

Process System Engineering (PSE) Analysis on Process and Optimization of the Isomerization Process

Awan, Zahoor Hussein*⁺

Department of Food Engineering, NED University of Engineering and Technology, Karachi, PAKISTAN

Kazmi, Bilal

Department of Applied Chemistry & Chemical Technology, University of Karachi, Karachi, PAKISTAN

Saud, Hashmi

Department of Polymer and Petrochemical Engineering, NED University of Engineering and Technology, Karachi, PAKISTAN

Raza, Faizan; Hasan, Sahzeb

Department of Chemical Engineering, NED University of Engineering and Technology, Karachi, PAKISTAN

Yasmin, Farzana

Department of Food Engineering, NED University of Engineering and Technology, Karachi, PAKISTAN

ABSTRACT: Oil refineries are facing the ever-strict restriction in terms of fuel specification in view of the several policies by the environmental impact agency (EIA). Strict rules have been enforced on the gasoline product specification. Isomerization is one of the key processes for increasing the octane number of gasoline. Hence a case study has been performed using the concept of hydrogen once-through technology to analyze the process constraints for optimal operation of the process using Aspen HYSYS. In addition to this, a rigorous process model of isomerase stabilizer was also used to compare the results of the stabilizer model and optimize those various variables affecting the octane number of gasoline. The model was validated by observing the effects of constraints on the efficiency of the process by comparing it with the operational isomerization unit to further verify the authenticity of the case study. Furthermore, a calculator has been generated for the reactor temperature with respect to high benzene contents in the feedstock (benzene in feed Vs reactors ΔT).

KEYWORDS: Isomerization process; Hotpenex; Simulation; Aspen HYSYS; Isomerase; Benzene controlling; Stabilizer.

INTRODUCTION

With the world moving towards emission reduction and pollution control, fuel-producing companies are facing

stringent policies of the various environmental protection agencies in order to provide the cleaner fuel products

* To whom correspondence should be addressed.

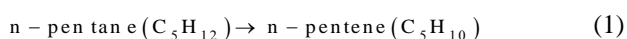
+ E-mail: zahoor@neduet.edu.pk

1021-9986/2021/1/289-302

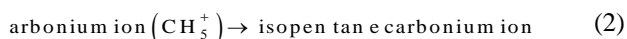
14/\$/6.04

that result in low emissions[1]. Therefore many processes are being used to enhance the quality of the product to meet the environmental specifications. One of which is to restructure the molecules of the feed components and produce a new molecular structure with the same number of carbon atoms[2]. This can be achieved by using the isomerization process. Isomerization is the chemical process where hydrocarbon molecules are rearranged from one structure to another, without changing the number of carbon or hydrogen atoms[1, 3].

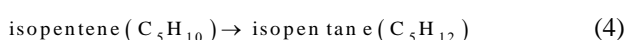
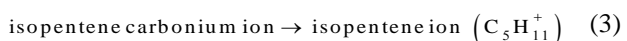
Isomerization reaction of normal paraffin to isoparaffin results in an exothermic reaction and it is favorable at a temperature range from 118–170°C [4,5]. Whereas Dehydrogenation of the n-paraffin due to the adsorption on the catalyst results in the formation of olefin as a side product.



Due to the low equilibrium conversion of paraffin isomerization, n-olefins can be converted to carbonium ions with the injection of strong chloride acid as initiator ion. This initiator help in the reaction by removing n-olefin components in order to start the hydrogenation reaction.



Hydrogenation reaction proceeds with a high reaction rate due to the higher acidity of the catalyst which causes the reaction to proceed at a higher rate. At that point, the carbonium particle changed over isoparaffin to iso-olefin by the dehydrogenation step.



The isomerization process is most productive to deliver high octane components of gasoline[4]. Isomerization process productivity further enhances the ability to produce enhanced motor gasoline (final product) having high octane number by removing aromatic and benzene contents. A catalytic isomerization process employing a platinum-based catalyst to convert low octane hydrocarbons (Light Naphtha) into higher-octane hydrocarbons (Isomerate) in the atmosphere of hydrogen [4, 6]. The process occurs in reactors at an operating

temperature range of 110–175 °C with a pressure of up to 35 bar. The reactor section is equipped with dual reactors, exchangers, a stabilizer, product separator, and a charged heater to heat the combined reactor feed material. The light naphtha feedstock (C₅/C₆), having a low octane value is then, mixed with the hydrogen gas stream and fed into the reactor. After heat exchanged with the reactor effluent, the combined feed passes through the heater and into the lead reactor. The inlet temperature is controlled using the heat input to the charged heater and the heater is heated using steam. High-temperature alarms and shutdowns around the reactor are tied into removing the heat from the charged heater and stopping the naphtha feed flow. The Isomerization Process also consumes hydrogen; therefore a continuous hydrogen gas supply is necessary for the once-through process[1, 7-8]. Unstabilized Isomerate after heat is exchanged in exchangers goes to Stabilizer and Stabilized Isomerate is directed to the storage tank. Stabilizers off-gases rich in hydrogen chloride are fed to a net gas scrubber for caustic treatment before sending to refinery gas fuel system. As high moisture and sulfur are poisons for the system so feed and hydrogen gas preparation are also required before going to the reactors section. This is being carried out by employing the sulfur guard bed on light naphtha to reduce the sulfur from 0.5 ppm to 0.1 ppm. Drying of naphtha and makeup hydrogen gas is also required in the feed so for this purpose makeup gas driers are utilized which can reduce the incoming streams to less than 0.1 ppm [9].

The more branched the hydrocarbon structure, the higher will be the octane number[10]. The more branched hydrocarbon structure of isopentane has a RON (Research Octane Number) of 93, whereas the less branched normal pentane has a RON of 61.8.[4, 11-12] Isomerization reactions are reversible, which means that they can proceed from either left to right (normal pentane to isopentane) or from right to the left (isopentane to normal pentane). High temperature favors the production of normal straight-chain molecules, and lower temperature favors the production of branched molecules[12].

Process simulation and assessment are considered as the vital step in designing new processes and technology in industries, especially for chemical engineering processes [13]. Through process simulation platform various different processes, their operating parameters, cost estimation, sensitivity analysis, and the scale-up results

can be carried out, which can be used for process optimization[14-15]. Considering the necessity of the isomerization unit and its future need a process simulation model of C₅-C₆ (penex) isomerization unit was developed using the process simulation platform for the whole process.[8, 16]. The components to represent Light Naphtha, and real-time plant scale design and operating data were utilized to observe the comparison between the actual and simulation scale models to optimize the system and improve the product properties with respect to its quality (i.e. RON) [4, 5, 8, 11].

THEORETICAL SECTION

Process variables

It is important to be able to relate the process variables with the performance of the unit and with catalyst life. This would ensure the effective operation of the process with greater efficiency. Following are the process constraints considered in Penex process as variables for the high efficiency of the process[1]:

Reactor temperature

Theoretically, Chemical equilibrium is the point when the reactions are in balance, and amounts of reactants and products are fixed, although not necessarily equal.

