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# INFLUENCE OF BENZENE ON THE PROCESS OF n-HEXANE ISOMERIZATION ON Pt/SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> CATALYST

## Abstract

*Isomerization of n-hexane is a process that produces high octane value isomers, which are ecologically acceptable components for blending of motor fuels. One of the latest generation isomerization catalysts is Pt/SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> catalyst, whose activity depends on feed properties and process parameters. Increased demand for petroleum products in last few years lead to the need for processing feeds of decreased quality, containing compounds that negatively affect the kinetics as well as thermo-dynamics of the process.*

*In this paper we studied the effect of benzene on the isomerization process of n-hexane. Solutions of benzene in n-hexane were used as feed, with benzene contents of 1, 2, 3 and 4 wt.%. The temperature range in which tests were conducted was 130-170 °C. Additional process parameters which were used to control process efficiency are hydrogen to hydrocarbon ratio and liquid hourly space velocity (LHSV). The results indicate a decrease in conversion of n-hexane with increasing benzene content in the feed, especially at lower temperatures and higher values of space velocity and the hydrogen to hydrocarbon ratio.*

## 1. Introduction

In the last 20 years increased number of vehicles all over the world has resulted in increased consumption of motor fuels, and therefore in growth of environmental impact. Combustion of motor fuels creates harmful carbon, nitrogen and sulphur compounds which are emitted into the atmosphere. For that reason current regulations and forthcoming ones will require even more reductions in content of unwanted compounds in fuels combusting in petrol and diesel engines. As a solution to achieve the required fuel quality, motor fuel treatment processes are necessary, wherewith product quality is increased and adverse impacts on environment as well as motors are reduced. One way of improving motor fuels quality is the production of high octane gasoline in isomerization process, by conversion of n-paraffins in light naphtha with the boiling point up to 80 °C into iso-paraffins<sup>1</sup>.

### 1.1. C<sub>5</sub>/C<sub>6</sub> isomerization process

During C<sub>5</sub>/C<sub>6</sub> isomerization process low octane straight-chained n-pentane (n-C<sub>5</sub>) is converted into high octane i-pentane, while hexanes (C<sub>6</sub>) with relatively straight chains (n-hexane, 2-methylpentane and 3-methylpentane) are converted into branched forms with double side chains (2,2-dimethylbutane and 2,3-dimethylbutane). Isomerization reactions are moderately exothermic reversible reactions, limited by thermodynamic equilibrium. Since the hexane content in feed is higher and hexane isomerization reactions are slower, hexane conversion is taken as relevant for monitoring and process control. This refers to achievement of optimum thermo-dynamic equilibrium which is shifted towards the highest amounts of iso-compounds in isomerizate. Isomerization of n-hexane results with 4 iso-hexanes: 2-methylpentane (2-MP), 3-methylpentane (3-MP), 2,3-dimethylbutane (2,3-DMB) and 2,2-dimethylbutane (2,2-DMB). The first three iso-hexanes form relatively easy and are intermediates to the creation of most branched and most desirable isomer 2,3-dimethylbutane. The molecule stability increases with increasing of branches in space, and to achieve stability, higher forming energy is required. For this reason, the formation of 2,3-dimethylbutane from intermediates is the slowest of all C<sub>5</sub>/C<sub>6</sub> paraffin isomerization reactions, with the highest activation energy value.<sup>1</sup>

Temperature at which isomerization process is conducted is the parameter that has the greatest impact on the yield and composition of the product; isomerizate gasoline. Given the fact that the isomerization reactions are slightly exothermic, C<sub>5</sub>/C<sub>6</sub> isomerization process, from the standpoint of thermodynamic equilibrium has greater efficiency at lower reaction temperatures. However, in such conditions, the reaction is kinetically limited due to slower reaction rates, and further lowering of the temperature leads to reduction of the isomerization reaction due to insufficient amounts of energy present in the system needed to start the reactions. At higher temperatures, reaction rate is higher, but the yield of the iso-compounds is lower due to the thermodynamic limitation of reaction; the balance shifts towards straight chain hydrocarbons, not their isomeric components.<sup>2</sup>

