

Enhancement of Octane Number of Gasoline by Isomerization Process

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Abstract: Upgrading light hydrocarbon (C_4 - C_7) streams in refineries, petrochemical plants and gas processing plants has continued to increase in commercial applications, as the world demand for gasoline and petrochemicals has experienced steady growth over the past decade. Increasingly stringent regulations have been enacted in most regions of the world, driving the increased demand for clean fuels. As a result, gasoline composition has been adjusted to a greater extent using C_5 - C_7 isomerization process. Light Naphtha isomerization technology plays a key role in meeting octane demand in the gasoline pool for clean fuels and premium grades. Low octane naphtha feedstock is processed into isomerate with increase octane number ranging from 70 to 89. This process involves the skeletal isomerization of a paraffin to highly branched paraffin with the same carbon number. The industrial practice of isomerization of light naphtha is discussed with focus on economic motivation, flow schemes, processing conditions, hazards and safety aspects and industrial process configurations in this project.

Keywords: Upgrading light hydrocarbon

I. INTRODUCTION

Naphtha is a general term used for low boiling hydrocarbon fractions that are a major component of gasoline. In petroleum engineering, full-range naphtha is the fraction of the crude oil boiling between 30°C and 200°C, and constitutes typically 15-30% by weight of the crude oil. This includes hydrocarbons ranging from C_5 to C_{12} , some sulfur, and small amounts of nitrogen. Metal containing compounds are usually not present. Light naphtha is the fraction boiling from 30°C to 90°C, containing C_5 and C_6 hydrocarbons. Heavy naphtha is the fraction boiling from 90°C to 200°C and consists of molecules with 6-12 carbons. The term 'medium naphtha' is sometimes used for the fraction that boils below 150°C and includes mostly C_7 - C_9 hydrocarbons. Aliphatic naphtha refers to those naphthas containing less than 0.1% benzene and along with carbon numbers from C_3 to C_{16} . Aromatic naphtha has carbon numbers from C_6 to C_{16} and contain significant quantities of aromatic hydrocarbons such as benzene, toluene and xylene. Naphtha is refined or partly refined light distillates with an approximate boiling point range of 27°C to 221°C. Blended further or mixed with other materials, to make highgrade motor gasoline or jet fuel. Also, used as solvents, petrochemical feed stocks, or as raw materials for the production of town gas.

1.1 Isomerization

Isomerization of light naphtha is the process in which low octane number hydrocarbons (C_4 , C_5 , and C_6) are transformed to a branched product with the same carbon number. This process produces high octane number products. One main advantage of this process is to separate hexane (C_6) before it enters the reformer preventing the formation of benzene which produces carcinogenic products on combustion with gasoline. Low octane naphtha fractions are produced not only by crude oil straight run distillation but also by secondary processes (middle distillate fractions, heavy vacuum gas oils- hydrotreatment, heavy residues conversion processes-Visbreaker unit). It is well known that two processes of low octane number naphtha upgrading exist. They are light naphtha (C_5 - C_6) isomerization and heavy naphtha (fraction C_7 - C_{11}) catalytic reforming. It is not desirable low octane naphtha fractions with initial boiling point below 80.6°C according to True Boiling Point Curve to be subject to catalytic reforming by reason of standard motor naphtha benzene content limitation not more than 1.0 % v/v. That is why, low octane naphtha fractions of typical

boiling range of 30-180°C have to be fractionated to light naphtha fraction of the range 30-81°C and heavy naphtha fraction of the range 81-180°C as the light naphthas has to be turn to isomerization and the heavy one to catalytic reforming.

1.2 Gasoline

Gasoline is a fuel produced by refining crude oil and is a complex liquid mixture of hundreds of individual hydrocarbons which have five to twelve carbon atoms per molecule. Among common wealth nations it is known as petrol. Gasoline specifications impose controls on the physical and performance properties of gasoline's constituents. The art of correctly formulating a gasoline that does not cause engines to knock apart; does not cause vapor lock in summer but is easy to start in winter; does not form gums or deposits; burns cleanly without soot or residues; and does not dissolve or poison the car catalyst or owner; is based on knowledge of the gasoline composition.