The equilibrium position at higher and lower temperatures favors the formation of normal paraffin and isoparaffins respectively. However, a minimum temperature is required to have a high enough reaction rate to approach the equilibrium curve.

As the temperature is increased, the equilibrium curve slopes approach downward, representing a decreasing isoparaffin concentration in the reaction product. The minimum temperature is required in order to have a high enough reaction rate to approach the equilibrium curve.

Additionally, space velocity also impacts the reaction rate. At low space velocities, as indicated by the 1.0 LHSV curve, a lower temperature can be used for enough reaction rate to approach the equilibrium curve[11]. When the feed rate is twice than the initial feed rate, as shown by the 2.0 LHSV curves than higher temperatures are required due to the shorter residence time.

Reactor pressure

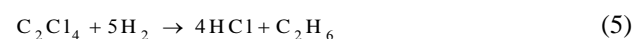
Isomerization units are ordinarily planned to function at 450 psig, although designed pressures are in the range

from 270 to 1025 psig[5]. At pressures higher than 450 psig, no significant change has been observed in iso-ratios. However, at reactor pressure lower than 450 psig, iso-ratios and octane number of the product also becomes low[4]. This is due to the impact of C₆ cyclic compounds which tend to adsorb on the catalyst, which results in lowering the catalyst activity[22]. The higher pressure is maintained in the reactor to avoid this impact.

Catalyst

Metal and acid sites promote different reactions. Paraffin isomerization reactions are catalyzed by both metal and acid sites in intermediate steps. Benzene saturation and Naphthenes ring-opening reactions are catalyzed by only these metal sites. It is useful to understand what reactions are catalyzed by which sites on the catalyst. For example, if the metal site is poisoned, then the benzene saturation reaction will be inhibited[6]. The resulting loss of reaction will appear as a reduction in the exothermic reaction across the reactor. Table 1 shows the reactions and catalyst sites that promote the reaction. Catalysts are usually susceptible to two types of poisoning. One is the temporary poisons. Temporary poisons attack the platinum sites of the catalyst but do not attack the chloride sites. Second is the Permanent poison which attacks the acid sites and either removes the chloride or blocks the active site which may be available for the reaction[22]. Water is an example of a permanent poison that would deactivate the chloride site. Heavy hydrocarbons (benzene, naphthenes, etc) are permanent poisons that block access to the active sites of the catalyst.

So to promote the functionality of the catalyst, perchloroethylene (PERC), an organic Chloride catalyst, is introduced in the process stream to maintain catalyst activity on the acidic side[19]. At a temperature of 104.4 °C or higher, PERC will be decomposed into hydrochloric acid and ethane in the presence of the Penex catalyst and hydrogen.



Performance factors

LHSV (Liquid Hourly Space Velocity)

Liquid Hourly Space Velocity is commonly referred to as LHSV which is defined as the hourly volume flow of reactor charge, divided by the volume of catalyst contained in all of the reactors[1].

Table 1: Catalyst functionality for various isomerization reactions.

Reaction	Catalyst site
Paraffin isomerization	Metal/acid
Benzene saturation	Metal
Naphthene isomerization	Acid
Naphthene ring opening	Metal
Hydrocracking	Acid
Heavier formation	Metal

$$\text{LHSV (hr}^{-1}\text{)} = \frac{\text{volumetric flow rate of feed (ft}^3\text{/h)}}{\text{catalyst volume (ft}^3\text{)}} \quad (6)$$

The design LHSV for isomerization units is normally between 1 and 2 h⁻¹. In general, increasing the LHSV leads to lower product iso-ratios, due to the shorter contact time with the catalyst.

H₂ to hydrocarbon ratio

There should be a minimum ratio for the hydrogen been used against the hydrocarbon in the reactor (0.05)[1]. The ratio is calculated from the contained hydrogen in the stabilizer off the gas, as indicated by FI-3, to the C₅/C₆ feedstock, as indicated by FI-1 in Fig. 2. This ratio ensures that there is an excess of hydrogen throughout the reactors.

The hydrogen to hydrocarbon(HC) ratio should be kept at or above the designed value to ensure that there is sufficient hydrogen for isomerization as well as other hydrogen-consuming reactions. Excess hydrogen will cause the product iso-ratios very low. By maintaining the ratio at the designed value will also help to avoid potential carbon deposition on the catalyst.

Product iso ratio

Iso-ratios are defined as the percentage of a component divided by the total sum of the paraffin of the same carbon number. These percentages are typically reported in weight percent. Due to their high octane value, the three iso-ratios of most interest are isopentane, 2,2-dimethyl butane(DMB), and 2,3-dimethyl butane.

Paraffin Isomerization Number (PIN)

The paraffin isomerization number (PIN) is a measure of the degree of isomerization in the product. The PIN

is deliberately added together with the iso ratios of isopentane, 2,2-dimethyl butane, and 2,3-dimethyl butane.

X-factor

The X-Factor is an indication of the heavy hydrocarbon components (benzene, cyclohexane) in the feed. The heavies consist of the C₆ cyclic and C₇₊ material in the feedstock. The X-factor is calculated by using the equation given below. Feeds with high X-factors are more difficult to isomerize and will have a lower product octane number.

$$\text{X factor} = (\text{wt\% methylcyclopentane}) + (\text{wt\% benzene}) + (\text{wt\% cyclohexane}) + (\text{wt\% C}_{7+}) \quad (7)$$

Herein, a rigorous simulation model was developed and the objective is to improve and discuss the quality of the product (RON) with the feed rate and composition. Since the controlling of Benzene and the reactor temperature is important as it would affect the RON. Therefore, keeping this in view a calculation methodology is depicted based on the optimization of simulation which predicted controlling the content of Benzene with respect to benzene in feed Vs reactors ΔT. The process was further optimized based on various analytical and performance aspects the obtained results were then compared to the actual plant scale model to check the results reliability.

Methodology

Penex process scheme has been used as the base case to study and analyze the process constraints for the isomerization of the light naphtha as shown in Fig. 1. The Penex process helps refiner in terms of flexibility for the choice of Feed stocks [9, 19]. Light straight Naphtha has been used as a feed source for the Penex unit [5, 11, 12, 17,18]. These include C₅/C₆ streams from any of the following units: hydrocracker fluidized catalytic cracker, visbreaker, delayed Coker, or catalytic reformer [3].

Hydrotreated feed flows through a discretionary sulfur guard bed and then through a traditional liquid feed drier. After dryers, the effluent is sent to the feed surge drum. Makeup hydrogen flows through an optional chloride treater and methanator, and then through a set of gas dryers and finally mixed with the feed. The hydrogen-feed mixture is preheated in the combined feed heat exchangers [3, 5, 12].

