

Model and Simulation of a Pentane Isomerization Reactor for Naphtha Stream in Oil Refining

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Abstract

Nowadays, the development of oil refining processes has taken a great importance in the industry, on account of new legislation which requires environmentally sustainable fuels. To complete these requirements, the refinery plants had been introducing processes to different streams to decrease their pollutant load. One of them is the isomerization used to increase the octane number in the stream. The reaction carries out in this process was achieved in a reactor catalyzed by Pt / SO₄²⁻ / ZrO₂, which is in charge of isomerizing the n-pentane (RON: 61.7) to i-pentane (RON: 92.3). The process was modelled using the Chao Seader model for hydrocarbon mixtures and subsequently simulated. In the reactor, it was necessary the hydrogen and the naphtha streams, which were adapted to reactor conditions. It was studied two variants of the process, the first one where the outlet reactor stream was not treated, while in the latter variant, the stream was cooled and sent to a flash separator, in order to obtain a hydrogen stream to recycle to the process and an isomerized product. The isomerization plant was optimized to achieve an adequate temperature in the reactor and in the separator to increase conversion and hydrogen purity for recycling. It was acquired 510 K and 310 K for temperature respectively. The conversion achieved was higher than 95% for the alkane.

Keywords: Chao Seader model, Chemical reactor, Chemical simulation, DWSIM, Light petroleum streams, Pentane

Introduction

Nowadays, the oil industry had decided to increase the commercial value for light streams, through different processes in the refinery plant [1]. Among the most used techniques are the hydrotreatment use to decrease the pollutants, the isomerization and the alkylation use to increase the octane number for the streams, the thermal cracking to take advantage of thick streams, among others [2], [3].

The isomerization is the process whereby a molecule transform in another one, where the new compound had the same atoms than the first, however, they are organized in a different way [4]. Both compounds are isomers. This technique is widely used by the petroleum industry, due to it is a reaction used to transform n-paraffin of low octane number into i-paraffins of high octane [5]–[7]. This process increases the fuel purity and the plant profitability [8].

To carry out the reaction it is necessary a catalyst with a precious metal. Additionally, the reaction requires the presence of hydrogen [9]. Exist three types of catalysts, the chloride alumina, the zeolitic and the sulphated metal oxide catalysts, which requires work with a lower temperature, to obtain a higher octane number in the outlet stream [10]. The chloride alumina type catalysts were developed in the 1930s, with the purpose of getting i-butane using n-butane as a reactant, however, the reactor also requires a chloride stream and a basic stream to neutralize the outlet stream [6], [11].

Currently, it has been developing new catalysts for isomerization able to admit pollutants in the feed stream, without decrease his activity and which in turn decreases the cost per barrel of the product [12]–[15]. In work made by Shaofeng et al. in 2013 were used bifunctional catalysts with a double reaction mechanism with the purpose of decrease their activation energy and increase the octane number in the outlet stream [16].

In this paper, it raises a pentane isomerization process, with heavy crude oil from Colombia, through the high-pressure isomerization of compounds. In previous phases of the project, it was obtained the characterizations for the outlet stream from a fractionated distillation column. The isomerization process was made with a light fraction called Naphtha 2, which had a high content of n-pentane and with low content of heavy metals, the reason why the stream had the suitable conditions to be processed.

Methodology

With the purpose of the model and simulate the isomerization process for a light stream from the fractionated distillation column, it starts with the characterization in Table 1. This flow contains a significant part of n-pentane which has a research octane number (RON) of 61.7, while for the i-pentane the value is 92.3 [6].

Table 1: Naphtha stream characterization.

