ANALYSIS OF OPTIMAL PROCESS FLOW DIAGRAMS OF LIGHT NAPHTHA ISOMERIZATION PROCESS BY MATHEMATIC MODELLING METHOD

Vjacheslav Chuzlov[1,*], *Konstantin Molotov*[2]

[1]Tomsk Polytechnic University, Lenin av. 30, Tomsk, 634050, Russia
[2]OOO "Kinef", Enthusiastov Highway 1, Kirishi, Russia;

Abstract. An approach to simulation of hydrocarbons refining processes catalytic reactors. The kinetic and thermodynamic research of light naphtha isomerization process was conducted. The kinetic parameters of hydrocarbon feedstock chemical conversion on different types of platinum-content catalysts was established. The estimation of efficiency of including different types of isomerization technologies in oil refinery flow diagram was performed.

1 Introduction

The increase of straight run normal alkanes C_5-C_6 fraction research octane rating to 92 points is an effective decision of important applied problem of changing the structure of native gasoline pool. The high octane flow of isomerate does not content a sulfur, aromatic and olefin hydrocarbon that is why it is an excellent component for finished gasoline compounding. The selection of optimal process flow diagram (PFD) of light naphtha isomerization is an important research and practice task which can be solved more efficiently with a help of mathematical modelling method.

2 Research Object

In this paper the research object is catalytic isomerization of light gasoline fraction unit on sulfated catalyst with different recycle flows direction (figure 1) and isomerization unit with recycle of unconverted hexanes on chlorinated Pt-content catalyst (figure. 2).

* Corresponding author: chuva@tpu.ru

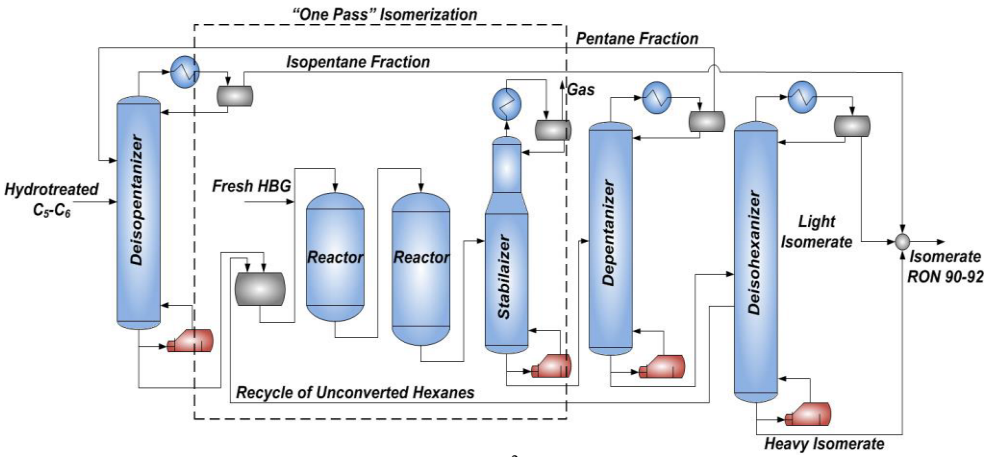

Fig. 1. Light naphtha isomerization PFD on $Pt/SO_4^{2-}/ZrO_2$ catalyst "One pass" and with recycles of n - C_5 and unconverted hexanes

Isomerization catalysts based on sulfated metal oxides combines high activity and resistance to poisons and have ability to regeneration [1-3]. "One pass" isomerization technology is the simplest, has minimal capital and operation costs and provides the production of isomerate with 80-82 RON. Including in "one pass" isomerization recycles of unconverted $C_5 - C_6$ hydrocarbons takes more difficult conditions of its operation but helps to reach the increase in RON about 10-12 points.