Isomerization reactions are carried out in the presence of a catalyst. Catalyst used for the isomerization process is active at lower temperatures, at which the thermodynamic equilibrium favors the creation of paraffin with side chains. Discovery of bifunctional catalysts primarily for the needs of the catalytic reforming, provided logical guidelines for the development of isomerization process catalyst. The desire for improved quality and increased production of motor gasoline was the driving force for further development of this catalyst. Bifunctional catalysts have two or more different catalytically active centers. They may consist of two or more phases of different activities, or from one phase with more active centers of different catalytic activity, as is the case with zeolites.<sup>3</sup> Bifunctional catalysts used in the process of C<sub>5</sub>/C<sub>6</sub> isomerization are chlorinated aluminum oxide, zirconium sulfate and zeolite catalysts. Light gasoline fractions depending on initial feed, can contain different proportions of benzene and cycloparaffins. In most cases, their separation

is not economically justified, therefore they are treated (desulphurization, the saturation of benzene, isomerization) together with the other fractions. To ensure benzene saturation and isomerization of n-paraffins and cycloparaffins is carried out in one process step; a special process configuration and catalyst are required. In parallel with the isomerization reactions, hydrogenation reaction of benzene to cyclohexane and its isomerization to methyl-cyclopentane take place or even a ring-opening reaction which results in paraffin components can occur.

Additionally, on highly acidic catalysts, the energy of adsorption of aromatic and naphthenic components is significantly higher than that of normal and single side chained paraffins, thus adversely affecting the process of isomerization of these compounds. Yield of liquid products increases because benzene inhibits hydrocracking reactions. Octane number of the mixture of products was higher than in the mixture before the isomerization process. It was observed that the increase of benzene content in the starting mixture results with gradual reduction in increase of octane number of products. Therefore, product octane number is lower than expected. It is the result of two opposing effects. Proportionally less isoparaffin hydrocarbons are formed due to benzene contained in the feed, since isomerization is inhibited by benzene presence. Octane numbers of the mixtures of cyclohexane (formed from benzene) and methyl-cyclopentane are higher than those of isoparaffin mixture formed by isomerization. The results showed that the sulfated metal-oxide catalysts are suitable for the simultaneous isomerization and hydrogenation of benzene and cycloparaffins in light naphtha fractions. Prior to the process it is desirable to determine the cyclohexane / ethyl-cyclopentane ratio of the mixture so that final concentration of cyclohexane (from the initial mixture and resulting hydrogenation) would be higher than the equilibrium at the given conditions, which results in isomerization of the cyclohexane into octane higher methyl-cyclopentane.<sup>4</sup>

## **2. Experimental**

### **2.1. Materials**

Feed in the process was n-hexane (puriss.,  $\geq 95\%$ ) with added benzene (puriss., min 99.7 %) in concentrations of 1, 2, 3 and 4 wt.%, respectively. The catalyst used in the process was a commercial sulfated zirconia catalyst. Carrier gas used in the experiments was 99.99 % hydrogen.

### **2.2. Apparatus**

Isomerization process was carried out in a laboratory apparatus located in Petroleum and Petrochemical Department, Faculty of Chemical Engineering and Technology, University of Zagreb. The apparatus is designed for conducting experiments and investigating continuous process of isomerization in a solid catalyst bed and in the presence of hydrogen. It consists of hydrogen system, system for feed drying, feed dosing pumps, tube type reactor with cooler for the effluent, slop tank, and a high pressure separator. The apparatus is equipped with a process controller, ultra-precise measurement and control technology, and the corresponding software that ensures easy handling and process control.

A detailed description of the apparatus and the scheme can be found in a previous paper.<sup>5</sup> Analysis of the products after isomerization process was carried out by gas chromatography. The method is based on the physical separation between the components of mobile and stationary phase within a chromatographic column. The gas chromatograph used in this work had a flame ionization detector.

### 3. Results and discussion

Influence of benzene content in the starting mixture of 0, 1, 2, 3, and 4 wt.% on conversion of n-hexane in the isomerization process on the Pt/SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> catalyst at 130 °C, 150 °C and 170 °C, is shown in Figure 1. The process was carried out at the LHSV of 2 h<sup>-1</sup>, and hydrogen to feed ratio, H<sub>2</sub>/HC, of 6. It is evident that the increase of benzene content in the feed results with conversion decrease. At the same conditions, the difference between the achieved conversion of pure n-hexane, and n-hexane with benzene content of 4 wt.% are between 50-60 %, depending on the temperature. The biggest difference is in conversion between 0 wt.% and 1 wt.% of benzene in the feed, while the difference between the 3 wt.% and 4 wt.% at all temperatures are negligible. It can also be seen that the isomerization favors higher temperatures, where the highest values of conversion were observed. From these results it can be concluded that the impact of level of benzene is very high, and that is very important to be familiar with the composition of feed entering the isomerization process in order to optimize the process conditions.