Stream	Naphtha 2
Temperature [°C]	260.596
Pressure [kPa]	1311.667
Molar flux[kgmole/h]	5.234
Mass flux [kg/h]	705.503
Std Volumetric flow [m3/h]	0.971
Molar enthalpy [kJ/kgmole]	-2.016E+05
Molar composition	
Ethane	0.0032
Propane	0.0010
i-Butane	0.0048
n-Butane	0.0008
i-Pentane	0.3686
n-Pentane	0.4890
n-Hexane	0.1278
n-Heptane	0.0028
n-Nonane	0.0019
n-Dodecane	0.0001

The stream had 12.3% of n-hexane, which could isomerize into 2-methyl pentane, however, this compound only has an RON of 73.4, wherewith the profitability of the process will decrease in comparison with a pentane isomerization. During this process, the maximum concentration of i-pentane at the reactor it is contained by the thermodynamic equilibrium between the three species, (

Figure 1), as shown in Equation (1).

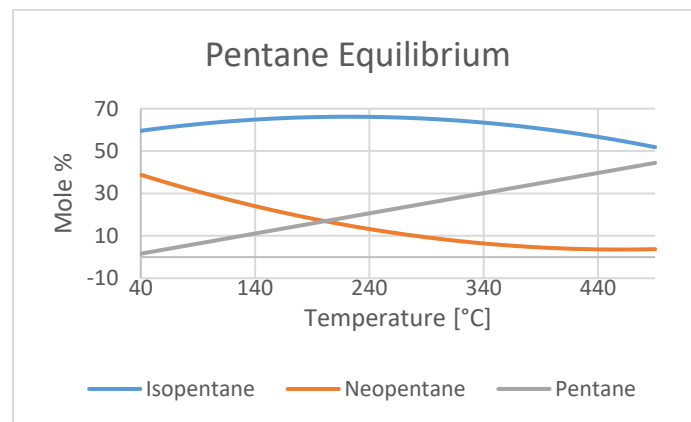
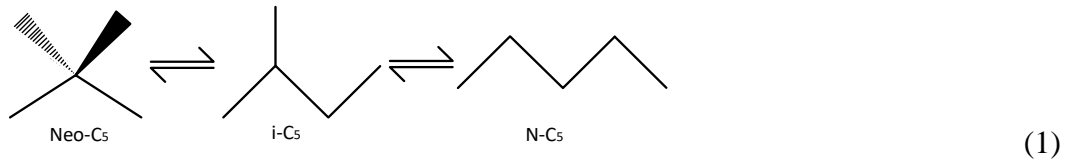


Figure 1: Thermodynamic equilibrium for the pentane.



The reaction occurs in a catalyzed reactor, using the simulation parameters in Table 2. These variables were obtained from values recommended in the literature for an adequate operation and accomplish with the isomerization conversion.

Table 2: Isomerization reactor parameters for steady state [6], [17].

Pressure (MPa)	2
Temperature (°C)	210
LHSV	3.0
H2 / nC5 Ratio	1.5

The physicochemical properties of the process were obtained through the model plant by K. C. Chao and J. D. Seader in 1961 for hydrocarbon mixtures [18]. The vapour-liquid equilibrium (VLE) for the system had as base semi-empirical parameters. The general way for this method is based on equation (2).

$$K = \frac{y}{x} = \frac{v^* \varphi}{\gamma} \quad (2)$$

Where:

- " v^* " is the fugacity coefficient for the pure liquid,
- " φ " is the fugacity coefficient for the component i in the vapor mixture and
- " γ " is the activity coefficient for the component i in the liquid solution.

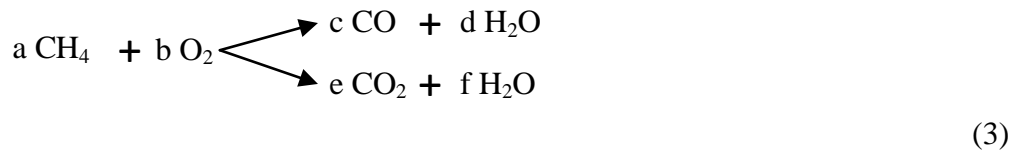
The calculus of the vapour phase is made through the Redlich-Kwong state equation, while for the liquid phase it was used the Scatchard-Hildebrand regulars solution theory [19].

The process was modelled and simulated in the Open Source DWSIM software made by Daniel Medeiros and Gregor Reichert. The simulation starts with the inlet stream to the process, which is adapted to accomplish with the system conditions. The hydrogen flow was set up using the data in Table 2.

