HUNGARIAN JOURNAL
OF INDUSTRIAL CHEMISTRY
VESZPRÉM
Vol. 39(1) pp. 117-120 (2011)

INVESTIGATION OF KINETICS OF HYDROISOMERIZATION OF C_5/C_6 AND C_6/C_7 ALKANES AND THEIR BINARY MIXTURES

ZS. SZOBOSZLAI✉, J. HANCSÓK

University of Pannonia, Department of MOL Hydrocarbon and Coal Processing
8200, Veszprém Egyetem u. 10, HUNGARY
✉E-mail: szzsolt@almos.uni-pannon.hu

Modern gasoline quality requirements globally became stricter. These specifications parallel with the applied developments of vehicle technologies contributing to the cleaner environment. Nowadays only the concentration of cyclo- and isoparaffins are not limited in gasoline, because they burn cleaner, have high octane number, lower sensibility and better combustion properties than aromatic or olefinic hydrocarbons. In the last decade because of the applied refinery investments both sulfur and aromatic content of gasolines decreased, but the octane mass of the gasoline pool significantly decreased against the increment of octane number requirement of spark ignition engines. Importance of isomerization of light paraffins has been publicized in many papers. However few of them investigated, studied and explained the individual hydrocarbons ($C_5/C_6/C_7$) interaction with each other in multicomponent mixtures practically in similar to industrial hydrocarbon feedstocks. Binary and multicomponent hydrocarbon mixture investigations can contribute to the understanding the results of isomerization of real, feedstocks from multiple sources; which contain higher boiling point hydrocarbons (cycloparaffins, benzene, and heptanes). Further these results can help to operate with higher flexibility, safety and economically a light naphtha isomerization units. The hydroisomerization of n-pentane (n-C_5), n-hexane (n-C_6), cyclohexane (c-C_6) and n-heptane (n-C_7) and their binary mixture were studied on Pt/sulfated zirconia catalyst at temperature 150–170 °C, total pressure 20 bar, 1:1 H_2-hydrocarbon molar ratio. The apparent activation energies of all individual components, further the reaction rates individually and in different composition binary mixtures were specified. Results of our experiments concluded that the rate of reaction of the higher carbon number hydrocarbon or in case of the same carbon number the cycloparaffins (lower volatility component) increased with increasing the concentration in the binary mixtures, while the rate of reaction of higher volatility component decreasing.

Keywords: Isomerization, light naphtha

Introduction

Nowadays the fractions rich in isoparaffin are the most important blending components of the gasolines because they have high octane number, low sensibility, they are practically free from sulphur, olefin, and aromatics, they have low toxicity, and undesired molecules are not generated under controlled combustion [1-4]. The continuous demands for the application of isoparaffin rich hydrocarbon fractions are the followings:

From 2000
- Low benzene and decreased aromatic concentration (research octane number and octane number distribution)
- Reducing the research octane number give away
- Supplementation of the octane number decrease of the deep desulphurization of cracked naphthas
- Regulation of the application of MTBE
- Balancing the boiling range shifting in case of heavier ether (ETBE, TAME) application in high concentration

From 2005
- Further deep desulphurization
- Further reduced aromatic and benzene content

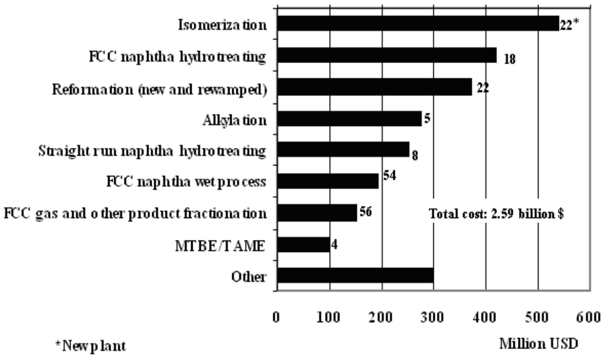

Figure 1: Constructed refinery investments in the EU for high quality gasoline production until 2005 to fulfill the 2005 gasoline regulations

The simultaneous reduction of the sulphur and aromatic content significantly decreased the octane number of the gasoline pool against the increasing octane number requirements of the Otto engines (higher compression ratio → higher octane number → higher volumetric efficiency and specific power with lower emission).

