Selection of Isomerization Process to Produce Upgraded Mogas Meeting EURO-IV Standards as per Government Regulations

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This report is submitted as a FYP thesis in partial fulfilment of the requirement for the degree of

BE Chemical Engineering

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Certificate

This is to certify that the work in this thesis has been carried out by **Mr. Muneeb Ur Rahman, Mr. Abdul Moiz and Mr. Hadi Safdar** and completed under supervision of Lec. Zaeem Aman in School of Chemical and Materials Engineering (SCME), National University of Sciences and Technology (NUST), H-12, Islamabad, Pakistan.

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Dedication

To our parents, who were a source of constant support and helped us become the people we are today.

Acknowledgements

Thanks to **Almighty Allah** for His countless blessings, He gave us courage to finish this project. A very special recognition to our Supervisor, **Lec. Zaeem Aman** for supervising this project and for his support us throughout the year. Because of his experience and knowledge we are able to complete this project. We express our profound gratitude to **Mr. Khalil Ur Rehman and Mr. Muhammad Arif**, for giving us this project and believing in us. Furthermore, we extend our gratitude to **Mr. Muhammad Nisar** and **Mr. Ahmed Rehman** for their continual provision and guidance. They have been an immense source of assistance. We couldn’t have completed all the necessary paperwork and delivered it properly without them. We are able to achieve this milestone due to love and prayers of our beloved **parents**.

Abstract

This project aims to select the most suitable isomerization process for producing motor gasoline of desired Research Octane Number (RON) meeting Euro IV standard. For this purpose, UOP Honeywell®'s Penex process is being used here. The whole process occurs in a H2 atmosphere and utilizes a metal-chloride catalyst. Plant is based on light straight run Naphtha feed of approx. 12500 bbl/day which is mixed with H2, perchloroethylene (a catalyst promoter) and recycle stream from DIH. Process operations can be categorized into three sections. The first section is reactor section, where two fixed bed reactors are installed. Following it is a stabilization section where impurities like H2S, NH3 and light hydrocarbons are removed. The third section is a de-isohexanizer/recycle section where unconverted hexanes and methyl pentanes are separated and recycled as they have low RON. Other than isomerization, the reactions occurring include benzene saturation, hydrocracking and ring opening. The final isomerate produced is blended with higher hydrocarbons to give a fuel of RON between 87 and 90. The target reduction in benzene (<1%), Sulphur (<50 ppm), aromatics (<35%) and lead(0.005 g/l) content has been achieved.

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Chapter 1 Introduction

1.1 Background

Started off as a joint venture between the government of Pakistan and Emirates of Abu Dhabi, Pak Arab Refinery Limited (PARCO) commissioned in the year 2000 and was built at a cost of 886 million $. It is located at Mahmoodkot, Multan and has increased Pakistan's refining capacity by around 100,000 BPD. It also holds the honor of being in the only five refineries in the world built at the beginning of the millennium.

Light straight run naphtha is a distillation cut made up of pentane and slightly heavier naphtha range material. Light naphtha can come either from crude distillation or from fractionation of NGLs (natural gasoline). The light naphtha distillation cut has three typical uses: a) Blending directly into a finished light naphtha product. b) Feed to the isomerization unit to make isomerate for blending into gasoline. c) Direct blending into gasoline

As a blend stock for making gasoline, light naphtha is of fairly low quality. It tends to have low octane and high vapor pressure. So it typically only makes up a very small portion of the gasoline pool.

As per government regulations, refineries are instructed to produce gasoline that meets Euro standards without addition of octane boosters. Euro standards are acceptable limits for vehicle exhaust emissions as regulated by European environmental organizations. These regulations include minimizing benzene, sulphur, aromatic content and lead. This task is done by installing an isomerization unit in the refinery. Light naphtha isomerization plays a key role in meeting the octane demand.

1.2 Problem Statement

At this time in Pakistan, additives such as Lead and Manganese are being added in motor gasoline to achieve the desired RON (Research octane number). These additives not only cause air pollution but also harm the vehicles' engines and are potential carcinogens. Environmental pollution is one of the most critical challenges faced at this time by our society and this project seeks to tackle it through a greener approach aiming to achieve the product without using harmful pollutants.

Chapter 2 Literature Review

2.1 The Penex Process

The Penex Process is a proprietary process developed by UOP LLC.catalytic isomerization of pentanes and hexanes is done in this process. The reactions occur in favorable conditions having hydrogen in it and at operating conditions that minimize side reactions and enhances isomerization.

Other than the normal process called hyrotreating, penex process dodnt have a lot of requirements or pre requisites including prefractionation of C6 cyclis or C7+. We can consider penex process to add fractionations either on upstream or downstream of unit to get the desired results. The major elements of the Penex Unit are the Feed Surge Drum, the Sulfur Guard Bed, the Gas Treaters, the Feed Driers, the Makeup Gas Driers, the Penex Reactors and their associated heaters and exchangers, the Makeup Gas Compressor, the product Stabilizer and the Net Gas Scrubber, the Recycle Gas Compressor and associated equipment such as the Product Separator and the Reactor Effluent Condenser (for the Recycle Gas Penex flow scheme).Although not essential to the success of the process, the Penex process will normally employ two reactors in a series. With time, the Penex isomerization catalyst will become deactivated mostly likely from oxygenates, in particular water, and not from hydrocarbon catalyst downstream of the deactivation front normally remains unaffected. Reactor is switched off when the catalyst is deactivated During the short period of time the reactor is out of service,; conversion may be moderately lower. Freshly loaded catalyst is normally placed in the lag position.

After we load the catalyst we can reversed the processing position of two reactors. The two-reactor design permits essentially 100% unit onstream efficiency and reduces catalyst consumption costs by making partial catalyst replacements practical. It also permits the unit to be designed for a smaller catalyst inventory (higher space velocity), thus reducing catalyst capital requirements. In Isomerization and benzene hydrogenation reactions temperature increases across both reactors so both are exothermic reactions. It's the requirement of Equilibrium that the outlet temperature should be as low as the catalyst permits. Not all isomerization catalysts are suitable for application of the inverse temperature gradient principle. Some might coke or sludge if operated at a higher inlet temperature, or else they might promote excessive hydrocracking and yield loss. Since the Penex catalyst does neither of these, the inverse gradient can be applied to economic advantage. The C_5 paraffin equilibrium mixture will consist of essentially normal and iso- pentane. The C_6 isomer equilibrium distribution is split approximately 50/50 between the higher octane dimethylbutane and lower octane methylpentane.

Not all isomerization catalysts are suitable for application of the inverse temperature gradient principle. Some might coke or sludge if operated at a higher inlet temperature, or else they might promote excessive hydrocracking and yield loss. Since the Penex isomerization catalyst does neither of these, the inverse gradient can be applied to economic advantage. The promoter of catalyst is added continuously in the feed. Since the catalyst functions with very small amounts of promoter (measured in parts per million), it is not necessary to provide separate equipment for recovery and re-use of hydrogen chloride. It is permitted to leave the unit by way of the Stabilizer offgas.

The quantity of the Stabilizer offgas is relatively small, due to the selective nature of the catalyst which permits very little hydrocracking of the pentane/hexane charge to occur. The Stabilizer offgas contains the hydrogen not consumed in the reactor and the light gases (C_1 through C_4) introduced with the Makeup gas and produced in the reactor as a result of hydrocracking. The Stabilizer offgas is sent to the Net Gas Scrubber for removal of Hydrogen Chloride by neutralization before entering the refinery fuel gas system or hydrogen recovery system. The Penex catalyst itself is non-corrosive in the plant and, despite the presence of hydrogen chloride in the Unit during operation, the dryness of the system permits construction of carbon steel. Extensive years of commercial service have demonstrated the adequacy of this inexpensive metallurgy and the viability of the process. Figure I - 1 and Figure I - 2 represent the simplified flow schemes for the basic UOP Recycle Gas Penex Unit and the UOP Hydrogen Once Through (H.O.T.) Penex Unit, respectively. These configurations depict the process without a hydrocarbon recycle back to the reactors. The typical C5+ isomerate octane obtained with the Penex Process without hydrocarbon recycle is in the 82-85 RONc range. Figures I - 3 to I - 6 are examples of additional process flowschemes within which the basic flowscheme of the Penex Unit can be integrated. The specific Penex Unit flowscheme is dependent on the fresh feed composition and the process requirements from the unit, in terms of desired octane and yields.

If fresh feed to the Penex Unit is significantly high in iso-pentane content, approximately 20-30 wt percent or greater, there is an advantage to be gained in the installation of a Deisopentanizer (DIP) upstream of the Penex Unit. The size of the unit can be reduced with the exclusion of iso-pentane in the feed to the Penex Unit. Iso-pentane, if sent to the Penex Reactors will essentially take up space and pass unconverted with the isomerate product. The n-C_5 fraction and C_6 paraffins are then isomerized to equilibrium levels and blended back with the DIP overhead. The isomerate product from this flowscheme is the combined DIP overhead and Stabilizer bottoms materials. Figure I - 3 represents the DIP/Penex flowscheme. Figure I - 7 shows the octane upgrade over once-through operation for the DIP/Penex flowscheme. If fresh feed to the Penex Unit is high in total C_6 material, there is an octane advantage to be gained in the installation of a Deisohexanizer (DIH) downstream of the Penex Unit. In the Penex/DIH process, the DIH column fractionates the stabilized isomerate material from the Stabilizer bottoms, producing an overhead isomerate product containing all pentane (NC_5 and IC_5) and dimethylbutane (2-2 DMB and 2-3 DMB). Normal hexane and some of the methylpentane are taken as a sidedraw from the column and recycled back to the reactors for further upgrading.

There is a small bottoms drag stream from the DIH column that can also be sent to gasoline blending or to the reformer. The typical C_5+ octane obtained with the Penex/DIH process is in the 87-89 RONc range. Figure I - 4 represents the Penex/DIH flowscheme. The actual octane upgrade over once-through operation is a function of the relative C_5/C_6 concentration in the isomerization feedstock (Figure I) and the split obtained in the fractionator. If fresh feed to the Penex Unit is high in iso-pentane coupled with high levels of total C_6, an option exists in which a DIP can be installed upstream of the Penex Unit, with a DIH downstream to recover unconverted methylpentane and normal C_6. This flowscheme provides the highest product octane number; all the normal pentane (nC_5) and low octane C_6 paraffins (normal hexane and methylpentane) are recycled back to achieve maximum overall conversion across the unit. The total isomerate product from this flowscheme consists of a C_6 sidecut and bottom product from the DIH and iso-pentane overhead material from the DIP.

In this configuration, the DIH column is sometimes referred to as a Super DIH column because of the upper sidedraw product in addition to the normal sidedraw recycle lower in the column. The DIP/Penex/(Super) DIH process can produce C_5+ isomerate octane in the 90- 92 RONc range. The DIP/Penex/(Super) DIH flowscheme is represented on Figure I - 5. In the Penex/Molex process, a Molex unit is used to separate the iso-paraffins and napthenes from the normal paraffins with the normal paraffins recycled back to the Penex Reactors. The Molex process is a molecular sieve separation process and operates at low temperature in the liquid phase. The principles of operation of the Molex unit are based on UOP's successful Sorbex^{TM} separation technology. Generally, the Molex recycle system has advantages of lower energy consumption and a relatively pure normal paraffin recycle stream back to the Penex Unit. The high activity of the Penex catalyst combined with the high efficiency separation of the Molex process enables the Penex Reactors to operate at high space velocity. This reduces the catalyst requirement. A flowscheme of the Penex/Molex process is shown in Figure I - 86. The Penex/Molex process produces high C_5+ isomerate octanes, typically in the 87-90 RONc range. The best octane upgrade for this system is obtained on feedstocks that are richer in C_5s than C_6s (Figure I - 9). The performance of a Penex/Molex process against that of a Penex/Deisohexanizer at various feed compositions is compared in Figure I - 10.

The typical limit of benzene in the Penex Reactor charge is approximately 5 volume percent. If the benzene concentration in the Penex Reactor feed begins to approach 5 volume percent or if the total exotherm across the Lead Penex Reactor exceeds 55°C (100°F), a Saturation Reactor is added upstream of the Penex Unit to reduce benzene to the inlet of the Penex Reactors. This flowscheme is called the Penex-Plus flowscheme. The conventional Penex-Plus flowscheme is shown in Figure I - 11. For existing units in which benzene content in the reactor feed has increased above the typical limit of 5 volume%, a revamp configuration change is possible with the addition of a benzene saturation reactor, feed-effluent exchanger and heater upstream of the existing reactors, but downstream of the feed driers. This Integrated Penex-Plus Process flowscheme is shown in Figure I - 12. Each flowscheme discussed above has an isomerate octane range associated with it. The higher the required isomerate octane, the more complex the flowscheme can become. A summary of the octane performance of each flowscheme is shown in Figure I - 13. Light naphtha typically has an octane number of 60-70 RONc, depending on the origin of the feed. Processing this feed across the Penex Unit provides an octane boost of 15-30 numbers, depending on the flowscheme and feed type. Figure I - 14 shows typical octane upgrade based on the amount of C_6 in the feeds and choice of hydrocarbon recycle flowscheme. The selection of the Penex unit configuration is dependent upon feed composition and octane targets.

2.2 Isomerization History

Light straight run naphtha is characterized by a low octane number, typically 65-70 research octane number clear (RONc). This straight run fraction was once blended directly into the gasoline pool without additional processing except perhaps treating for mercaptan removal. This placed the C_5/C_6 straight run naphtha cut in the position of being that segment of the gasoline pool helped most by the addition of lead and least in need of upgrading by processing.

Refiners throughout the world are now faced with regulations regarding minimizing benzene, sulfur, aromatics and lead content in gasoline. The Penex process plays a key role in meeting the octane demands of the gasoline pool that result from changing gasoline specifications. The isomerate product contains no aromatics, benzene, sulfur or olefins. It is an ideal blending component to assist refiners in meeting new gasoline regulations. Compared to alternate means of replacing pool octane numbers lost when lead is removed, Penex isomerization offers several distinct advantages:

1. **Overall Yields** – Volumetric yields from isomerization are close to 100 percent. Most of the octane lost from straight run C_5/C_6 by lead removal can be replaced by once-through Penex isomerization. With recycle, the clear octane of the isomerate can be higher than the leaded octane number of the

straight run C_5/C_6 with isomerization. As lead is removed, some increase in catalytic reforming severity will be needed to maintain the octane number of the bulk of the gasoline pool at a satisfactory level. There will be an unavoidable yield loss associated with this reforming severity increase. The refiner has the option of isomerizing the C_5/C_6 or increasing the reforming severity to compensate for the octane numbers lost from the C_5/C_6 by lead removal and thereby incurring yield loss.

2. **Motor Octane** – Due to the high paraffin content, Penex isomerate has an excellent motor octane number. Although opinions differ concerning the exact quality and lead content of the gasoline which will be marketed in the United Sates and other countries a few years hence, it seems to be a distinct possibility that Motor rather than Research octane number may control the total amount of processing needed. Isomerization can permit C_5/C_6 to enter the gasoline pool at a clear Motor octane number at least as high as that of a 98 to 100 Research clear reformate.

3. **Non-Aromaticity** – The aromaticity of the gasoline, at the same pool octane numbers, will tend to be higher without C_5/C_6 isomerization than with it. Although there is some lack of agreement concerning possible adverse environmental effects of high aromatic concentrations, proposed legislation in some areas would restrict the aromatic content of the gasoline. All of the benzene in the feedstock is saturated in the Penex process.

4. **Front End Octane** – Completely apart from any consideration of lead reduction, European refiners began to construct isomerization units to meet the demand imposed by the high performance European-type engine for a fuel whose lower boiling components possess relatively high octane number, i.e., one with a relatively good “front end” octane number. The carburetor/manifold system tends to segregate the gasoline into lighter and heavier boiling fractions with the result that some cylinders receive a disproportionate amount of low boiling fuel and also an uneven amount of lead compounds. The European engine, normally operated with a manual transmission and having small displacement and high specific power output, is rather prone to knock during low speed acceleration in top gear. It is essential, therefore, that the fuel which enters each cylinder has some minimum octane number if knocking is to be avoided.

2.3 Catalysts

2.3.1 Aluminum chloride catalysts

The isomerization catalysts that were used in World War II were the majority of the Friedel-Crafts type. Hydrocarbon/aluminum chloride complex (the sludge process) contain aluminium chloride. They were proposed to work at extremely low temperatures [49-129°C (120-265°F)] and to approach the entirely appropriate equilibrium temperatures normal for these temperatures.

The catalyst would in general devour itself by response with the feedstock as well as item. At the point when temperature was brought a little up with an end goal to make up for loss of catalyst and to speed the response to impact more isomerization, light sections were framed by breaking and these, when vented, caused an inordinate loss of the catalyst promoter.

2.3.2 Hydro-Isomerization Catalysts [Below 199°C (390°F)]

They work in a hydrogen air and may utilize a promoter whose focus in the reactor may go from parts per million to considerably more elevated amounts. They by and large all require a dry, low sulfur feedstock; notwithstanding, they may contrast significantly in their resistance of particular kinds and atomic loads of hydrocarbons. Hydrocracking to light gases is commonly slight, so fluid item yields are high. This type of catalyst is used in the Penex Unit. Due to its high product octanes and yields, UOP’s Penex process is the most popular of the isomerisation unit types.

2.3.3 Hydro-Isomerization Zeolitic Catalysts [Vapor Phase]

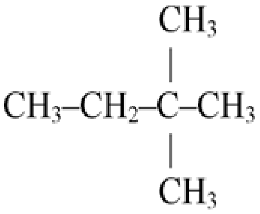
In the early 1970’s, an isomerization catalyst based on a zeolite was introduced. This system operated in the vapor phase at relatively mild conditions, 220-315°C (420-600°F) and 14-31.5 kg/cm^2g (200-450 psig). The advantage of this system was no catalyst promoter was required and the catalyst is more tolerant of feedstock impurities such as water and sulfur. The disadvantages of this system are it requires a recycle gas compressor (e.g. high H_2:HCBN), the laydown of coke requires periodic regeneration, and the high temperature limits the conversion due to the lower equilibrium.

2.3.4 Hydro-Isomerization Metal Sulfate Catalysts

Sulfated zirconium catalysts form one of the newest types of isomerisation catalysts, whereupon zirconium sulfate is used as the source of the acid sites. It was first commercialized in a Par-Isom unit in 1996. The activity of UOP’s newest zirconium sulfate catalyst approaches that of the chloride alumina type catalysts, although at lower yields.

2.4 Abbreviations

1. **2-2 DMB (2,2-dimethylbutane)** – a branched 6-carbon chain isomer of hexane with 2 methyl groups attached to the second carbon; the resulting chemical structure is :



$$\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{CH_3{-}CH_2{-}C{-}CH_3}\\ |\\ \mathrm{CH_3}\end{array}$$

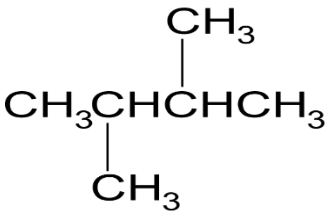
2. **2-2 DMB / C_6 P** = 2-2 DMB / (2-2 DMB + 2-3 DMB + 2MP + 3MP + NC_6) * 100,

normally in weight or mole percent; product isomer ratio of 2-2 DMB.

3. **2-3 DMB / C_6 P** = 2-3 DMB / (2-2 DMB + 2-3 DMB + 2MP + 3MP + NC_6) * 100,

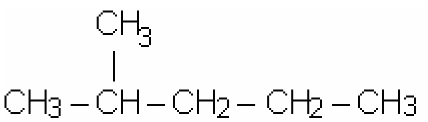
normally in weight or mole percent; product isomer ratio of 2-3 DMB.

4. **2-3 DMB (2,3-dimethylbutane)** – a branched 6-carbon chain isomer of hexane with methyl groups attached to the second and third carbons; the resulting chemical structure is :



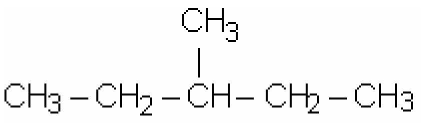
$$\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{CH_3CHCHCH_3}\\ |\\ \mathrm{CH_3}\end{array}$$

5. **2 MP (2 methylpentane)** – a branched 6-carbon chain isomer of hexane with a methyl group ($-CH_3$) attached to the second carbon; the resulting chemical structure is :



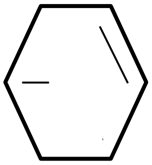
$$\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{CH_3-CH-CH_2-CH_2-CH_3}\end{array}$$

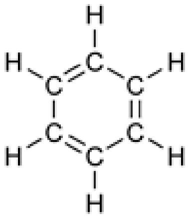
6. **3 MP (3 methylpentane)** – a branched 6-carbon chain isomer of hexane with a methyl group (-CH_3) attached to the third carbon; the resulting chemical structure is :



$$CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_3$$

7. **Bz (Benzene)** – an aromatic compound ring structure with the molecular formula C_6H_6; the resulting chemical structure is :





8. **C_7^+ (C7 Plus)** – Feed material heavier than heptane, including normal heptane

9. **CH (Cyclohexane)** – a cycloalkane with the molecular formula C_6H_{12}; the resulting chemical structure is:

10. **DIH** –A fractionator that separates the C_6 isomers from light naphtha, typically an 80-tray column. The overhead material, mostly dimethylbutanes (2-2 DMB+ 2-3 DMB) are sent to gasoline blending; the bottoms material can be sent to gasoline blending or to a Naphtha Splitter. There is a sidedraw, comprised mostly of methylpentanes (2MP + 3MP) and normal hexane (NC_6) that is recycled to the reactors for further processing. An upper sidedraw can sometimes be employed to further segregate C_6 isoparaffins.

