Study of C5/C6 isomerization on Pt/H-zeolite catalyst in industrial conditions

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Abstract. This is an experimental study of C5/C6 isomerization on Pt/H- zeolite conducted in industrial conditions. The goal of the work was to find the kinetic parameters of the main isomerization reactions, by considering the industrial reactor as an ideal plug flow reactor. This assumption is fair, taking into account the high pressure and low linear velocity of the effluent in the reactor. The kinetic model can be used for the prediction of isomerizate production and quality.

Keywords: kinetic parameters, isomerization, LSRG

1. Introduction

The increasing demand for gasoline pool with high octane number, cost-effective and environmentally sound, led to the development of new technologies but also to the improvement of old solutions, such as the isomerization of light straight run gasoline (LSRG) [1, 2, 3].

With the goal of maintaining the gasoline pool octane, without adding lead compunds and having in view the reduction of benzene concentration, the isomerization of light straight run gasoline- LSRG - is a very attractive solution.

Light naphtha cuts result in good yield at oil processing, so a high quantity of improved octane naphtha can be obtained. The branched molecules resulting in the process increase the octane number of the LSRG with approx. 20 units. The resulting gasoline fraction has a higher vapour pressure than the feed, so ignition will be improved.

The present study of C5/C6 isomerization on Pt/H- zeolite was conducted in industrial conditions. The goal of the work was to find the kinetic parameters of the main isomerization reactions, by considering the industrial reactor as an ideal plug flow reactor.

The yield and composition of obtained products in the process are of highest importance. The knowledge of the mechanism and a good model based on it, predicting the production and the quality of the isomerizate is useful for the production forecast of the industrial unit.

2. Theoretical aspects

Straight light run gasoline with boiling points range of 27-72°C is mainly composed of n-Parrafins : n-Pentane and n-Hexane. The main reactions are presented in **Fig.1**.
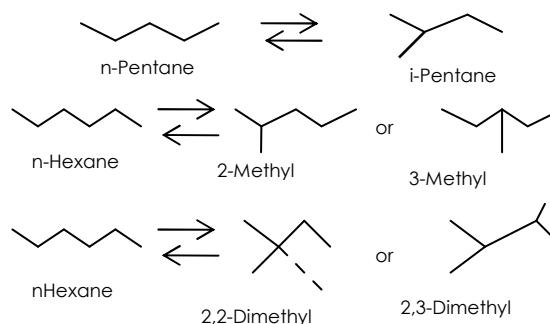
Fig. 1. Main reactions at the isomerization of C6/C6 naphtha on zeolitic catalyst

The secondary reactions with neglictible yield are: hydrogenation of olefins and hydrocracking.

The isomerization reactions occur on alumina or zeolites based catalyst. New catalysts are bifunctional with metallic and acid centers [3], and the mechanism described in [4, 5] involves the following steps:

1.Dehydrogenation: the n-Paraffinic molecule is adsorbed on a metallic center and an olefinic molecule is formed

2. Isomerization: the formed molecule is transferred on an acid center where it gains a proton, the hydrocarbon chain is branched and the resulting i-Olefin releases the proton

3. Hydrogenation: the i-Olefin is transferred back on the metallic center where it is fast hydrogenated.

The kinetics of the isomerization reaction depends on the catalyst type. Bremer *et al* [6] considered the main reactions as pseudo-first order reactions for bifunctional catalyst NiH/NaY zeolite.Other authors found different order for the main reactions. Spivey and Bryant [7] modelled the isomerization on Pt/CaY zeolite with the Eq.1 and 2:

$$r_{C5} = 134(1 + 0.294 \cdot P_{C5})^2 \cdot P_{H2} \qquad (1)$$

$$r_{C6} = 366(1 + 0.124 \cdot P_{C6})^2 \cdot P_{H2} \qquad (2)$$

Where *r* is the reaction rate [kmol/h], P_{C5}, P_{C6} and P_{H2} are the partial pressure of C_5, C_6 and H_2 respectivelly, in bar.

In [8], Ahari *et al* found more complicated equations for the catalyst Pt/H zeolite where the reaction rate of every hydrocarbon depends on the partial pressure of all the other compounds in the reactor. Also, Ahari *et al* produced two sets of equations, one for the temperature 260°C and one for the temperature 270°C.

The goal of this study was to find kinetic equations valid for the Pt/H zeolite in the range of running parameters of the industrial reactor, taking into account that the temperature varies in narrow limits.