The kinetics reaction for the reactor was adapted from the work made by Kimura in 2003, in which was developed a platinum catalyst on Sulfated zirconium oxide [15]. To increase the performance and reduce costs in the process, it was implemented a cooling and a separation system for the hydrogen in the outlet stream. Also, the plant was optimized through a sensibility analysis to find the optimum reactor temperature and the optimum separator temperature, which enhance the quantity of i-pentane produce and the purity of the hydrogen for recycling.

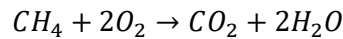
With the aim of cooling the reactor outlet stream, it was proposed an energy removal system using water. For this process, it was taking into account a minimum energy delta of 10 °C, in order to ensure an adequate heat transfer.

The boiler used to adapt the reactor inlet stream was feed with a mixture of methane, which was in a mix with an excess of oxygen. Using the simulator, it was obtained the heat necessaire to increase the Naphtha temperature. With this value, it is possible to know the quantity of required methane to produce this energy, through the methane combustion reaction (Equation 3).



Where the parameters a, b, c, d, e and f, were the stoichiometric variables of the reaction.

For a complete combustion reaction:



Due to co-exist two simultaneous reaction (Complete and incomplete combustion), it was estimated an occurrence probability, taking into account the Gibbs free energy for the reaction;

$$\Delta G_{rxn} = (\Delta G_{\text{CO}_2} + 2 * \Delta G_{\text{H}_2\text{O}}) - (\Delta G_{\text{CH}_4} + 2 * \Delta G_{\text{O}_2})$$

$$\Delta G_{\text{CH}_4 \rightarrow \text{CO}_2} = -818.255 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta G_{\text{CH}_4 \rightarrow \text{CO}} = -561.048 \frac{\text{kJ}}{\text{mol}}$$

The probability was calculated using the equation (4), for which were obtained the following occurrences:

$$P_{A \rightarrow B} = \frac{\Delta G_{A \rightarrow B}}{\sum(\Delta G_{A \rightarrow \dots})} \quad (4)$$

$$P_{\text{CH}_4 \rightarrow \text{CO}} = \frac{\Delta G_{\text{CH}_4 \rightarrow \text{CO}}}{\Delta G_{\text{CH}_4 \rightarrow \text{CO}} + \Delta G_{\text{CH}_4 \rightarrow \text{CO}_2}}$$

$$P_{\text{CH}_4 \rightarrow \text{CO}} = 0.407$$

$$P_{\text{CH}_4 \rightarrow \text{CO}_2} = 0.593$$

Results and discussion

The system temperature is an important variable, due to it affects the maximum concentration that could be obtained from the iso-pentane in the solution. These variables had a direct relationship, the reason why to a higher temperature the quantity

of n-pentane increase, which mainly affects the neo-pentane concentration as shown in Figure 1. For the case of iso-pentane, the maximum concentration was approximately 70% with a temperature near to 260°C. It should be noted that the maximum composition was the maximum obtained from the thermodynamic equilibrium.

Considering the previous theme and the values in Table 2, it was designed an isomerization catalytic reactor for light naphtha as shown in Figure 2. It has a packaged zone with catalysts which match with the 70% of the total reactor volume.

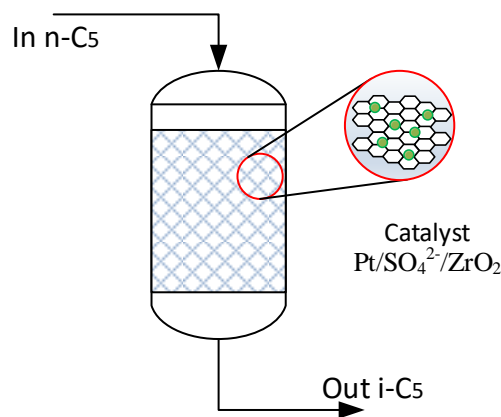


Figure 2: Isomerization reactor.