11. **DIP** – A fractionator that separates isopentane from light straight naphtha, typically an 80-tray column. The overhead material, mostly IC_5, is sent togasoline blending. The bottoms material NC_5 and heavier material are sent to the Penex unit for processing.

12. **DMB or Dimethylbutane** – 2-2 DMB and 2-3 DMB are collectively known as DMB or Dimethylbutane. Refer to 2-2 DMB and 2-3 DMB.

13. **Equilibrium Product Ratio** – Since the isomerization is an equilibrium reaction, a balance of iso-and ordinary paraffins will be come to at the reactor effluent. At the point when this balance is achieved, max product proportion or balance product proportion will be gotten. Any endeavor to surpass equilibrium proportion with delivering more isoparaffins in the reactor gushing would just outcome in less iso-paraffins yield and an expansion in propane and lighter yield.

14. **IC_5 (Isopentane)** – a branched chain alkane with 5 carbon atoms; an isomer of normal pentane.

15. **IC_5 / C_5P** = $IC_5 / (IC_5 + NC_5) * 100$, normally in weight or mole percent; product isomer ratio of IC_5.

16. **MCP – Methylcyclopentane** – a chemical compound with an alkyl group attached to a 5-ring carbon compound. The molecular formula is (C_5H_{10})-CH_3; the resulting chemical structure is :

17. **MONc (Motor Octane Number clear)** – The performance of anti knocking agents in engine is represented by octane number

18. **MP or Methylpentanes** – 2MP and 3MP are collectively known as MPs or methylpentanes. Refer to 2MP and 3MP.

19. **NC_5 – Normal Pentane** – a straight chain alkane with 5 carbon atoms; the resulting chemical structure is :

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

20. **NC_6 – Normal Hexane** – a straight chain alkane with 6 carbon atoms; the resulting chemical structure is :

$$CH_3 – CH_2 – CH_2 – CH_2 – CH_2 – CH_3$$

21. **Product Ratio** – The product ratio is a term used to define the degree of isomerization taking place in the reactors. It is the weight or mol percent of isoparaffins in the total paraffins found in the reactor effluents.

22. **RONc (Research Octane Number clear) –** The anti knock performance of petroleum is represented by octane ratings.

