

INVESTIGATION OF THE EFFECTS OF METYL- CYCLOPENTANE IN FEED OF ISOMERIZATION UNIT

Jafar Sadeghzadeh Ahari*, Seyed Javad Ahmadpanah, Alireza Khaleghinasab,
Majid Kakavand

*Process Development Division, Research Institute of Petroleum Industry
(RIPI), Tehran-Iran, (*Corresponding author, e-mail: sadeghzadehj@ripi.ir)*

Received October 23, 2005 ; accepted December 21, 2005

Abstract

In isomerization process, linear and cyclic paraffins existing in light naphtha, are converted to branched isomers resulting in a considerable increase in the octane number of produced gasoline. Isomerization units have found very important roles in oil refineries as they considerably improve the quality of oil products. The product of isomerization process can lower the aromatic percentage of the gasoline in accordance with EURO 2005. In this paper, effects of methylcyclopentane (MCP), existing in the light naphtha produced by most of the Iranian refineries, has been investigated on the quality of gasoline and efficiency of the isomerization process. Results of the experiments show that increase of the MCP in isomerization unit feed, leads to a considerable decrease in the octane number of gasoline, increase in the efficiency of the isomerization process and increase in the utility consumption.

Key words: methylcyclopentane, isomerization, alkanes

1- Introduction

Isomerization of light naphtha will considerably increase the octane number of the produced gasoline. Increase of the iso-alkanes has always been an important challenge in oil industries because of its low amount in naphtha cut.

One of the main methods for production of iso-alkanes is isomerization of normal hydroparaffins existing in naphtha. In this process, normal paraffin chain is converted to branched paraffin (isomer) in the vicinity of catalyst and in suitable temperature and pressure conditions, which leads to improvement of gasoline octane number without any increase in the cyclic components.

Nowadays, incorporation of isomerization units has found a considerable importance in refineries to ensure quality improvement of the products and optimum consumption of raw materials. Increase of efficiency and quality improvement of products are very important factors for an effective introduction of a technology and license to industries, which make it competitive in compare with the other licenses. Research Institute of Petroleum Industry (RIPI) and National Iranian Oil Engineering and Construction Company (NIOEC) as the first and sole owner of the license for isomerization of light paraffins in Iran have always tried to optimize the operational conditions and quality of the products. As a small achievement, this paper has been prepared to investigate the effects of MCP on efficiency and quality of the final products in isomerization process.

In literature lots of research has been done on this subject. Wu et al.^[8] has investigated the effects of different catalysts on cycloalkanes (C₅-C₁₀) Isomerization reactions. They concluded that when aluminum chloride catalysts which contain bromphosphate on silica or active carbon bases are used, MCP will more severely show its negative effects. Rahlwes^[9,10] investigated two similar processes for isomerization of a group of hexanes including normal hexane, iso-hexane, methylhexane, methylcyclopentane and cyclohexane. One of the processes included one isomerization stage and two separation stages and the other one isomerization stage and three separation stages. Both processes aimed at maximizing the conversion rate of cyclopentane to cyclohexane. They also concluded that MCP included in the feed of isomerization unit has some negative effects on this process.

2- Investigation of MCP effects on isomerization process

To study the effect of MCP on isomerization process yield, thirteen case studies have been investigated using Hysys Refinery software. The feed under investigation is a mixture of n-C₆ and MCP. The only difference between the case studies is the weight percentage of the MCP content of the feed, which has been depicted in table 1.

Table 1 – Weight Percentage of feed components

Case	MCP(wt%)	n-C ₆ (wt%)	Case	MCP(wt%)	n-C ₆ (wt%)
1	0	100	8	50	50
2	5	95	9	60	40
3	10	90	10	70	30
4	15	85	11	80	20
5	20	80	12	90	10
6	30	70	13	100	0
7	40	60			

Process description is the same for all thirteen cases.

2-1- Process Description

Naphtha isomerization is a process in which hydrogen reacts with heavy paraffins such as normal pentane and normal hexane to yield their isomers (without any change in their total molecular weights). This process increases the gasoline octane number.

