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ISOMERIZATION OF *n*-HEXANE ON Pt/SO₄-ZrO₂ CATALYST

Abstract

C5/C6 hydrocarbon isomerization is a mild reforming process, which is used to obtain gasoline with high octane number. Zirconium sulfate catalyst is a representative of a new generation of catalysts in the isomerization process, which has properties of high efficiency and is environmentally more acceptable than the current commercial chlorinated aluminum oxide.

*In order to study isomerization process on the zirconium sulfate catalyst (Pt/SO₄-ZrO₂), laboratory apparatus for the isomerization process of light hydrocarbons in the presence of hydrogen is designed. By conducting a series of experiments and analysis of five key components: *n*-hexane, 2-methylpentane, 3-methylpentane and 2,2- and 2,3-dimethylbutanes, as well as cracking products, the impact of temperature and space velocity on the product composition of the isomerization process of *n*-hexane on zirconium-sulfate catalyst is described and explained. Obtained results show *n*-hexane conversion increase with the temperature increase and space velocity decrease in the investigated range of values, but is accompanied with the unwanted cracking reactions increase.*

1. Introduction

The quality of automotive fuels in the European market is based on standards prepared by the European Committee for Standardization CEN (Comité Européen de Normalisation), and represents the minimum requirements that were accepted and referred to in the oil and automotive industries. Requirements for the quality of motor fuels, which are related to sulfur, olefins, aromatics and vapor pressure, and considering the amount of volatile hydrocarbons, are increasingly stringent due to, increased global environmental concerns. As a solution to achieve the required quality of fuel, motor fuels treatment processes are imposed, which increase product quality and reduce harmful impacts on environment, as well as on the motor itself. The process of hydrocarbons isomerization is an efficient and economically acceptable way of increasing the octane number of motor gasoline, and gasoline isomerizate represents an ideal product that can satisfy the most stringent environmental requirements¹.

2. Isomerization process

With C5/C6 isomerization process low octane straight-chained *n*-pentane is converted into a high-octane *iso*-pentane, while hexanes with relatively straight chains are converted into branched forms with double-side chains. Isomerization reactions are slightly exothermic reversible reactions, limited with thermodynamic equilibrium. Isomerization reactions of *n*-pentane are very quick, and share of isopentane in isomerate is directly related to the balance of *n* / *iso*-pentane. Since the hexane isomerization reaction is slower than *n*-pentane, hexane conversion is taken as a measure for monitoring and process control. This refers to the optimum thermodynamic equilibrium shifted towards the higher proportion of iso-compounds in isomerate. With isomerization of *n*-hexane four forms of *iso*-hexane can be produced: 2-methylpentane (2 MP), 3-methylpentane (3 MP), 2,3-dimethylbutane (2,3 DMB) and 2,2-dimethylbutane (2,2 DMB)². Differences in molecular structure between *n*-alkanes and their isomers are the cause of differences in the chemical and physical properties. The consequence is higher resistance of iso-compounds to detonation in the cylinder of Otto-type internal combustion engines, respectively higher octane number compared to the straight chain alkanes. Therefore, the preferred compounds in the motor fuels are isomers like *iso*-pentane, 2,2 DMB and 2,3 DMB which have up to 80 units higher-octane value than their paraffin forms.

C5/C6 isomerization reactions are conducted in a layer of catalyst in the presence of hydrogen. Isomerization process uses a catalyst that is active at lower temperatures, at which thermodynamic equilibrium favors the creation of alkanes with side chains. Catalysts which are used in the C5/C6 isomerization process are chlorinated aluminum oxide (Pt/Al₂O₃-CCl₄), zeolite catalysts (Pt/zeolite) and recently zirconium sulfate on platinum (Pt/SO₄-ZrO₂)³. Isomerization mechanism on all of this catalyst is bifunctional catalysts mechanism on metal and acid center. The available technologies for the isomerization process of light gasoline can be compared on the basis of performance, the octane number of the product and operation cost. Processes based on zirconia-sulfate catalysts have the lowest price with a much larger effect than zeolite catalyst. However, this effect is slightly smaller than that obtained in the process with chlorinated aluminum catalyst. Process efficiency can be increased with the recirculation of the low octane product back to the isomerization process. Currently, the highest efficiency has the process with Pt/Al₂O₃-CCl₄, with recirculation of the product with deisohexanizer (DIH). Modern zirconia-sulfate catalysts achieve performance similar to that of Pt/Al₂O₃-CCl₄, with the price that falls in the category of the process in the presence of Pt/zeolite catalysts. Zirconium sulphate catalyst has a considerably higher activity than zeolite catalyst, but it is still somewhat lower than the activity of the Pt/Al₂O₃-CCl₄. On the other hand, zirconia-sulfate catalysts have the possibility of easy regeneration and high resistance to catalyst poisons. In addition, zeolite and zirconia-sulfate catalysts require a higher ratio of hydrogen toward hydrocarbons; therefore, such processes require the compressor for recirculation of hydrogen back in the process⁴.