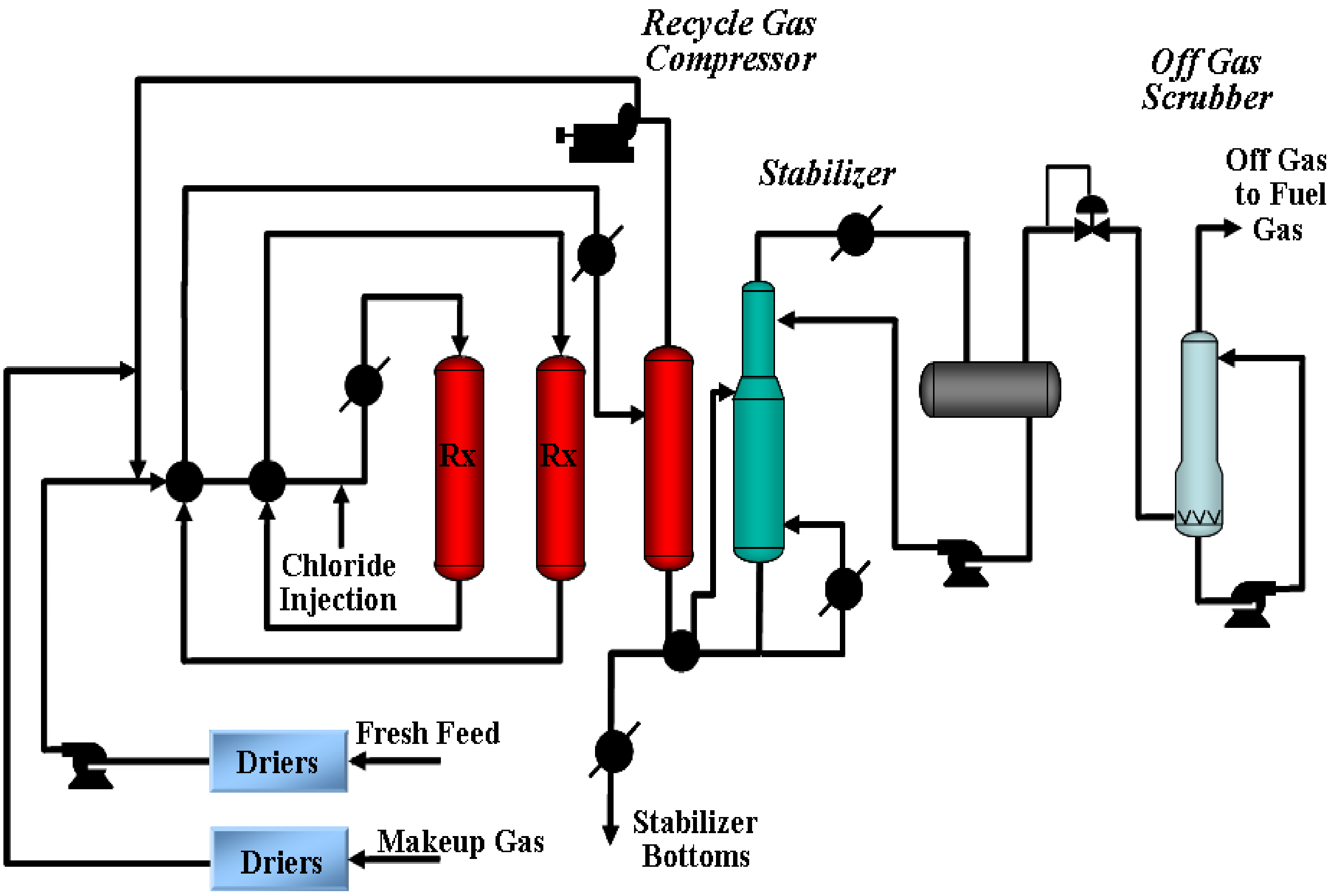


Figure 1 (Recycle Gas) Penex Process

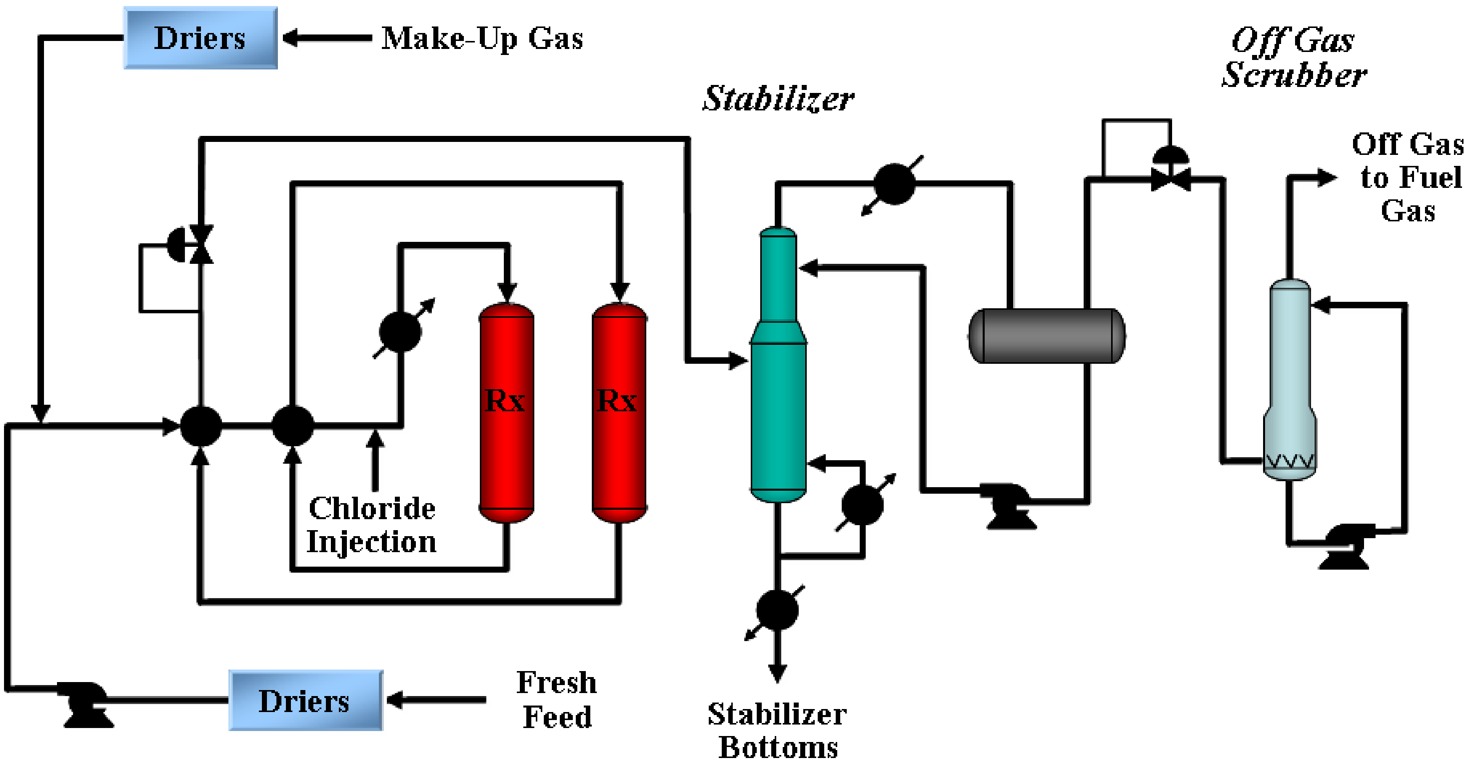


Figure 2 (Hydrogen Once Through) HOT Penex Process

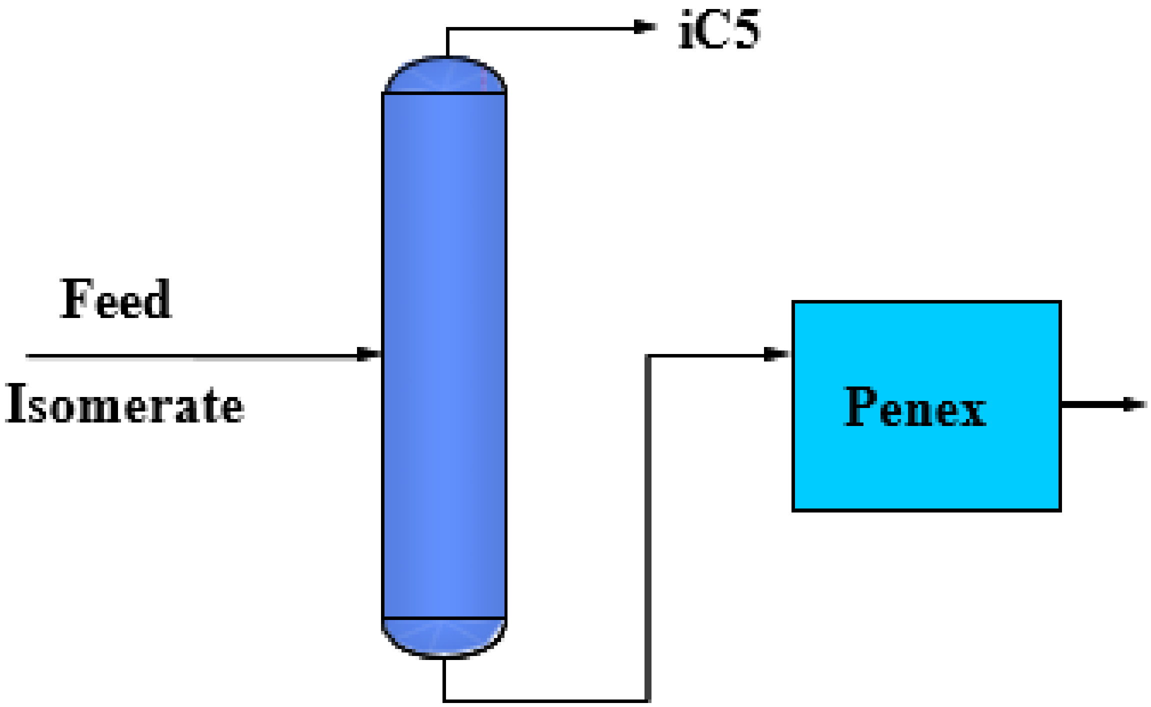


Figure 3 DIP / PENEX Flowscheme

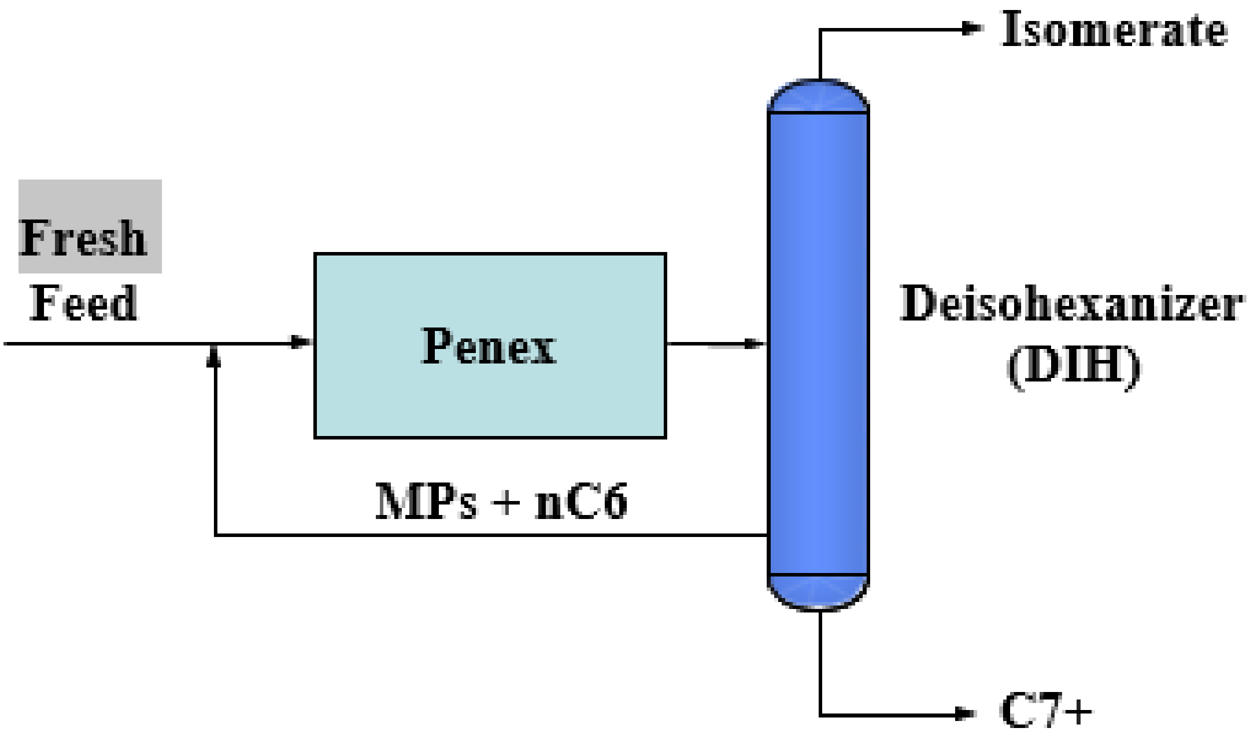


Figure 4 PENEX / DIH Flowscheme

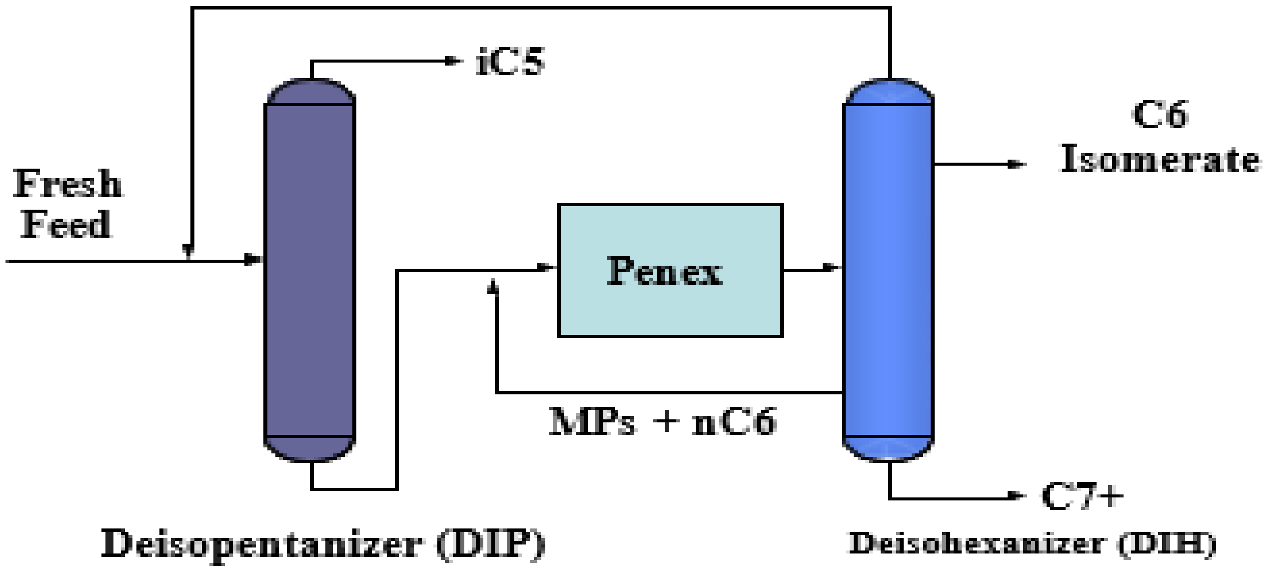


Figure 5 DIP / PENEX / (SUPER) DIH Flowscheme

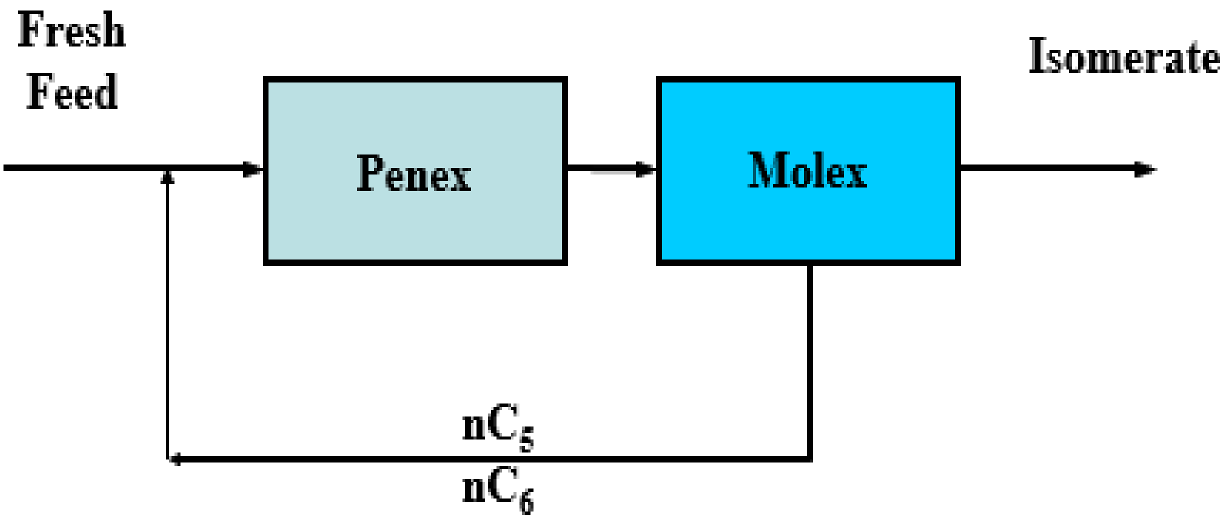


Figure 6 PENEX / MOLEX Flowscheme

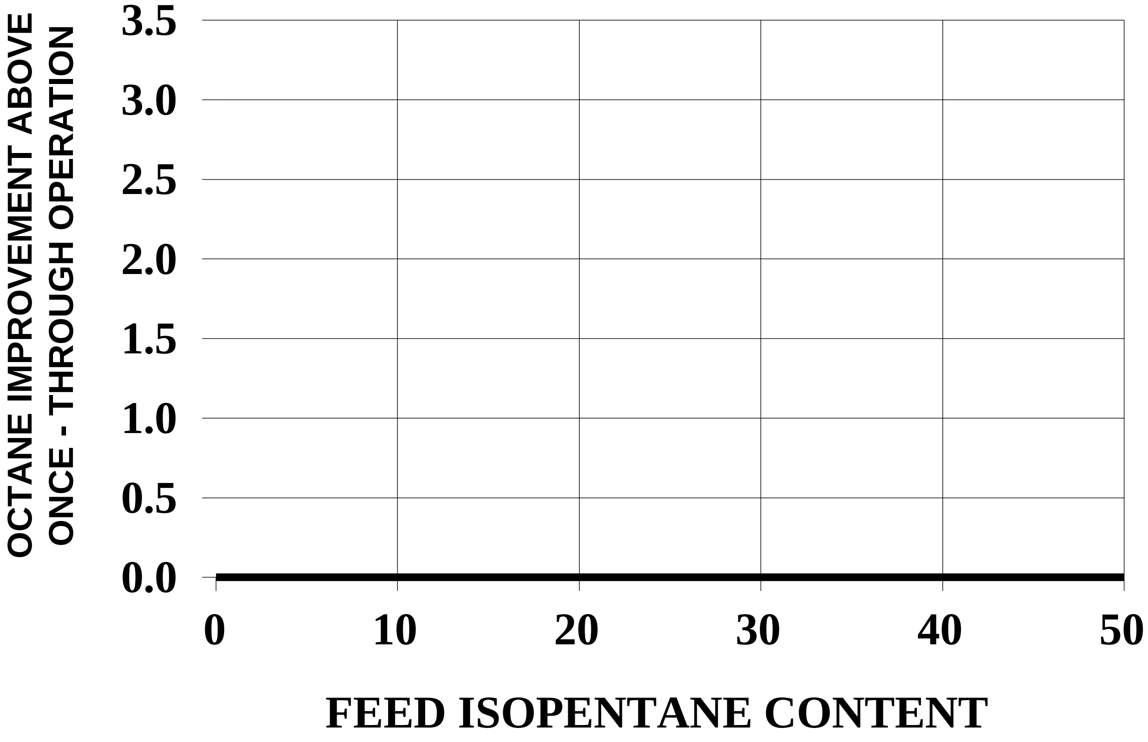


Figure 7 DEISOPENTANIZER Octane Increase

BASIS: C_5/C_6 PARAFFIN ISOMERIZATION FEED

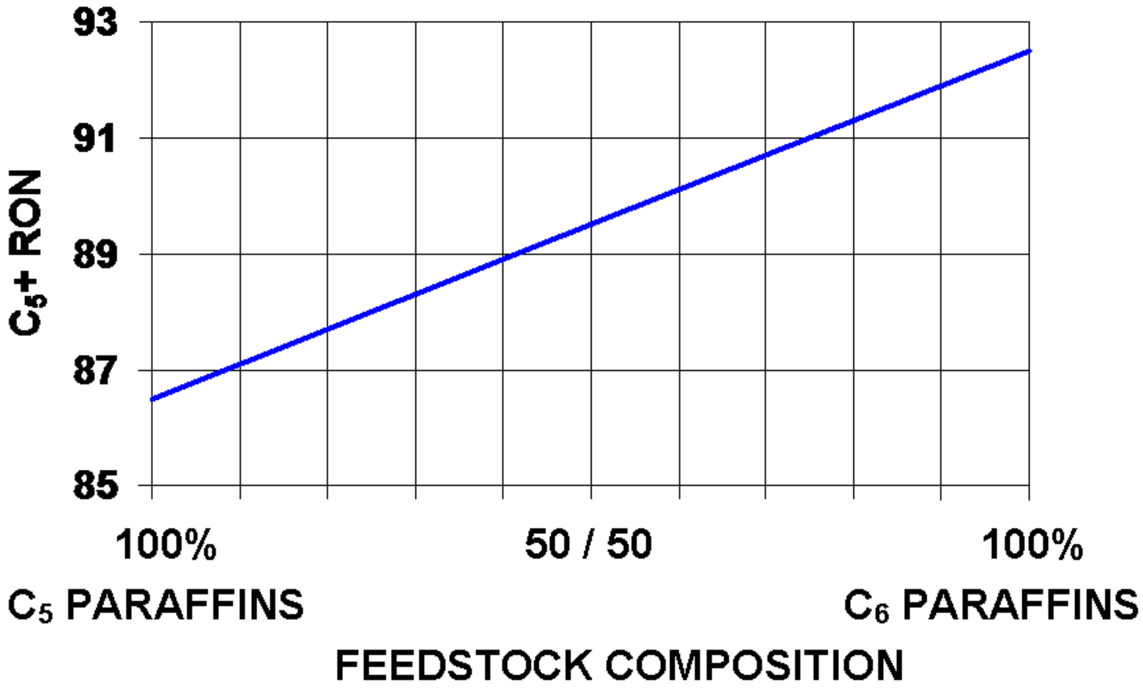


Figure 8 DEISOHEXANIZER Octane

BASIS: C_5/C_6 PARAFFIN ISOMERIZATION FEED

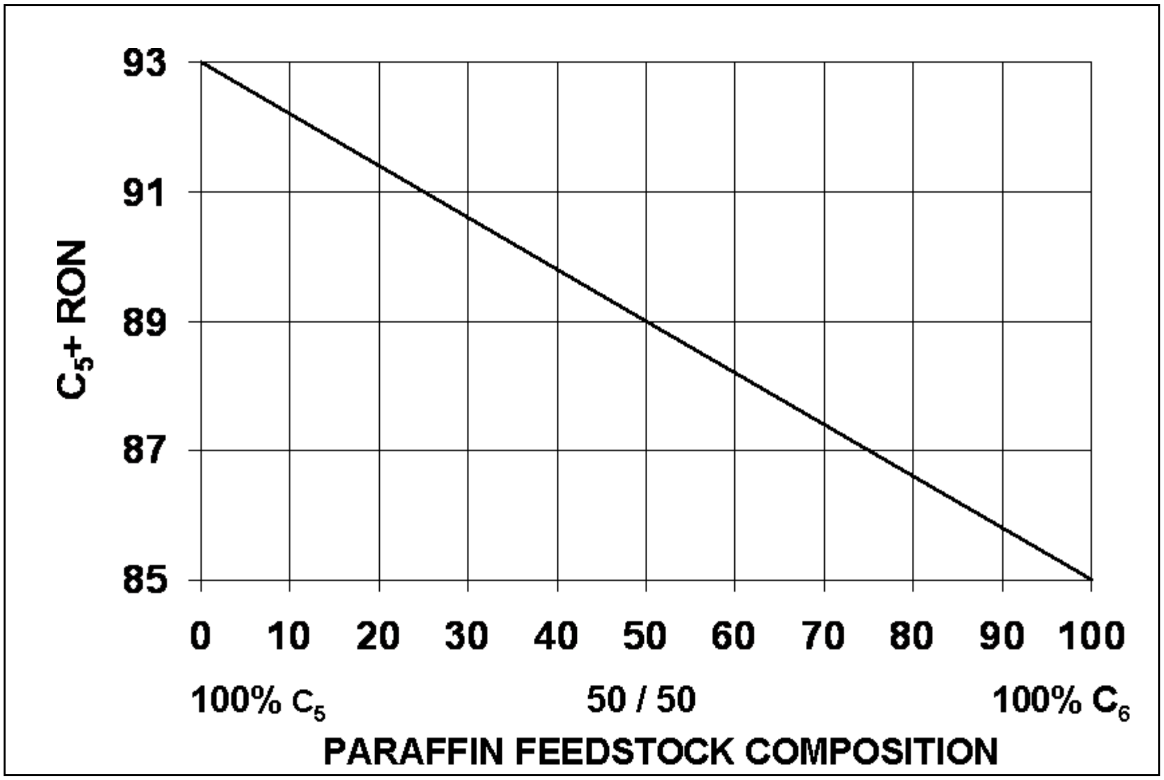


Figure 9 PENEX / MOLEX Octane vs Feed Composition

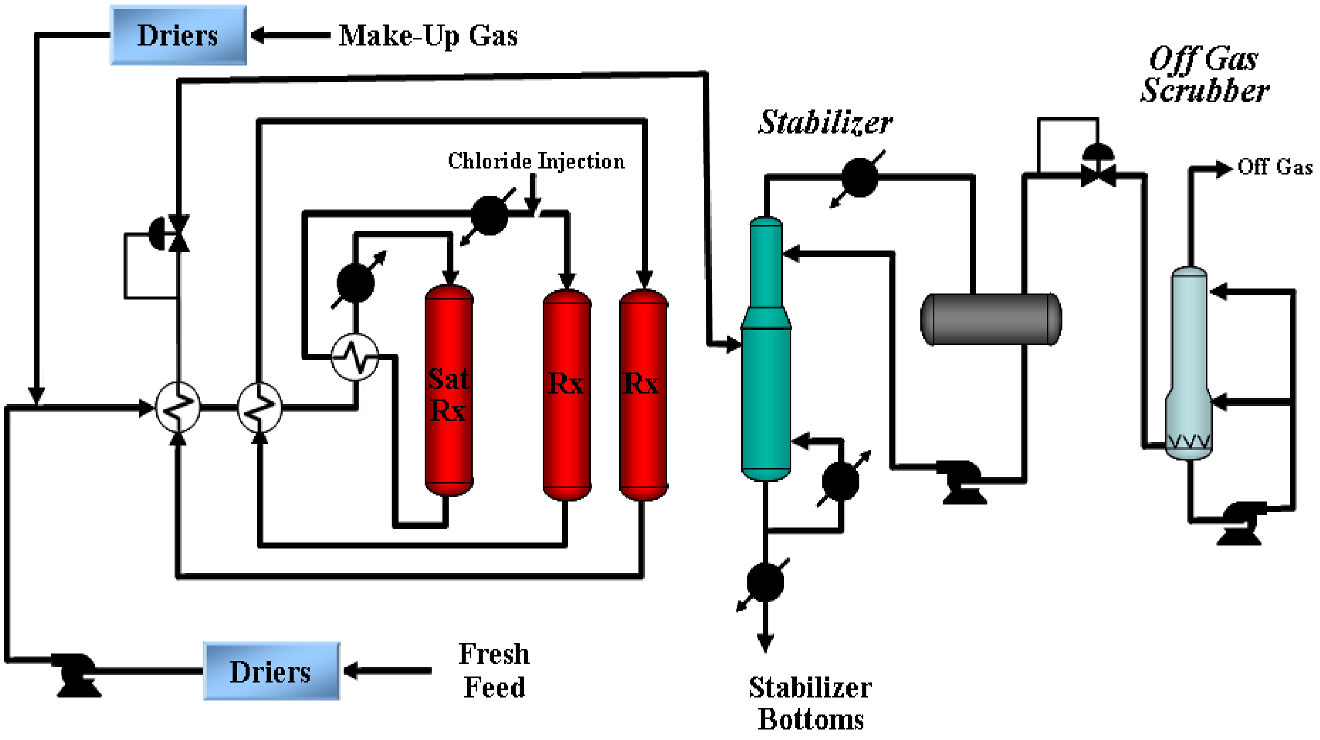


Figure 10 Integrated PENEX-PLUS Flowscheme

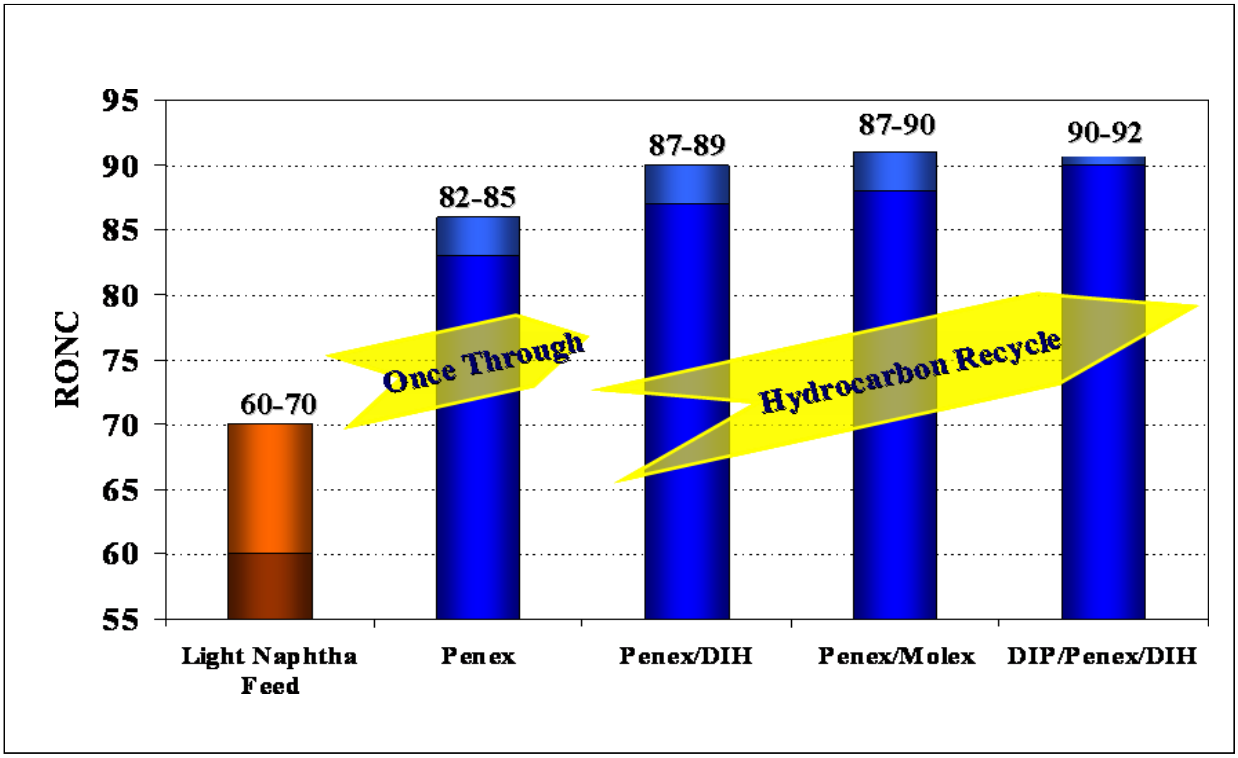


Figure 11 PENEX PROCESSES Octane Portfolio

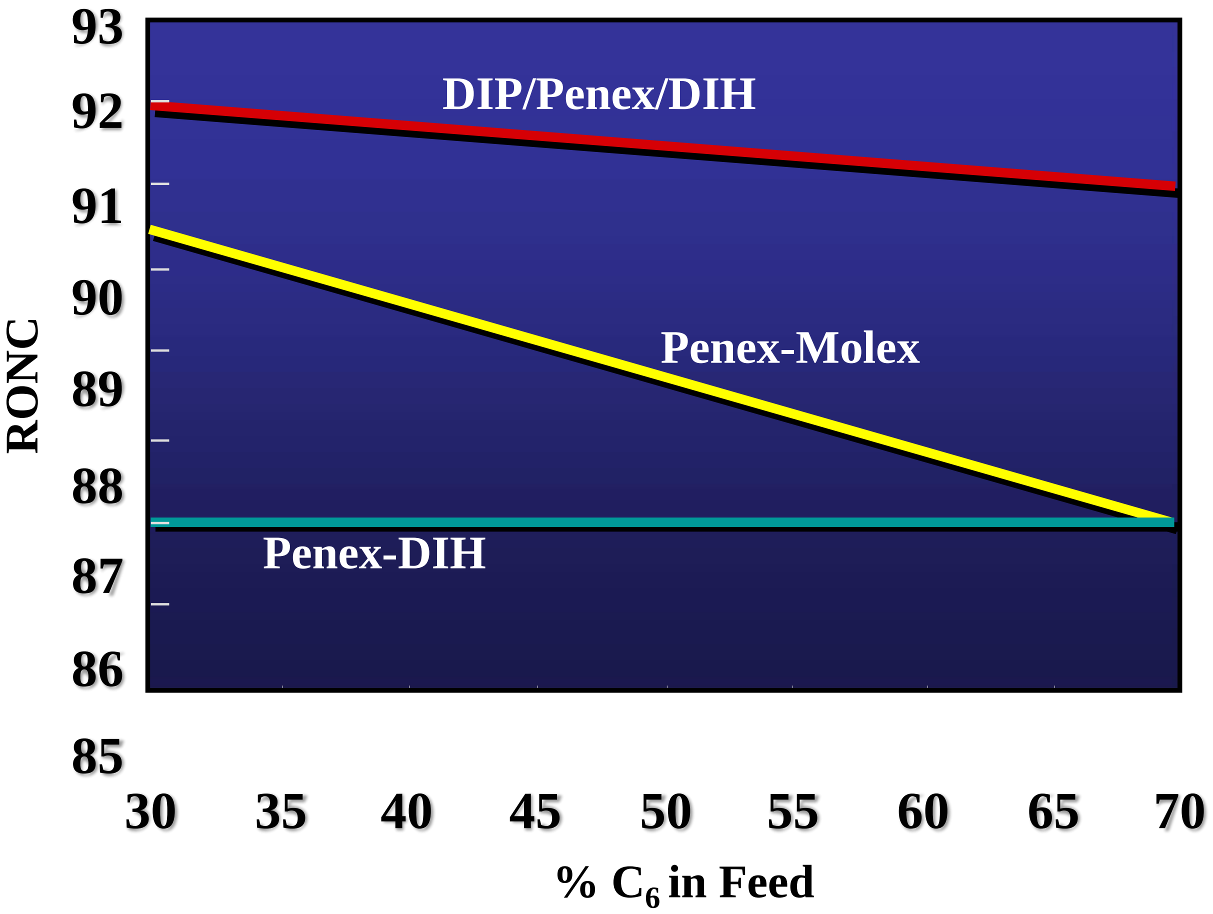


Figure 12 Selecting A Recycle Flowscheme

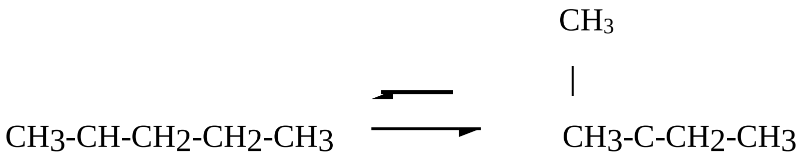
2.5 Process Principles

2.5.1 Reaction Mechanisms

Paraffin isomerization catalysts falls into two categories

(1)Friedel-Crafts catalysts as known as aluminum chloride/hydrogen chloride, or (2) dual-function hydro-isomerization catalysts. No attempt is made to present a discussion of mechanisms of a degree of sophistication acceptable to a chemist specializing in the area. The intention is simply to provide those practicing engineers who have not previously had reason to consider isomerization with a basic introduction to the subject. Isomerization by either Friedel-Crafts or dual-function catalysts is generally thought to entail intramolecular rearrangements of carbonium ions as illustrated - for pentane:

(1)



$$CH_3\text{-}CH\text{-}CH_2\text{-}CH_2\text{-}CH_3 \rightleftharpoons CH_3\text{-}\overset{\overset{\displaystyle CH_3}{|}}{C}\text{-}CH_2\text{-}CH_3$$

There appear to be two schools of thought regarding the Friedel-Crafts mechanism. Perhaps each mechanism is operative and the disagreement is merely over their relative importance under specific circumstances.

Friedel-Crafts isomerization is believed by some to require the presence of traces of olefins or alkyl halides as carbonium ion initiators, with the reaction thereafter proceeding through chain propagation. The initiator ion, which needs to be present in small amounts only, may be formed by the addition of HCl or $HAlCl_4$ to an olefin, which is present in the paraffin as an impurity or which is formed by cracking of the paraffin:

(2) $RCH = CH_2 + HAlCl_4 \;\square\; RCHCH_3 + AlCl_4{}^{\Theta}$

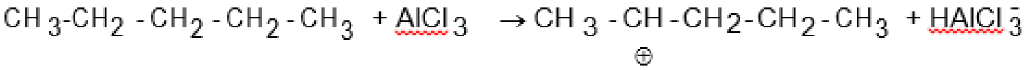
The initiator then forms a carbonium ion from the paraffin to be isomerized:

(3) $RCHCH_3 + CH_3 - CH_2 - CH_2 - CH_2 - CH_3\ RCH_2CH_3 + CH_3 - CH - CH_2 - CH_2 - CH_3$

Isopentane is then formed and the chain propagated by the generation of a new normal carbonium ion.

Naturally, the same sequence could have been illustrated starting with isopentane and ending with n-pentane and an iso-carbonium ion to propagate the chain, i.e., reactions (3), (4), and (5) are reversible, as are all of the reactions to be shown later. The composition of the final mixture is, of course, that set by thermo-dynamic equilibrium, assuming that sufficient reaction time has been provided.

Another Friedel-Crafts route which has been suggested is direct hydride ion abstraction:

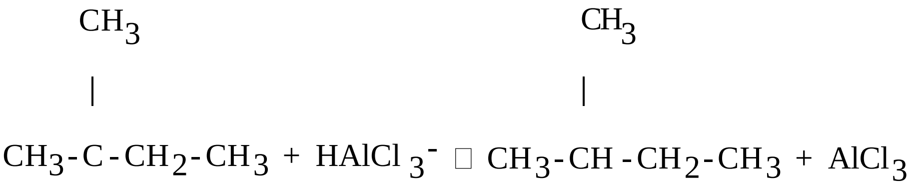


$$CH_3-CH_2-CH_2-CH_2-CH_3 + AlCl_3 \rightarrow \underset{\oplus}{CH_3-CH}-CH_2-CH_2-CH_3 + HAlCl_3^-$$

The carbonium ion, as before, rearranges

$CH_3CH_3-CH-CH_2-CH_2-CH_3$ □ $CH_3-C-CH_2-CH_3$

Finally, iso-pentane is formed:



$$CH_3-\overset{\overset{CH_3}{|}}{C}-CH_2-CH_3 + HAlCl_3^- \;\square\; CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_3 + AlCl_3$$

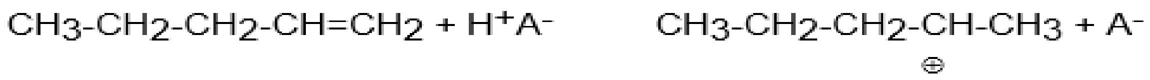
Abstraction of the hydride ion is energetically favored by the fact that the aluminum atom can thereby complete its electron octet. Since there is always some hydrogen chloride present, either by design or from hydrolysis of aluminum chloride by traces of water, a Bronsted (protonic) acid could have been shown for Reactions (6) and

instead of a Lewis acid:

$CH_3-CH_2-CH_2-CH_2CH_3 + H^+(AlCl_4)^-$ $CH_3-CH-CH_2-CH_2-CH_3 + (AlCl4)^- + H_2$

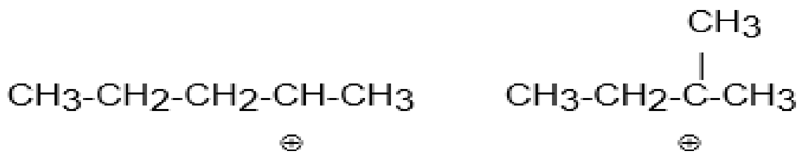
Some chemists feel uncomfortable with the above because of the required postulation of hydrogen formation. The dual-function hydro-isomerization catalysts are thought by some to operate through an olefin intermediate whose formation is catalyzed by the metallic component.