As illustrated in Fig. 1, isomerization process includes the following three main units:

- 2-1-1- Unit 100: Feed pre-heating and reaction unit
- 2-1-2- Unit 200: Stabilizer unit
- 2-1-3- Unit 300: Deisohexanizer unit

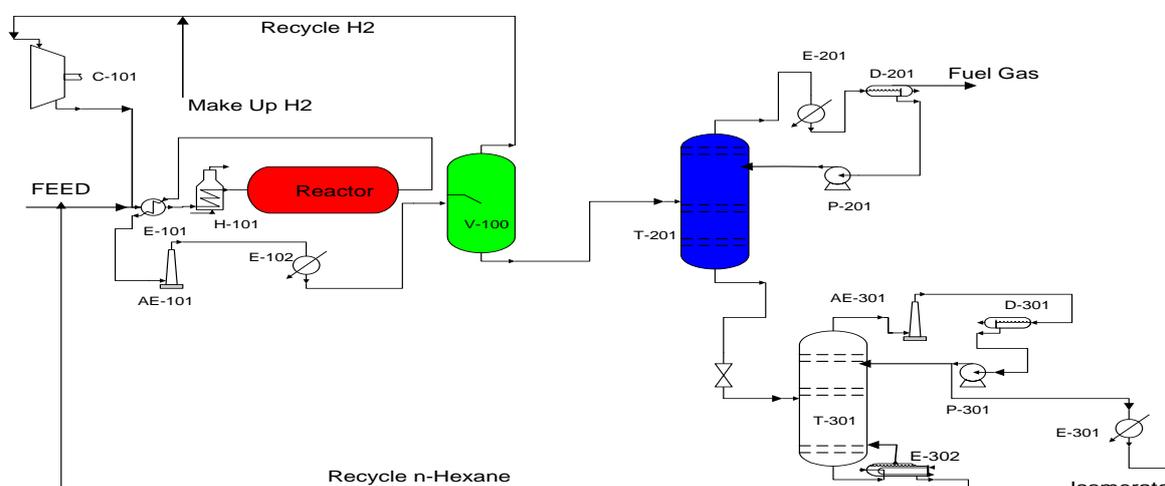


Fig. 1 - Block diagram of isomerization process for the 13 case studies

2-1-1- Unit 100: Feed pre-heating and reaction

The feed including normal hexane and methylcyclopentane is fed into the system at a temperature of 37°C and a pressure of 3.5 bar-g. The pressure of the feed can be increased up to 26 bar-g via a pump. This feed is first mixed with the recycled n-hexane including heavy paraffins coming from deisohexanizer tower (T-301) and then fed into the process. The recycled hydrogen from liquid-steam

separator (V-100) is first mixed with make up hydrogen with a purity of 93.6 weight percentage and then is pressurized to 25 barg via a compressor (C-101), which is then added to the feed. The amount of make up hydrogen is selected such that the weight ratio of hydrogen to hydrocarbons becomes 1.2 in the input feed to reactor. The final feed containing approximately 60% gas, is first heated in heat exchanger (E-101) and then transferred through furnace (H-101) where it is completely converted to gas and its temperature increases to 200°C until 210°C. Now the feed has got the required activation energy for the reaction to be carried out in reactor.

As the hydro-cracking reactions generate heat, the output temperature of the reactor increases. The output product of the reactor 60% of which is formed of light gases like hydrogen is conducted to exchangers E-101, AE-101 and E-102 through which its temperature reaches 38°C and is then sent to separator V-100.

2-1-2- Unit 200: Stabilization

Hydrogen and light gases, after separation in V-100, in accompany with make up hydrogen are mixed with feed through the compressor C-101 and are then conducted to the reactor feed pre-heating unit.

The output liquids from the bottom of V-100 are conducted to pressurized stabilizer tower T-201. Stabilizer tower contains 20 trays (theoretically) and the feed is entered into its 7th tray. The water condenser E-201 is used to condense the light components of the top product of the tower. Output gases, which are mainly propane at 38°C and 5 barg, are sent to gas recovery unit (SGRU) from the top of D-201 vessel. Products from the bottom of tower T-201 are first depressurized to 1 bar through a control valve and then conducted to deisohexanizer tower.

2-1-3- Unit 300: Deisohexanizer

The stabilized feed from unit 200 is transferred to the 36th tray of deisohexanizer tower (T-301) which theoretically includes 60 trays. Tower T-301 is equipped to an air cooler (AE-301) which acts as a condenser for the light components in top of the tower at 64°C. Pump P-301 is used for recycling of liquids to tower T-301 and transfer of product to gasoline tank.

The isomerized products from top of the deisohexanizer tower is cooled down from 64°C to 38°C in water cooler E-301 and is then transferred to gasoline storage tank at a pressure of 3.5 barg.

Products of bottom of the tower including heavy components are sent to reactor feed pre-heating unit. The re-boiler of the deisohexanizer tower (E-302) is of kettle type for heating of which LP(low pressure) steam is used.