2.1 Distribution of products of the isomerization process

According to the bifunctional catalysis mechanism 2,3 DMB is formed in steps over methylpentane, with simultaneous creation of 2,2 DMB (Fig. 1).

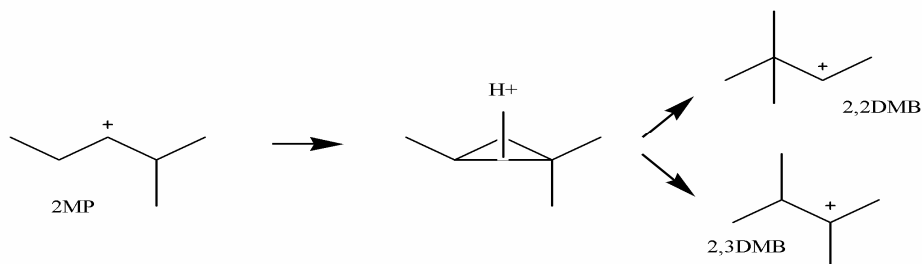


Figure 1: Formation of 2,3 DMB and 2,2 DMB

2,2 DMB formation is the slowest isomerization reactions, because it involves creation of a secondary carbocations⁵. 2,3 DMB involves the creation of a tertial carbocations which is much more favorable from the energy point of view. Since 2 MP and 3 MP are created with a similar mechanism (Fig. 2), they emerge with similar speed and are created in similar amounts.

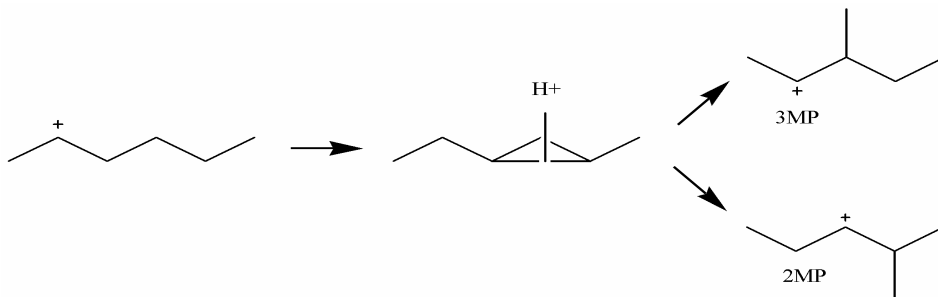


Figure 2: Formation of 2 MP and 3 MP

The described mechanism of 2 MP and 3 MP is present in cases of low conversion. As conversion increases, the ratio between the 2 MP and 3 MP approaches thermodynamic equilibrium due to rapid isomerization reactions with methyl groups' shift, as shown in Fig. 3.

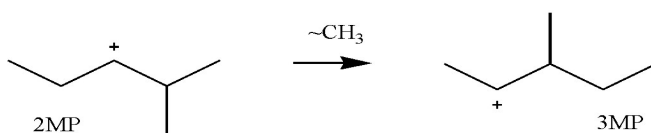


Figure 3: Formation of 3 MP from 2 MP

2.2 Cracking reactions in isomerization process

Isomerization of *n*-alkanes on acid and bifunctional catalysts is accompanied by cracking reactions. C-C bond opening occurs when it is in the β -position in relation to the positively charged carbocation. This mechanism is known by the name β -splitting. Weitkamp et al.⁶ classify the basic principles of β -splitting based on the type of splitted and generated carbocation. It is proved that the isomerization reaction of *n*-hexane on sulfate zirconia/platinum catalysts are always accompanied by hydrocracking reactions, while reactions of hydrogen addition on the single C-C bond are not noticed⁷.