The reactor was designed in Microsoft Excel and assemblies with the DWSIM software. First, the process was modelled without recycling as shown in Figure 3. The naphtha stream originating from the fractionated distillation column was adapted to ensure the process pressure. Subsequently, it was added a hydrogen atmosphere to facilitate and promote the reaction.

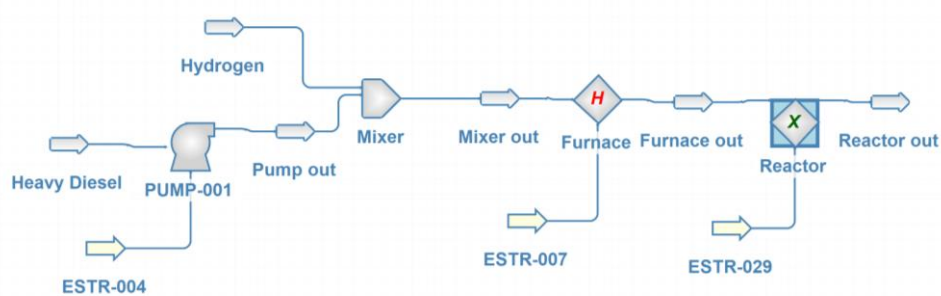


Figure 3: Isomerization process without recycling.

The resulting mixture was heated to obtain the sufficient reactor temperature, for this case, the temperature was located on 210°C. At the end of the reaction, it was got a flux ratio of 0.735 between the iso-pentane with the n-pentane.

Table 3: Outlet reactor stream without recycle

Stream	Out Reactor
Temperature [°C]	467.16
Pressure [kPa]	1760000
Molar flux[kgmole/h]	5.9651753
Mass flux [kg/h]	0.20265143
Std Volumetric flow [m3/h]	0.01293254
Density[kg/m3]	1.57E+01
Mass Flow	
Ethane	2.5517E-04
Propane	1.1694E-04
i-Butane	7.3982E-04
n-Butane	1.2330E-04
i-Pentane	1.6283E-01
n-Pentane	1.2522E-03
n-Hexane	2.9205E-02
n-Heptane	7.4401E-04
n-Nonane	6.4621E-04
n-Dodecane	4.5170E-05
Hydrogen	6.6788E-03

In Table 3 was the reactor outlet stream characterization for the process without recycle. The catalyst used achieved a conversion of 95.3%. However, it was observed a flow of 0.00668 kg/s of hydrogen, which equivalent to 3.3% from the current. In order to decrease the costs, it was made a hydrogen recycle, through its separation falling the stream temperature. The process scheme was shown in Figure 4.

The process was designed taking into account the process without recycle, through the addition of a cooler, a flash separator and a compressor necessary to achieve the removal and the adaptation for the hydrogen stream from the outlet reactor stream.

From the isomerization, the plant was detected two critical sections for the optimization process. The first one was the outlet furnace temperature, while the second one was the outlet cooler temperature. These variables affect the behaviour and performance of the catalyst with the purpose of obtaining the highest quantity of isomer, considering the physical limitations and the costs generated. Also, the second variable modified the separator performance which is highly correlated with the purity in the hydrogen separated.

