaffins also significantly decreased with about 40 - 55 % and the quantity of these components decreased in the liquid products. N-hexane and its branched isomers were formed only at higher temperatures with a high concentration which gives good correlation with the fact that cycloparaffin isomerization reactions are dominant in the mixtures even in case of their low concentrations. The isomers of n-hexane in the gained liquid products were the 2-MP, 3-MP and 2,3-DMB components, and their thermodynamic equilibrium concentration approached more than 95 % in case of the most strict applied parameters. The degree of the approach of the equilibrium concentration of the 2,2-DMB component just about 35 – 45 % that can also be a reason that the other hexane isomer can be formed through cyclopropane ring closing and opening route, but the quaternary carbon formation needs higher activation energy or it can be formed through the bigger (bi)molecule, but the structure and physical-chemical characteristics of the catalyst do not support it.

## 4. Summary

In our experimental work we investigated the hydroisomerization of n-hexane and cyclohexane and its kinetic correlation as well as their binary mixtures. During this were based on the measured and calculated results we concluded that with increasing the partial pressure of individual components positive effect on conversion was experienced while the increasing hydrogen partial pressure inhibited the isomerization reactions. Reaction rate of cyclohexane was multiple than n-hexane despite of their not too much difference in apparent activation energy. Reaction rate of cyclohexane in binary mixtures decreased but the differences in reaction rates were much higher than observed in itself. The cyclohexane and methylcyclopentane in low concentration in hydrocarbon mixtures significantly reduced the conversion (isomerization) rate of the other lower boiling point components. This adversely affects the isomerization degree of high n-paraffin content mixture s (feedstocks). In case of of cycloparaffins on higher tempreture (160-200 °C) by itself and in 50-50% binary mixture isomerization found that the gas phase primarily content isobutene that suggest bimolecular isomerization of cycloparaffins. In addition, we concluded that by itself and also in the investigated mixture the methylcyclopentane ring opening the typical and higher degree reaction (than cyclohexane). However in case of the investigated hexane fractions we concluded that the cyclohexane (RON: 86) ring opening degree is very significant which adversely affect the available octane number because mostly the n-hexane (RON: 25) is formed. In all case of the investigated hexane fractions the decrement of the cycloparaffin yield was remarkable. The gas yield was more significant parallel the increasing cycloparaffin content of the mixtures and with the strictening the parameter combinations. So the conclusion is that the presence of cycloparaffins adversely affected – beyond others - the available yields of liquids, iso- and cycloparaffins, thereby the available octane number as well as the octane mass (yield of iso- and cycloparaffins) based on the non-kinetic results was also confirmed. Important to note that the octane number of the equilibrium composition of cycloparaffin mixture (cyclohexane-methylcyclopentane) is higher than the n-hexane and its isomers octane number on this investigated temperature range. So the investigated catalytic system in one stage was limited to the simultaneously isomerization of high cycloparaffin containing hexane fractions. The gained results are very important because these cycloparaffins in also be formed in the hydrogenation of benzene and benzene containing naphtha fractions which is very important because of the further reduction of benzene content of gasoline in the near future.

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