1.3 : Selection of Process:

Various Processes for increasing the octane number of gasoline:

1. Alkylation Process
2. Catalytic Cracking
3. Catalytic Reforming
4. Isomerization

1. Alkylation Process: Alkylation, in petroleum refining, chemical process in which light, gaseous hydrocarbons are combined to produce high-octane components of gasoline. The light hydrocarbons consist of olefins such as propylene and butylene and iso-paraffins such as isobutane. These compounds are fed into a reactor, where, under the influence of a sulfuric-acid or hydrofluoric-acid catalyst, they combine to form a mixture of heavier hydrocarbons. The liquid fraction of this mixture, known as alkylate, consists mainly of isooctane, a compound that lends excellent antiknock characteristics to gasoline.

2. Catalytic Cracking: Fluid catalytic cracking (FCC) is the conversion process used in petroleum refineries to convert the high boiling point, high molecular weight hydrocarbon fractions of petroleum (crude oils) into gasoline, olefinic gases and other petroleum products. The cracking of petroleum hydrocarbons was originally done by thermal cracking, now virtually replaced by catalytic cracking, which yields greater volumes of high octane rating gasoline; and produces by-product gases with more carbon-carbon double bonds, that are of greater economic value than the gases produced by thermal cracking.

3. Catalytic Reforming: Catalytic reforming converts low-octane, straight-run naphtha fractions, particularly heavy naphtha that is rich in naphthenes, into a high-octane, low-sulfur reformate, which is a major blending product for gasoline. The most valuable by product from catalytic reforming is hydrogen to which satisfies the increasing demand for hydrogen in hydrotreating and hydrocracking processes. Most reforming catalysts contain platinum as the active metal supported on alumina, and some may contain additional metals such as rhenium and tin in bi- or tri-metallic catalyst formulations. In most cases, the naphtha feedstock needs to be hydrotreated before reforming to protect the platinum catalyst from poisoning by sulfur or nitrogen species.

4. Isomerzation: The isomerization unit converts light naphtha into a higher-value gasoline blend stock by changing its molecular shape and raising its octane number. The primary product from isomerization is called isomerate. The value from isomerization is its ability to upgrade light naphtha into gasoline. While the resulting isomerate is not high octane (typically 82-87 RON), it is much better than light naphtha at around 70 RON.

Selection of Process:

Isomerization:

1. The isomerization process is gaining importance in the present refining context due to limitations on gasoline benzene, aromatics, and olefin contents. The isomerization process upgrades the octane number of light naphtha fractions and also simultaneously reduces benzene content by saturation of the benzene fraction.
2. Isomerization complements catalytic reforming process in upgrading the octane number of refinery naphtha streams. Isomerization is a simple and cost-effective process for octane enhancement compared with other octane-improving processes.
3. Isomerate product contains very low sulfur and benzene, making it an ideal blending component in refinery gasoline pool.
4. Due to the significance of isomerization to the modern refining industry, it becomes essential to review the process with respect to catalysts, catalyst poisons, reactions, thermodynamics, and process developments. The present research thrust in this field along with future scope of work is also discussed briefly.

II PROCESS DESCRIPTION

Feed: Light Naphtha from Crude Distillation Unit, Hydro Cracking Unit, Continuous Catalytic Regeneration and Storage.