Chloride, in the form of perchloroethylene, is added

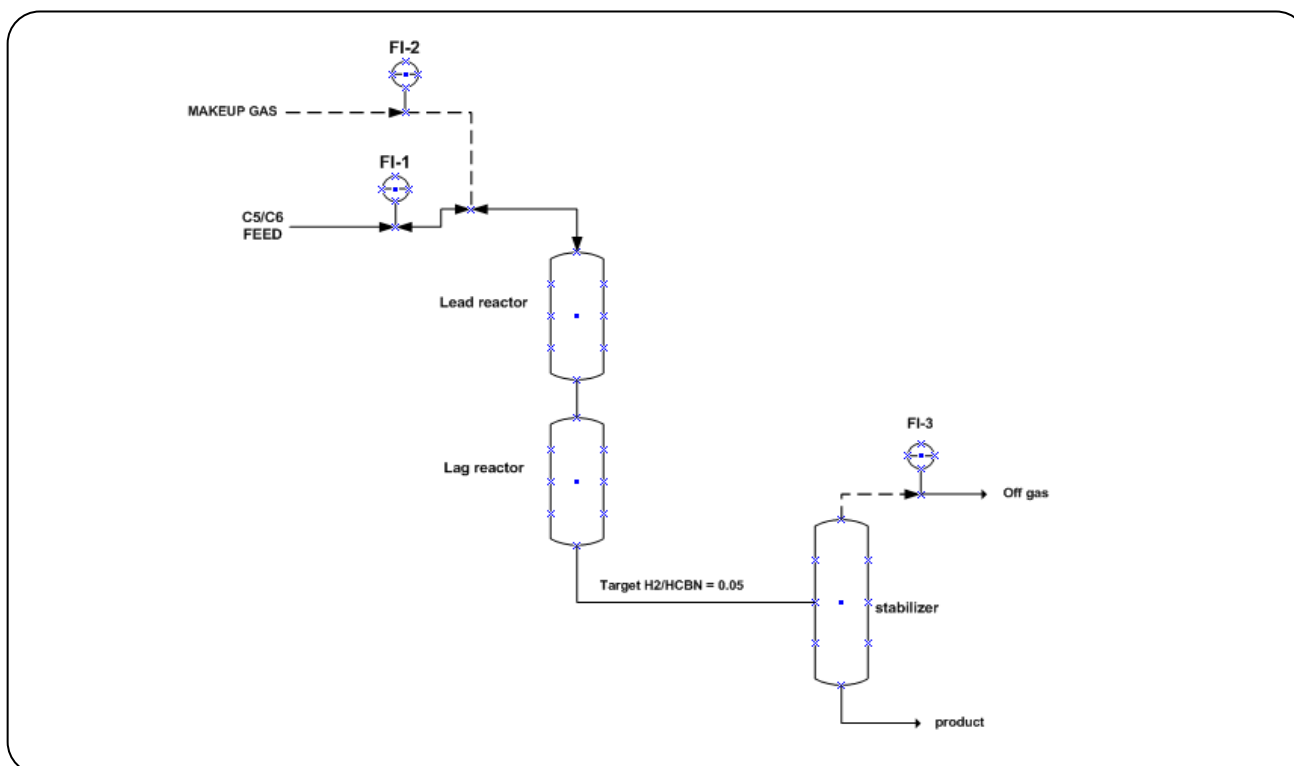


Fig. 1: H₂/HC ratio controller arrangement.

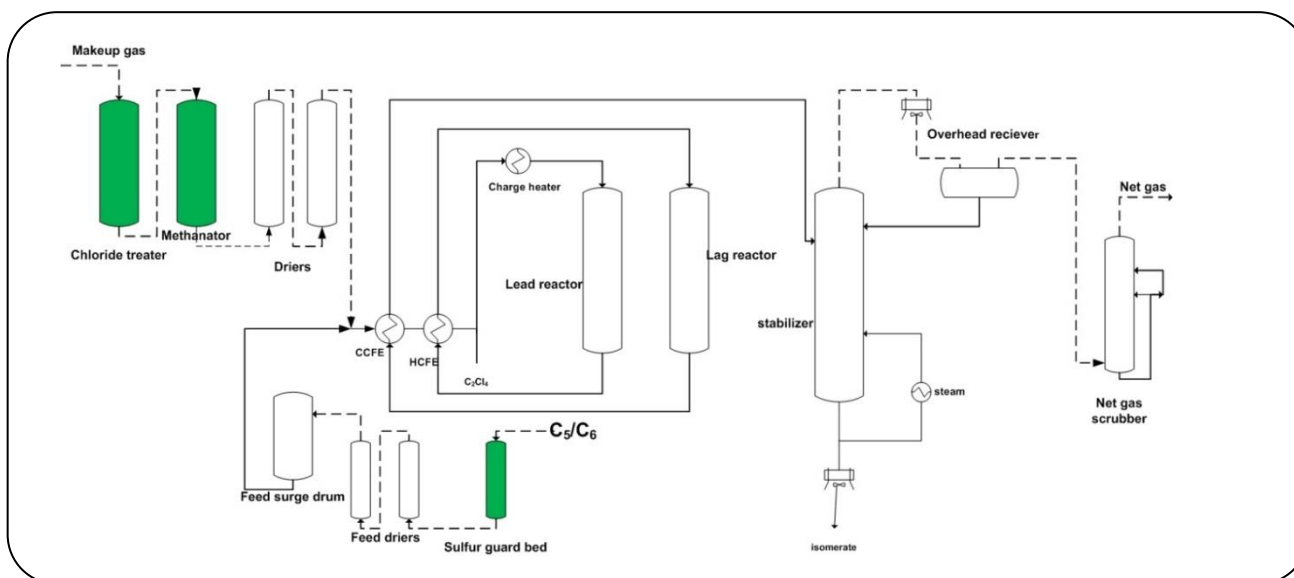


Fig.1: Penex Process Flow Methodology

to the feed before entering into the charged heater. The charged heater heats this mixture until it attains the operating temperature. After each reactor, the effluent is cooled via the combined feed heat exchanger, transferring heat to the incoming hydrogen-feed mixture[19].

The lag reactor outlet stream is cooled and routed directly to the isomerization stabilizer. The effluent from the reactor, section goes to the stabilizer column. The stabilizer column removes light ends such as hydrogen, methane, ethane, propane, butane, and hydrochloric acid

from the Isomerase and the stabilizer overhead gas is sent to the net gas scrubber where the hydrochloric acid is neutralized from the gas stream. The scrubbed gas is typically routed to fuel gas or to a gas recovery system. The isomerase is drawn off as the bottoms product.

Process simulation

Feed composition

Liquid Fresh feed Naphtha composition was collected to represent the components of cyclopentane, methyl cyclopentane, and methylcyclohexane to represent various naphthenic, as well as paraffinic natures of contents, see Table 2 [1, 7]. In order to produce gasoline having a lower content of benzene, the catalytic reformer feed is a key component. Benzene has been identified as a carcinogen and therefore the amount of benzene allowed in gasoline has been greatly reduced. The splitter bottoms stream contains the C₇₊ and heavier components which are sent to a catalytic reforming unit. Due to restrictions on benzene in gasoline, benzene and its precursors, Methyl cyclopentane and cyclohexane, must be processed in the isomerization unit [5, 12, 23]. The splitter overhead now includes cyclohexane. As a result, some of the C₇₊ paraffin are carried overhead. The overhead C₇₊ content should be carefully monitored and minimized.