This response is, obviously, reversible and, since these impetuses are utilized under considerable hydrogen weight, the harmony is far to one side. Be that as it may, the corrosive capacity of the catalysts devours the olefin by arrangement of a carbonium particle and accordingly allows more olefin to shape regardless of the troublesome equilibrium. This stepis entirely analogous to Reaction (2) shown for Friedel-Crafts, except that it is better to denote the acid function by a more general “H^+A^-.”



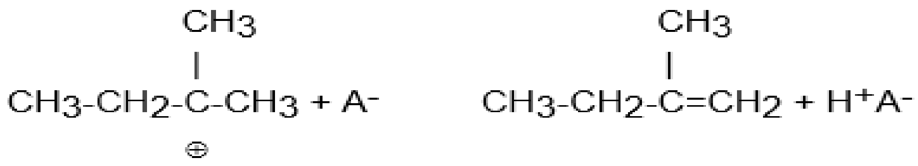
$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH{=}CH_2 + H^+A^- \qquad CH_3\text{-}CH_2\text{-}CH_2\text{-}\underset{\oplus}{CH}\text{-}CH_3 + A^-$$

usual rearrangement ensues:



$$CH_3\text{-}CH_2\text{-}CH_2\text{-}\underset{\oplus}{CH}\text{-}CH_3 \qquad CH_3\text{-}CH_2\text{-}\underset{\oplus}{\overset{\overset{\displaystyle CH_3}{|}}{C}}\text{-}CH_3$$

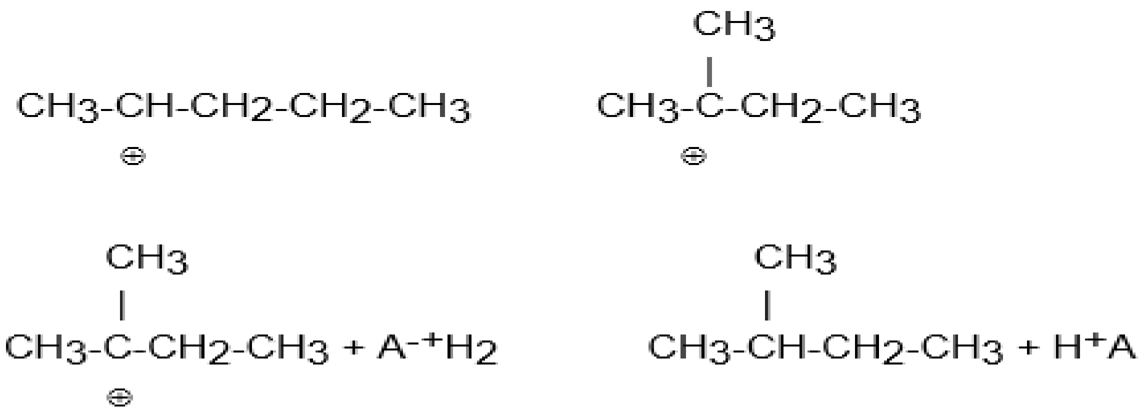
iso-olefin is then formed by the reverse analog of (11):



$$CH_3\text{-}CH_2\text{-}\underset{\oplus}{\overset{\overset{\displaystyle CH_3}{|}}{C}}\text{-}CH_3 + A^- \qquad CH_3\text{-}CH_2\text{-}\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2 + H^+A^-$$

The iso-paraffin is finally created by hydrogenation:

$$CH_3\text{-}CH_2\text{-}CH_2CH_2CH_3 + H^+A^- \qquad CH_3\text{-}CH\text{-}CH_2\text{-}CH_2\text{-}CH_3 + A^- + H_2$$



$$CH_3\text{-}\underset{\oplus}{CH}\text{-}CH_2\text{-}CH_2\text{-}CH_3 \qquad CH_3\text{-}\underset{\oplus}{\overset{\overset{\displaystyle CH_3}{|}}{C}}\text{-}CH_2\text{-}CH_3$$

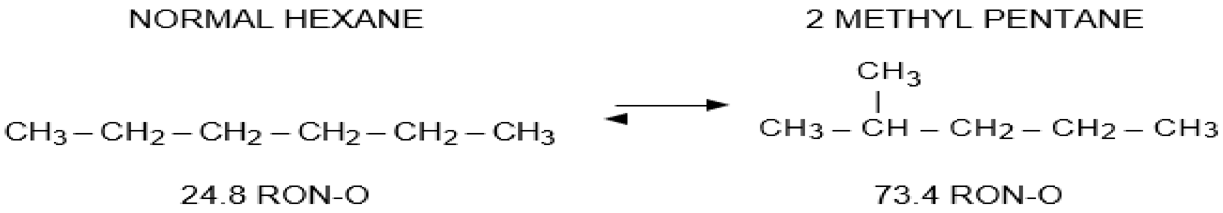
$$CH_3\text{-}\underset{\oplus}{\overset{\overset{\displaystyle CH_3}{|}}{C}}\text{-}CH_2\text{-}CH_3 + A^- {}^+H_2 \qquad CH_3\text{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}\text{-}CH_2\text{-}CH_3 + H^+A$$

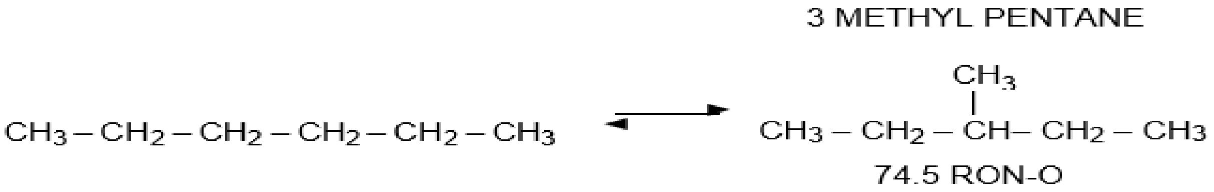
The last reaction is in lieu of the displacement type chain propagation step (Reaction 5) discussed earlier.

Since the reaction with hydrogen is relatively fast, acid sites are readily liberated for further reaction. This may account, at least in part, for the higher activity of such dual functional catalysts.

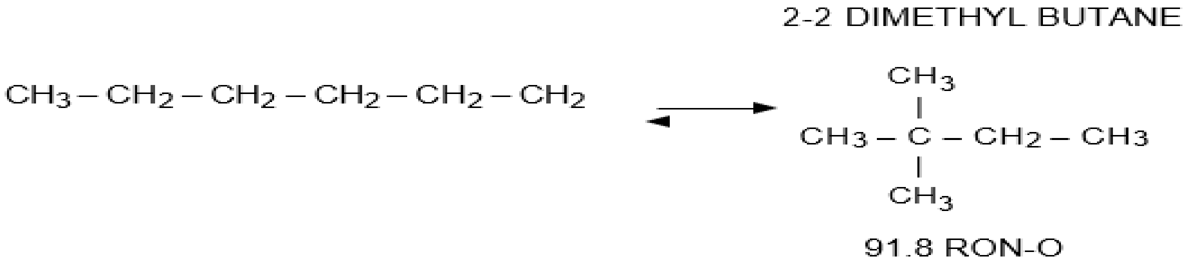
2.5.1.1 Hydro-Isomerization Catalysts [below 199°C (390°F)]

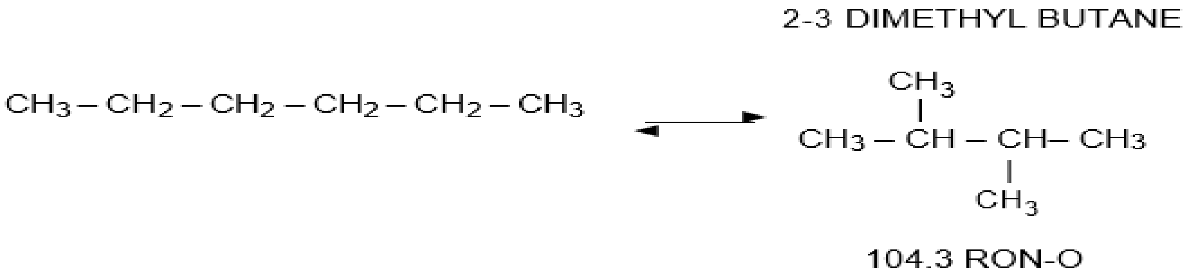
The reactions in Hydro-Isomerization catalysts are as follows:

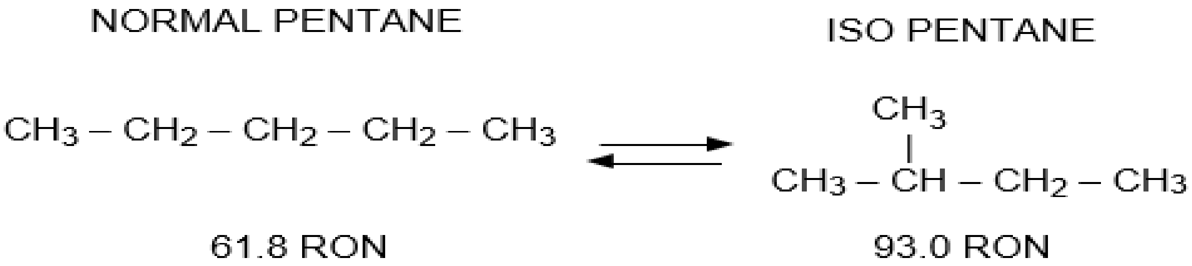




The C5/C6 reactions that occur are written below







$$CH_3 - CH_2 - CH_2 - CH_2 - CH_3 \rightleftharpoons CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_2 - CH_3$$

2.5.1.2 Other Reactions

Aside from the paraffin isomerization reactions these are some extra

A. Naphthene ring opening.

B. Naphthene isomerization.

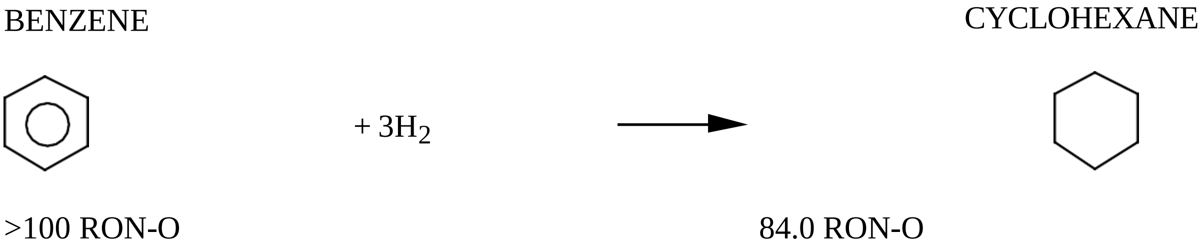
C. Benzene saturation

D. Hydrocracking.

Ring Opening: The three naphthenes cyclopentane (CP), methyl cyclopentane (MCP) and cyclohexane (CH). The naphthene rings will hydrogenate to produce paraffins.

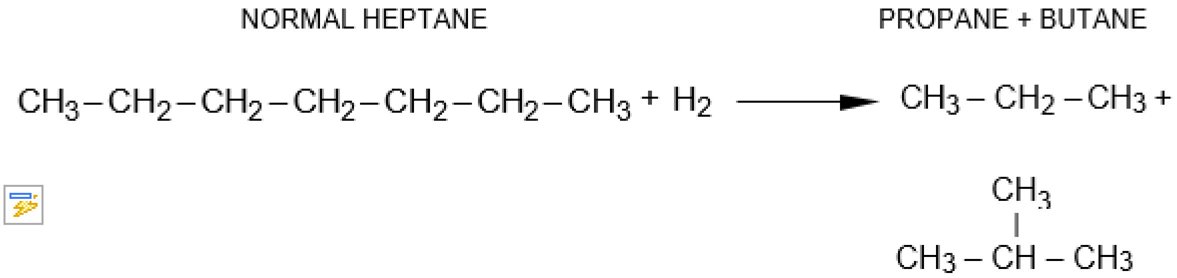
2.5.2.3 Benzene Saturation:

The isomerization area is commonly intended for 2 LV% benzene. The Penex catalyst will immerse benzene to cyclohexane. This response continues all around rapidly and is accomplished at extremely low temperatures.Saturation of benzene isn't balance constrained at the isomerization reactor conditions and change ought to be 100%.



2.5.2.4 Hydrocracking:

Hydrocracking happens in the Penex reactors to a degree which relies upon the feed quality and seriousness of activity. C7+ hydrocrack more than the little ones. C5 and C7 will hydrocrack too



$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3 + H_2 \longrightarrow CH_3-CH_2-CH_3 + CH_3-CH(CH_3)-CH_3$$

2.5.2.5 Acidizing

Hydrogen chloride (HCl) goes into the process stream where it reacts with iron oxide (Fe_2O_3) to form Iron Chloride ($FeCl_3$) and water. This reaction will continue to take place until the rust present in the unit is depleted.Analyzers, will signify that the reaction has gone to completion.

Hydrogen Chloride + Iron Oxide ⟶ Iron Chloride + Water

$$6HCl + Fe_2O_3 \longrightarrow 2FeCl_3 + 3H_2O$$

2.5.2.6 Chloride Promoter

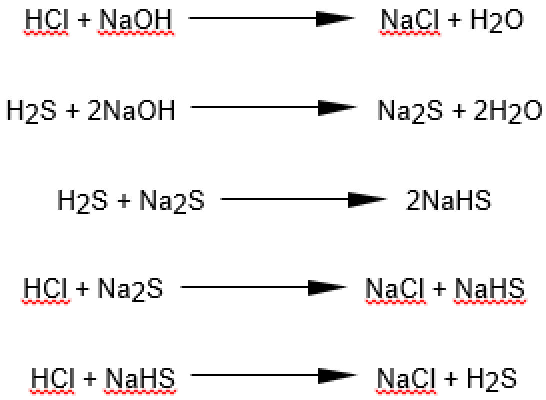
After we add catalyst promoter (perchloroethylene C_2Cl_4) to the stream going into the mixture is proposed to keep up the corrosive capacity of the impetus with chloride iotas (Cl). When the reactor temp hits 105°C (220°F) or higher, the chloride will change to HCl during the presence of Penex catalyst.

Perchloroethylene + Hydrogen ⟶ Hydrogen Chloride + Ethane

$$C_2Cl_4 + 5H_2 \xrightarrow[\text{Heat}]{\text{Catalyst}} 4HCl + C_2H_6$$

2.5.2.7 Caustic Scrubbing

Stabilizer Net Gas Scrubber is used to neutralized the hydrogen chloride by neutraliazation base reactions between sodium hydroxide (NaOH) and hydrogen chloride (HCl). An outline of the burning scouring task is appeared in Figure II-1. The quality of the caustic ought to be observed by deciding the complete alkalinity of the arrangement. If a hydrogen stripping operation is performed, hydrogen sulfide (H_2S) will be present in the stabilizer off gas and will react with sodium hydroxide to form sodium sulfide (Na_2S), sodium bisulfide (NaHS) and water. During the sulfur stripping procedure it is important to monitor the total alkalinity and the percent spent (the difference between the total alkalinity and the strong base) as shown in Figure II-2 and Figure II-3.