Products: Light and Heavy Isomerate

The **ISOM unit** is broadly classified as

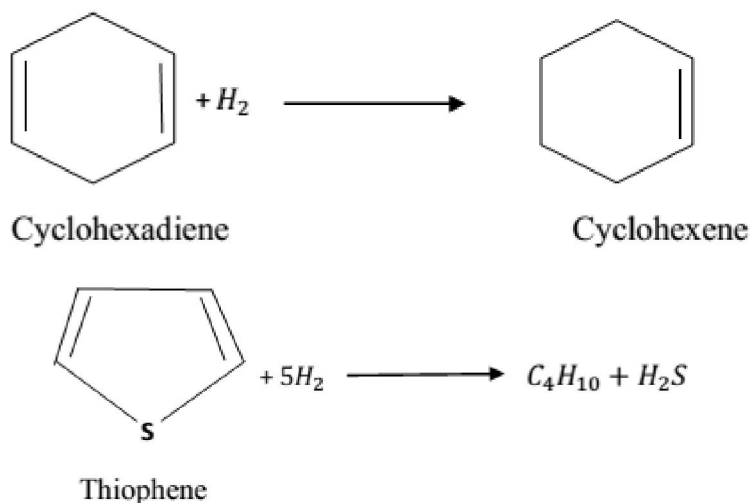
LNHT Reactor Unit

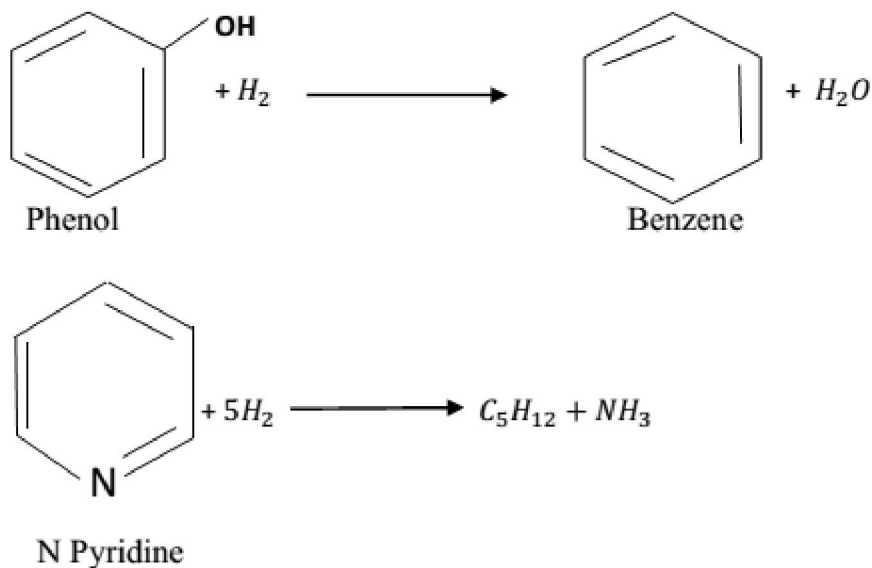
BENSAT Reactor Unit

PENEX Reactor Unit

LNHT Reactor Unit: Purpose of the Light Naphtha hydrotreating (LNHT) unit is to remove sulphur, nitrogen compounds, metals, olefins and aromatics from petroleum distillates. These are the contaminants that contaminate the PENEX reactor. So, this LNHTU unit removes such contaminants. Hydrogen (recycle hydrogen) is used along with the feed here and are heated prior to entering a reactor up to 370°C. The naphtha hydrotreating unit uses a cobalt molybdenum catalyst (CoMoX) to remove sulphur by converting it to hydrogen sulphide that is removed along with unreacted hydrogen. The stripper used here has 30 trays. Condensed liquid feed is inserted, and steam is inserted from the bottom of the stripper. From the top of the stripper, we obtain C₁ to C₄ and H₂S. From the bottom of the stripper, we obtain C₅ to C₇. Some of the hydrogen sulphide - hydrogen mixture is recycled back to the reactor to utilize the unreacted hydrogen using a compressor. Reactor conditions for naphtha hydrotreating unit are around 205°C - 260°C and pressure of 350-650 psi (25-45 bar).

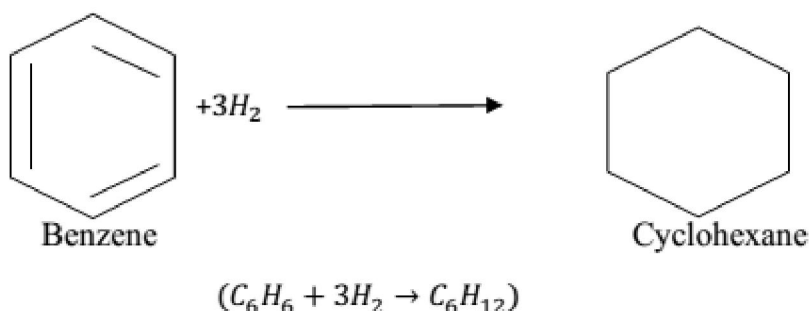
Reaction involved in LNHT Reactor:





BENSAT Reactor Unit: This process consists of aromatic saturation to reduce the benzene contained in the distillate, in order to avoid product contamination and catalyst poisoning. It is realized to complete the C_5 - C_6 isomerization, to remove the natural benzene concentrated by aggressive reformer feed pre-fractionation and also to remove the benzene that has been produced handles up to 30 vol% more benzene in the feed. Benzene is saturated to C_6 naphthenes so that the reactor effluent contains less than 0.5 volume%. The catalyst used in this process is highly selective the heat of reaction from benzene saturation is carefully managed to control the temperature rise across the reactor make up hydrogen to the BENSAT process is provided in an amount slightly above the stoichiometric level required for benzene saturation. The liquid feed stream is pumped to the feed effluent exchange and then to the pre-heater used only for start-up purpose once the unit is operating, the heat of reaction provides the required heat input to the feed via the feed – effluent exchanger. Benzene is saturated to C_6 naphthenes in the presence of hydrogen using a noble metal catalyst. The effluent is passed through the feed effluent exchanger and is sent to a PENEX reactor.