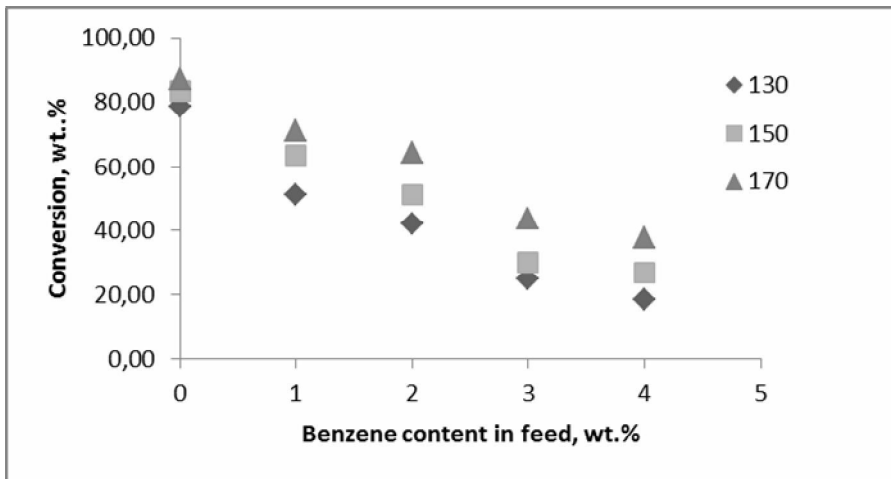


Figure 1: Effect of benzene content on the conversion of n-hexane at different temperatures (H<sub>2</sub>/HC = 6 mol mol<sup>-1</sup>, LHSV = 2 h<sup>-1</sup>)

Although the catalyst has the possibility of simultaneous hydrogenation of benzene, and isomerization of components in the mixture, a small reduction of benzene content in the initial feed, can lead to improved product quality, and hence the financial and energy savings. Figure 2 shows the effect of temperature on conversions for pure n-hexane (NHX), and for different concentrations of benzene in the initial feed. The process is carried out in the above mentioned conditions. As previously stated, increasing the temperature increases the yield of the isomers of n-hexane. These results are consistent with the theory, according to which although the isomerization reaction is exothermic, the kinetic constraints require a higher temperature to make the process economically feasible. Specifically, at higher temperature molecules are more mobile and thus facilitate the number of collisions, and it is also easier for molecules to overcome the activation energy barrier.

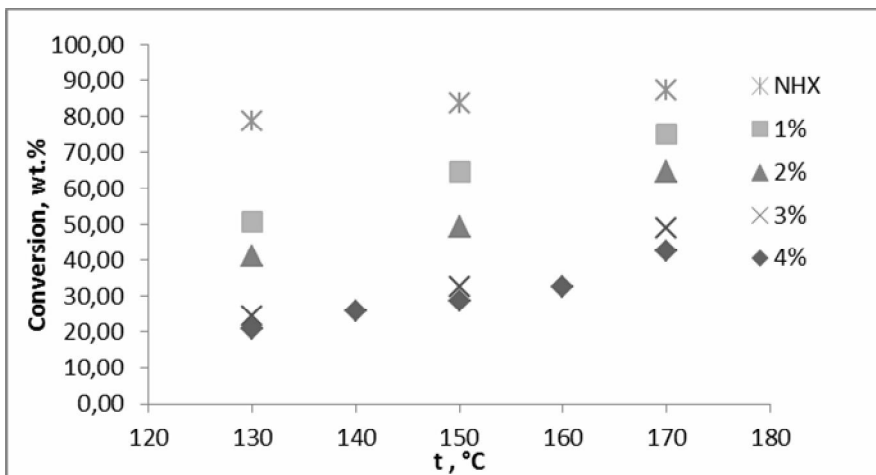


Figure 2: Effect of temperature on the conversion of n-hexane for different levels of benzene in the feed ( $H_2/HC = 6 \text{ mol mol}^{-1}$ ,  $LHSV = 2 \text{ h}^{-1}$ )