3. Experimental

3.1 Materials

The feed for the C5/C6 isomerization process was 99.5% *n*-hexane (Sigma-Aldrich). Carrier gas used in all experiments was 99.99% hydrogen (Messer). The catalyst used in the isomerization process is the commercial zirconia-sulfate on platinum catalyst.

3.2 Apparatus

Apparatus for the implementation of experiments on the continuous process of isomerization in a catalyst bed in the presence of hydrogen (Fig. 4) was designed at the Petroleum and Petrochemical Department, Faculty of Chemical Engineering and Technology. The apparatus consists of a hydrogen system, systems for feed drying, dosing pumps, tubular reactor with outlet cooler, slop vessel and a high pressure separator. The program allows programming of experiments, monitoring and acquisition of all measured and calculated data.

Feed from the feed tank (1) continuously circulates through the column filled with the silica gel granules (2). In this way, all the water from feed is removed prior to its entry into the reactor; which is constantly monitored on the exit position from the feed tank with moisture sensor. Hydrogen and feed are heated in the preheater (3) and then introduced into the reactor (4) with the 61,5 cm³ volume with 10 cm³ of the catalyst, where the isomerization reactions take place. After isomerization process, gaseous mixture from the reactor goes to the high pressure separator (6) where is cooled, sampled and analyzed on the gas chromatograph GC-2010 Shimadzu with FID detector. Before the beginning of the experiment catalyst has been activated by the manufactures recommendations. The first step of the isomerization is starting of hydrogen flow through the apparatus, than we can begin with the preheater and reactor heating in determined steps. When reactor temperature reaches 100 °C feed flow through apparatus is started, and reactor heating can be continued till we reach the desired temperature. After reaching the given values of process parameters, process is stabilized during the period of 4 hours, after which liquid sample can be taken and analyzed. Time period between sampling and analysis is reduced to minimum achievable value, so the sample composition change does not occur.

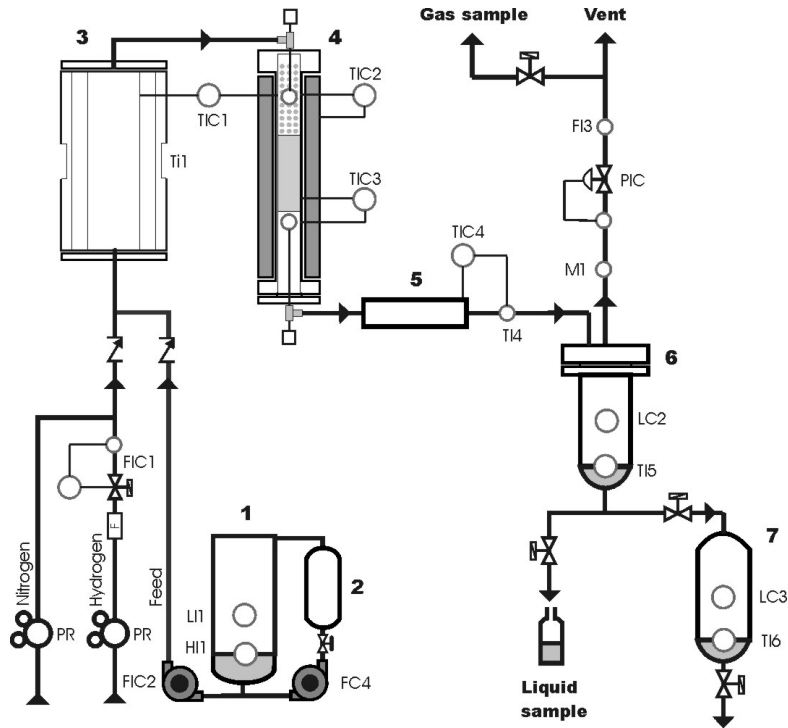


Figure 4: Isomerization apparatus:

(1) feed tank, (2) adsorption column, (3) preheater, (4) reactor, (5) cooler, (6) high pressure separator, (7) slop vessel

4. Results and discussion

Conversion of *n*-hexane was calculated according to equation:

$$X(nC_6) = 100 \times \frac{(nC_6)_{in} - (nC_6)_{out}}{(nC_6)_{in}} \quad (1)$$

Investigated range of values of process parameters influence on the composition of the isomerization products was selected based on preliminary research, and attempted to cover the area of standard conditions in the refinery application process isomerization on zirconia sulfate catalysts. This is especially relevant to the temperature, which is about 160 °C in refinery process. Influence of catalyst bed temperature of 160 °C ± 10 °C on *n*-hexane conversion and distribution of isomers in isomerizate-gasoline was investigated, at constant values of hydrogen to hydrocarbon ratio ($H_2/HC = 3$) and pressure of 25 bar.