$$HCl + NaOH \longrightarrow NaCl + H_2O$$

$$H_2S + 2NaOH \longrightarrow Na_2S + 2H_2O$$

$$H_2S + Na_2S \longrightarrow 2NaHS$$

$$HCl + Na_2S \longrightarrow NaCl + NaHS$$

$$HCl + NaHS \longrightarrow NaCl + H_2S$$

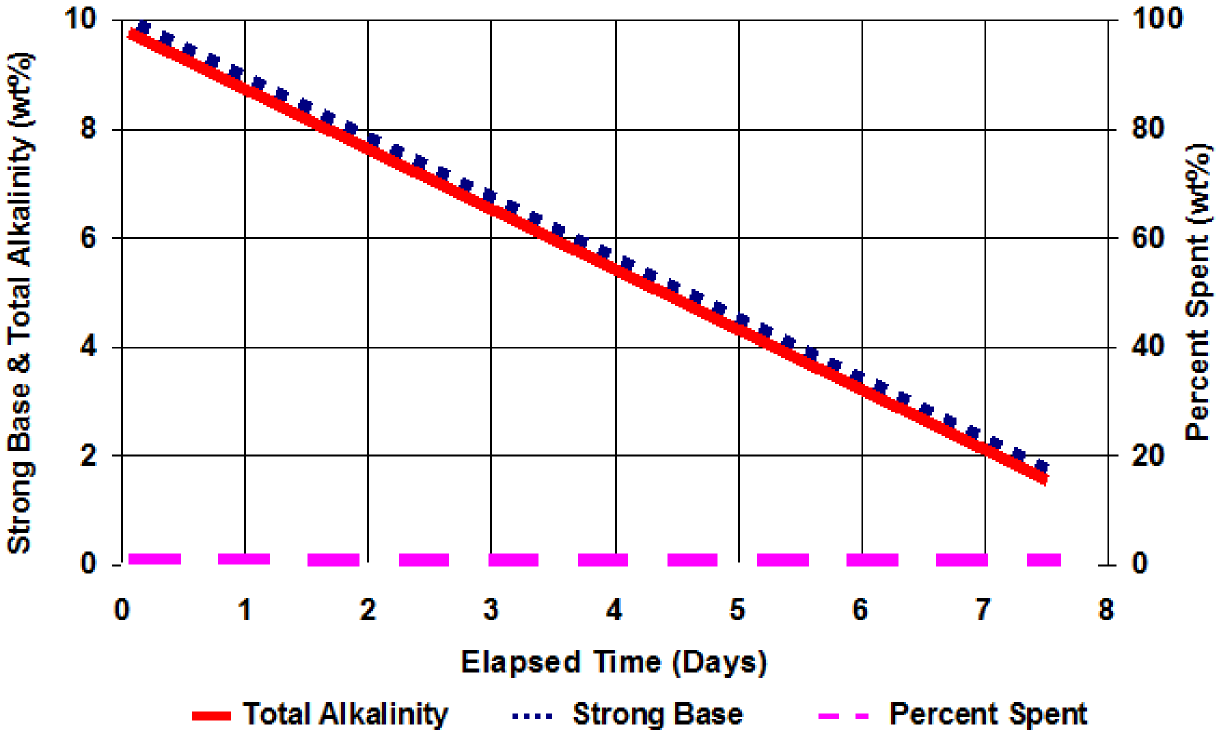


Figure 13 HCl Scrubbing Caustic Scrubbing Operation

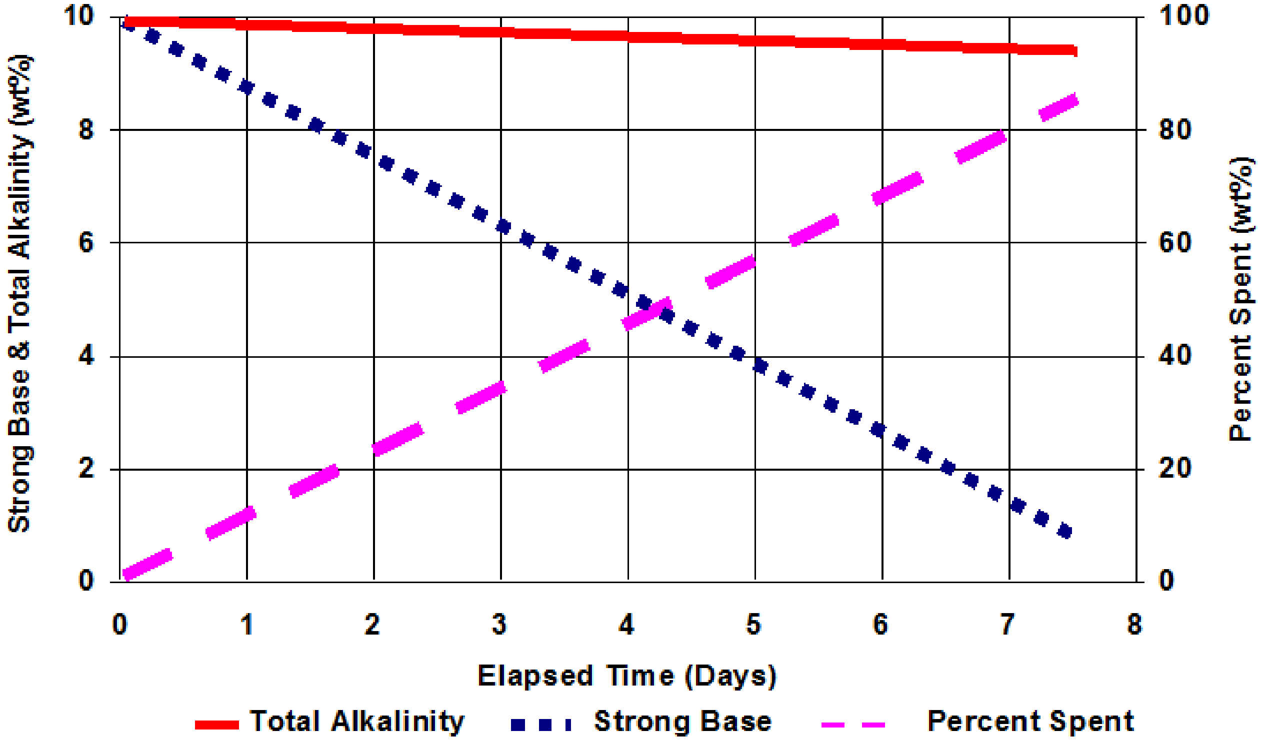


Figure 14 H2S Scrubbing Caustic Scrubbing Operation

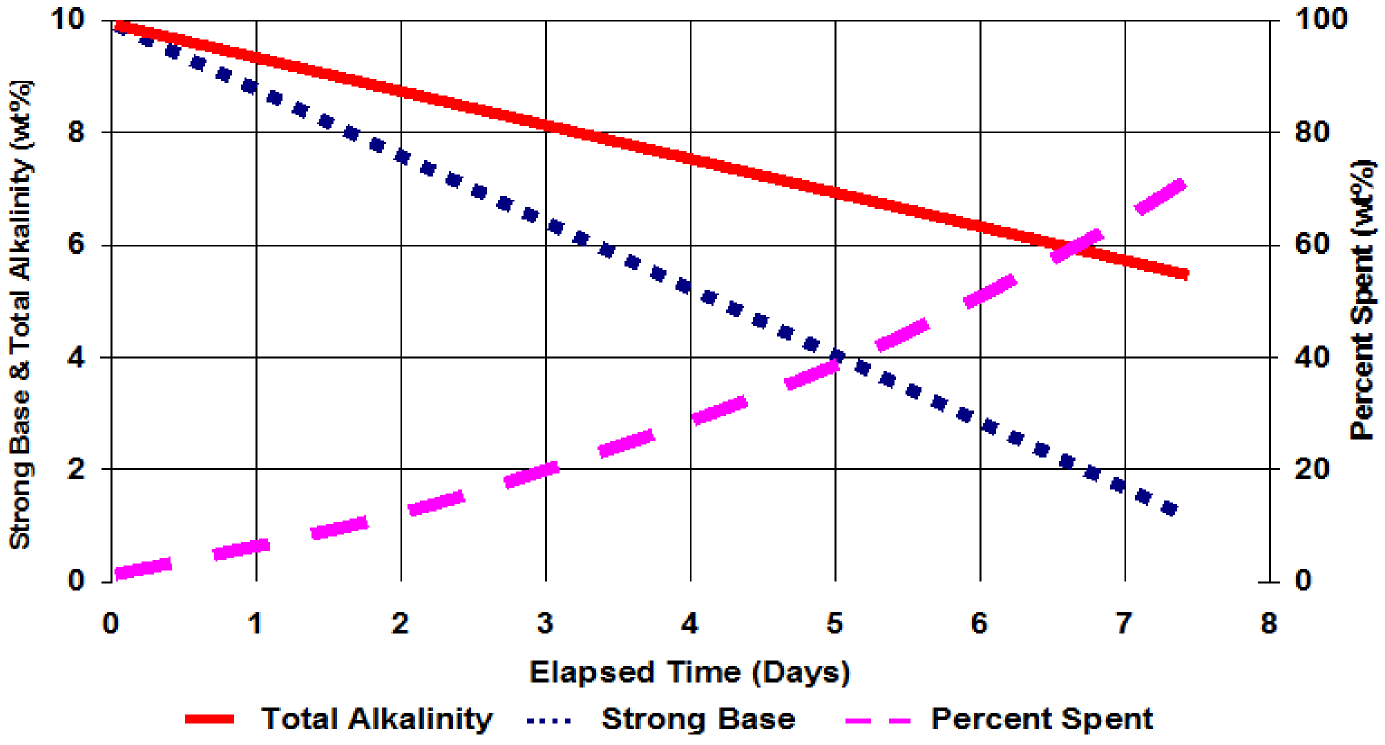


Figure 15 HCl and H2S Scrubbing Caustic Scrubbing Operation

2.6 Process Variables

In the every day use of Penex process it is usually necessary to adjust the inlet temperature Nevertheless, it is to the operator's advantage that he has a thorough understanding of the influence process variables will have on performance of the unit and the life of the catalyst. When we move the catalyst to the unit, the process after which the catalyst goes and all the treatment it gets when in administration will to a substantial degree impact its effectiveness. In rolling out any improvements to the activity, the safety of the catalyst must be the number 1 thought for it tends to be viewed as the core of the task on which the nature of the outcomes got will depend. In the discussion which follows, the “product isomer ratio” refers to the weight percentage ratio of isopentane to total C_5 aliphatic paraffins, or the weight percentage ratio of 2,2 and 2,3 dimethyl butane in the total C_6 aliphatic paraffins in the stabilizer bottoms stream. The term "Liquid feed”, “reactor charge”, and “combined feed,” refer to the C_5/C_6 charge to the liquid feed driers of the unit, the effluent from the liquid feed driers, and the reactor charge plus makeup hydrogen respectively.

2.6.1 Reactor Temperature

Fundamental procedure control is done by reactor temperature, as shown in Figures III-1, III-2 and III-3 you can see the upper and lower limit. This is the equilibrium forced by thermodynamics, and it tends to be achieved simply after a boundless period of time, for example with a boundlessly extensive reactor. By and by, consequently, the item will contain not as much as this harmony grouping of iso-paraffins. When reactor temperature is increased the rate of isomerization, the balance sythesis will be moved toward all the more intently. Grouping of iso-paraffins in the product will really diminish in light of the descending movement in the equilibrium curve, despite the fact that the high temperature gives a higher response rate. The equilibrium curves provided in Figures III-1, III-2 and III-3 show vapor and liquid phase equilibrium. At the process conditions in the H.O.T. Penex reactor the composition is mixed phase. The amount of liquid is determined by the feed composition, reactor temperature and pressure. The equilibrium values for liquid phase operation are lower than for vapor phase operation. The actual equilibrium values for isopentane and 2-2 DMB for the mixed phase content of the reactor lie between the liquid and vapor curves shown in Figures III-1, III-2 and III-3. Although the first reactor system temperature is normally selected without regard to the isomer content of the final stabilizer bottoms product, there are the possible interactions which should be considered for optimum overall operation, the quantitative relationships for which will be developed through operating experience on each unit and which will vary with catalyst age. Provided the final product can be made as rich in isopentane and 2,2 dimethyl butane (after optimization of the second reactor temperature) then the first reactor is better operated with a lower iso-pentane and 2,2 dimethyl butane content in its effluent, because this implies a lower first-reactor temperature and, therefore, slightly less hydrocracking and slightly higher liquid yield. This situation is more likely to arise in the early stages of a run when all of the catalyst is fresh. The second interaction may occur with feeds which are rich in C_6 cyclics. Since these materials tend to reduce the rate of paraffin isomerization, it may be beneficial with very C_6 cyclic rich feed stocks to choose the first reactor temperature to control the amount of cyclics which enter the second reactor. By raising the first reactor temperature, more of the cyclics can be converted to hexanes and the rate of isomerization in the second reactor system thereby increased. The best combination of reactor temperatures for each plant will be easily determined through operating experience.

2.6.2 Liquid Hourly Space Velocity (LHSV)

The LHSV is the volumetric flow rate of reactor divided by catalyst volume.The plan LHSV for C5/C6 Penex task is typically somewhere in the range of 1 and 2. If we expand LHSV past this limit it will cause lower item isomer proportions.

2.6.3 Hydrogen to Hydrocarbon Mol Ratio

This is known as the amount of hydrogen moles at the outgoing stream of reactor divided by moles of reactor charge other than the catalyst.

2.6.4 Pressure

C5/C6 Penex Units are ordinarily intended to work at 31.6 kg/cm2g (450 psig) at the reactor outlet. The rate of isomerization is decreased by adsrobtion of methylcyclopentane and cyclohexane. Higher weight counterbalances this impact of the C6 cyclic mixes. C5/C6 The rate of isomerization is decreased by adsrobtion of methylcyclopentane and cyclohexane

2.6.5 Catalyst Promoter

For catalyst to work continuously the addition of chloride is important. The plant should not be run continuously for more than 6 hours without the addition of chloride. Restarting the plant will in general return the action of catalyst to its previous self but we might see that it is not working upto its full potential thus no chloride will be produced. (C2Cl4) is UOP's choice. For catalyst to work continuously the addition of chloride is important.

2.7 Process Contaminants

General

The purpose of this section is to discuss and highlight the effects of the following contaminants and undesirable components on the Penex Process.

Contaminants:

1. Sulfur
2. Water or other Oxygenated Compounds
3. Nitrogen
4. Fluoride

Undesirable Hydrocarbons:

1. Olefins
2. Cyclic Compounds
3. C7+ Hydrocarbons
4. Butane

As the Penex Unit's feed is hydrotreated and dried, it is highly unlikely that any of these contaminants will manifest themselves to any degree.However, as it is possible for unit upsets and misoperation, their detrimental impact on the process is presented.

2.7.1 Contaminants

2.7.1.1 Sulfur

The sulfur presence decreases the activity of the catalyst. This decrease in activity is temporary and recovery is normally rapid once the sulfur has been removed. An increase in reactor temperatures to purge sulfur from the catalyst more rapidly may be desirable after the sulfur has been removed from the combined feed. While sulfur is present in the feed, an increase in temperature may help to partially compensate for the reduced catalyst activity. A sulfur stripping operation will be necessary if performance is unacceptable after elevating reactor temperatures.

2.7.1.2 Water or Other Oxygenated Compounds

The deactivation resulting from water or an oxygenated compound is permanent. The oxygenated compounds, in any form, will convert to water across the Penex catalyst. Water will react chemically with the active chloride on the catalyst. This chloride is chemically bound into the alumina structure during manufacture. Deactivation with water occurs whereby oxygen, “O”, is chemically bound to the alumina and permanently displaces an active chloride site, “Cl”. Approximately 1.6 kilogram (pound) of oxygen in any form will deactivate 100 kilograms (pounds) of the current generation of chloride alumina based Penex catalysts, I-82 and I-84. This is an update to UOP’s long standing guideline 1.0 kilogram (pound) of oxygen deactivates 100 kilograms (pounds) of catalyst; this deactivation rate was developed for UOP’s first generation of chloride alumina based catalyst to communicate to customers the need to prevent water poisoning of the catalyst during loading and operation.

2.7.1.3 Nitrogen Compounds

Nitrogen compounds usually react with chloride during the presence of HCL to form salts compounds which cannot be prove to be good for the catalyst, loss of chloride or maldistribution due to salt deposits.

2.7.1.4 Fluoride Compounds

This material is also a permanent catalyst poison. Approximately one pound of this material will deactivate 100 lbs. of catalyst.

2.8 Undesirable Hydrocarbons

2.8.1 Olefins

The UOP Penex Process has been operated with an olefin content of as much as 2%. The amount and types of olefins present in, say, a C_5/C_6 fraction from a catalytic reformate are acceptable,. The adverse effect of appreciable quantities of olefins is thought to be due to their physically coating the catalyst following polymerization.

2.8.2 Cyclic Compounds

Although this is not a cumulative effect at normal operating pressures, cyclic compounds are absorbed on the catalyst and therefore reduce the active sites available for paraffin isomerization. (Should the amount of benzene in the charge stock exceed about 5%, additional catalyst inventory would be required in the reactors.

Unsaturated cyclic hydrocarbons consume considerable quantities of hydrogen resulting in an exothermic reaction which is undesirable from the standpoint of isomerization equilibrium. Benzene is quickly hydrogenated and then behaves as an equivalent amount of cyclohexane. Cyclohexane and other C_6 naphthenes are converted to C_6, paraffins. This results in a decrease in octane number for this portion of the charge stock. With normal fractionation, however, any attempt to eliminate C_6 cyclics will result also in an exclusion in part of the normal hexane. Special fractionation facilities are not required for the UOP Penex Process.

2.8.3 C7+ Hydrocarbons

It is preferable to restrict the C7+ content of the feedstock to the UOP Penex Process to 2 or 3%. C7 paraffins hydrocrack easily to C3 and c4. C7 naphthenes have the same adverse effect as the C6 naphthenes described above, but to an even greater degree. Of course, the levels of the cyclic and C7 hydrocarbons above mentioned are not normally expected unless there are plant upsets on the prefractionation equipment upstream of the Penex unit.

2.8.4 Butane

There is no particular concern as to the actual limits as far as harm which could occur to the reaction process with the inclusion of butanes in the feedstock. Normally, 4 LV-% is acceptable.

Table 1 Typical Limits On Stream Impurities

PENEX REACTOR CHARGE

Impurity	**Typical Limit**	**Laboratory Method**
Total Sulfur	0.1 ppmw	UOP-987
Total Nitrogen	0.1 ppmw	UOP-981
Total Oxygenates	0.1 ppmw	UOP 960*
Water	0.05 ppmw	On-Line Analyzer
Copper	Nil ppbw	UOP-962
Lead	Nil ppbw	UOP-952
Arsenic	Nil ppbw	UOP-946
Fluorides	0.5 ppmw	ASTM D-7359
Bromine Number	4	UOP 304
Total Chloride	0.5 ppmw	UOP-395

*Present method dependent on type of oxygenate.

PENEX MAKEUP GAS

Impurity	**Typical Limit**	**Laboratory Method**
Hydrogen Sulfide	1 mole-ppm	Detector Tube
NH_3	1 ppmw	Detector Tube
Water	0.1 ppmv	On-Line Analyzer
HCl	5 mole-ppm	Detector Tube
Total Carbon Oxides	10 mole-ppm	UOP-603
CO	1 mole-ppm	UOP-603

Table 2 Properties Used In Predicting Isomerate Qualtiy

Component	Sp. Gr. 60F/60F	RVP psi	Molecular Weight	Octane RON-0	Octane RON+3	Octane MON-0	Octane MON+3
Isobutane	0.5631	71.90	58.120	100.2	106.7	97.6	120.0
n-Butane	0.5844	51.50	58.120	95.0	105.0	93.5	106.0
Isopentane	0.6248	18.93	72.146	93.5	104.5	89.5	106.9
n-Pentane	0.6312	14.42	72.146	61.7	84.7	61.3	83.8
Cyclopentane	0.7505	9.18	70.130	102.3	111.1	85.0	95.2
2,2 Dimethylbutane	0.6540	9.13	86.172	94.0	104.5	95.5	114.5
2,3 Dimethylbutane	0.6664	6.85	86.172	105.0	112.0	104.3	110.0
2 Methylpentane	0.6579	6.27	86.172	74.4	92.2	74.9	92.4
3 Methylpentane	0.6690	5.56	86.172	75.5	92.3	76.0	92.6
n-Hexane	0.6640	4.59	86.172	31.0	65.3	30.0	63.5
Methylcyclopentane	0.7535	4.17	84.156	96.0	104.5	85.0	91.1
Cyclohexane	0.7834	3.02	84.156	84.0	97.4	77.2	87.3
Benzene	0.8846	2.98	78.108	120.0	120.0	114.8	114.8
C_7+ (Feed)	0.6915	1.97	100.198	55.0	78.0	55.0	79.0
C_7+ (Product)	0.6830	2.10	100.198	82.0	88.0	71.0	88.0

NOTES: 1 – Octane values should be calculated based on liquid volume percent blending.

2 – RVP values should be calculated based on mole percent blending.

Table 3 Naphtha Fractionation

Component	Boiling Point (F)	Boiling Point (C)	Relative Volatility
Isopentane	82	28	3.18
n-Pentane	97	36	2.71
2,2 Dimethylbutane	122	50	1.90
2,3 Dimethylbutane	136	58	1.59
2 Methylpentane	140	60	1.53
3 Methylpentane	146	63	1.42
n-Hexane	156	69	1.26
Methylcyclopentane	161	72	1.21
Benzene	176	80	1.25
Cyclohexane	177	81	1.00

Table 4 Properties Of Perchloroethylene

	Perchloroethylene
Formula	C_2Cl_4
Molecular Weight	165.8
Boiling Point	121°C (250°F)
Melting Point	-23°C (-9°F)
Specific Gravity (20/20°C)	1.62
Chloride Content, wt%	85.5