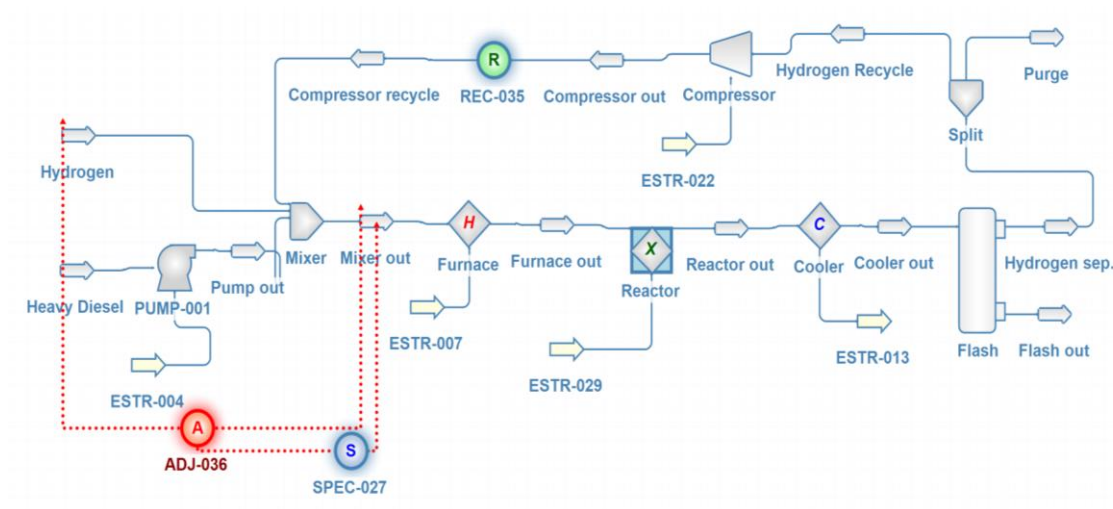


Figure 4: Isomerization process with recycle.

With the complete system, it was made a sensibility analysis changing the inlet temperature for the inlet temperature stream in function of the *i*-C₅ fraction in the reactor outlet stream (Figure 5).

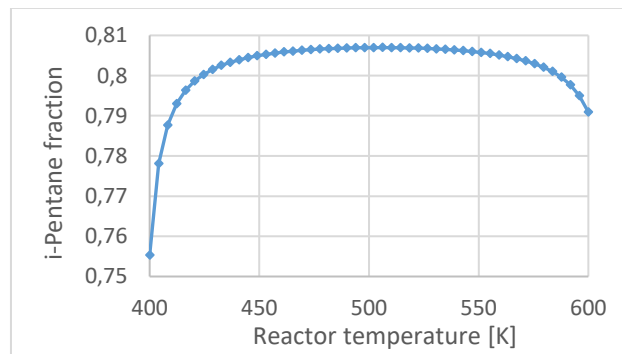


Figure 5: Reactor temperature variation vs *i*-C₅ fraction.

The furnace temperature was raised between 400 K to 600 K (126.8 – 326.8 °C), which was the optimum range to work in this reactors from the literature. It was found that the *i*-pentane mass fraction from the outlet reactor stream had a variation of 0.86% between 423 K and 588 K.

The operation point with the maximum *i*-C₅ concentration in the mixture was at 510 K, with a mass fraction of 0.807. However, it should be noted that there was not a significant change in this value since 423 K to the maximum point. The reason why it was not relevant increase the temperature beyond this stage in the absence of a substantial change in conversion. While, reach a higher temperature requires a big economic and energetical costs, as the equipment dimensioning and the day-to-day management.

Furthermore, it was realized a sensibility analysis for the operating temperature in a flash. It was considered two exit variables (Figure 6), the first one was the hydrogen

mass fraction in the separator's heavy stream, while the second was the hydrogen mass fraction to recycle.

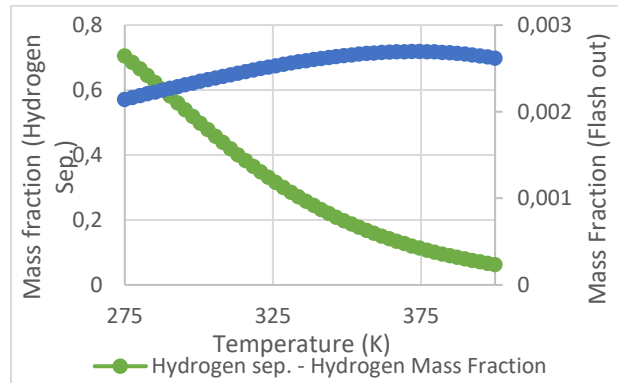


Figure 6: Cooler temperature vs hydrogen fraction.

In this case, the system compartment was analyzed between 275 K and 400 K. It should be distinguished that the outlet stream temperature was 467.17 K. For the hydrogen mass fraction in recycle stream, it was founded that had an inverse relationship, while for the second variable, exists a direct relation. However, for this variable, there was a maximum point at 377K and the behaviour for the system change.