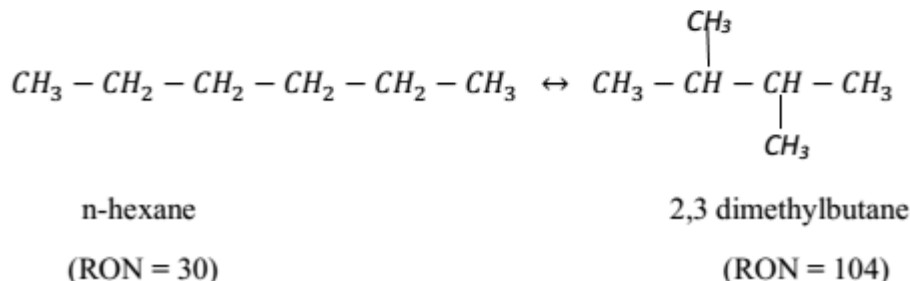
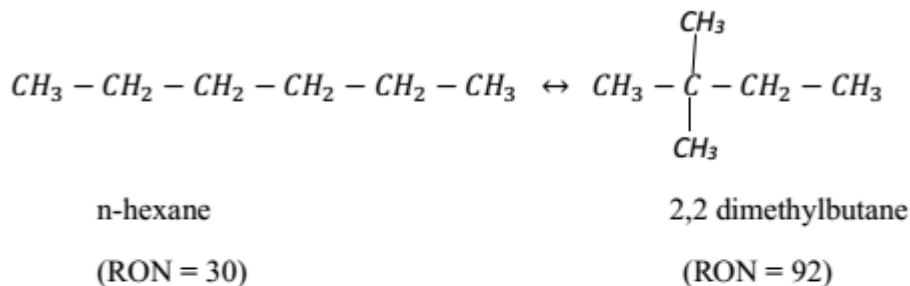
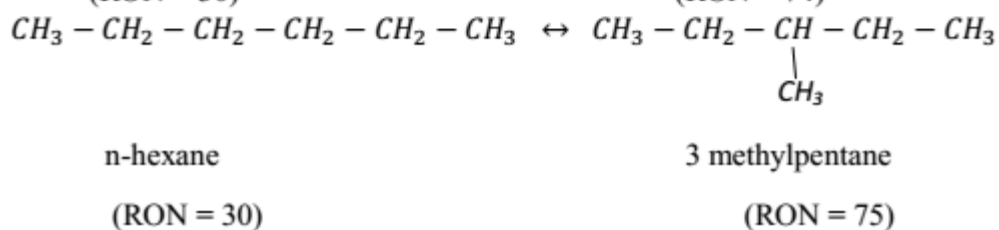
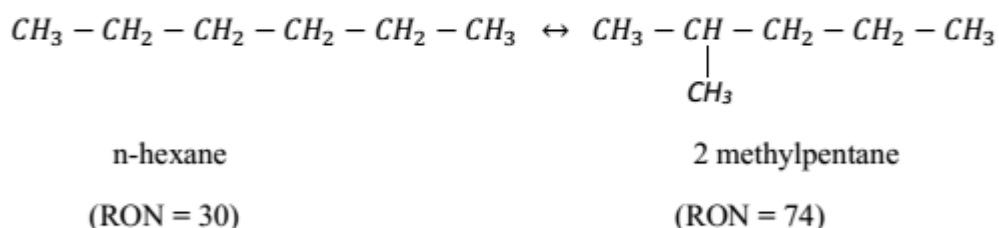
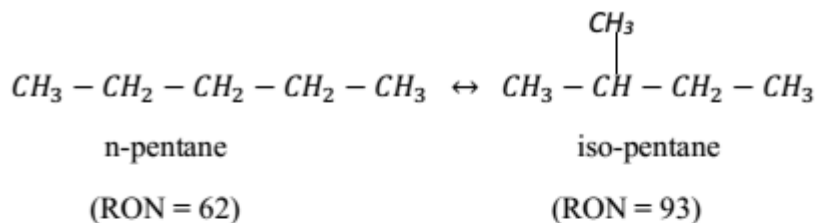
Reaction involved in BENSAT Reactor:



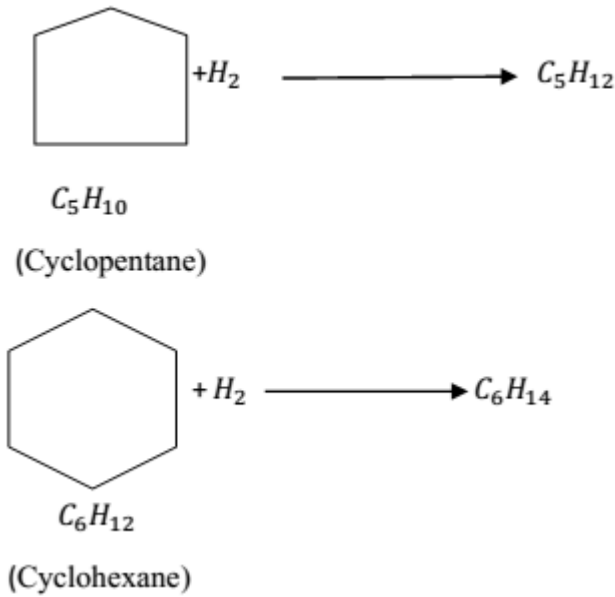
PENEX Reactor Unit: The PENEX process is a continuous process used to isomerize light straight run naphtha (C_5/C_6) into higher octane, branched C_5/C_6 molecules. The PENEX process uses fixed bed catalysts containing chlorides. Catalyst used is platinum base and aluminium oxide and promotor is perchloroethylene (C_2Cl_4). The main Isomerization reaction occurs in this section. A single pass of feed stock with octane rating 50-60 through such bed typically produces an end product rated at 82-87. The feed stock is subsequently passed through a DIH (De Iso Hexanizer) column to separates the light Isomerate and Heavy Isomerate. Light Isomerate has the octane rating around 87-89.

Reaction involved in PENEX Reactor:

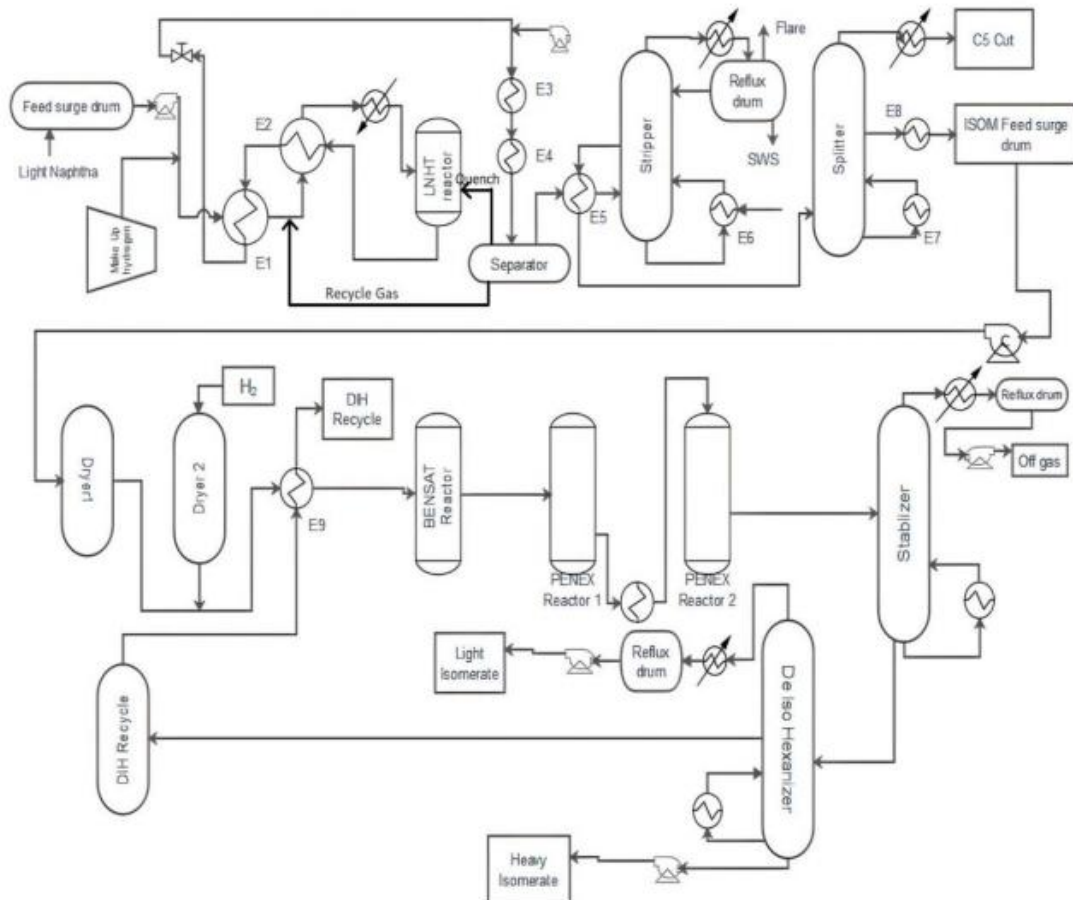
1. Isomerization:



2.NaphtheneRing Opening:



Process Flow Sheet



III APPLICATION OF GASOLINE

1. Gasoline is used as a fuel for internal-combustion engines
2. It is also used as a solvent for oils and fats. Gasoline effectively dissolves oils and even grease.
3. Gasoline became the preferred automobile fuel because of its high energy of combustion and capacity to mix readily with air in a carburetor
4. A gasoline heater is a small gasoline fuelled space heater. Fixed versions were originally used mainly for supplemental heat for passenger compartment of auto mobiles and air crafts
5. Gasoline used in an electricity generator for portable and emergency power supply
6. Serves as a popular cleaning agent in the United States.
7. It is used as raw material in several chemical industries.
8. It is used in industries that depends heavily on gasoline such as companies that manufacture pesticides, insecticides and fungicides.

IV LITERATURE REVIEWS

1. INVESTIGATION OF THE EFFECTS OF METHYL- CYCLOPENTANE IN FEED OF ISOMERIZATION UNIT, Jafar Sadeghzadeh Ahari, Seyed Javad Ahmadpanah, Alireza Khaleghinasab, Majid Kakavand (Dec 21, 2005).

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.

2. SOLID ACID CATALYSTS IN HETEROGENEOUS n-ALKANES HYDROISOMERISATION FOR INCREASING OCTANE NUMBER OF GASOLINE Galadima A., Anderson J. A. & Wells R. P. K (Jan, 2009).

As the current global environmental concerns have prompted regulations to reduce the level of aromatic compounds, particularly benzene and its derivatives in gasoline, hydroisomerisation of n-alkanes is becoming a major alternative for enhancing octane number. Series of solid acid catalysts comprising of Freidel crafts, zirconias, MoO₃-based (MOB), chlorinated Al₂O₃, heteropoly acids and bifunctional zeolite based catalysts have been tested in this respect. This paper reviewed important studies conducted on these catalysts with the aim of identifying areas requiring further investigation(s). Freidel craft catalysts are currently abandoned due to corrosion and disposal problems. MOB and heteropoly acids have good resistance to nitrogen and sulphur in a reaction stream but have poor thermal stability, difficult to regenerate and with mechanism their action only partly resolved. Bifunctional zeolites on the other hand are increasingly becoming promising catalysts due to resulting high acidity, activity and easy regeneration properties. Both solid and gaseous acid modifiers could similarly modify their textural characteristics. The activities of all catalysts could under uncontrolled conditions lead to side reactions such as cracking, aromatization and dehydrogenation.

3. DETERMINATION OF THE OCTANE NUMBER OF AUTOMOTIVE GASOLINES BY FTIR SPECTROMETRY WITH CHEMOMETRICS, Ivana Hurtova, Marie Sejkorova, (Feb, 2022).

The quality of motor fuels is more and more strictly controlled in connection with many factors - users are particularly interested in the anti-knock resistance of automotive gasolines, quantitatively expressed by the value of the research octane number (RON). The paper presents FTIR spectrometry in conjunction with chemometry as an alternative method to the standardized determination of the octane number of gasoline by a research method according to ČSN EN ISO 5164. An FTIR-PLS regression model working with spectra in the range of 650–4000 cm⁻¹ was proposed for ON prediction. With this model, a very strong dependence (R=0.996) was achieved between the predicted of octane number values and the values determined by the standardized method; the calibration error was 0.414.

4. RAISING THE RESEARCH OCTANE NUMBER USING AN OPTIMIZED SIMULATED MOVINGBED TECHNOLOGY TOWARDS GREATER SUSTAINABILITY AND ECONOMIC RETURN, Tasneem Muhammed, Begum Tokay, Alex Conradie (Nov, 2022).