On Figure 3 we can see the negative impact of increased space velocity on the isomerization process. It is evident that the best results are achieved for the marginal value of  $LHSV = 2 \text{ h}^{-1}$ . Furthermore, after a sharp fall in the value of conversion between  $LHSV = 2 \text{ h}^{-1}$  and  $LHSV = 6 \text{ h}^{-1}$ , additional increase in the space velocity or flow of feed, the impact is almost negligible in all cases, regardless of the initial content of benzene in the feed. These results corroborate the fact that longer contact time between the feedstock and catalyst results in improved product quality and higher yields of isomeric components. Figure 4 shows the influence of hydrogen to hydrocarbon ratio on n-hexane conversion for different concentrations of benzene in the feed (1-4 wt.%). Other process parameters were set according to the optimum levels determined in previous papers. The maximum conversion process is achieved when the value of ratio is  $H_2/HC = 6$ .

Subsequent increases or decreases in the ratio result with the decrease in conversion, especially at higher ratios. In Figure 4, it can also be seen that the impact of hydrogen to hydrocarbon ratio on the final conversion decreases as the content of benzene in the feed increases.

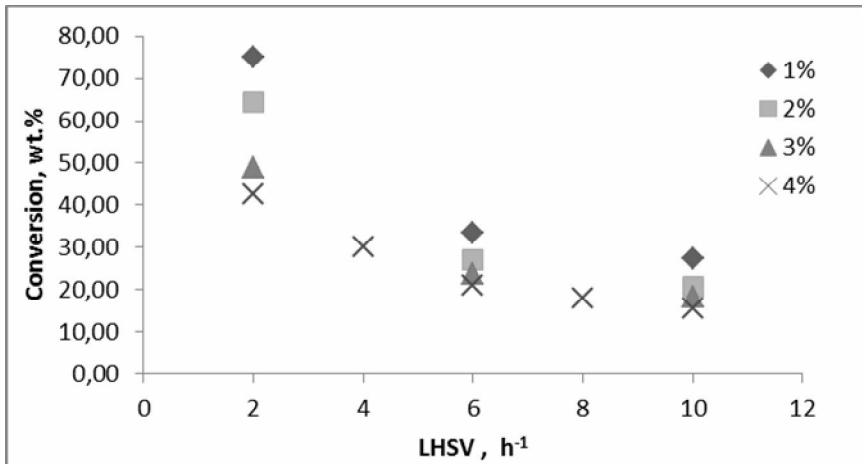


Figure 3: Effect of space velocity on the conversion of n-hexane for different levels of benzene in the feed ( $t = 170\text{ }^{\circ}\text{C}$ ,  $\text{H}_2/\text{HC} = 6\text{ mol mol}^{-1}$ )

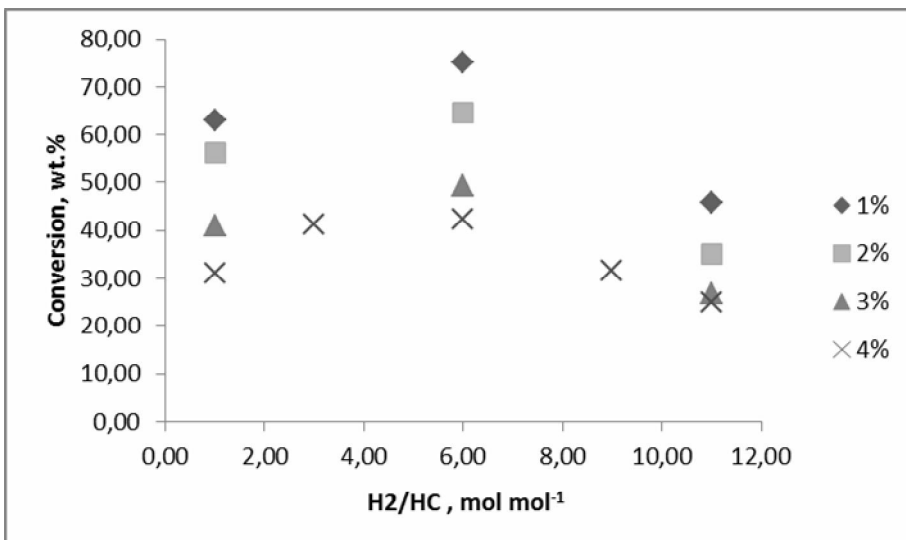


Figure 4 Effect of  $\text{H}_2/\text{HC}$  ratio on the conversion of n-hexane for different levels of benzene in the feed ( $t = 170\text{ }^{\circ}\text{C}$ ,  $\text{LHSV} = 2\text{ h}^{-1}$ )