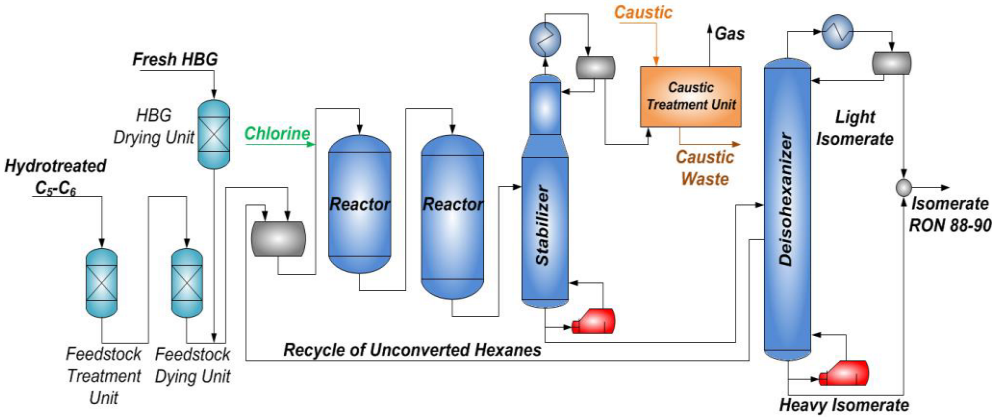

Fig. 2. Light naphtha isomerization PFD on $Pt/Cl^-/Al_2O_3$ catalyst with recycle of unconverted hexanes

Catalysts based on chlorinated alumina oxide due to longtime operation lose chlorine. In result its activity is decreased. In addition it requires a caustic treatment unit to utilize organic chlorine. Chlorinated catalyst can't be regenerated and its operation cycle is 3-5 years.

3 Methods

In this paper for description of unsteady catalytic processes of hydrocarbon feedstock isomerization the method of mathematical modelling is used. According to characterized methodology [4-15] the construction of mathematical model of complicated chemical-engineering process consist in sequential implementation of following stages: conducting of thermodynamic analysis, estimation of kinetic parameters of thermodynamically possible reactions, construction of reactor model and chemical-engineering system at all.

The full mathematical description of hydrocarbon feedstock catalytic isomerization process is formatted on components material and heat balances:

$$\begin{cases} G \cdot \frac{\partial C_i}{\partial z} + G \cdot \frac{\partial C_i}{\partial V} = \sum_{j=1}^{m} a_j \cdot r_j \\ \frac{\partial T}{\partial z} + G \cdot \frac{\partial T}{\partial V} = \sum_{j=1}^{m} a_j \cdot r_j \cdot \Delta H_j \end{cases}$$

if Z=0, C=0, where r=0, $C=C_0$, if Z=0, $T=T_0$, where r=0, T=Tin;

where G is a feedstock flow rate, m^3/h; z = G*t (t is a overall time of catalyst work starting from the new catalyst load, h); Ci is a concentration of ith component, mol/m^3; V is a volume of the catalyst bed,m^3; a is a catalyst activity; ρ is density of hydrocarbon mixture, kg/m^3; Cmp is a specific heat capacity of hydrocarbon mixture, J/(kg*K); Q_j is jth reaction heat, J/mol, T is temperature, K; rj is jth reaction rate, $mol/(m^3\ h)$, a – activity of catalyst.

The program realization of this model is implemented in Delphi 7. The initial data for calculation are feedstock composition and operation parameters of the process. The adequacy of the model is estimated by comparison of experimental data from industrial isomerization plant with calculated values [10]. The activity of catalyst is decreased due to processes of coke formation, poisoning and ageing.

4 Results and Discussion

The research of kinetic parameters of purposeful reactions of light naphtha isomerization process for chlorinated and sulfated catalysts is presented in table 1.