The scale of CO₂ emissions from light-duty vehicle (LDV) fleets worldwide has led governments to mandate substantive improvements in vehicle fuel economy, thereby mitigating climate change. Raising the Research Octane Number (RON) of fuel through isomerization, alongside mandates to recalibrate existing LDV engines, promises to contribute substantially to climate action. This study has aimed to develop a highly efficient adsorption separation technology for isomerization refining that can contribute significantly to the sustainability and economics of the overall “well-to-wheel” outcome for LDV fleets globally. This study developed a rigorous dynamic model for a Simulated Moving Bed (SMB), comparing the SMB to conventional distillation as the next best alternative. The SMB was optimized using a genetic algorithm, maximizing RON and Gross Margin as objective functions. This study showed that SMB effectively separates high octane components from low octane components, producing a fuel with a RON of 95 when maximizing the RON, thereby enabling lower emissions associated with recalibrated LDV engines. Compared to 11 MW of steam duty associated with conventional distillation, the SMB unit utilized 3.4 MW and 5.7 MW of electricity when optimizing the RON and the Gross Margin respectively, appreciably reducing comparative greenhouse gas emissions. Finally, compared to conventional distillation as measured by Gross Margin, the optimized SMB unit increased the economic return by 47% when maximizing the RON and by 82 % when maximizing the Gross Margin. In summary, this study motivated for rapid capital investment into retrofitting isomerization facilities with SMB unit operations, replacing outmoded distillation as the primary separation technology. Future work will focus on optimizing the separation technology alongside the overall isomerization process using a rigorous techno-economic analysis as the objective function for optimization.

5. IMPROVING GASOLINE QUALITY PRODUCED FROM MIDOR LIGHT NAPHTHA ISOMERIZATION UNIT, M.F. Mohamed , W.M. Shehata , A.A. Abdel Halim , F.K. Gad (Feb 21, 2016).

Isomerization process became one of the best gasoline production sources, as it gives a high octane product while saving environment from pollution impacts. This paper presents a practical study that aims to improve the gasoline quality and economic income of an existing light naphtha isomerization unit used for octane improvement. The study included selecting the optimum combination of isomerization unit equipment that gives better product specifications for a specified feed. Eight scenarios were studied and simulated to predict the product specs. The original studied unit is MIDOR light naphtha isomerization unit at Alexandria-Egypt that recycles the unconverted hexane (C6). The other studied scenarios were adding fractionators for separating feed iso-pentanes, and recycling unconverted pentanes, hexanes and/or combinations of these fractionators. The results show a change in octane number of gasoline product for a specific feed. Once through process with no extra fractionators has lower octane number of 81 while that with de-isopentanizer, de-pentanizer and de-hexanizer produces gasoline with 92.3 octane number. Detailed economic study was done to calculate the return on investment “ROI” for each process option based on equipment, utilities, feed and product prices. Once through simple isomerization unit had the lowest ROI of 14.3% per year while the combination of De-iso-pentanizer with the De-hexanizer had the best ROI of 26.6% per year.

6. BOOSTING THE RESEARCH OCTANE NUMBER (RON) OF AN INDUSTRIAL SCALE LIGHT NAPHTHA ISOMERIZATION UNIT BY USING ADAPTIVE NEURO-FUZZY INFERENCE SYSTEM (ANFIS), Sepehr Sadighi, Seyed Reza Seif Mohaddecy, Mahdi Talebbeigi, (July 21, 2020).

In this work, an optimization approach is proposed to increase the research octane number (RON) of a commercial scale light naphtha isomerization unit. To represent the isomerization plant, an adaptive neuro-fuzzy inference system (ANFIS) is developed. The input layer of the network includes days on stream, temperature of the deisopentanizer condenser, light naphtha feed flowrate, inlet temperature of the isomerization reactor, hydrogen to hydrocarbon molar ratio, flow rate of n-hexane recycle, and temperatures of the de-pentanizer, de-isohexanizer and de-isopentanizer reboilers. The output variable of ANFIS is the RON of the product (i.e. isomerate). At first, it is confirmed that by using the Gaussian membership function, the model is capable of predicting the RON of isomerate with the AAD% of 0.913, confirming the reliability of the ANFIS model. Then, the actual RON of isomerate is boosted by manipulating

the significant variables of the plant i.e. temperatures of de-isopentanizer condenser and reboiler, inlet temperature of the isomerization reactor, hydrogen to hydrocarbon molar ratio, and temperatures of the depentanizer and deisohexanizer reboilers. During 280 days of study and considering all operational constraints, results confirm that the optimized decision variables can increase the RON of isomerate close to the designed value (about 86) which is the main concern of the target isomerization plant.