Figure 5 shows the effect of temperature on the yields of some isomerization products, with initial benzene content of 4 wt.%. From the results it is clear that the predominant isomer is 2-methylpentane, followed by 3-methylpentane, while the 2,2-dimethylbutane and 2,3-dimethylbutane are represented in smaller amounts. These results follow the theoretical considerations according to which the formation of 2-methylpentane is the fastest process step, followed by the formation of 2-methylpentane, and 2,3-dimethylbutane. Formation of 2,2-dimethylbutane is the slowest reaction of all the above, therefore, its content in product mixture is the lowest. It is evident that the temperature has very small influence on the formation of this compound, except at the highest temperature which probably slightly favors the kinetics of the process. The amount of 2-methylpentane in the product is constantly increased simultaneously with the temperature, while the increase in the amount of 3-methylpentane in the product is most pronounced at the highest temperature.

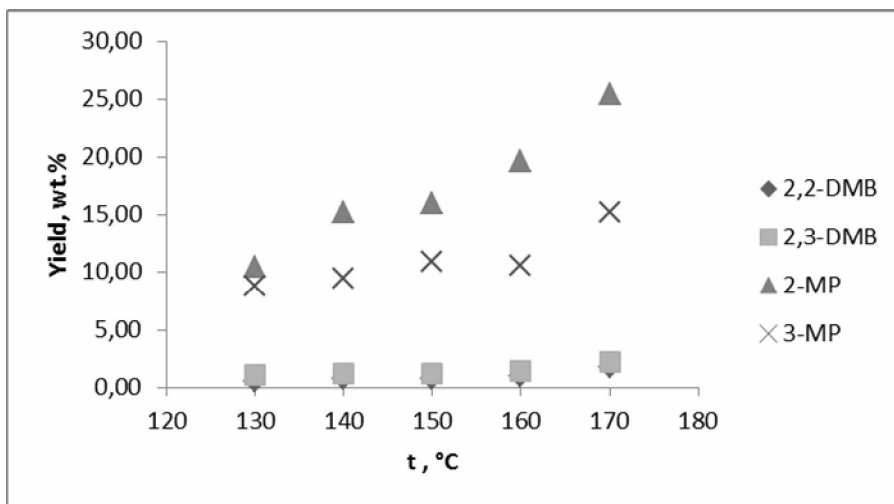


Figure 5: Effect of temperature on n-hexane isomers yield

#### 4. Conclusion

In this paper the influence of the most important process parameters on the isomerization of n-hexane in the presence of the latest generation isomerization catalyst, zirconium sulfate, were observed. It was found that benzene has a significant negative effect in the isomerization reaction of n-hexane. A small amount of benzene in the feedstock results in a much higher net decrease in conversion compared to pure n-hexane. Further increase of benzene content in feed results in additional lowering of the conversion. Benzene has higher energy absorption compared to n-hexane, and occupies the active sites on the catalyst where the reactions of hydrogenation of benzene, followed by isomerization of cycloparaffins

are occurring. This resulted in a smaller methylpentane and dimethylbutane yield, while increasing the proportion of cyclo compounds in the product. Methylpentane isomers are predominant in the mixture of products after isomerization process. Temperature rise in the investigated range of 130-170 °C increases n-hexane conversion.

Increase of the space velocity leads to reduced value of n-hexane conversion. Experiments have confirmed that the optimum value of the LHSV is 2 h<sup>-1</sup>, which is the lowest value in the tested interval (2-10 h<sup>-1</sup>). From this we can conclude that the increase in contact time between catalyst and feed results in conversion increase. Hydrogen to hydrocarbons ratio H<sub>2</sub>/HC greatly contributes to the final result of the conversion of n-hexane. It was determined that the optimal value of the H<sub>2</sub>/HC ratio is 6. Increasing or decreasing of this value results in conversion decrease. The impacts of all parameters on the conversion were found to be reduced by increasing benzene content in the feed, and that benzene content is the factor which affects process the most.

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