Thermodynamic model

The thermodynamic model selection is important before proceeding with the process because it permits you to foresee properties of blends extending from well-defined light hydrocarbon frameworks to complex oil blends and exceedingly non-ideal (non-electrolyte) chemicals. It also gives us an upgraded parameter for Peng-Robinson (PR) [15, 18] and Peng-Robinson Stryjek-Vera (PRSV) [13, 15, 17] for a thorough treatment of hydrocarbon frameworks; semi-experimental and vapor weight models for the heavier hydrocarbon frameworks; steam relationships for precise steam property forecasts; and action coefficient models for chemical frameworks [24]. All of these conditions have their claim inalienable impediments and you are energized to end up more recognizable with the application of each condition.

Simulation details

Fresh gasoline feed with the endpoint of around 80–82 °C is pressurized at 22.5 bar through a booster pump, then it

Table 2: Feed composition of the light naphtha.

Components	Mass %
Methyl cyclopentane	6.23
Cyclopentane	2.14
3-methyl pentane	0.74
2-methyl pentane	11
n-pentane	24.21
Cyclohexane	5.58
n-hexane	18.15
Benzene	3.38
i-pentane	18.08
n-butane	0.09
2,2,3-trimethyl butane	0.09

is entered into the preheat exchanger from where its temperature increased to 100 °C. The steam heater further increases the temperature to around 135 °C and then this stream goes into the sulfur guard bed which contains adsorbent to selectively reduce the sulfur-based impurities (less than 0.1 ppm) from the gasoline stream. The gasoline stream with lower sulfur content is then introduced into the heat exchanger where it exchanges heat and lowers the temperature to around 38 °C. Later this stream heads towards Moisture adsorber which removes moisture from the stream, moisture is a permanent poison for catalyst and it should be less than 0.1 ppm shown in Fig. 3.

A rule of thumb states that 1 kg of moisture can deactivate 100 kg of catalyst. After that feed enters into feed surge drum. The charge pump pumped the liquid at a higher pressure at about 43 Kg/cm² and the gas feed mixes with a liquid stream upstream of the Cold combine feed exchanger. The gas passes from the reformer unit and it is first treated in dryers to remove moisture.

Makeup gas is compressed and after passing through Moisture adsorbers it is mixed with a liquid stream coming from feed surge drum Fig. 4.

This combined stream enters into the Shell side of CCFE (cold combine feed exchanger) and HCFE (hot combined feed exchanger) and then enters into the charge heater from where it gets the required temperature. PERC (tetrachloroethylene) is also injected into this stream at upstream. PERC is used to maintain the acid site of the catalyst. Now the combined feed enters into the Lead reactor

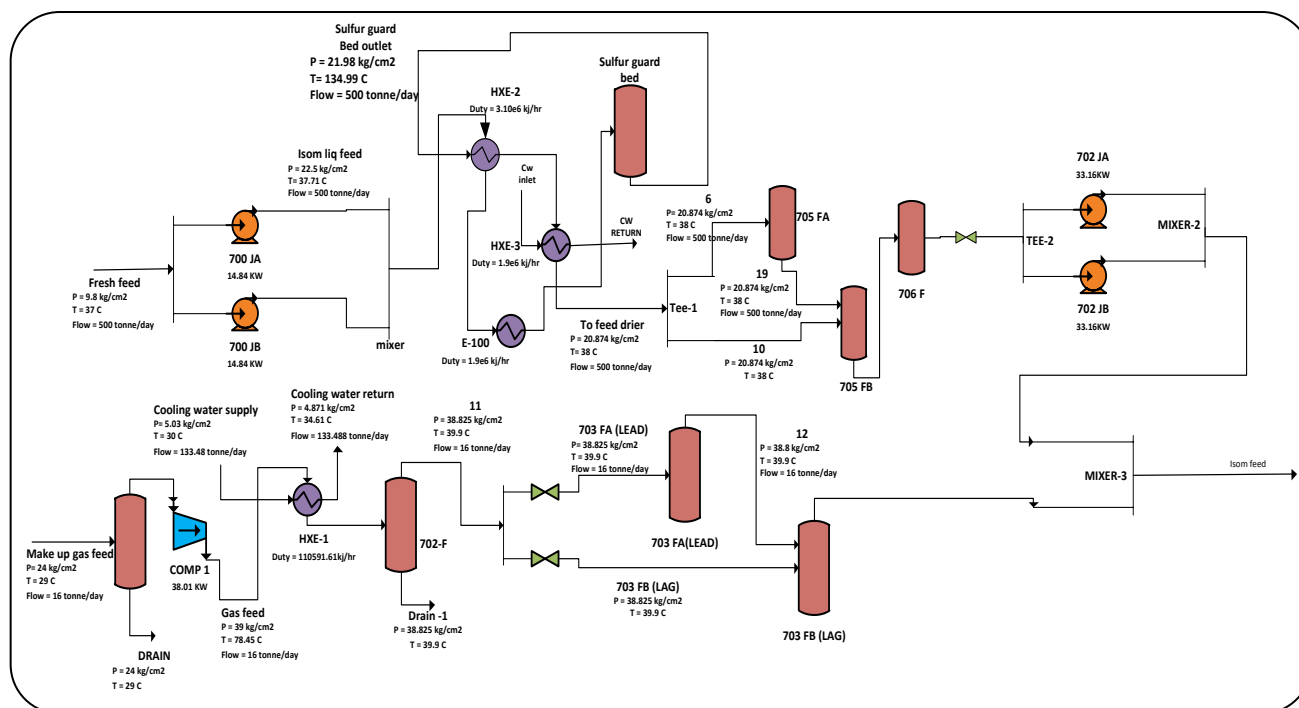


Fig. 2: Isomerization process flow diagram (part 1).

by attaining a temperature of 130°C and exits at 162 °C this effluent stream enters into the *t/s* of HCFE (hot combined feed exchanger) and then enters into the lag reactor at a temperature of 120 °C the effluent stream from the lag reactor enter into the *t/s* of CCFE (cold combine feed exchanger) and then heading towards stabilizer. The stabilizer has 30 trays and the gas leaving the stabilizer from the top, the pressure in the reflux drum is maintained and reboiler duty is set to achieve the desired RVP of isomerate. H₂/HC ratio at reactor outlet is set normally greater than 0.05 to ensure better consumption of hydrogen during the reaction. Net Gas Scrubber (NGS) is also installed in the penex unit scheme downstream of the stabilizer to neutralize the HCl in the stabilizer overhead gas by using caustic and water circulation.

Table 3 contains the tag name of the equipment used in the process diagram Figs. 4 and 5 with their tag names as well.