Table 1. The comparison of major reactions kinetic parameters of isomerization process

Reactions	**Relative rate constants**	
	$Pt/SO_4^{2-}/ZrO_2$	$Pt/Cl^-/Al_2O_3$
$n\text{-}C_5 \rightarrow i\text{-}C_5$	1	0.31
$i\text{-}C_5 \rightarrow n\text{-}C_5$	1	0.96
$nC_6 \rightarrow$2Methylpentane	1	0.47
2Methylpentane →2.3 Dimethylbutane	1	0.16
2Methylpentane →3Methylpentane	1	1.72
2.2 Dimethylbutane →2.3 Dimethylbutane	1	0.85

Rate constants of major reactions for sulfated catalyst are taken as 1, rate constants for chlorinated catalyst are performed as a part of 1. In such a way major reactions of isomerization process pass faster on sulfated catalyst.

The isomerate composition for different light straight run cuts isomerization technologies is presented in table 2.

Table 2. Calculated isomerate composition

Component	Isomerization Technology

	$Pt/SO_4^{2-}/ZrO_2$ System		$Pt/Cl^-/Al_2O_3$ System
	"One Pass"	With n-C_5 and C_6 Recycle	With Unconverted C_6 Recycle
n-butane	0.16	0.42	0.44
i-butane	0.13	0.00	0.06
n-pentane	14.32	0.00	11.47
i-pentane	33.38	2.32	30.72
n-hexane	6.01	6.87	0.54
2-methylpentane	15.13	0.00	5.20
3-methylpentane	7.70	9.87	0.75
2,2-dimethylbutane	11.74	61.75	36.12
2,3-dimethylbutane	4.41	14.90	5.20
n-heptane	0.04	0.13	0.00
Sum i-C_7	3.28	3.74	0.00
Sum C_8	1.79	0.00	0.00
Cyclopentane	0.84	0.00	9.11
Methylcyclohexane	1.06	0.00	0.40
Isomerate RON	***80.20***	***91.58***	***82.85***

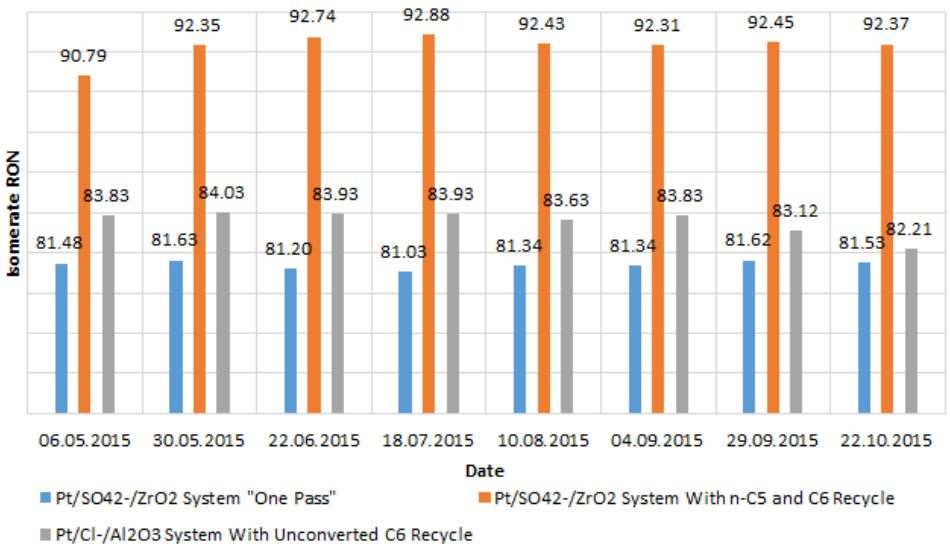

Fig. 3. Isomerate RON vs different types of catalyst and PFD

Application of catalyst based on sulfated zirconia in industrial isomerization process with recycles of unconverted hydrocarbons C5-C6 allows to produce isomerate with RON 10-12 points higher than traditional “one pass” isomerization technology and with RON 8-9

points higher than technology based on chlorinated catalyst with unconverted C_6 hydrocarbons recycle (figure 3).

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