The importance of isoparaffin rich fractions is presented in *Fig. 1* which shows what the most important investments are in the refineries to satisfy the demands and meet the new specifications [1-4]. It can be clearly seen that the highest investments in the refinery were the light paraffin isomerization processes (though the application of light paraffins was slightly reduced by the bioethanol blending, in spite of the significant effect of the ethanol on the gasoline physical-chemical application properties the etherification and alkylation capacity can be significantly increased by taking advance of the isomerization capacity), but the alkylation unit installation and revamping was also important. The possible ways to produce industrial economically isoparaffin rich fractions are the following:

- The proper naphtha fraction separation to iso- and normal paraffin fractions
- Alkylation of isobutane with C_3-C_5 olefins (direct alkylation)
- Dimerization of C_3-C_5 fractions rich in olefins (indirect alkylation) after hydrogenation
- Isomerization of C_5-C_7 fractions rich in n-paraffins
  - Isomerization of benzene containing fractions
    - Two-steps → two reactors and different catalysts
    - One step
      - isomerization of benzene containing fractions (the saturation of benzene and isomerization of the n-paraffins is done in the same reactor and on the catalyst) [5-6]
      - in the same reactor with segmented beds with different catalysts [4]

The specifications of the benzene concentration of the naphtha fraction can be ensured by adequate pre- and post-treating so the feed of reformation does not contain benzene precursor or after the reformation they have to be fractionated (if the reformation is gasoline purpose) from the product and saturated in the isomerization plant.

The feedstock of both of the etherification and alkylation technologies are the C_4-C_5 isoparaffins consequently the light paraffin isomerization will be one of the key processes just partly producing internal components/feeds for other technologies.

Experimental

Aim of our experimental work was the investigation of isomerization of hydrocarbons with different volatility and their binary mixtures. We investigated that the isomerization effects/rate on each other further how influenced the individual hydrocarbon the other in laboratory scale reactor on steady state activity catalyst. The inspiration of this research work was the absent of large scale, long term catalytic studies with near industrially parameters [7-14].

Experimental eqipment

The applied catalytic system contains a 100 cm^3 vertical reactor and every instrument which can be found in a commercial scale light naphtha isomerization unit.

The catalytic system contains a gas regulator/control and pretreatment system and an on-line gas chromatograph.

Materials

We applied 60cm^3 of in situ dried and activated Pt/sulphated-zirconia (extrudated, D: 1.5mm) catalyst and the empty space was filled with Raschig rings.

The feedstocks were analytical grade, sulphur free n-pentane, n-hexane, cyclohexane and n-heptane. The concentration of components was varied between 0–100% (0, 25, 50, 75 and 100% theoretically) in binary mixtures. The practically sulfur free hydrocarbons continuous demoisturising was done with Linde 4A molecule sieve.

Catalyst and test methods

The applied catalyst was Pt/sulfated-zirconia. Main properties of the catalyst were shown by *Table 1.*

Table 1: The main characteristics of applied catalysts

Properties	**Values**
Pt-content, %	0.415
Pt-dispersion, %	69
Acidity, mmolNH_3/g	0.56
$Sa_{metalic}$ (metal (Pt) surface on the catalyst), m^2/g metal	25.91
S_{metal} (specific metal surface), m^2 metal/g cat.	0.108
APS (average particle size of the metal), nm	2.0
Specific acidity, mmolNH_3/m^2 cat.	0.0043
BET surface, m^2/g	130
Microporous surface, m^2/g	12.2
Microporous volume, cm^3/g	0.0045
Mezoporous volume, cm^3/g	0.2874
Mezo-/microporous volume ratio	63.9
Average pore size, nm(Å)	8.5(85)

Standard measurements methods were used. Pt content of the catalyst was measured by UOP-274 standard. BET surface area and total acidity of the catalyst was measured by NH_3 sorption according to ASTM D3663 and D4824 standards, while pore size distribution and pore volume was measured by mercury intrusion porosimetry method according to ASTM D4284 and D6761 standards respectively. The feeds and products composition was measured with gas chromatograph according to ASTM-D5134 standard.

The sulphur content of all feeds and products (GREENLAB Ltd./Analytik-Jena - Multi EA 3100-type device) with EN ISO 20846 (2003), water content (GREENLAB Ltd./KEM - MKA-610-type device) with ISO 12937:2001 standard was determined.

Process parameters

Experiments were measured on steady state activity catalyst. Based on preliminary results the experiments was taken on 20 bar total pressure, 1.0–4.0 LHSVs, H_2/HC molar ratio was 1.0:1.0. Fine changes of the parameter combination kept measuring where the low conversion rates (5–15%) of the individual hydrocarbon were not inhibited by the products.