RESULTS AND DISCUSSION

Benzene calculator

As high benzene in feed has a high impact on the reactor temperatures sometimes temperature excursion is carried out. An idea was developed to make such a calculator that not only predicts the temperature rise in the reactors but also give us an idea about the quantity

of benzene coming with the feed. For this purpose by varying the benzene in the feed and monitoring the temperature rises in the reactor the results of the simulation model is indicated in Table 4 which further illustrates that 1 % wt. benzene in the feed will give a temperature rise of 11 °C approx. across the reactor. Also when the reactor inlet temperature is set at a maximum operating value of 145 °C it didn't follow the trend as shown by *Shehata* [1]. The reason for such deviation is due to vaporization at a high temperature which alters the liquid to vapor conversion resulting in a low rise in temperature until all the feed vaporizes at the outlet stream. This was further clarified from Fig. 6 which shows that increasing the temperature will further increase the vapor fraction in the feed thereby shifting the equilibrium of isomerization reaction.

Isomerization activity ΔT rise

Firstly the naphtha feed interacts with the catalyst to remove the heavy hydrocarbon content (benzene). So a benzene saturation reaction occurs on the surface of the catalyst in which all the benzene in the feed is converted into cyclohexane by taking hydrogen. This reaction is highly exothermic as it has been proved above that 1 % wt. benzene will raise the reactor bed temperature to 11°C.

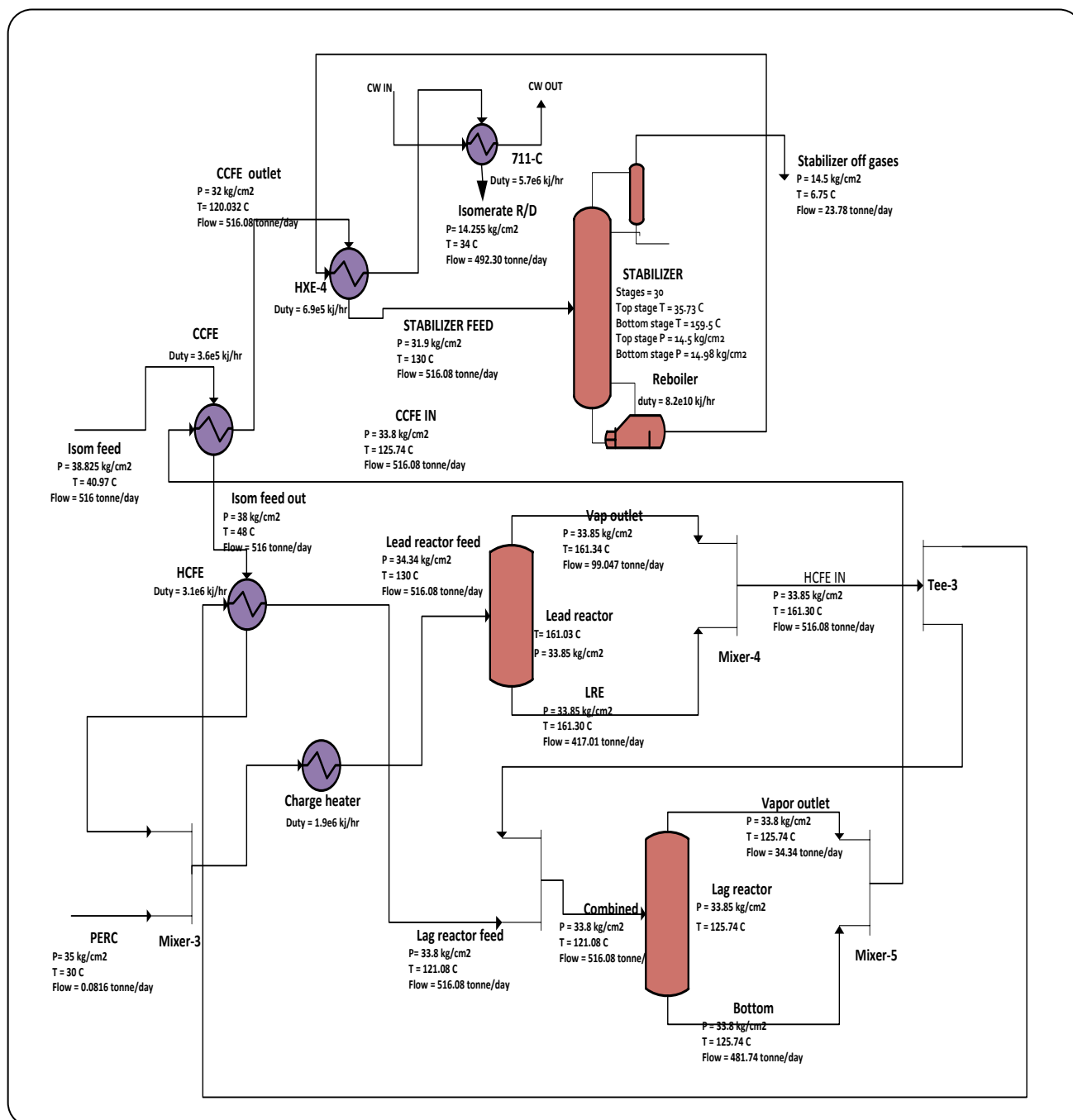


Fig. 3: Isomerization process flow diagram (part 2).

Since isomerization reaction is occurring on the acid site of the catalyst. Therefore, it is difficult to decide how much extent of isomerization reaction is taken place in the reactor. If the deactivation occurs in the reactor then at first the temperature in the top bed thermocouple reduces to zero and in the second-bed thermocouple, the reaction starts to become active since it is occurring in annular

fashion inside the reactor. Due to moisture and nitrogen, permanent deactivation occurs on acid site. Temporary poison like sulphur only affects the metal site and it can be offset through online and offline sulfur stripping thereby the metal sites could be recovered

Our main objective is to find out the total isomerization reaction ΔT that generally arises when the volume

Table 3: Tag names of the equipment used in the process diagram.

Equipment	Tag name
Heat exchanger	HXE-1, HXE-2, HXE-3, HXE-4
	E-100
	Isomerase R/D
	CCFE
	HCFE
	Charge heater
	711-C
Compressor	Comp-1
pumps	700 JA, 700 JB (feed pumps)
	702 JA, 702 JB
Separating Vessel	Sulfur guard bed
	703 FA, 703 FB
	705 FA, 705FB
	702 F
	706 F
Reactor	Lead reactor
	Lag reactor
Distillation column	stabilizer

Table 4: Results of the benzene calculator.

% Benzene Vs Temp rise across the reactor Calculator.		Values	Unit
Input	% benzene in light Naphtha =	3.309	
Output	Delta T across Reactor =	38.2366	
	At RIT = 120 C, ROT will be =	158.2366	°C
	At RIT = 130 C, ROT will be =	168.2366	°C
	At RIT = 140 C, ROT will be =	178.2366	°C
% error in calculator		0.001839	°C
Input	Enter Delta T across reactor	39	°C
output	Predicted benzene in feed	3.361833	% wt.

of catalyst in the reactor is not more than 11 m³. Mostly the licensor of the unit suggests the dense loading of a catalyst which therefore increases the bed density to 835 kg/m³. Results show that a temperature rise of around 12–13 °C across the reactor bed which will result in an iso ratio of about 70–75 respectively.