7. MATERIAL BALANCE AND REACTION KINETICS FOR PENEX ISOMERIZATION PROCESS IN DAURA REFINERY, Adel Sharif Hamadi, Rawnak Adnan Kadhim (2017).

Penex Deisohexanizer isomerization of light straight run naphtha is a significant process for petroleum refining and proved to be effective technology to produce gasoline components with a high octane number. Modelling of the chemical kinetic reactions is an important tool because it is a better tool for optimization of the experimental data into parameters used for industrial reactors. The present study deals on the isomerization process in Daura refinery. Material balance calculations were done mathematically on the unit for the kinetics prediction purpose. A kinetic mathematical model was derived for the prediction rate constants K_1 and K_2 and activation energy E_a at operating temperatures range 120-180°C. According to the model, the results show that with increasing of temperature leads to increased K_1 directly, where the K_2 values proportional inversely. The activation energy results show that $E_{a1}(nC_6) < E_{a1}(C_5) < E_{a1}(CH)$, and for $E_{a2}(iC_5) < E_{a2}(2,2-DMB) < E_{a2}(2,3-DMB) < E_{a2}(MCP)$.

8. PREDECTIVE MODELING AND OPTIMIZATION FOR AN INDUSTRIAL PENEX ISOMERIZATION UNIT - A CASE STUDY, Mohanad M. Said, Tamer S. Ahmed, Tarek M. Moustafa (Dec,2014).

This work presents a model for UOP Hydrogen Once Through (HOT) Penex Process using Aspen HYSYS Petroleum Refining module. The model relies on routinely taken industrial data of process streams during normal operating conditions. Acquired data sets have been tested and screened to ensure data validity for building the model and avoiding erroneous results. A reaction network with 20 reactions and 19 components has been used for the reactors model. The reactors model has been validated using 4 months of industrial plant data. In addition, rigorous tray-to-tray simulation of isomerate stabilizer has been utilized to match the performance of plant stabilizer. The model validated has been used for studying the effects of each process variable on plant performance. In addition, the model has been used in optimizing the operating conditions of the process. This optimization showed a potential for notable fuel savings in the process.

9. PROCESS SYSTEM ENGINEERING (PSE) ANALYSIS ON PROCESS AND OPTIMIZATION OF THE ISOMERIZATION PROCESS, Awan Zahoor Hussein, Kazmi, Bilal, Saud, Hashmi, Raza, Faizan; Hasan, Sahzeb Yasmin, Farzana (Nov 1,2021).

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 isomerate 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).

10. REACTOR TEMPERATURE OPTIMIZATION OF THE LIGHT NAPHTHA ISOMERIZATION UNIT, Ana Vukovic, INA Petroleum Industry, Petroleum Refinery Sisak (Feb 20,2013).

Isomerate, the product of an Isomerization unit, is a high octane number gasoline blending component characterized by low (or none at all) aromatic and sulphur content which also satisfies both economic and ecological demands. Quality of the isomerate is affected by a number of parameters, such as feed composition, process parameters, process engineer

attention to daily operation, etc. Some process parameters are set by the design basis or production planning while some others, like reactor temperatures, are optimized by a process engineer. During the optimization, reactor outlet temperatures are adjusted in the lead and lag reactors to maximize the reaction rate in the lead reactor and to manipulate the equilibrium concentrations in the lag reactor. This combination will maximize desired component product ratio, the so-called iso-ratio. The optimum can be chosen out of two options: to produce maximum isomerate barrels (maximum liquid yield) or to produce maximum product octane number. This paper deals with reactor temperature optimization background and results. The optimum inlet start-of-run temperature for the lead reactor was set to 117°C and for the lag reactor around 120°C.

V CONCLUSION

The isomerization process is gaining importance in the present refining context due to the limitations of benzene, aromatics, and olefin contents in gasoline. The isomerization process upgrades the octane number of light naphtha fractions and also simultaneously reduces benzene content by saturation of the benzene fraction. The low value of benzene percentage makes this process remarkable than the other processes with less carcinogenic effect. Isomerization complements catalytic reforming process in upgrading the octane number of refinery naphtha streams. Isomerization is a simple and cost-effective process for octane enhancement compared with other octane improving processes. Isomerate product contains very low sulphur and benzene, making it ideal blending component in refinery gasoline pool.

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