Results and discussion

Near low conversion rates the individual hydrocarbons initial reaction rates were measured then the logarithmized values were presented versus the inverse of temperature. These methods were applied to determine the apparent activation energies of hydrocarbons. Based on the given data they had relatively high deviation, and these values can be given with relatively high inaccuracy. Our values and the publicized values are relevated well *(Table 2)* but the most of them were determined in different catalytic system and with different parameter combinations [11-15]. For example in case of the cyclohexane the measured values are well correlated with publicized data (100–150 kJ/mol).

Table 2: The apparent activation energies of individual hydrocarbons

Hydrocarbon	n-pentane	n-hexane	n-heptane	cyclo-hexane
$E_{apparent}$, measured values, kJ/mol	130–170	99–107	149–163	113–146
$E_{apparent}$, publicized values, kJ/mol	145–153	120	109–135	100–150

The targeted quantity was added to n-hexane and above 20% concentration it caused significantly lower reaction rate. So the reaction rate of the main component decreased causing lower effectiveness under isomerization consequently the adequate composition of the feed(s) has to be kept assured!

Based on our measurement the reactivity of the individual hydrocarbons were the following: c-C_6>n-C_7>n-C_6>n-C_5, the main cause was that the adsorption energies of cycloparaffins is higher than the same carbon number linear paraffins on strongly acidic catalysts so in their mixtures increasing the individual component reaction rate change with different degree with the concentration interdependently (*Fig. 2-4*). In the hexane the other component concentration more than 20–30% the n-hexane reaction rate was approximately halved and its component reaction rate was comparable/similar to the other individual component reaction rate. In case of cycloparaffin isomerization the lower H_2 pressure was beneficial though it increased the selectivity of ring opening reaction. On stricter parameter combinations the ring isomerization selectivity becomes higher and near the equilibrium concentration (cyclohexane↔methylcyclopentane) the cracking reaction come to front that ascribe to methylcyclopentane. In the examination of the gas phase composition it was observed that the C_2/C_4 molar ratio was very low so the isomerization and cracking reaction probably to take place through C_{12}-C_8 intermediate products.

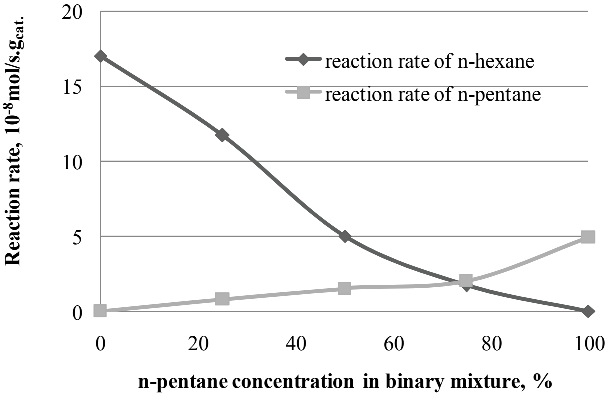

Figure 2: Changes in reaction rate of individual components in the binary mixture (T: 150 °C, LHSV: 1.5 h^{-1}, P: 20 bar)

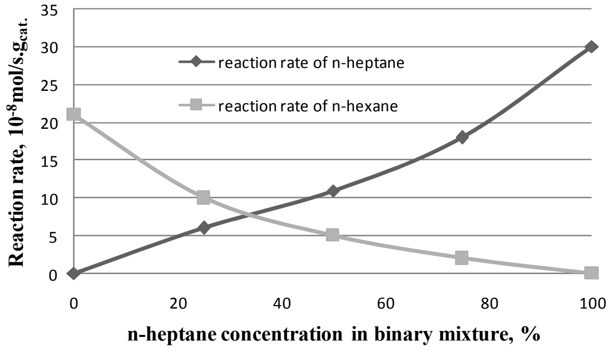

Figure 3: Changes in reaction rate of individual components in the binary mixture (T: 150 °C, LHSV: 1.5 h^{-1}, P: 20 bar)

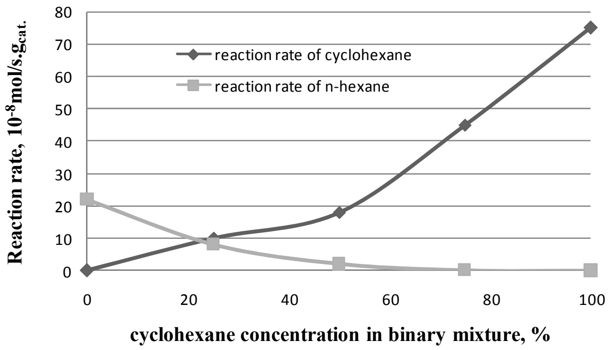

Figure 4.: Changes in reaction rate of individual components in the binary mixture (T: 150 °C, LHSV: 1.5 h^{-1}, P: 20bar)

Conclusions

The individual component reaction rates were lower in every case than in their binary mixtures. The reaction rates were significantly decreased in the mixtures with increasing the concentration of individual paraffin hydrocarbons.