Effect of X-factor on pin

The relationship between Pin and X-factor is linear. As shown in Fig. 8, changes in feed X-factor of 10 will cause an alteration in the item PIN of 4.

Effect of ron with a feed rate

In order to find out the effect of feed with an increase in RON (research octane number) further evaluation was performed on the simulation model because upon increasing feed will reduce the feed contact time with the catalyst bed. Fig. 9 shows that with the increasing loading of raw materials per 500 MT/Day RON of Isomerase reduced by 0.3–0.5 points depending on the feedstock composition. On the basis of these results, one can predict the change in quality with respect to the change in feed rate.

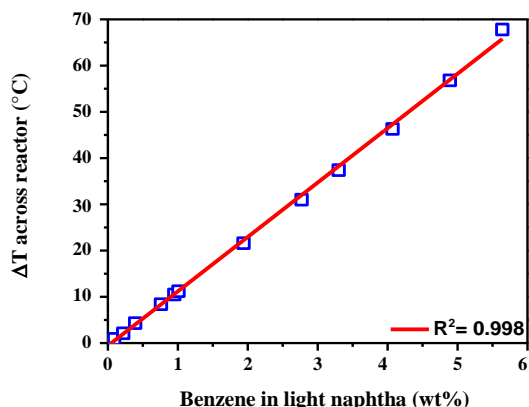


Fig. 5: Benzene Vs Temp rise across the reactor Calculator.

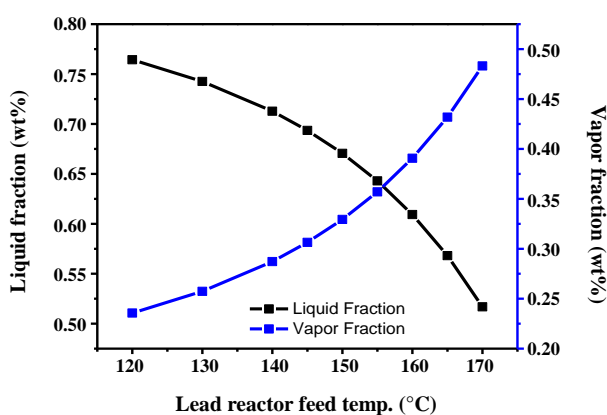


Fig. 6: Feed temperature Vs Liq-Vap Fraction.

H₂ consumption

As the amount of benzene in the feed increases which results in an increase in the amount of H₂ consumption in the lead reactor which is quite evident from Fig. 10. Therefore benzene loading should be kept at a minimum level upstream. On the basis of results, it can be summed up that the feed composition and rate are the prevailing factors and Benzene composition is assumed to be the most critical constraint. At inlet temperature, the Paraffin Isomerization Number (PIN) directly affects the amount of benzene which is present in feed and it can help in the persistent monitoring of feed containing benzene inside the lead reactor. So for this calculation (numerical expression), a benzene calculator is created which can help in controlling the benzene levels by foreseeing the delta T of the lead reactor.

Altering the amount of benzene in the feed would enhance the efficiency of the isomerization process.

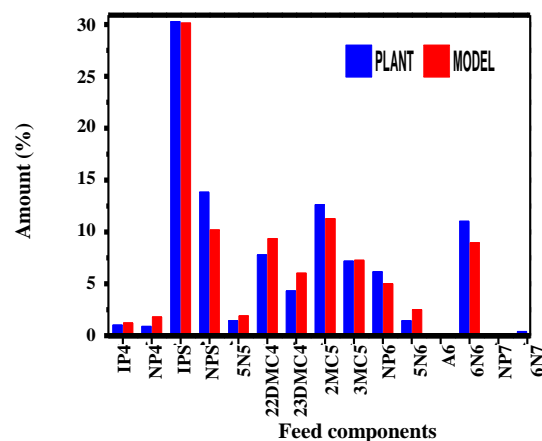


Fig. 7: Plant scale vs simulation model results in comparison.

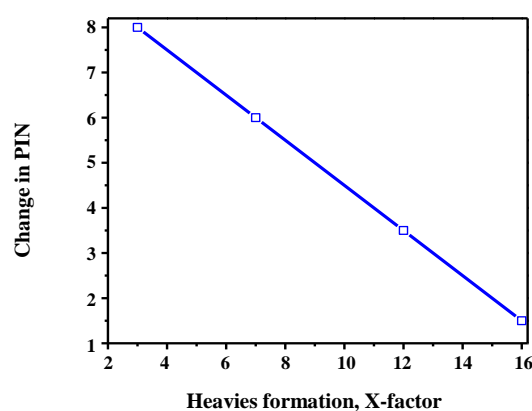


Fig. 8: Effect of X-factor on PIN (Change in PIN vs X-Factor).

Refiners minimize this effect by changing the temperature of the lead reactor. so as to have a constant temperature rise through the reactor. Gradual temperature increase can be due to an increment in the feed rate. This working strategy may be effective; in the event that the feed contains frequent variations in benzene level. Another important variable is the H₂(hydrogen) to hydrocarbon ratio in the reactor. Sometimes hydrogen is considered necessary for completing isomerization and diminishing coke lay-down on catalyst. For this reason, an additional rise in the fractional weight of hydrogen inside the reactor may lead to an increase in the hydrocracking process and decreases isomerate yield. In this manner, the reactors ought to be working with the most reduced conceivable hydrogen fractional weight. So based on this, the reactors should not be worked below 0.05 (hydrogen) H₂ to hydrocarbon (HC) ratio at the lag reactor outlet.

Table 5: Operational Conditions of the Unit at the Base Case and the constraints sanctioned by the licensor.

Process Variable	Base operating point	Bounds
H ₂ :HC ratio at Rx outlet	0.1055	0.05 minimum
Lead reactor inlet T	130°C	105-204°C
Lag reactor inlet T	120°C	105-204°C

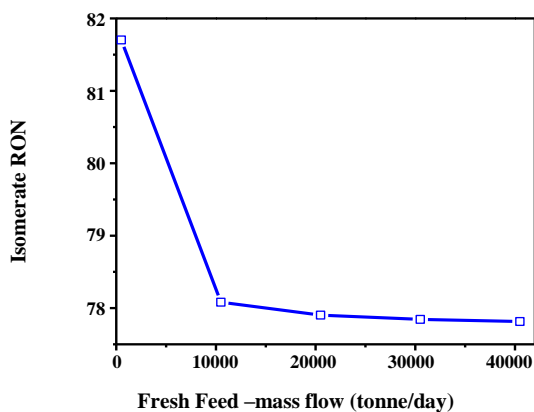
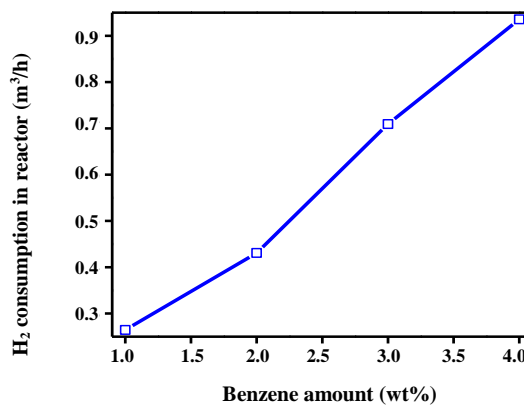
**Fig. 9: Isomerate RON vs. fresh feed rate.****Fig. 10: Hydrogen Consumption Vs Benzene.**