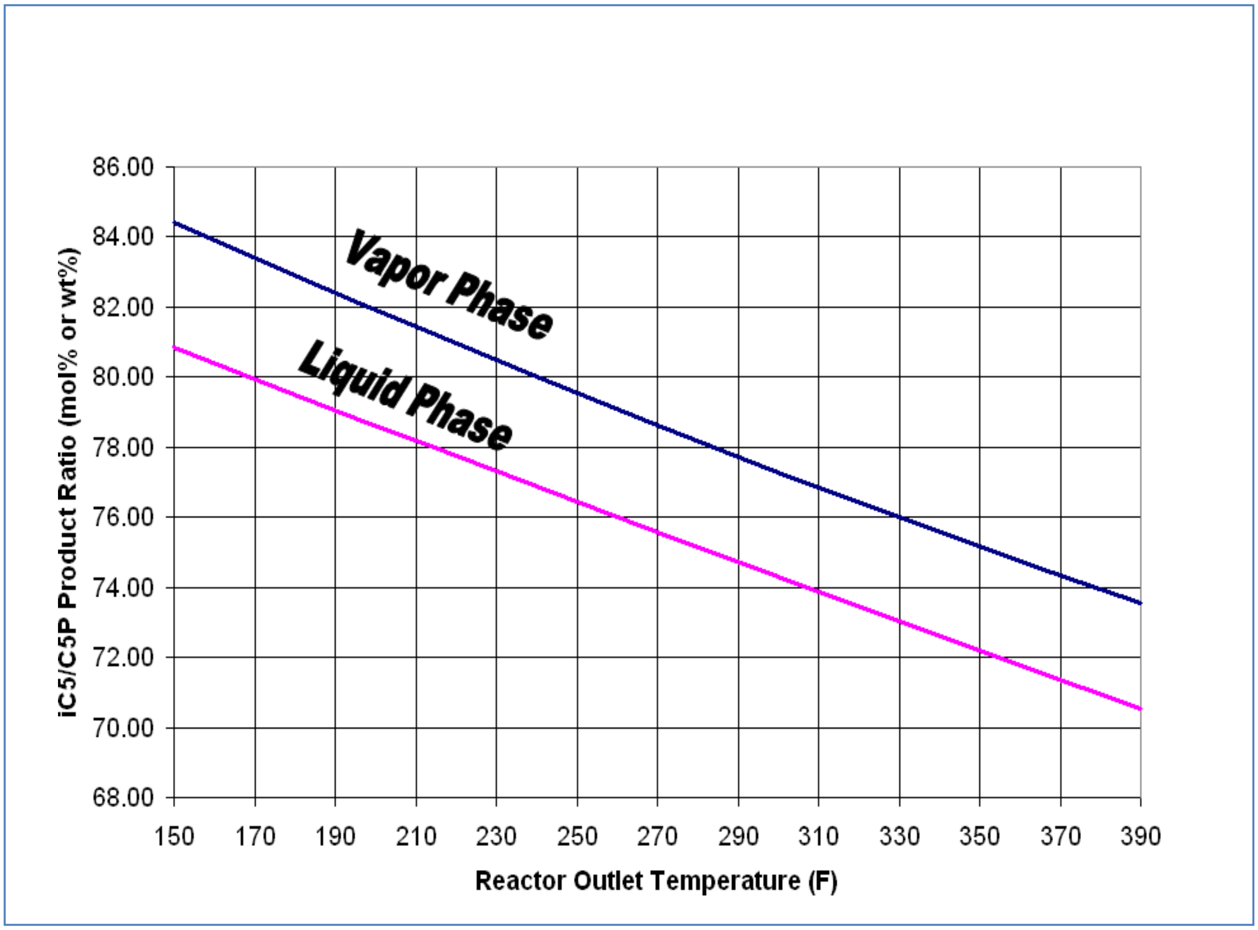


Figure 16 Iso-Pentane Equilibrium Curves

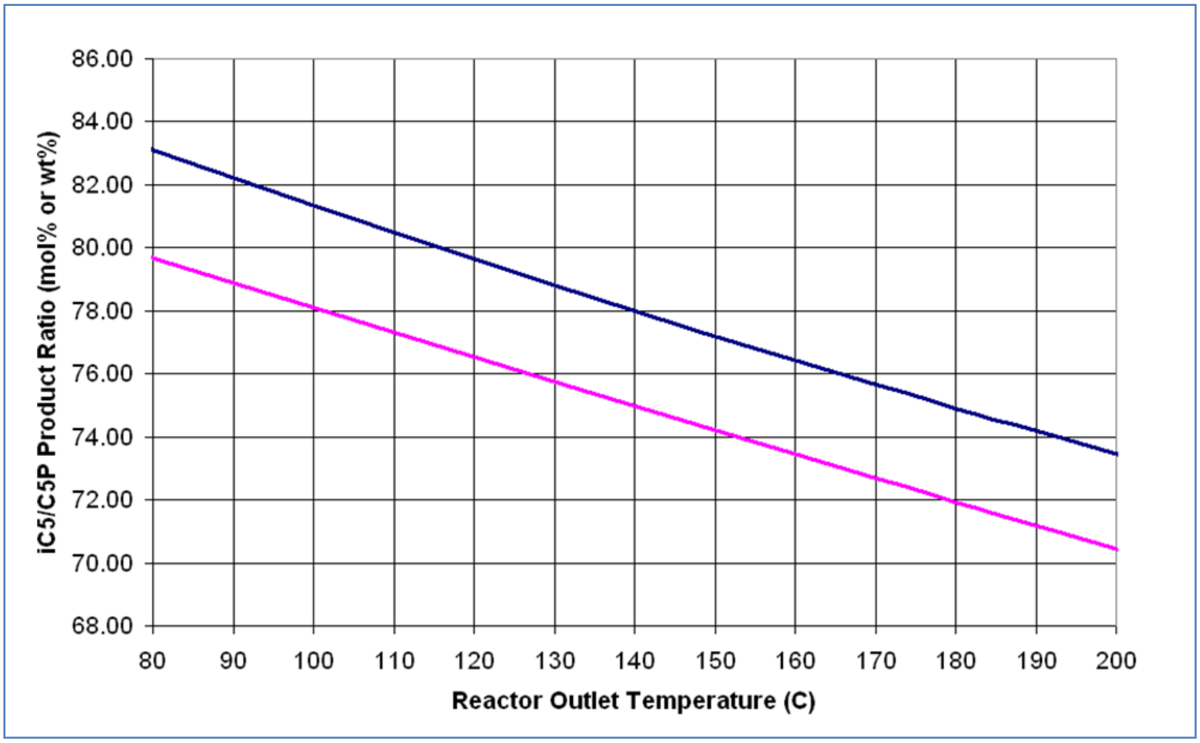


Figure 17 2,2 Dimethylbutane Equilibrium CurvesFigure

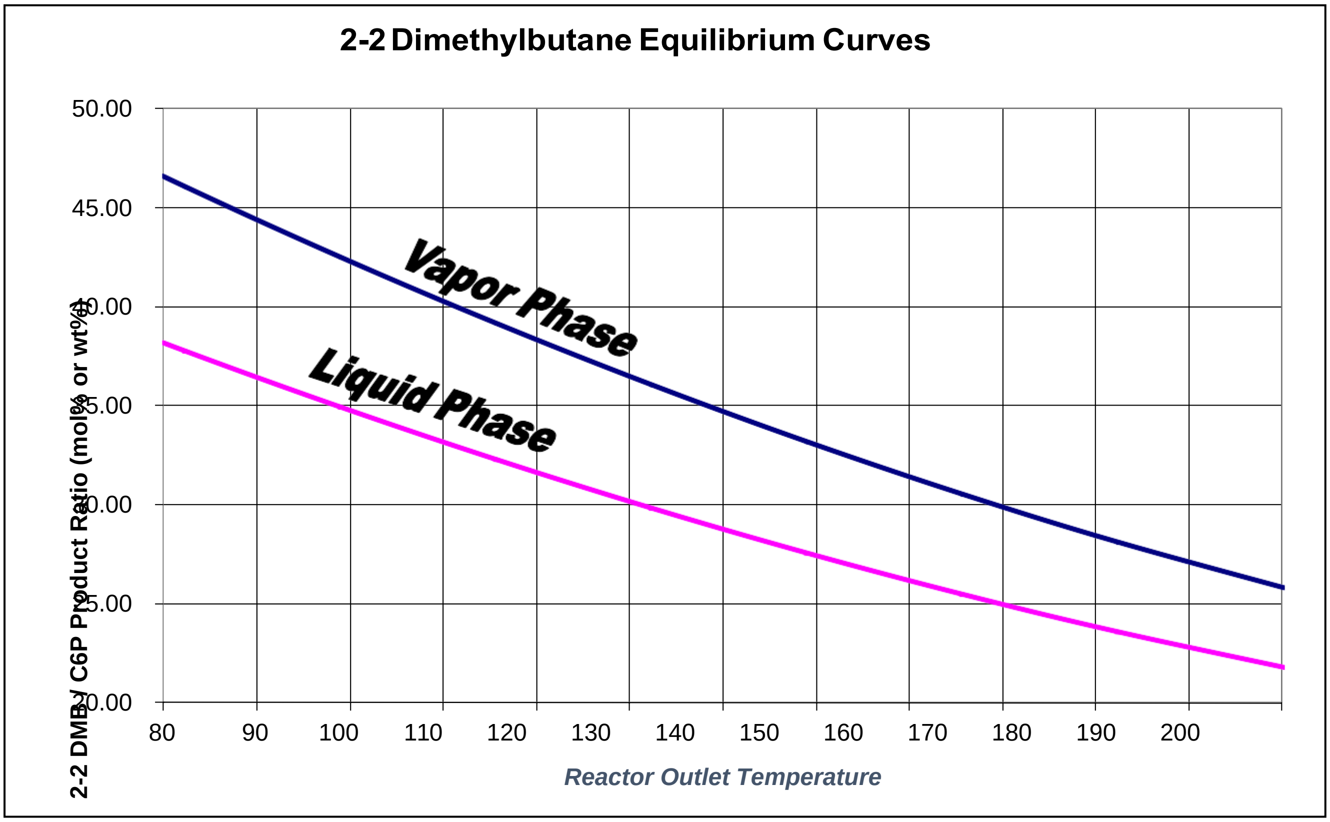


Figure 18 2,2 Dimethylbutane Equilibrium Curve

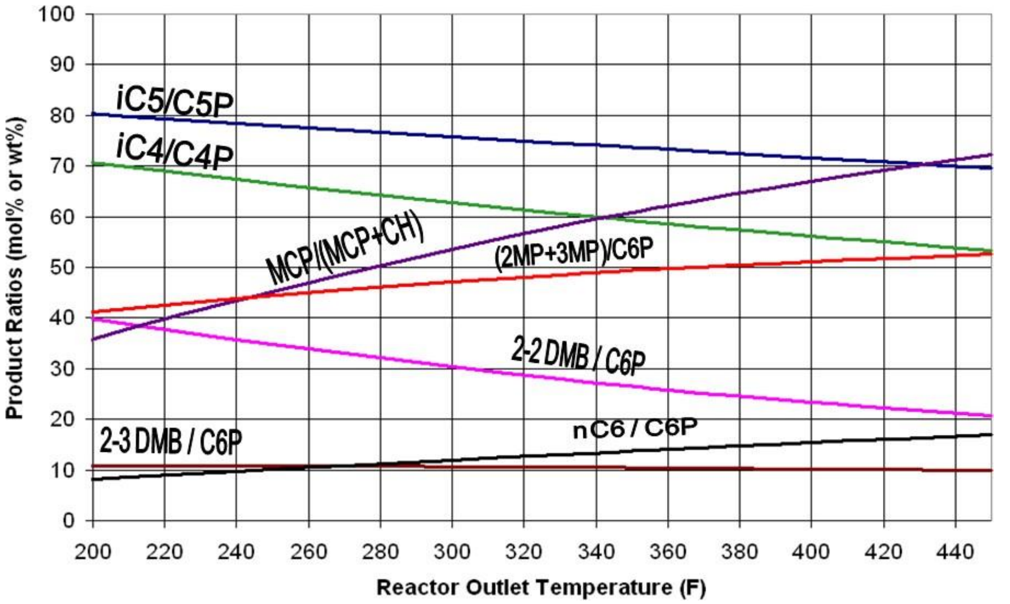


Figure 19 Penex Process Equilibrium Curves

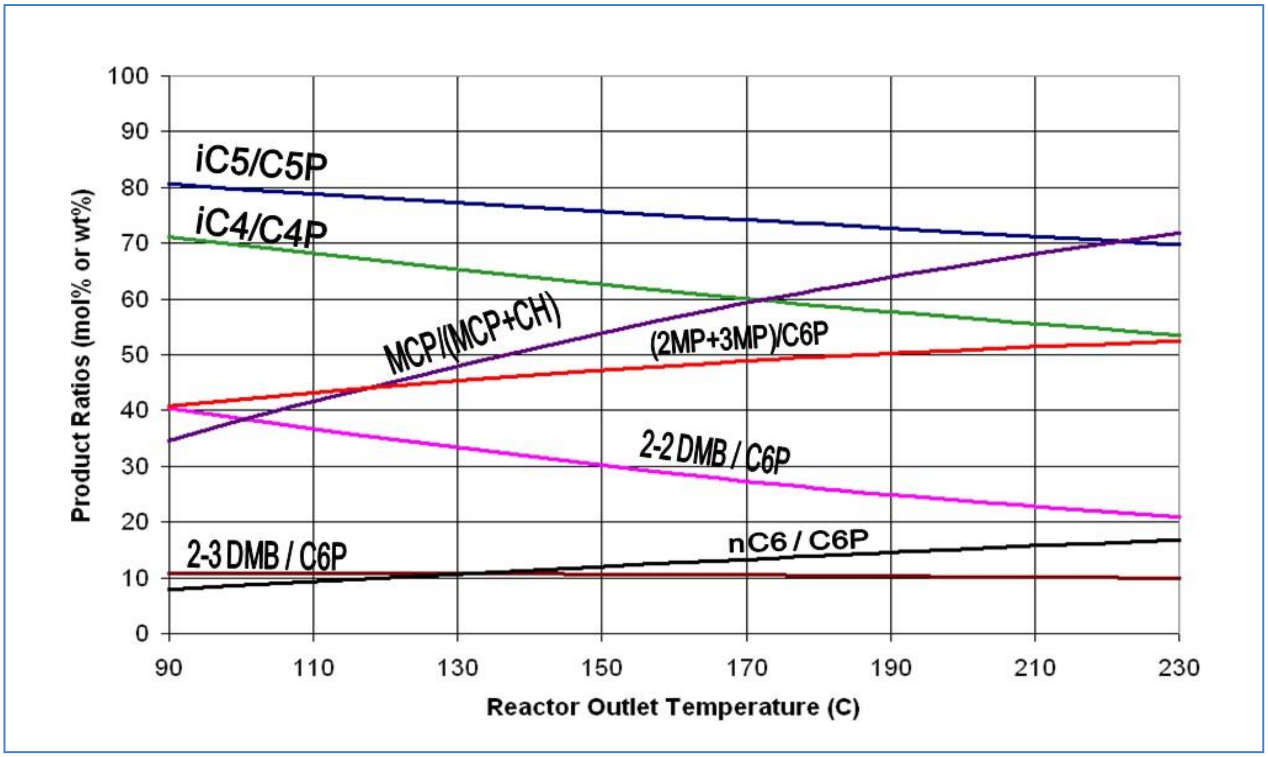


Figure 20 Penex Process Equilibrium Curves

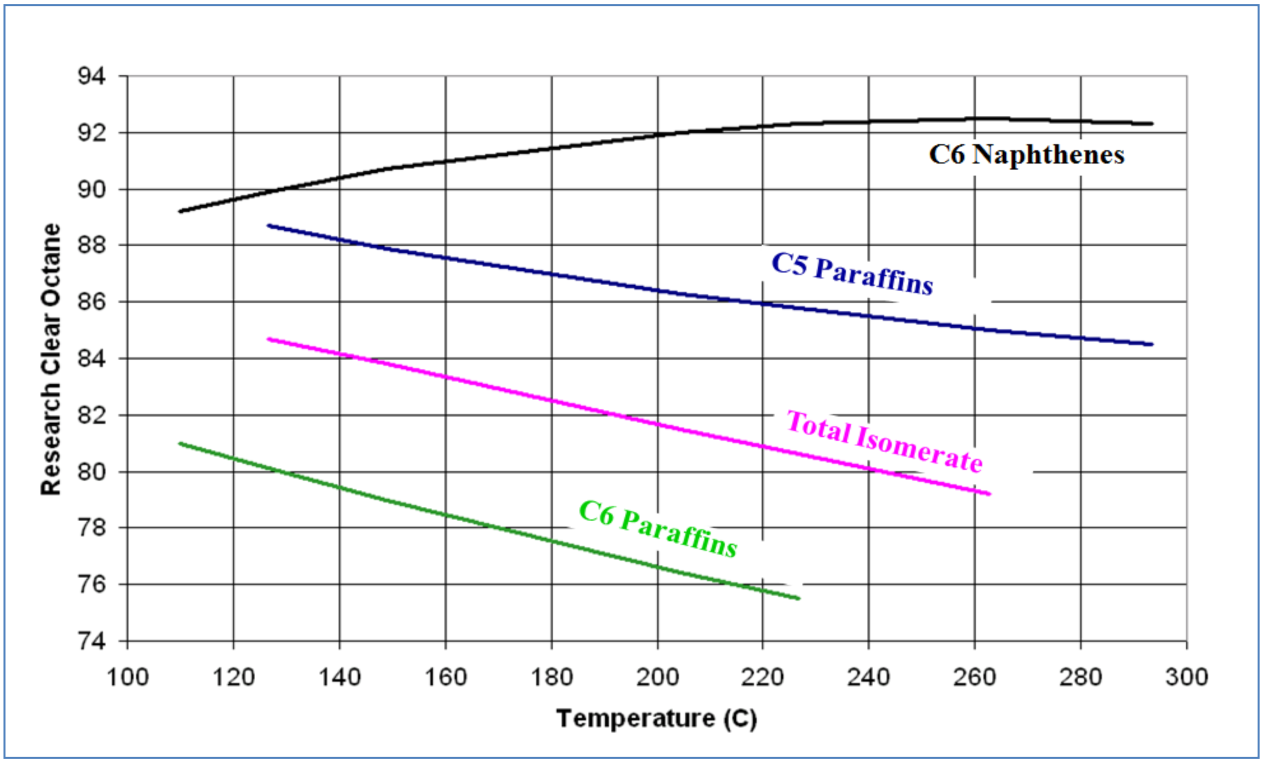


Figure 21 Octanes of Mixtures at Equilibrium

PIN

Paraffin

Isomerization

Number

PIN = iC5/C5P + 2-2 DMB/C6P + 2-3 DMB/C6P

X-Factor

Summation of:

- % Methylcyclopentane
- % Benzene
- % Cyclohexane
- % C7+

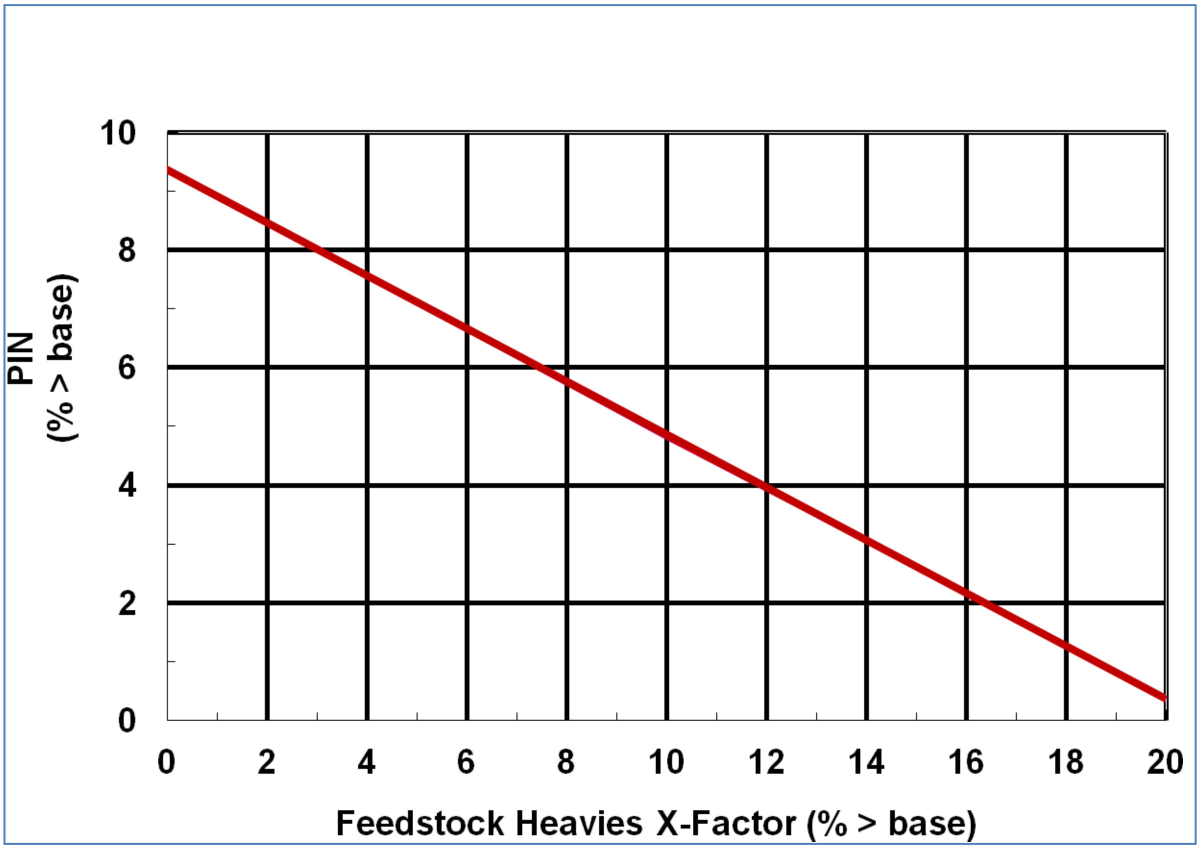


Figure 22 Effect of Heavies on PIN

2.9 Process Flow and Control

This section will present a description of each major piece of equipment, its function in the process and its place in the process flow. Details relating to operation will be discussed in another section.

2.9.1 Sulfur Guard Bed

The reason of use of sulful is to keep safe Penex catalyst .The hydrotreater will expel the vast majority of the sulfur in the Penex feed. The watchman bed decreases the sulfur to a sheltered dimension for H.O.T. Penex task and fills in as security in case of surprises in the NHT which could result in higher than ordinary dimensions of sulfur in the feed.

For sulfur removal in a hydrocarbon liquid stream, the following adsorbents can be used:

- ADS-11, nickel-based
- ADS-11L, nickel-based
- ADS-12, copper-based
- ADS-120, copper-based
- ADS-130, copper-based

The feed to the Sulfur Guard Bed is heated to the given temperature for maximum sulfur removal, usually between 250°F (121°C) to 150°C (300°F), and passed downflow over the adsorbent. The Sulfur Guard Bed is designed and operated to ensure liquid phase in the Sulfur Guard Bed is maintained at all times during operation.

2.9.2 Feed Driers

Feed Driers are used to dry the hydrocarbon steam before it is entered into the catalytic unit.The driers are worked in arrangement with the exception of when they are in the recovery mode when around then just a single will be in administration. The C5/C6 stream which is treated with feed drier at the base goes to the top and then moves out from the top. The stream is then moved from drier hybrids to next fluid fleed drier. The dried hydrocarbon is than again moved to feed surge drum. Over some undefined time frame, the drier ahead of the pack position will wind up spent as shown by the dampness analyzer situated between the two driers. As of now, it will wind up important to recover this drier. The Feed Driers ought to be recovered on a calendar visit enough to maintain a strategic distance from dampness leap forward. The spent drier is removed from administration by shutting the proper square valves. The main drier is actually doing all the work currently so the second drier is currently free. The dampness analyzer tap is changed to screen this in-administration drier. After the drier recovery has been finished, it is currently prepared for administration.. Over some undefined time frame the lead drier will wind up spent and is currently set up for recovery with the tail drier presently being the just a solitary one in administration. This is the only arrangement driers will be arranged .The recovery technique for the Feed Driers is itemized in Section XIII Special Procedures.

2.9.3 Makeup Gas Treater

The purpose of the Makeup Gas Treater is to remove contaminants, such as HCl and H_2S, in the gas stream to the Penex unit. The configuration can consist of a single vessel or two vessels operating in series. The gas stream flows downflow through the treater(s) and onto the Penex Makeup Gas Driers. Once contaminant breakthrough occurs i.e. the bed is saturated with the contaminants, the single guard bed is taken offline and reloaded with fresh adsorbent material. The Penex and alternate process units can operate during the short time that the treater is being reloaded. A bypass line is provided to bypass the treater during loading. This provides the flexibility to operate the units when the treater is being loaded if the refiner decides to operate in absence of the Makeup Gas Treater.

2.9.4 Makeup Gas Driers

A dried makeup gas must be used in order to protect the Penex catalyst. The two Makeup Gas Driers and Feed Driers have same operating process. The driers operate upflow, in series. The regeneration procedure for the gas driers is detailed in Section XIII Special Procedures.

2.9.5 Penex Reactors

Penex unit reactors have isomerization unit. They are made of carbon. The main stream containing naphtha and and hydrogen along with catalyst promoter enters the reactor through top inlet and leaves from the bottom. To ensure the distribution of the hydrocarbon stream there is a vapor liquid distributor tray installed above the catalyst bed.. Check fig V-9 and V-10.The bottom head of the reactor has an outlet basket that allows the process stream to pass through it, but prevents any catalyst or ceramic support material from migrating downstream into the unit.Ceramic support material is also placed on top of the catalyst bed to prevent disturbance of the top layer of catalyst. The top layers of support material consist of a layer of 19mm (3/4") and a layer of 6mm (1/4") ceramic balls. Refer to Figure V-11 for a diagram of the bottom head of the Penex Reactors.

2.9.6 Stabilizer

The main purpose of stabilizer is to remove impurities like HCL, Hydrogen from certain c3 and c4 compounds and bottom stream conatin paraffins that are sent to recycle stream.Feed usually enters the column through a distributor located at the bottom of the conical section of the column. Two liquid traps are placed below tray 1 in order to create a liquid seal in the tray downcomer. This prevents vapor from bypassing the tray. Refer to Figure V-12 for a diagram of the Stabilizer.

2.9.7 Net Gas Scrubber

The Stabilizer offgas enters the Net Gas Scrubber through an inlet gas distributor located near the bottom of the vessel. The gas flows upflow through the Net Gas Scrubber, which is filled with caustic, to remove hydrogen chloride. The scrubbed gas leaves the top of the vessel and is typically routed to the fuel gas system on pressure control. In some designs, offgas from alternate process units can be sent to the common Net Gas Scrubber, if operating conditions allow. Makeup caustic is pumped from the refinery to the reservoir section of the Net Gas Scrubber when caustic addition is required. The caustic in the reservoir section is pumped by the caustic circulation pumps to the top of the scrubbing section of the Net Gas Scrubber above a packed bed of carbon rings where a counter current contact with the rising acidic gas is made. Caustic is also continuously circulated to the distributor under the packed section. The caustic level in the scrubber is maintained about 0.3 meter (1 foot) below the distributor under the packed section. The flowrates of the upper and lower circulating caustic circulations are monitored by local or board mounted flow indicators.