It is evident from the results shown in Fig. 5 that hexane conversion increases with temperature increase of 10 °C by an average of 15-20 wt.%. Increasing space velocity (LHSV, Liquid Hourly Space Velocity, expressed as a feed flow through the layer of catalyst per hour) also means reducing the contact time between feed and catalyst, and results in lower hexane conversion. The highest conversions was 63 wt.% obtained at 170 °C and LHSV values of 1 h⁻¹, while at the same LHSV values at the temperature of 160 °C the conversion was 49 wt.%. At 150 °C conversion was lowest, only 30 wt.%, whereas with a further increase in LHSV values above 9 h⁻¹ product contained no isomeric compounds, which means that feed hasn't been enough time in contact with catalyst and isomerization reactions didn't occurred.

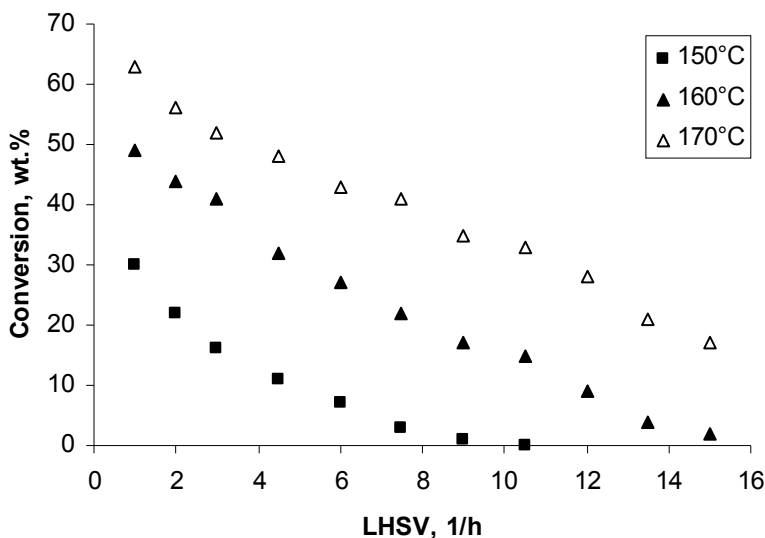


Figure 5: Effect of space velocity (LHSV) on n-hexane conversion with Pt/SO₄-ZrO₂ catalyst at different temperatures of 150 °C, 160 °C and 170 °C

Isomer that is produced in highest quantities was 2 MP and makes about 50 wt.% of the total occurred isomers. Share of 2 MP in the product at 160 °C and 170 °C and low values of LHSV was about 25 wt.% (Fig. 6). 3 MP occurs in somewhat smaller amounts, and makes about 35 wt.% of the total amount of isomers formed. Highest conversion to 3 MP was obtained at 170 °C and low LHSV in the amount of 17 wt.% in the product (Fig. 7).

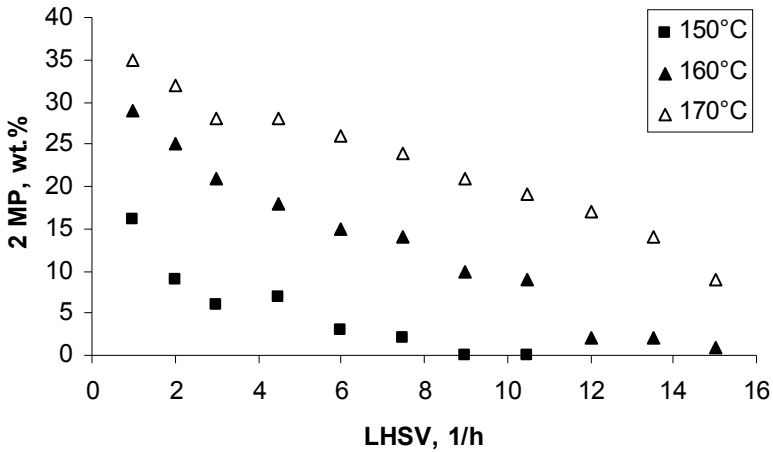


Figure 6: Effect of space velocity (LHSV) on the content of 2 methyl pentane (2 MP) in the product of *n*-hexane isomerization with Pt/SO₄-ZrO₂ catalyst at different temperatures of 150 °C, 160 °C and 170 °C