3. Experimental

The experiment was conducted in an industrial reactor on Pt/H zeolite catalyst. The installation is presented in **Fig.2.** The parameters of the reactor were collected during a month. The main fluxes indicated in Fig.2 are: 1- feed, 2-recirculated paraffins, 3- effluent and 4- isomerizate. The fluxes were analysed by GC-FID daily and chromatographic data served to calculate conversions and yields. The C5+C6 n- paraffin

content in feed varied between 55-68% as seen in **Fig.3**.
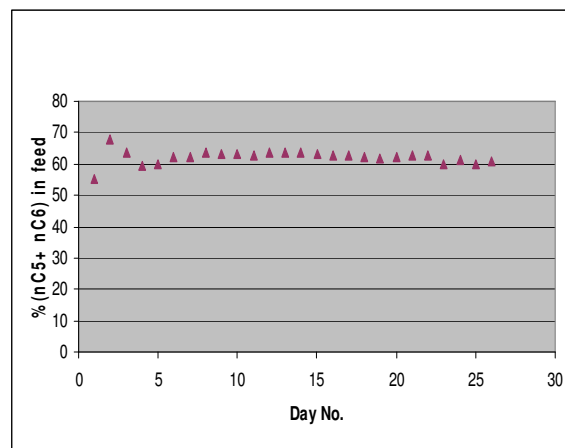
Fig.3. n-Paraffin content in feed during the test run

The parameters of the reactor during the test run are presented in **Table 1**:

Table 1. Parameters of the isomerization reactor during the test

| Parameter	Unit	Value (limits)
Reaction zone volume	m^3	10
Flowrate	m^3/h	9-11
Liquid Hourly Space Velocity (LSHV)	h^{-1}	0.99-1.1
Average temperature in the reactor	^{o}C	258-263
Pressure	bar	20-24
Molar ratio H$_2$/feed	-	1.1-1.7

4. Results and Discussions

The data collected in the test served to calculate the conversion of Paraffin in the reactor (**Fig.4**).

The conversion of nC$_5$+nC$_6$ varied between 18.3-27.2%. Since the catalyst was a performant one, the feed had the recommended composition and all the parameters in the reactor were those indicated by the designer, this low conversion should be due to the poisoning of the catalyst with H$_2$S present in the hydrogen flow; usually, the H$_2$ used in this process is residual from refinery.
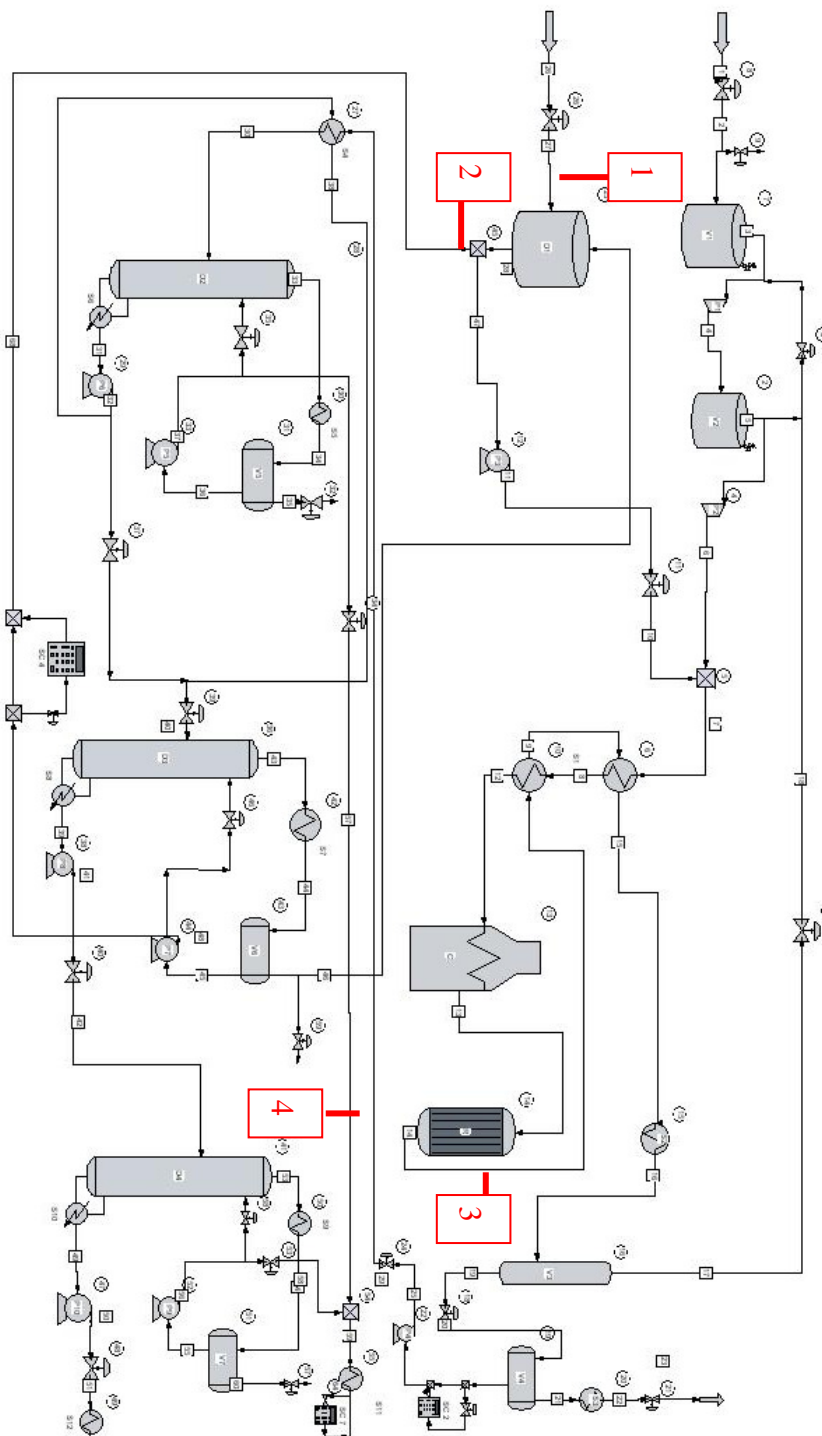
Fig. 2. The industrial C5/C6 isomerization unit.. 1- feed; 2-recirculated paraffins; 3- effluent; 4- isomerizate
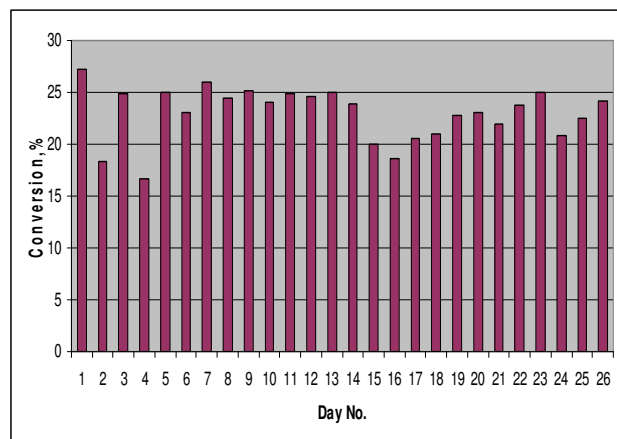
Fig.4. The conversion of n-Parrafin in the reactor, during the test