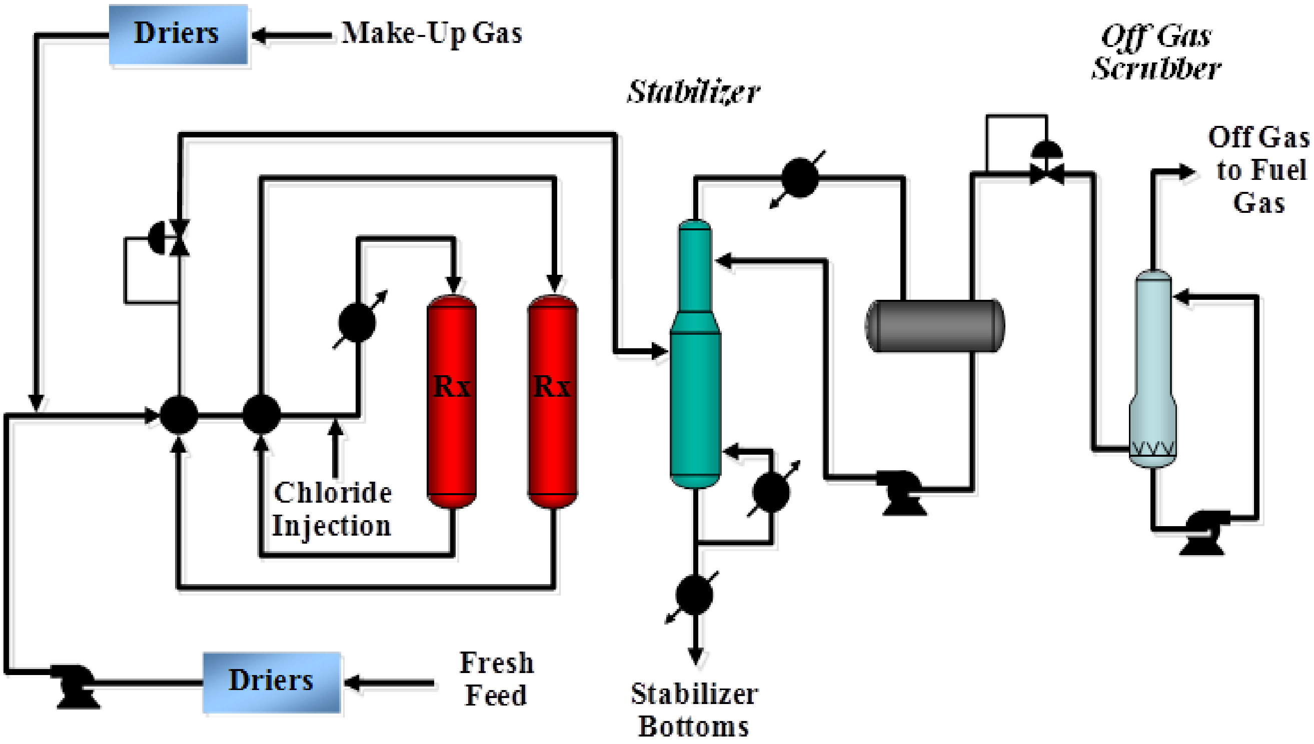


Figure 23 UOP Penex Process (Once Through)

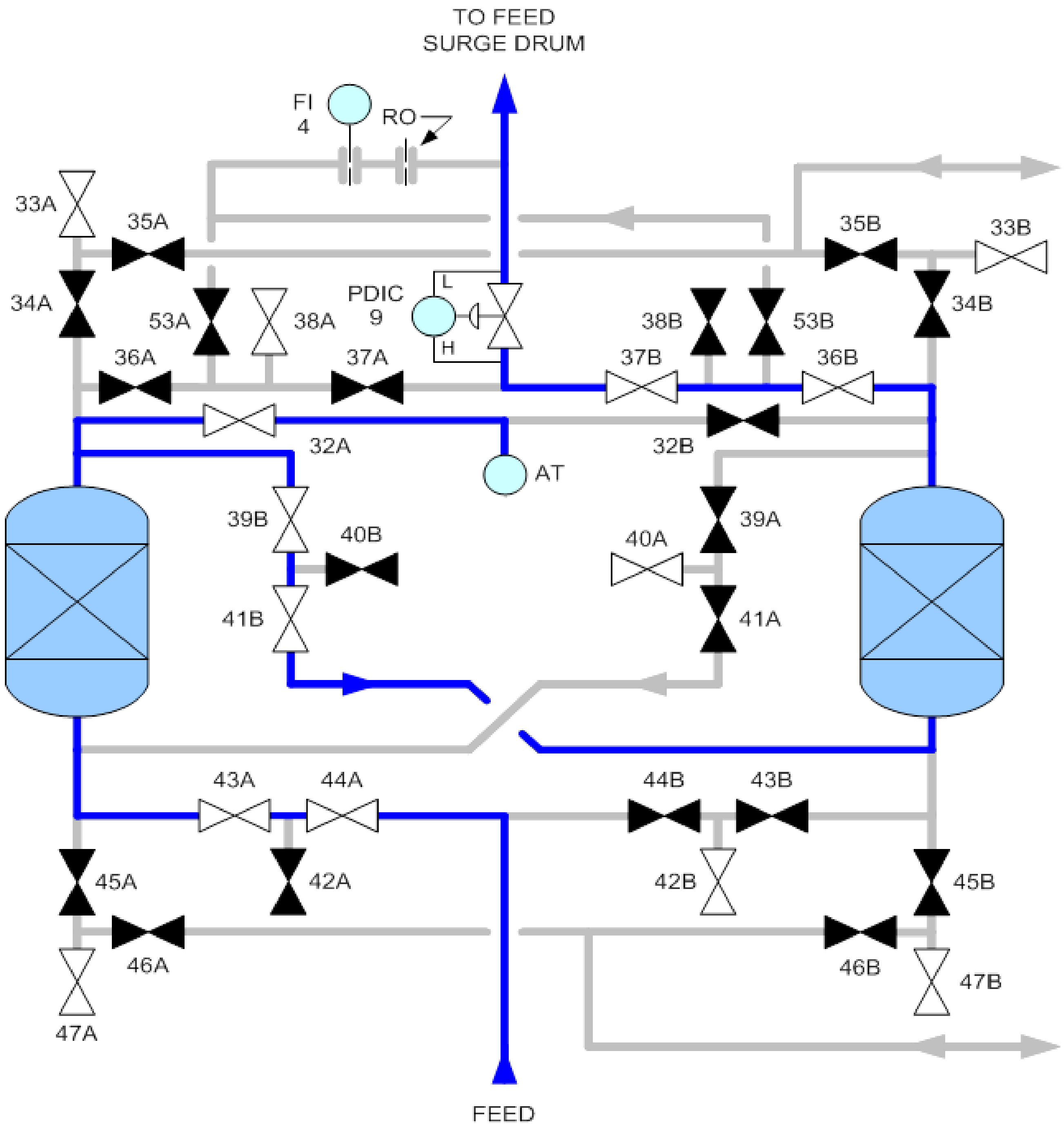


Figure 24 Liquid Feed Drier

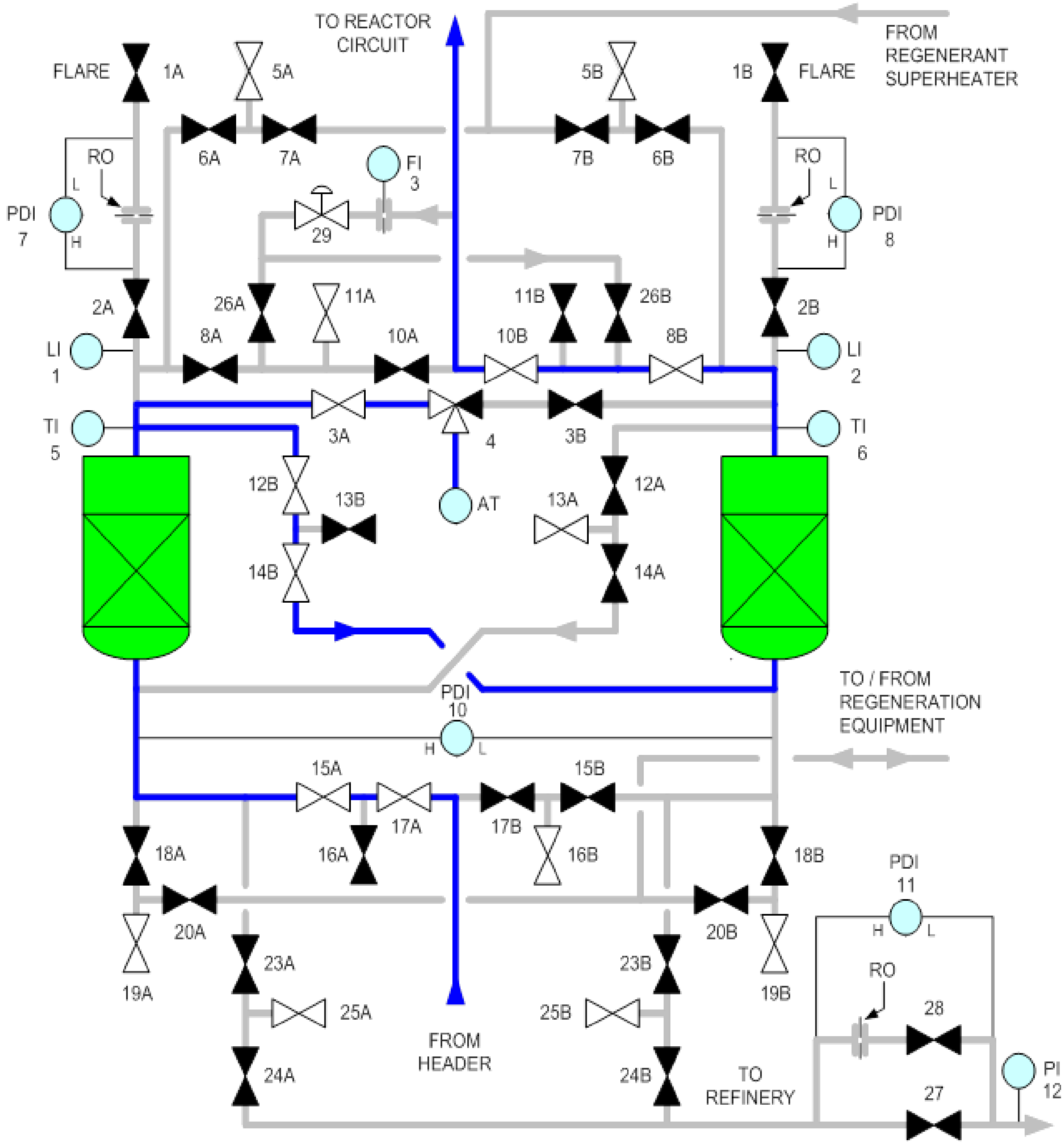


Figure 25 Makeup Gas Drier

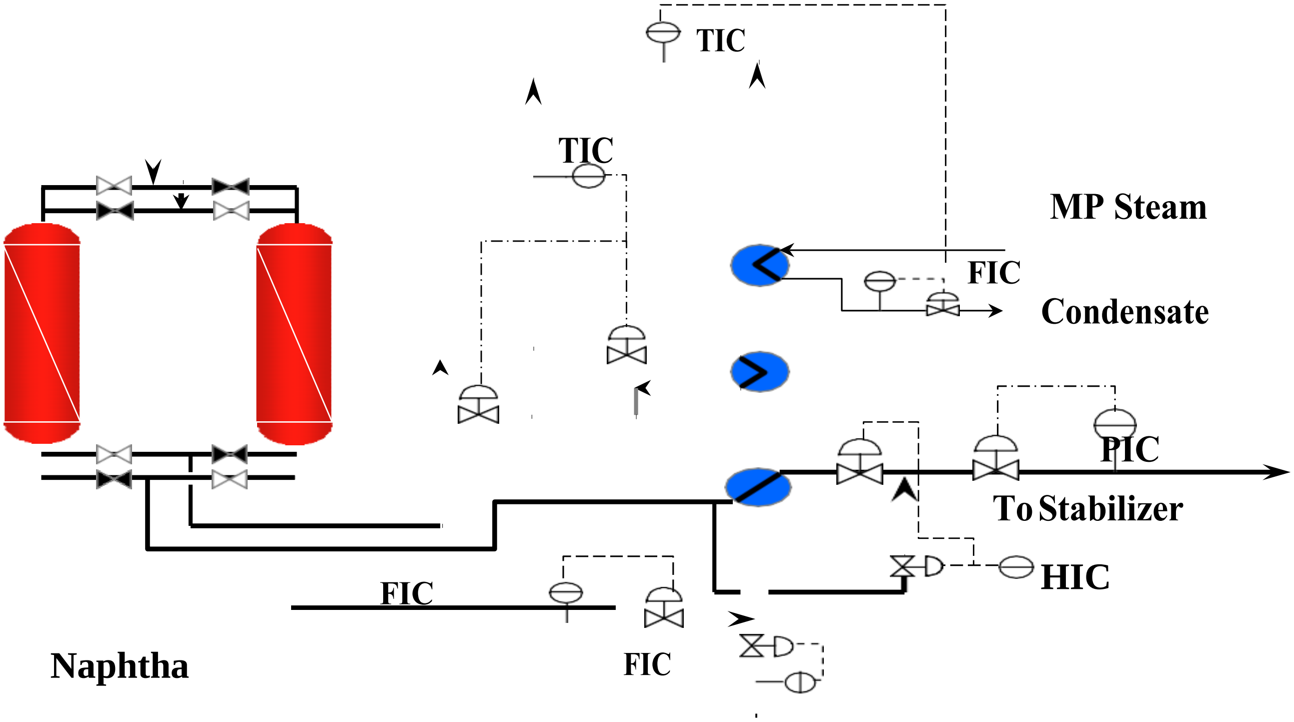


Figure 26 Penex Reactor Section

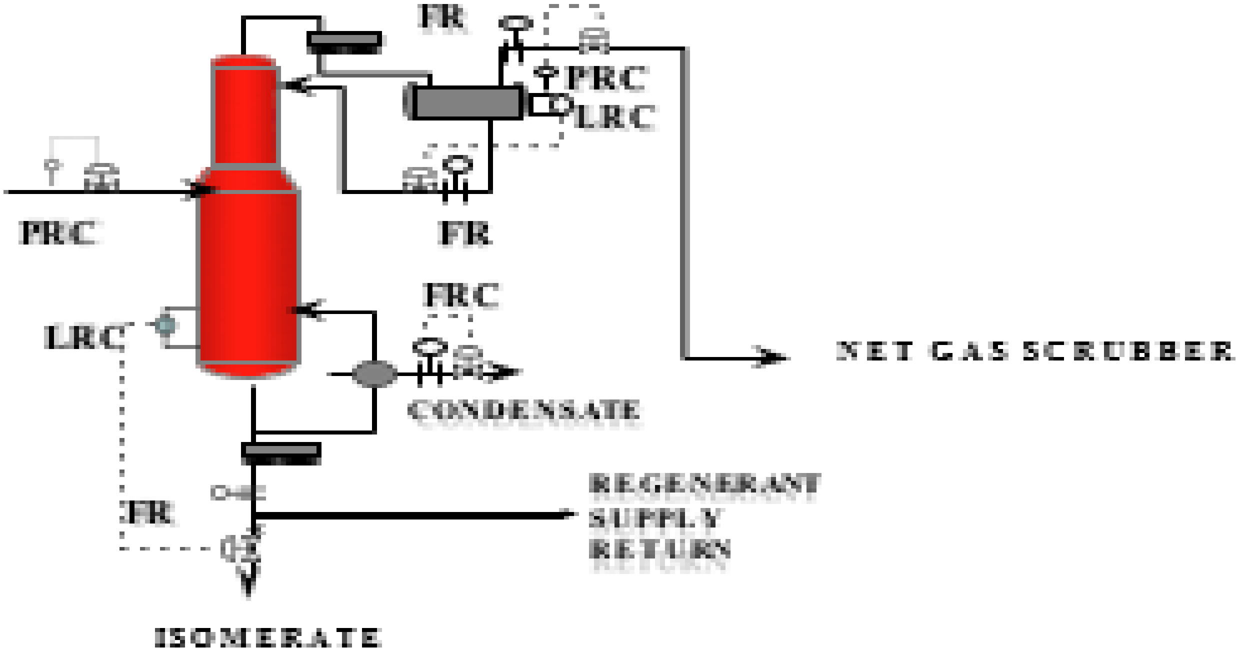


Figure 27 Stabilizer Section

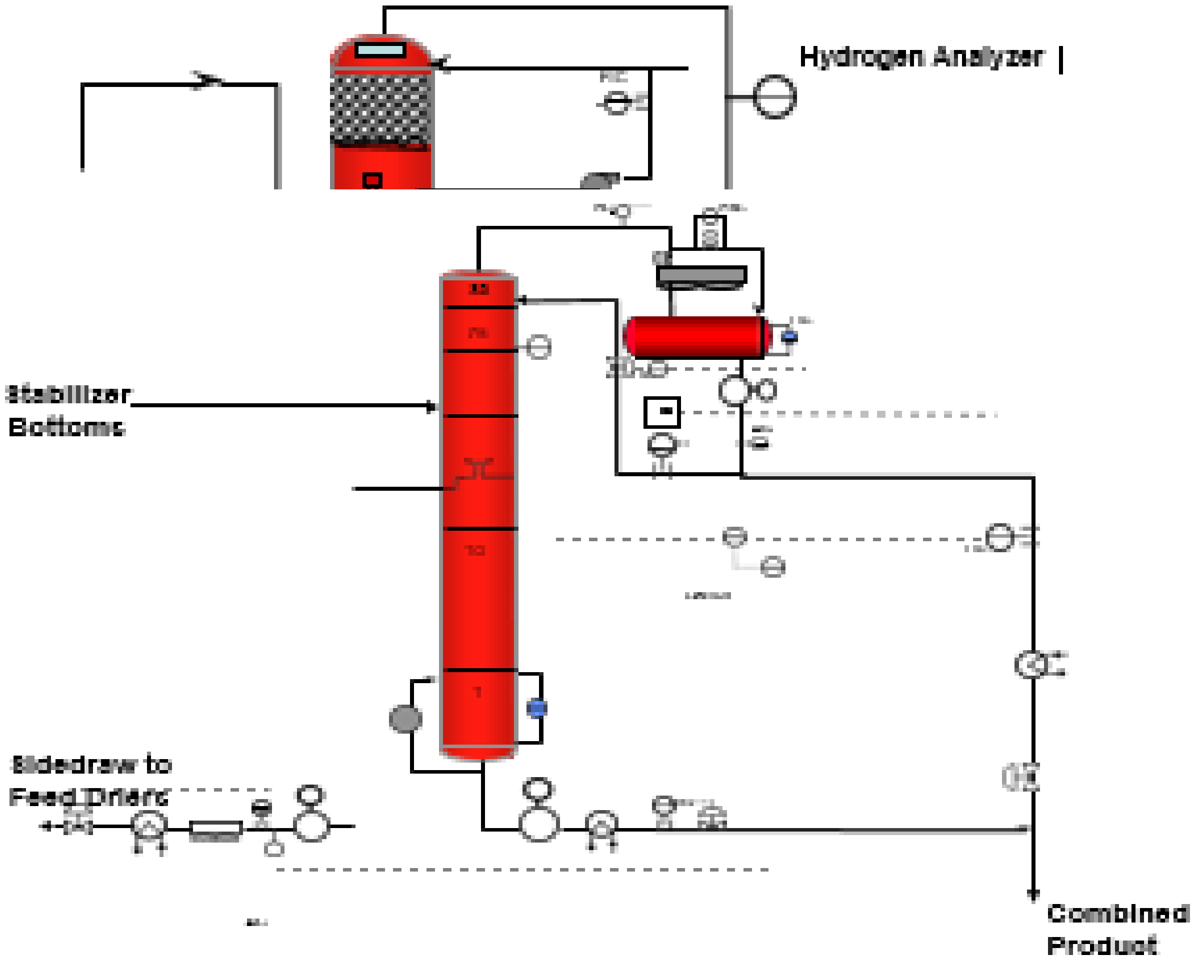


Figure 28 DIH Section

2.10 Process Equipment

This section will present a description of each major piece of equipment, its function in the process and its place in the process flow. Details relating to operation will be discussed in another section.

2.10.1 Sulfur Guard Bed

The Sulfur Guard Bed vessel is constructed of carbon steel. The bottom of the vessel is equipped with an outlet collector to prevent loss of adsorbent or support material. The adsorbent is loaded between a graduated system of ceramic/alumina inert balls. The vessel operates liquid full with the feed entering the Guard Bed through an inlet pipe.Refer to Figure V-1 for an example loading diagram of the Sulfur Guard Bed.

2.10.2 Makeup Gas Treater

The purpose of the Makeup Gas Treater is to remove contaminants, such as HCl and H_2S, in the gas stream to the Penex unit.The gas treater vessels are typically constructed of carbon steel. The configuration can vary and will depend on refinery demand for flexibility. The configuration can consist of a single vessel or two vessels operating in series. The gas stream flows downflow through the treater(s) and onto the Penex Driers. The bottom of the vessel is equipped with a carbon steel outlet basket, covered with a steel mesh screen, to prevent loss of adsorbent or support material.The adsorbent is loaded between a graduated system of ceramic/alumina inert balls. A wire mesh screen is placed between the top holddown material and the bed to prevent migration of the holddown material into the treater bed. The treater(s) contains a bed of activated alumina, molecular sieve or adsorbent to either adsorbed or chemisorbed the contaminant(s) onto the treater bed material. The choice of bed material is dependent on the contaminant chosen for removal.Figure V-2 depicts an example loading diagram of a Makeup Gas Treater.

2.10.3 Feed Surge Drum

The function of the Feed Surge Drum is to provide surge capacity for the Penex Unit. This vessel is constructed of killed carbon steel.Refer to Figure V-3 for a diagram of the Feed Surge Drum.

2.10.4 Liquid Feed And Makeup Gas Driers

Due to the sensitivity of the Penex catalyst to water and other contaminants, the feedstock and the makeup hydrogen for the Penex Unit must be routed through molecular sieve driers. These driers are designed to remove contaminants before they can enter the Penex Reactors and deactivate the catalyst. The Makeup Gas Driers are loaded with UOP Molsiv Adsorbent PDG-418 or HPG-429, a molecular sieve which removes water. The Feed Driers and Makeup Gas Driers are constructed from carbon steel. The bottom of the vessel is equipped with a carbon steel outlet basket to prevent migration of molecular adsorbent and support material. The molecular sieve are loaded between several layers of graded support material. A holddown grating or screen is used on top of the bed between the molecular sieve and the support material to prevent sieve migration.Refer to Figures V-4 and V-5 for example loading diagrams of the Feed Drier and Makeup Gas Drier respectively.