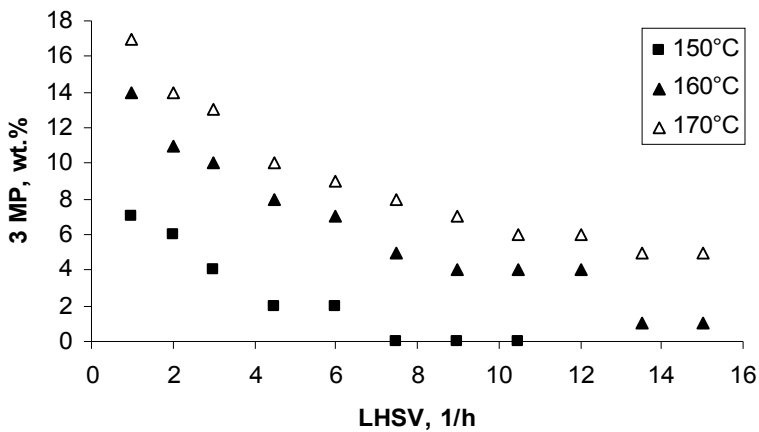


Figure 7: Effect of space velocity (LHSV) on the content of 3-methyl pentane (3 MP) in the product of *n*-hexane isomerization with Pt/SO₄-ZrO₂ catalyst at different temperatures of 150 °C, 160 °C and 170 °C

Compounds 2,2 and 2,3 DMB, which largely contribute to octane number value, are created in the smallest quantities, making a total of less than 15 wt.% of the total amount of isomers formed. As shown in Figs. 8 and 9 hexane conversion to these compounds does not change significantly with temperature increase, and comprise about 5 wt.% of the product. Smaller amounts of these compounds are found in product at higher LHSV values.

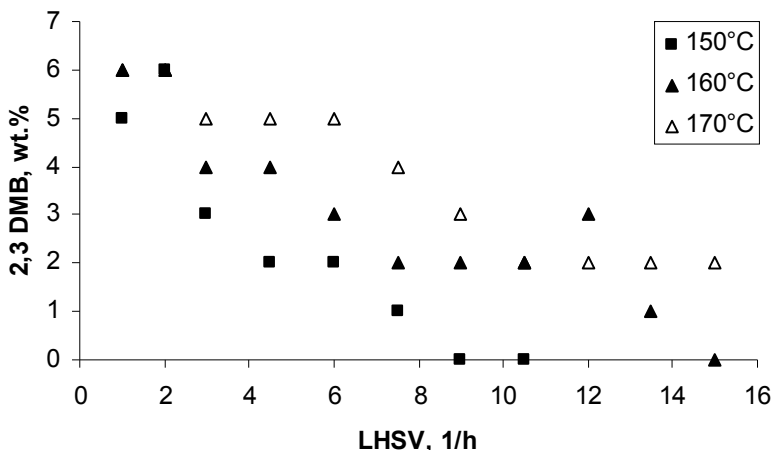


Figure 8: Effect of space velocity (LHSV) on the content of 2,3 dimethyl butane (2,3 DMB) in the product of *n*-hexane isomerization with Pt/SO₄-ZrO₂ catalyst at different temperatures of 150 °C, 160 °C and 170 °C

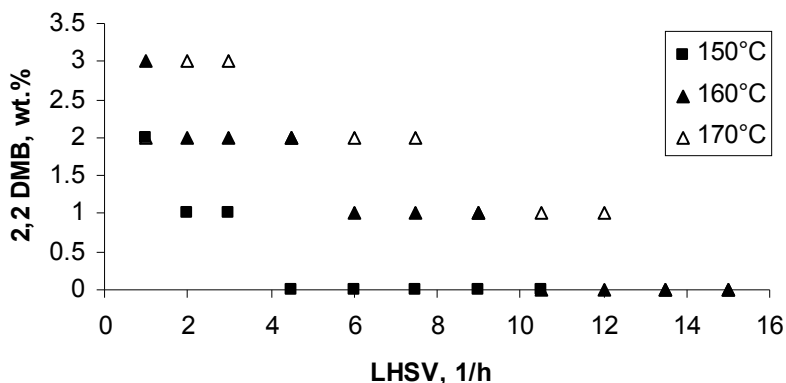


Figure 9: Effect of space velocity (LHSV) on the content of 2,2-dimethyl butane (2,2 DMB) in the product of *n*-hexane isomerization with Pt/SO₄-ZrO₂ catalyst at different temperatures of 150 °C, 160 °C and 170 °C