3- Results

3-1- Effects of MCP weight percentage included in the feed on the RON of the product

The reactions achieved in isomerization unit reactor is divided to the following two groups:

1. Molecular cracking reactions
2. Isomerization reactions

In molecular cracking reactions, heavy molecules like heptane, hexane, pentane, MCP, etc., as a result of reacting with H₂, are converted to light components like ethane, methane, propane, etc. Isomerization reactions which are carried out in equilibrium, change the molecular configuration (isomerization).

One of the isomerization reactions carried out is as below:



According to Lechatelier principle, increase of MCP in feed causes more MCP to be more converted to CH and as the octane number of MCP (91) is higher than that of CH (83), it is expected that the RON of the final product increases with decrease of MCP weight percentage. (Fig. 2)

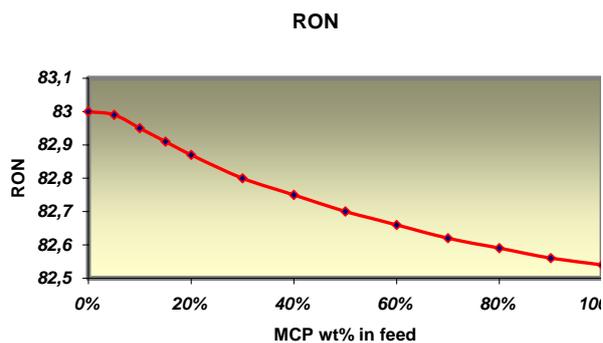


Fig. 2- Effect of increase of MCP weight percentage on RON of the final product

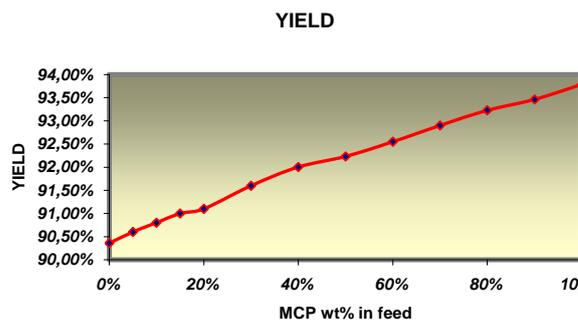


Fig. 3- Effect of increase of MCP weight percentage on process yield

3-2- Yield

Yield in the case studies has been defined as below:

$$YIELD = (Weight\ of\ the\ Final\ Product / Wight\ of\ the\ Feed) * 100$$

As illustrated in Fig. 3, increase of MCP in feed results in increase of the process yield.

3-3- Make Up Hydrogen

As depicted in Fig. 4, make up hydrogen is increased with increase of MCP weight percentage in feed which can be verified as below:

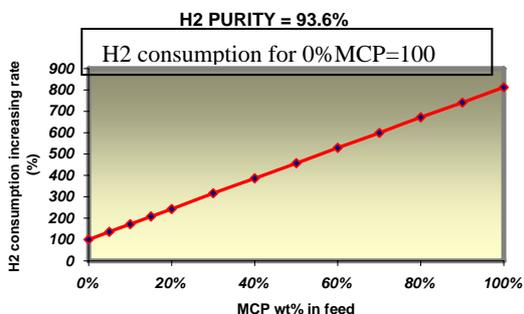
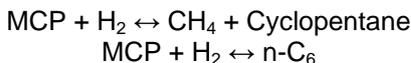


Fig. 3- Effect of increase of MCP weight percentage on make up hydrogen

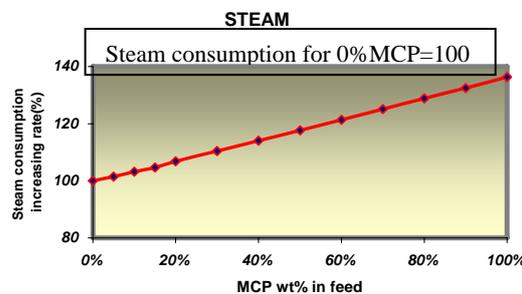


Fig. 4- Effect of increase of MCP weight percentage on steam consumption

3-4- Consuming Utility

Fig. 5, 6 and 7 show that utility consumption increases as the MCP content of the feed is increased.