The feed only contained n-Paraffin, i-Parrafin and cyclo-Paraffin, without aromatics.

Based on our experimental data, a mathematical model is proposed (Eq.3 and 4), close to Spivey and Bryant's model but even simpler:

$$r_1 = k_{C5} P_{C5}^2 \cdot P_{H2} \qquad (3)$$

$$r_2 = k_{C6} P_{C6}^2 \cdot P_{H2} \qquad (4)$$

The meaning of the terms in Eq.3-4 is the same as in Eq.1-2. k_{C5} and k_{C6} are the kinetic constants for the C_5 transformation and for C6 respectivelly [kmol h^{-1}bar^{-3}].

The goal of the work was to find the kinetic parameters of the main isomerization reactions (k_{C5} and k_{C6}), by considering the industrial reactor as an ideal plug flow reactor. This assumption is fair, taking into account the high pressure and low linear velocity of the effluent in the reactor. So, the characteristic ecuation of the plug flow reactor (Eq.5):

$$\tau = c_{A0} \int_0^{X_A} \frac{dX_A}{r} \ , \qquad (5)$$

was customized for the said reactions (Eq.6 and 7):

$$\tau = \frac{1}{k_{C5} P_{C5} P_{H2}} \int_0^{X_{C5}} \frac{dX_{C5}}{(1 - X_{C5})^2} \qquad (6)$$

$$\tau = \frac{1}{k_{C6} P_{C6} P_{H2}} \int_0^{X_{C6}} \frac{dX_{C6}}{(1 - X_{C6})^2} \qquad (7)$$

In Eq. 5, τ is the residence time in the reactor, A denotes the reactant (nC5 or nC6), c_{A0} is the concentration of the reactant in the feed and X denotes the conversion (as fraction).

Equations (6) and (7) were integrated and the mathematical expression of k_{C5} and k_{C6} (Eq.8-9) resulted:

$$k_{C5} = 1/[\tau \cdot p_{C5} \cdot p_{H2} \cdot (1-X_{C5})] \qquad (8)$$
$$k_{C6} = 1/[\tau \cdot p_{C6} \cdot p_{H2} \cdot (1- X_{C6})] \qquad (9)$$

The parameters k_{C5} and k_{C6} [kmol h^{-1}bar^{-3}] were calculated for each set of experimental data and the mean value and relative errors were determined:

- k_{C5}=0.0217 with a medium error 6.5% and a maximum error 21.2%;
- k_{C6}=0.1877 with a medium error 6.1% and a maximum error 17.1%;

The errors are acceptable. This conclusion was drawn taking into account that similar study [8] gave higher errors (medium error 11.1% and maximum error 26.3%) and, in general, in chemical engineering studies, such errors are frequent and acceptable.

5. Conclusions

This experimental study of C5/C6 isomerization on Pt/H- zeolite conducted in industrial conditions had the goal to find the kinetic parameters of the main isomerization reactions. The kinetic constants were found with reasonable errors.

The kinetic model is valid for the range of parameters in the test period: temperature 260^{0}C±3^{0}C, LHSV=0.99-1.1 h^{-1}, pressure 20-24 bar, H$_2$/feed molar ratio: 1.1-1.7. This range of parameters is tight but the industrial process doesn't exceed it.

The practical result of this study is that the kinetic equations proposed here can be used for the prediction of isomerizate production and quality.

6. References

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