Cracking reactions are present at the temperature values above 160 °C and space velocities under 12 h⁻¹ (Fig. 10). At 170 °C and high residence time of feed in catalyst bed, cracking products reach a value of 6 wt.% in the product.

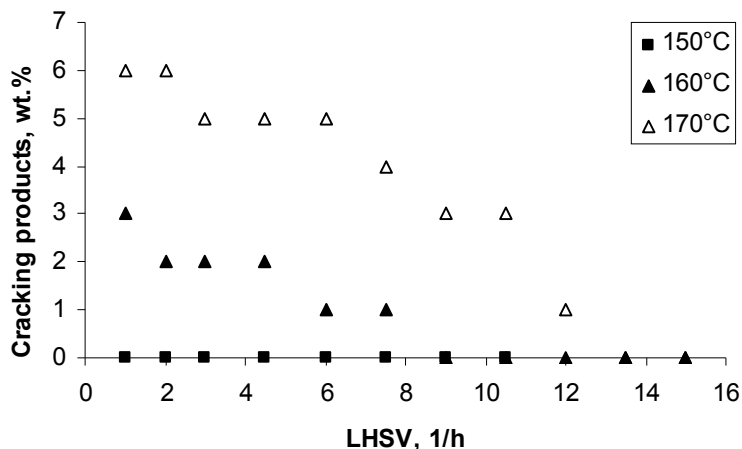


Figure 10: Effect of space velocity (LHSV) on the content of cracking products in the product of *n*-hexane isomerization with Pt/SO₄-ZrO₂ catalyst at different temperatures of 150 °C, 160 °C and 170 °C

5. Conclusion

Zirconium sulfate catalysts in the C5/C6 isomerization process in the last few years attracted attention, mostly due to its properties of high efficiency and low sensitivity to impurities in the system. With this paper we tried to give a contribution to the understanding of how the selected process parameters (temperature and space velocity) influence the conversion and distribution of products of the isomerization process of *n*-hexane with Pt/SO₄-ZrO₂ catalyst.

At the Faculty of Chemical Engineering and Technology apparatus for the study of catalytic conversion processes of hydrocarbon compounds in the presence of hydrogen has been designed and constructed. Results indicate that conversion of *n*-hexane into its isomeric compounds increases with temperature increase in the researched area from 150 to 170 °C, and LHSV decrease, so the highest *n*-hexane conversion was achieved at 170 °C and LHSV value of 1 h⁻¹, and was 63 wt.%. At the conditions of the highest conversion, the highest content of light hydrocarbons in the product in the amount of 6 wt.%, as a result of the cracking reactions, has been noticed. With the analysis of the product it has been proven that methyl pentanes (2 MP and 3 MP) together made 85 wt.% of the isomers, as well that their content was highest at the conditions of the highest conversion.

Dimehyl butanes (2,2 DMB I 2,3 DMB) together made 15 wt.% of the isomers, and their content did not depend on the temperature, but only on the LHSV value. Highest content of dimethyl butanes in the product was obtained at the lowest value of LHSV of 1 h^{-1} and was 3 wt.% for 2,2 DMB and 6 wt.% for 2,3 DMB.

With this paper, high efficiency of the zirconium sulfate catalyst was proven, so the continuation of our research will include further investigation of the process parameters influence on the product yield and composition, as well as the kinetic modeling of the process, which will allow us to better describe and optimize isomerization process.

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UDK	ključne riječi	key words
665.656.2	izomerizacija C5/C6 u razgranate alifate	isomerisation C5/C6 to branched chains
665.658.2	hidrogenacija	Hydrogenation
66.097.3	katalizator Pt/SO4-ZrO2	Pt/SO4-ZrO2 catalyst
66.097.36	postojanost katalizatora na trovanje	catalyst poisoning resistance
66-94	protok tekuće šarže na sat	liquid hourly space flow velocity LHSV
66-97	temperatura postupka	process temperature

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