For this process, it is recommended to work with lowers temperatures, with the aim of remaining the isomer stream in the liquid phase, while the hydrogen would be in the vapour phase to remove it. Even so, reach these lower temperatures involve a high cost and complicated process. The reason why it was recommended work at 310 K as the optimum temperature in which the cooler costs were reduced, and it's obtained an adequate separation.

With the optimum parameter for the system and the hydrogen recycle, it was achieved a flow relation of 0.7371, between the i-pentane with the n-pentane in the outlet reactor stream. This value was similar to the point obtained without the gas recycle in the system. However, the hydrogen make-up pass from 0.00668 kg/s to 0.000899 kg/s, which was equivalent to 13.5 times the quantity required. It transforms in a significant costs reduction for the raw materials in the system. The plant conversion reaches 99.7% for the n-pentane.

The cooling system used in the cooler for the separator was designed using water as heat transfer fluid, with an initial temperature of 293.15 K. The inlet water receives an initial process as shown in Figure 7. Which was obtained for a centrifugal pump from a tank, which increases the pressure to 4.0 bars, to be entered to the exchanger design in countercurrent flow as shell boilers.

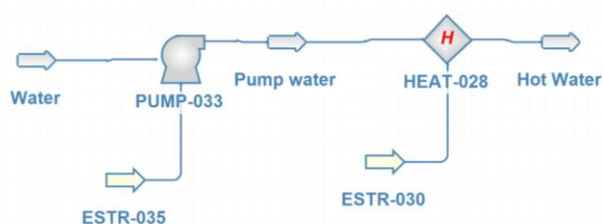


Figure 7: Water cooling system.

Finally, the water lets the system with a temperature of 321.21 K. It was necessary a flow of 1 kg/s achieves the desired temperature. It should be noted that the heat transfers its possible due to the countercurrent flow to ensure the delta of temperature in the system.

The preheating system for the reactor mixture uses methane as fuel, wherewith to obtain the required energy flux it was required 0.0005 kg/s of fuel. The quantity of reactants and products for the reaction were shown in Table 4.

Table 4: Preheating furnace fluxes for the combustion reaction.

Compound	Flux [kg/h]
Methane (CH ₄)	1.812
Oxygen (O ₂)	6.512
CO	1.290
CO ₂	2.956
H ₂ O	4.078
T ₁ [K]	298.15
T ₂ [K]	550.00

The temperatures 1 and 2 were the inlet fuel temperature and the outlet combustion gases respectively. For the furnace, the 40.7% of the admitted methane to the combustion zone produce carbon monoxide, while the other part will produce carbon dioxide. It should be considered that the outlet's streams, as the combustion gases and the outlet crude oil had a delta temperature of 40 K, wherewith is ensured the heat transfer in the system.

Conclusions

Currently, the development and implementation of processes in oil refining had taken a great acceptance, due to it comes necessary to accomplish the current laws for fuels. To design and optimize these processes there is a need to use an adequate software for simulating and predicting the physicochemical properties from the streams, furthermore, it decreases the time to develop calculus. In the isomerization process, a molecule is reorganized generating a new molecule with different properties, for the petroleum industry, the new molecules usually have a higher RON.

The system was designed with a separation part, to take advantage of the hydrogen in the reactor outlet stream. Wherewith, it was achieved a reduction of 13.5 times in the hydrogen make up. The system was optimized through two sensibility analysis, one for the reactor temperature, with a maximum point of 510 K, however, there was not a noticeable change in the mass fraction of i-C₅ in the range of 423 K and 588 K. For the second analysis, the separator to lower temperature the system achieved a better hydrogen separation, nevertheless, decrease the temperature is an expensive process, the reason why, it was recommended to work at 310 K, as operations conditions.

The stream used in the process was the naphtha stream taken from the fractionated distillation column. The characterized stream had an n-pentane content of 48.9% with an octane number (RON) of 61.7. Wherewith the stream was a perfect candidate for isomerization to i-pentane, increasing the RON to 92.3. The process with recycling achieved a conversion of 99.7% with the optimal conditions.

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