Table 5 shows the base working conditions of the explored industrial unit and the restrain bounds actuated by process licensor. It is clear that the Reactors are designed to work with H₂

H₂ to Hydrocarbon proportion much higher than required. The first step is to reduce the hydrogen per weight for the same reactor inlet temperature. Really, the most reduced conceivable H₂ ratio to HC proportion at the reactors 'outlet should be (0.06–0.08) for the safe side against the vendor recommendation, which is still far from the minimum allowable. Lower H₂(hydrogen) to hydrocarbon, ratios could be obtained either at a lower lead reactor temperature or higher lag reactor inlet temperature because the amount of makeup hydrogen used affects heat transfer coefficients in both the hot and cold combined exchangers and consequently affects the outlet temperatures.

Hence to achieve an optimum value of H₂: HC ratio also, based on the results shown in Table 6,

- Reducing the heat duty of hot & cold combined feed exchangers.
- Saving almost 4 million tons per day of Makeup gas directly to the Fuel gas system from the reformer unit.
- Heater duty also reduces to 0.0646 MMBtu/h

Lead and Lag reactor temperatures

Lead and lag reactor temperatures mainly depend upon the activity of the catalyst and the extent of reactions. There is also a benzene saturation reaction which is important to consider because we have to remove benzene from the final product. Isomerization reactions started at a lower temperature normally after 105 °C but the refiners also expect the desired performance results and the breakthrough of benzene at the lead reactor outlet. The benzene saturation reaction is metal-catalyzed, and in the presence of hydrogen, it is rapid and 100% complete at the top bed layers of the lead reactor. Benzene reaction over isomerization catalyst is always an irreversible & highly exothermic reaction high temperature favors the activity of benzene reaction to convert benzene into cyclohexane so it is important to note that the feed benzene content should always be low in light naphtha feed. With the passage of time, temporary deactivation occurs due to sulfur for which the refiners increase the reactor temperatures to get a breakthrough at the lead reactor outlet and to set a minimum load on the lag reactor.

A few key components in the Penex reactor the charge which may impact catalyst execution are the C₆ cyclic and C₇₊ compounds. The sum of three components i-C₅/C₅pentene, 2,2-DMB/C₆pentene, and

Table 6: Makeup gas optimum Values.

State	Makeup gas feed - Mass Flow	Lead reactor outlet Temperature	Lag reactor outlet Temperature	HCFE - Exchanger Duty	CCFE - Exchanger Duty	H ₂ : HC Ratio
	Tone/day	°C	°C	kJ/h	kJ/h	
Case 1	10	167.1	125.6	3117407.3	1119483.9	0.036
Case 2	11	165.8	125.4	3123388.8	1151425.1	0.051
Case 3	12	164.6	125.3	3130407.1	1182585.1	0.065
Case 4	13	163.6	125.1	3137263.1	1214131.0	0.079
Case 5	14	162.7	125	3144470.7	1245521.6	0.093
Case 6	15	161.8	124.9	3151798.9	1276964.7	0.108
Base case	16	161.1	124.8	3159256.7	1308430.9	0.122

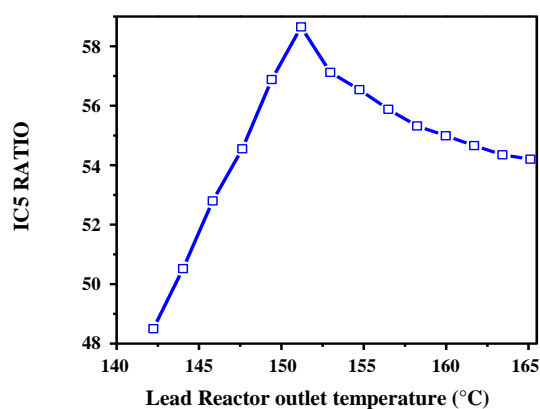


Fig. 11: Lead Reactor Iso ratio Vs Reactor Outlet Temperature.

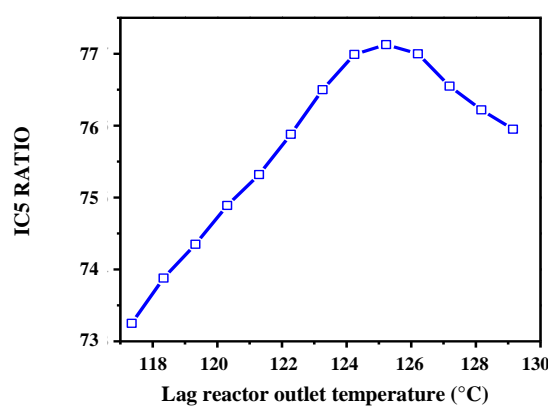


Fig. 12: Lag Reactor Iso ratio Vs Reactor Outlet Temperature.

2,3-DMB/C₆pentene is referred to as the paraffin isomerization number (PIN). To include the changes into the feed and losses in product PIN results due to a decrease in the C₆ cyclic and C₇₊ components which are being retained into the catalyst.

In order to increase the space velocity, higher reactor temperatures are needed for a maximized product PIN. On the other hand, a decrease in the space velocity will require lower reactor temperatures for a maximized PIN and related octane. The inlet temperature is controlled and utilized to accomplish the desired reactor outlet temperature. A normal working space velocity and X factor need to be kept high during the optimization of temperature. The results would help us to keep the unit stabilized and working efficiently at optimal conditions by interpolating the optimal reactor outlet temperature [4].

On the basis of this analysis, the iso-ratio is calculated and plotted as shown in Fig. 11 and Fig. 12. It was observed that after the 175°C temperature, the Isopentane ratio starts

to decline. Therefore the lead reactor optimal temperature is about 151°C. The lag reactor is always operated at a low temperature which indicates that the lower reactor rate can be obtained at a lower temperature; the lag reactor curve is flatter than the lead reactor curve as shown in Fig. 11. The lag Reactor's optimal temperature is about 125 °C. In some cases, refiners increase the reactor inlet temperature by considering benzene breakthrough at the reactor outlet on compromising optimal iso ratios of the lead reactor.

Stabilizer model

An optimization is performed on the isomerization model by including the stabilizer model which would increase the Isomerate yield and would further optimize the plant performance. The standard inside-out strategy was utilized for the stabilizer model which would meet rapidly with an assortment of specifications.