Based on the measured and calculated values it was concluded that in case of the non-adequate feed or in case of non-adapted isomerization catalyst – where accordingly to the demands the changes of process parameters have not indicated any opportunity – influence of some component on the isomerization efficiency become significant degree hereby the main linear chain components with low octane number reactions rate of isomerization was interfered.

ACKNOWLEDGMENT

We acknowledge the financial support of this work by the Hungarian State and the European Union under the TAMOP-4.2.1/B-09/1/KONV-2010-0003 project.

REFERENCES

1. U. Szalkowska: Fuel quality - global overview, 7th international colloquium on fuels 2009, TAE, Stuttgart/Ostfildern (Germany)
2. H. Weyda, E. Köhler: Modern refining concepts - an update on naphtha-isomerization to modern gasoline manufacture, Catalysis Today, 81(1), (2003), 51–55
3. Sz. Magyar, J. Hancsók, A. Holló: Key Factors in the Production Of Modern Engine Gasolines, 6th International Colloquim, Fuels 2007, Germany, Esslingen, 2007, In Proceedings (ISBN 3-924813-67-1), 273–284
4. J. Hancsók, Sz. Magyar, Zs. Szoboszlai, D. Kalló: Investigation of energy and feedstock saving production of gasoline blending components free of benzene, Fuel Processing Technology, 88(4), (2008), 393–399
5. J. Hancsók, Sz. Magyar, K. V. S. Nguyen, Zs. Szoboszlai, D. Kalló, A. Holló, Gy. Szauer: Simultaneous desulphurization, isomerization and benzene saturation of n-hexane fraction on Pt-H/MOR, Studies in Surface Science and Catalysis (ISBN 0 444 52083 X), - Porous Materials in Environmentally Friendly Processes 158, (2005), 1717–1724
6. Zs. Szoboszlai, J. Hancsók, Sz. Magyar: Upgrading of Benzene Containing Hexane Feeds by Simultaneous Isomerization at Low Temperature and Saturation of Benzene, 6th International Colloquium, Fuels 2007, Germany, Esslingen, 2007, In Proceedings (ISBN 3-924813-67-1), 293–302
7. G. D. Yadav, J. J. Nair: Sulfated zirconia and its modified versions as promising catalysts for industrial processes, Microporous and Mesoporous Materials 33, (1999), 1–48
8. J. M. Serra, A. Chica, A. Corma: Development of a low temperature light paraffin isomerization catalysts with improved resistance to water and sulphur by combinatorial methods, Applied Catalysis A: General, 239(1-2), (2003), 35–42
9. W. Takemi, M. Hiromi: Reaction of linear, branched, and cyclic alkanes catalyzed by Brönsted and Lewis acids on H-mordenite, H-beta, and sulfated zirconia. Journal of Molecular Catalysis A. 239, (2005), 32–40
10. J. C. Duchet, D. Guillaume, A. Monnier, C. Dujardin, J. P. Gilson, J. van Gestel, G. Szabo, P. Nascimento: Isomerization of n-Hexane over Sulfated Zirconia:Influence of Hydrogen and Platinum, Journal of Catalysis 198, (2001), 328–337
11. A. Holló, J. Hancsók, D. Kalló: Kinetics of hydroisomerization of C_5-C_7 alkanes and their mixtures over platinum containing mordenite, Applied Catalysis A: General, 229(1-2), (2002), 93–102
12. T. Løften, E. A. Blekkan: Isomerisation of n-hexane over sulphated zirconia modified by noble metals, Applied Catalysis A: General 299, (2006), 250–257
13. M. Guisnet, V. Fouche: Isomerization of n-hexane on platinum dealuminated mordenite catalysts, II. Kinetic Study, Appl. Catal, 71, (1991), 295–306
14. H. Liu, G.D. Lei, W. M. H. Sachtler: Alkane isomerization over solid acid catalysts. Effects of one-dimensional micropores, Appl. Catal., 137(1), (1996), 167–177
15. C.-L. Li, L. Shi, G-X. Huang, R.-Y. Wang: Scale-up for Alkane Isomerization, Chem. Eng. Comm., 121, (1993), 1–8