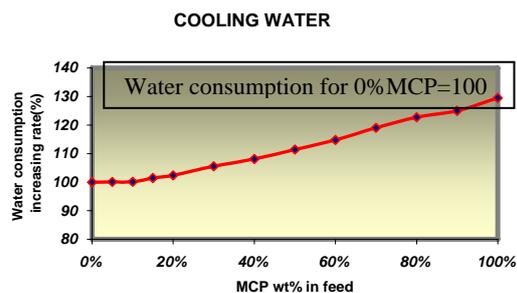


Fig. 5- Effect of increase of MCP weight percentage on cooling water consumption

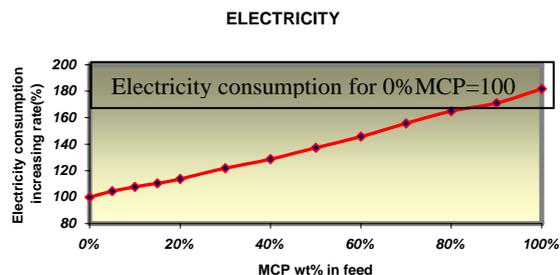


Fig. 6- Effect of increase of MCP weight percentage on electricity consumption

3-5- Catalyst Consumption

Considering that the reactions achieved are mostly similar to isotherm ones, the consumption of catalyst can be easily calculated by means of its LHSV.

Increase of MCP in feed results in increase of the recycling flow which in turn increases the mass flow rate to the input of the reactor and hence the consumption of catalyst must also increase which has been depicted in Fig. 8.

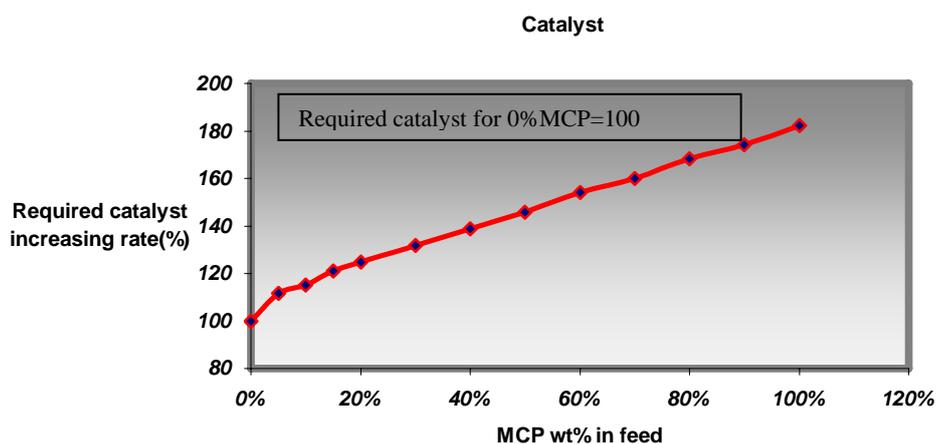


Fig. 8- Effect of increase of MCP weight percentage on catalyst consumption

References

- [1] Schlögl R. "Recent Developments in the Department of Inorganic Chemistry" <http://www.fhi-berlin.mpg.de/fbr2005/green/AC.pdf>
- [2] Ksenofantav V.A. Pryalchin A.N. Kustar L.M. And Lunin V.V. " Mutual Trans formation of C₆- Cycloalkanes in ionic liquids. Rep. 1 Isomerization of Cyclohexane and Methyleyclopentane in ionic liquid of three methyl amonia hydrochloride- AlCl₃ (1:2) Production of monochloroacetic acid. Rep. 1: Processing of subsidiary. Dichloroacetic acid by technique of catalytic hydrogenetation " *Catalysis in Industry* / 5 / 2003.
- [3] Boer M. Johnson C. "More Performance out of your isomerization unit Industrial examples an the benefit of improved catalysts " *Catalyst Courier* 33 / 1997.
- [4] Gagea B.C. Pârvulescu A.N. Pârvulescu V.I. Pârvulescu V. Grange P. and Poncelet G. " Isomerization of Cyclohexane and Hexane over silica- embedded Triflate Derivatives Catalysts " ARKAT USA Inc.
- [5] Keesom W.H. Kuchar P.C. " Penex and Platforming Synergy for Efficient Naphtha Processing and Benzene Control " 1995, UOP.
- [6] Belloun M. " Study of hydro isomerization of paraffinic C₄ to C₇ hydrocarbons and of Naphthenic C₆ hydrocarbons in presence of Pt/H- mordenite catalyst " Fischer- Tropsch

- Archive, Mar 90, 195p.
- [7] Abbot J. Wojciechowshi B. "Catalytic Reaction of Methylcyclopentane on Zeolite" The Can. J. of Chem. Eng., 1989, pp- 833.
- [8] Wu et al. "Cycloalkane isomerization process." United States Patent No. 5254791, Oct.19, 1993.
- [9] Rahlwes "Isomerization process" United States Patent No. 4655484, Apr.7, 1987.
- [10] Rahlwes "Isomerization process" United States Patent No. 4654452, Mar.31, 1987."
- [11] Optimization of Deisohexanizer Tower for Separation of MCP", Ripi report, 2003