The work of the isomerate stabilizer is to control isomerate by isolating light ends. Hence, the Reid vapor pressure

of isomerate indicates the recovery of light ends. To include the full reflux constraint to the stabilizer model, another specification was included in the model. Subsequently, the component recovery was specified as an execution specification. Since the condenser operates with significant vapor flows. Moreover alter in fluid or gas feed will not disturb the stabilizer operation.

Since $i-C_5$ & $n-C_5$ were not found in the stabilizer off-gas against the plant normal results of 2~2.5 vol% and 0.1~0.2 vol%. Theoretically, calculated RVP is always less than the actual RVP, the more the RVP the greater the chance of octane loss in storage tanks due to the high volatility of lighter components.

CONCLUSIONS

Benzene feed substance and H_2 ratio to hydrocarbon proportion were the most noticeable components which affect the process performance. A separate study has also been done on the benzene behavior with respect to change in delta T across reactor; through this study, a correlation is developed, this would help to predict the quantity of benzene in feed by analyzing the temperature rises across reactors. Isomerization reaction total delta T was also part of the research study. It will also help to examine the deactivation of the acid site across beds. Results obtained from the simulation model shows that economic saving in product yield can be accomplished by bringing down hydrogen partial pressure inside reactors to the most reduced conceivable practical value. The overflow in makeup gas may be directed to fuel gas which results in significant fuel savings. Additionally, the stabilizer model was optimized to control the RVP of the product against market requirements.

Nomenclature

RON	Research Octane Number
RVP	Reid Vapor Pressure
PENEX	Pentane-Hexane
PIN	Paraffin Isomerization Number
LHSV	Liquid Hourly Space Velocity
HC	Hydrocarbon

REFERENCES

- [1] Shehata W.M., Mohamed M.F., Gad F.K., [Monitoring and Modelling of Variables Affecting Isomerate Octane Number Produced from an Industrial Isomerization Process](#), *Egypt. J. Petro.*, **27**: 945-953 (2018).
- [2] Ivanchina E.D., Sharova E.S., Anna A., Syskina; Yakupova I.V., [Computer Modelling System Application for Catalytic Reforming Unit Work Optimisation](#), *Procedia Chem.*, **10**: 192-196 (2014).
- [3] Chuzlov V.A., Chekantsev N.V., Ivanchina E. D., [Development of Complex Mathematical Model of Light Naphtha Isomerization and Rectification Processes](#), *Procedia Chem.*, **10**: 236-243 (2014).
- [4] Hayati R., Abghari S.Z., Sadighi S., Bayat M., [Development of a Rule to Maximize the Research Octane Number \(RON\) of The Isomerization Product from Light Naphtha](#), *Korean J. Chem. Eng.*, **32**: 629-635 (2015).
- [5] K. Watanabe N.C., Kawakami T., [Development of New Isomerization Process for Petrochemical By-Products](#), *18th Saudi Arabia-Japan Joint Symposium*, Dhahran, Saudi Arabia, November 16–17 (2008).
- [6] Sadighi S., Zahedi S., Hayati R., Bayat M., [Studying Catalyst Activity in an Isomerization Plant to Upgrade the Octane Number of Gasoline by Using a Hybrid Artificial-Neural-Network Model](#), *Energy Technol.*, **1**: 743-750 (2013).
- [7] Chuzlov V.A., Ivanchina E.D., Chekantsev N.V., Molotov K.V., [Efficiency Improvement of the Light Gasoline Fractions Isomerization by Mathematical Modeling](#), *Procedia Eng.*, **113**: 131-137 (2015).
- [8] Chuzlov V.A., Ivanchina, E.D., Dolganov I.M., Molotov K.V., [Simulation of Light Naphtha Isomerization](#), *Process. Procedia Chem.*, **15**: 282-287 (2015).
- [9] [UOP Penex Reactor Temperature Optimization Procedure](#) (2013).
- [10] Robert A. Smiley, Harold L. Jackson., "Chemistry and the Chemical Industry: A Practical Guide for Non-Chemists", CRC Press (2003).
- [11] Mohamed M.F., Shehata W.M., Abdel Halim A. A., Gad F.K., [Improving Gasoline Quality Produced From MIDOR Light Naphtha Isomerization Unit](#), *Egypt. J. Petro.*, **26**: 111-124 (2017).

Received : Jul. 1, 2019 ; Accepted : Nov. 18, 2019

- [12] Valavarasu G., Sairam B., [Light Naphtha Isomerization Process: A Review](#), *Pet. Sci. Technol.*, **31**: 580-595 (2013).
- [13] Hamid M.K.A., [HYSYS®: “An Introduction to Chemical Engineering Simulation”](#), (2007).
- [14] Haydary J., [“Chemical Process Design and Simulation: Aspen Plus and Aspen Hysys Application”](#), Wiley-AIChE (2018).
- [15] Rao K. N., [“HYSYS and Aspen Plus in Process Design: A Practical Approach”](#), Lambert Publishers (2017).
- [16] Chekantsev N., Gyngazova MS., Ivanchina E.D., [Mathematical Modelling of Light Naphtha \(C5, C6\) Isomerization Process](#), *Chem. Eng. J.*, **238**: 120-128 (2014).
- [17] L.Luyben W., [“Principles and Case Studies of Simultaneous Design”](#), John Wiley & Sons, Inc. (2011).
- [18] Smith R., [Chemical Process Design and Integration](#). John Wiley & Sons, Inc. (2016).
- [19] UOP Penex [“Process Hydrogen Once Through, A. Isomerization Unit”](#), UOP (2017)
- [20] Kennicutt M.C., "Oil and Gas Seeps in the Gulf of Mexico. In [Habitats and Biota of the Gulf of Mexico: Before the Deepwater Horizon Oil Spill: Volume 1: Water Quality, Sediments, Sediment Contaminants, Oil and Gas Seeps, Coastal Habitats, Offshore Plankton and Benthos, and Shellfish](#)", Ward C.H. (ed.), Springer, New York, NY, 275-358 (2017).
- [21] Mokhatab S., Towler B., Manning F.S., Thompson R.E., ["Oilfield Processing of petroleum, Vol. 1—Natural Gas"](#), Published (1991) 408, ISBN: 0-87814-342-2; Vol. 2—Crude Oil, Published 1995, 434pp., ISBN: 0-87814-354-8. Tulsa, OK: PennWell Publishing Company. Vol. 31, p 2253-2255 (2006).
- [22] Azarpour A., N.G. Borhani T., R. Wan Alwi S., A. Manan Z., I. Abdul Mutalib M., [A Generic Hybrid Model Development for Process Analysis of Industrial Fixed-Bed Catalytic Reactors](#), *Chem. Eng. Res. Des.*, **117**: 149-167 (2017).
- [23] Joly M., [Refinery Production Planning and Scheduling: the Refining Core Business](#), *Braz. J. Chem. Eng.*, **29**: 371-384 (2012).
- [24] Boles Y.A.C.a. M.A., [“Thermodynamics: An Engineering Approach”](#), McGraw-Hill (2015).