2.10.5 Heat Exchangers

Reactor Section Heat Exchangers

The Penex Reactors have combined feed/reactor effluent heat exchangers. These exchangers are shell and tube type,. The Charge Heater for the Penex Reactors typically uses steam that is below or let down below the process pressure. During operation, the driving force would tend to leak process fluid into the condensate system. The Charge Heater also utilizes strength welded and fully rolled tube sheets (see Figure V-6) in order to minimize the potential for leakage.

Regenerant Vaporizer

The regenerant vaporizer utilizes low weight steam to warm the regenerant stream before it achieves the electric superheater. The vaporizer, appeared in Figure V-7, is an upstanding warmth exchanger which utilizes knife type tubes that have been quality welded and completely rolled. This warmth exchanger is outfitted with a dimension marker and an abnormal state alert, and is intended to work with the top bit of the cylinders revealed. Low weight steam within the pike tubes exchanges warmth to the regenerant outwardly of the pike tubes.. This avoids the regenerant from gathering which could harm the electric packages in the superheater while working. Allude to Figure V-7 for a graph of the Regenerant Vaporizer.

Methanator Feed Effluent Exchanger

The Methanator Feed-Effluent Exchanger is a hairpin type exchanger that is used in the Methanator flow scheme. The exchanger is usually made up of killed carbon steel throughout.

2.10.6 Electric Heater

Regenerant Superheater

The regenerant superheater is used to raise the temperature of the vaporized regenerant to a temperature of 315C. The steam is warmed by Inconel electric components.

Methanator Heater

The Methanator Heater provides the final heat input for makeup gas to the Methanator Reactor. Typically, an electric heater is used as the Methanator Heater. The Methanator Heater raises the temperature of the makeup gas to the required temperature for the Methanator Reactor of about 232°C (450°F).

2.10.7 Reactors

Penex Reactors

Penex unit reactors have isomerization unit. They are made of carbon. The main stream containing naphtha and and hydrogen along with catalyst promoter enters the reactor through top inlet and leaves from the bottom. To ensure the distribution of the hydrocarbon stream there is a vapor liquid distributor tray installed above the catalyst bed.. Check fig V-9 and V-10.The bottom head of the reactor has an outlet basket that allows the process stream to pass through it, but prevents any catalyst or ceramic support material from migrating downstream into the unit. Ceramic support material is also placed on top of the catalyst bed to prevent disturbance of the top layer of catalyst. The top layers of support material consist of a layer of 19mm (3/4") and a layer of 6mm (1/4") ceramic balls. Refer to Figure V-11 for a diagram of the bottom head of the Penex Reactors.

Methanator Reactor

Penex catalysts are very sensitive to water contamination. The acceptable makeup gas contamination levels are:

Total Sulfur	1 mol-ppm
Total N	1 mol-ppm
Water	Saturated at design temperature *
HCL	5 mol-ppm

Total Carbon Oxides	10 mol-ppm
CO	1 mol-pp

The Makeup Gas Driers are designed to handle the water and CO_2 concentrations listed above. However, the HPG-250 and HPG-429 drier absorbents typically used in the Makeup Gas Driers cannot absorb CO. If the makeup gas CO concentrationis greater than 1 mol-ppm, a Methanator Reactor or other alternate means for lowering the CO is required.The Methanator Reactor converts CO and CO_2 to water and methane. The Methanator Reactor utilizes a Johnson Matthey catalyst, Puraspec 2443, which is sensitive to sulfur and chlorides in the makeup gas. The acceptable levels for sulfur and chloride are < 1 mol-ppm each in the gas stream to a Methanator Reactor. If the makeup gas sulfur and chloride levels are higher than 1 mol-ppm each, gas treaters are required upstream of the Methanator Reactor.

2.10.8 Stabilizer Column

The reason we use stabilizer coloumn is to remove impurities like HCL, light Hydrocarbons and other impurities. From lower side parafins are removed .The top half of the Stabilizer Column has less space for fluid to flow than the bottom half of the column, due to the smaller amount of vapor / liquid traffic that occurs in the top portion of the column. Feed usually enters the column through a distributor located at the bottom of the conical section of the column. Two liquid traps are placed below tray 1 in order to create a liquid seal in the tray downcomer. This prevents vapor from bypassing the tray. Refer to Figure V-12 for a diagram of the Stabilizer.

2.10.9 Deisohexanizer (DIH)

The idea behind using this is because it is to recover isohexane and pentanes from the stabilizer products. The feed coming to DIH is from stabilizer bottom. Steam boiler provides the heat input, generally serviced by low pressure steam on condensate flow control. The reboiler heat input is adjusted to generate adequate reflux. Part of the overhead vapor bypasses the air fin condenser on overhead vapor pressure control. The operating pressure at the column overhead line is typically about 0.7 kg/cm^{2}g (10 psig). The overhead product which is mainly C_5's and di-methylbutanes is sent to storage on flow control reset by the DIH tower TRC located above one of the upper trays. An increase in the tray temperature will indicate the movement of heavier methylpentanes up the column which will require that the reflux be increased. The increase in the TRC indication will close off the product flow causing the overhead receiver level to rise which will cause an automatic increase in the reflux flow which is reset by the receiver level.In some cases, the overhead product and reflux instrument are attached to a signal summing device which will adjust the reflux flow to changes with the product flow in order to maintain the same net flow. In this way, the reflux is adjusted with changes in the control tray temperature before the receiver level changes making reflux response to control tray temperature faster.

The bottoms product from the column is generally a small flow. It is yielded from the column on flow control. The DIH column operation is fairly straightforward; the basic guidelines are to remove all the pentanes and 2-2DMB overhead while minimizing the 3 methylpentane content. The composition of the overhead is set by the TRC setpoint. The DIH recycle stream is taken off as a lower sidedraw. The sidedraw is pumped back to the Penex Feed Driers on flow control reset by the DIH bottoms liquid level. The heavies in the sidecut stream should be minimized to obtain the best performance in the Penex reactor section. The majority of the cyclohexane and C_7+ material should be rejected out the bottom of the tower.

The octane of the overhead product depends on the pentane composition of the upper stream. the entire quantity of pentane during this stream is about by the feedstock composition. The iso-pentane content is then set by the degree of C5 conversion within the reactors. For a given feedstock composition the hydrocarbon of the overhead is improved by increasing the IC5/C5P magnitude relation within the overhead product. Since the pentanes within the product square measure processed “once through,” the upper the concentration of pentanes within the feedstock, the lower the merchandise hydrocarbon are going to be.

2.10.11 Pumps

Centrifugal pumps are used for very small applicants in the unit. Normal applications for the radial siphons are for reactor charge siphons, reflux siphons for the fractionation sections, and harsh distribution siphons. Siphons are utilized for chloride infusion into the feed stream and cosmetics water to the net gas scrubber.The oil is persistently siphoned between the two seals. In case of a seal disappointment, hydrocarbon will spill into the oil framework and cause a weight increment in the supply. The seal oil store is furnished with a weight caution and weight check to alarm the administrator to a seal disappointment. The store is normally vented to flare through an opening plate.

2.10.12 Fin-Fan Heat Exchangers

An air fin exchanger comprises of a fan with at least one warmth exchange areas mounted on a level plane on an edge. The warmth exchange areas comprise of finned tubes fixed between header boxes. Stipend for warm extension of the cylinders is practiced by tying down just a single header box and allowing the opposite end to move. A fan that is mounted above the tubes is called an induced draft fan because air must be drawn (induced) past the tubes. A fan mounted below the tubes is known as a forced draft fan because air must be blown (forced) past the tubes.

Chapter 3 Material & Energy Balance

3.1 Material Balance

Material balances are important first step when designing a new process or analyzing an existing one. They are almost always prerequisite to all other calculations in the solution of process engineering problems.

Material balances are nothing more than the application of the law of conservation of mass, which states that mass can neither be created nor destroyed. Thus, you cannot, for example, specify an input to a reactor of one ton of naphtha and an output of two tons of gasoline or gases or anything else. One ton of total material input will only give one ton of total output,

i.e. total mass of input = total mass of output.

Conservation Law

FLOW IN (S) + GENERATION (S) = FLOW OUT (S) + ACCUMULATION (S)

The quantity S can be any one of the following quantities:

- Mass
- Energy
- Momentum
- Component Mass (Mole)

Total Mass Balance

Since mass is always conserved, the balance equation for the total mass (m) of a given system is: Rate of mass in - Rate of mass out = Rate of mass accumulation

Component Balance

The mass balance for a component A is generally written in terms of number of moles of A. Thus, the component balance is:

$$\begin{array}{c}\text{Flow of}\\ \text{moles (A)}\\ \text{in}\end{array} + \begin{array}{c}\text{Flow of}\\ \text{mole of (A)}\\ \text{out}\end{array} + \begin{array}{c}\text{Rate of}\\ \text{Generation of}\\ \text{moles of (A)}\end{array} = \begin{array}{c}\text{Rate of}\\ \text{Accumulation of}\\ \text{moles of (A)}\end{array}$$

BASIS:

Naphtha Feed Stream:

13500 BPSD of Naphtha is to be isomerized Mass Flow Rate: 59050 kg/hr

Molecular Weight: 78.73 kmol/kg

Density: 616.9 kg/m^3

Hydrogen Feed Stream:

Mass Flow Rate: 2118 kg/hr

Molecular Weight: 5.149 kmol/kg

Density: 8.980 kg/m^3

Perchloroethylene:

Mass Flow Rate: 8.200 Rate PPM

Molecular Weight: 165.8 kmol/kg

Density: 1578 kg/m^3

3.2 Energy balance

The First Law of Thermodynamics is a statement of energy conservation. Although energy cannot be created or destroyed, it can be converted from one form to another (for example, internal energy stored in molecular bonds can be converted into kinetic energy; potential energy can be converted to kinetic or to internal energy, etc.).

Energy can also be transferred from one point to another, or from one body to a second body. Energy transfer can occur by flow of heat, by transport of mass (transport of mass is otherwise known as convection), or by performance of work.

The general energy balance for a process can be expressed in words as:

Accumulation of Energy in System = Input of Energy into System – Output of Energy from System

Table 5 Representation of Streams Number

Stream	**Number**	**Stream**	**Number**
LSR_Naphtha	1	To_101	9
Naph_Feed	2	To_Stab	10
Hydrogen	3	Off_Gases	11
Perchloroethylene	4	Penexate	12
Mix_Feed	5	To_DIH	13
To_100	6	Isomerate	14
Lead_Prod	7	Recycle	15
From_100	8	C7+	16

3.1.1 Mass & Energy Balance on Mixer-100

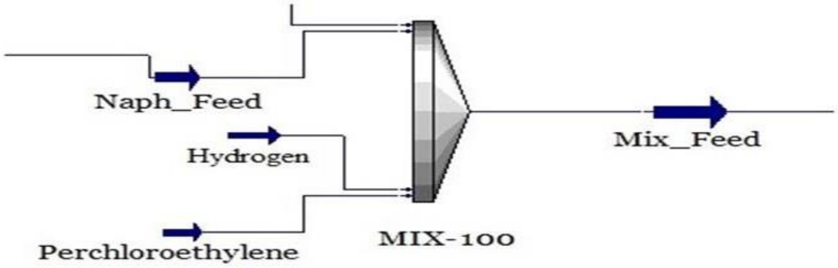


Table 6 Mass Balance on Mixer-100

Stream In	Mass Flow In	Stream Out	Mass Flow Out
LSR	1.302×10^5 lb/hr	Mixer Output	1.590×10^5 lb/hr
Hydrogen	4669 lb/hr	Recycle Feed	-2.411×10^4 lb/hr
Perchloroethylene	18.08 lb/hr	-----	-----
Total In	1.34×10^5 lb/hr	Total Out	1.34×10^5lb/hr

Table 7 Energy Balance on Mixer-100

Stream	Mass Flow	Mass Enthalpy	Heat Duty
LSR	1.302×10^5 lb/hr	912.6 Btu/lb	118.82×10^6 Btu/hr
Hydrogen	4669 lb/hr	835.4 Btu/lb	3.90×10^6 Btu/hr
Perchloroethylene	18.08 lb/hr	122.2Btu/lb	2.20×10^3 Btu/hr
Total	-------------	---------------	122.72×10^6 Btu/hr

3.1.2 Mass & Energy Balance Around Heat Exchanger E-100

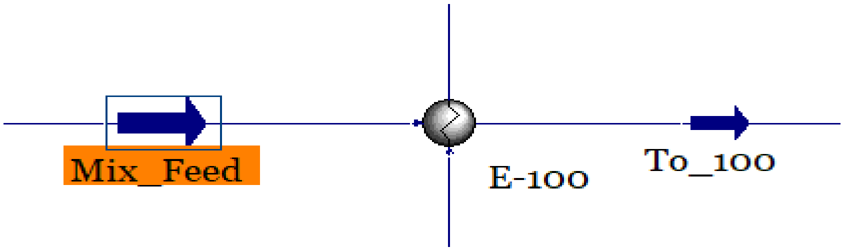


Table 8 Mass Balance Around Heat Exchanger E-100

Mass Flow In	Mass flow out
1.59×10^5 lb/hr	1.59×10^5 lb/hr

Table 9 Energy Balance Around Heat Exchanger E-100

Mass Flow In	**Mass Enthalpy In**	**Heat Duty In**
1.59×10^5 lb/hr	905.3 Btu/lb	143.94×10^6 Btu/hr
Mass Flow out	**Mass Enthalpy out**	**Heat Duty Out**
1.59×10^5 lb/hr	867.7 Btu/lb	137.94×10^6 Btu/hr

3.1.3 Mass & Energy Balance Around Reactor R-100

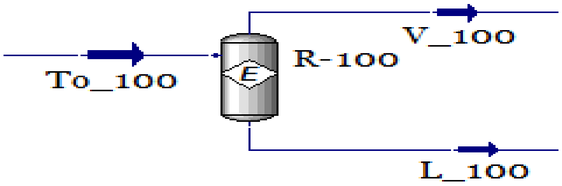


Table 10 Mass Balance Around Reactor R-100

Mass Flow In	**Mass Flow Out**
1.590×10^{5} lb/hr	3.781×10^{4} lb/hr
----------------------	1.212×10^{5} lb/hr
Total=1.590×10^{5}lb/hr	Total=1.590×10^{5}lb/hr

Table 11 Energy Balance Around Reactor R-100

Mass Flow In	**Mass Enthalpy In**	**Heat Duty In**
1.59×105 lb/hr	867.7 Btu/lb	137.96×10^{6} Btu/hr
Mass Flow out	**Mass Enthalpy out**	**Heat Duty out**
3.78×10^{4} lb/hr	794 Btu/lb	30.02×10^{6} Btu/hr
1.212×10^{5} lb/hr	890.7 Btu/lb	107×10^{6} Btu/hr
Total	------------	137.97×10^{6} Btu/hr

3.1.4 Mass & Energy Balance Around Mixer -102

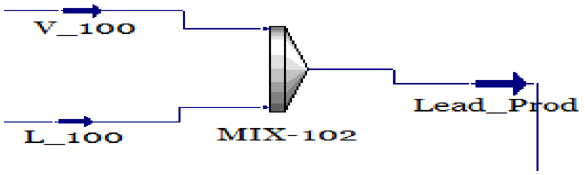


Table 12 Mass Balance Around Mixer -102

Mass Flow In	**Mass Flow Out**
3.781×10^{4} lb/hr	1.590×10^{5} lb/hr
1.212×10^{5} lb/hr	----------------
total=1.590×10^{5} lb/hr	total=1.590×10^{5} lb/hr

Table 13 Energy Balance Around Mixer -102

Mass Flow In	**Mass Enthalpy In**	**Heat Duty In**
3.78×10^4 lb/hr	794 Btu/lb	30.02×10^6 Btu/hr
1.212×10^5 lb/hr	890.7 Btu/lb	107×10^6 Btu/hr
Total	-----------------	137.97×10^6 Btu/hr
Mass Flow out	**Mass Enthalpy out**	**Heat Duty Out**
1.59×10^5 lb/hr	867.7 Btu/lb	137.96×10^6 Btu/hr

3.1.5 Mass & Energy Balance Around Cooler E-103

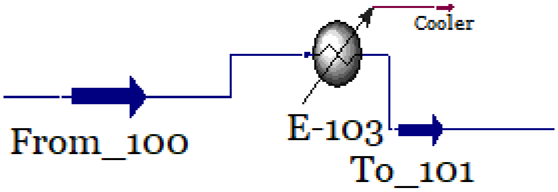


Table 14 Mass Balance Around Cooler E-103

Mass Flow In	**Mass flow out**
1.59×10^5 lb/hr	1.59×10^5 lb/hr

Table 15 Energy Balance Around Cooler E-103

Mass Flow In	**Mass Enthalpy In**	**Heat Duty In**
1.59×10^5 lb/hr	867.7 Btu/lb	137.96×10^6 Btu/hr
Mass Flow out	**Mass Enthalpy Out**	**Heat Duty Out**
1.59×10^5 lb/hr	918.4 Btu/lb	146.08×10^6 Btu/hr

3.1.6 Mass & Energy Balance Around Reactor R-101

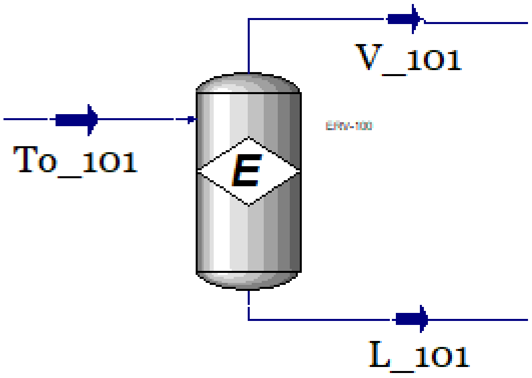


Table 16 Mass Balance Around Reactor R-101

Mass Flow In	**Mass Flow Out**
1.590×10^5 lb/hr	2.169×10^4 lb/hr
--------------------	1.373×10^5 lb/hr
Total=1.590×10^5lb/hr	Total=1.589×10^5lb/hr

Table 17 Energy Balance Around Reactor R-101

Mass Flow In	**Mass Enthalpy In**	**Heat Duty In**
1.59×10^5 lb/hr	918.8 Btu/lb	146.08×10^6 Btu/hr
Mass Flow Out	**Mass Enthalpy Out**	**HEAT DUTY Out**
2.164×10^4 lb/hr	819.8 Btu/lb	17.74×10^6 Btu/hr
1.373×10^5 lb/hr	934.4 Btu/lb	128.29×10^6 Btu/hr
Total	--------------------	146.03×10^6 Btu/hr

3.1.7 Mass & Energy Balance Around MIX_103

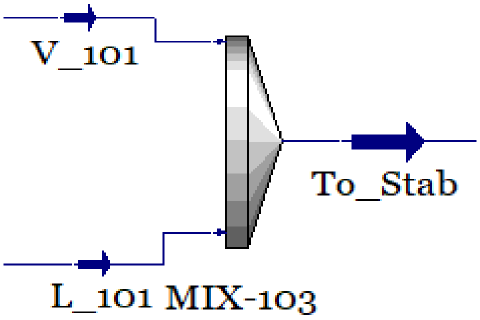


Table 18 Mass Balance Around MIX_103

Mass Flow In	Mass Flow Out
2.590×10^5 lb/hr	1.590×10^5 lb/hr
1.373×10^5 lb/hr	-------------------
Total=1.589×10^5lb/hr	Total=1.590×10^5 lb/hr

Table 19 Energy Balance Around MIX_103

Mass Flow In	**Mass Enthalpy In**	**Heat Duty In**
3.78×10^4 lb/hr	794 Btu/lb	30.02×10^6 Btu/hr
1.212×10^5 lb/hr	890.7 Btu/lb	107×10^6 Btu/hr
Total	-----------------	137.97×10^6 Btu/hr
Mass Flow Out	**Mass Enthalpy Out**	**Heat Duty Out**
1.59×10^5 lb/hr	867.7Btu/lb	137.96×10^6 Btu/hr

3.1.8 Mass & Energy Balance Around Stablizer Tower T-100

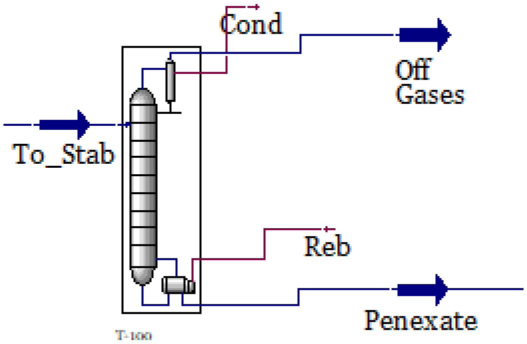


Table 20 Mass Balance Around Distillation Tower T-100

Mass Flow In	Mass Flow Out
1.580×10^{5} lb/hr	1891 lb/hr
---------------	1.561×10^{5} lb/hr
Total=1.580×10^{5} lb/hr	Total=1.578×10^{5} lb/hr

Table 21 Energy Balance Around Distillation Tower T-100

Mass Flow In	Mass Enthalpy In	Heat Duty In
1.580×10^{5} lb/hr	1022 Btu/lb	161.48×10^{6} Btu/hr
Mass Flow Out	**Mass Enthalpy Out**	**Heat Duty Out**
1891 lb/hr	1452 Btu/lb	2.745×10^{6} Btu/hr
1.561×10^{5} lb/hr	913.5 Btu/lb	142.59×10^{6} Btu/hr
Total	---------------------	145.34×10^{6} Btu/hr

3.1.9 Mass & Energy Balance Around DIH

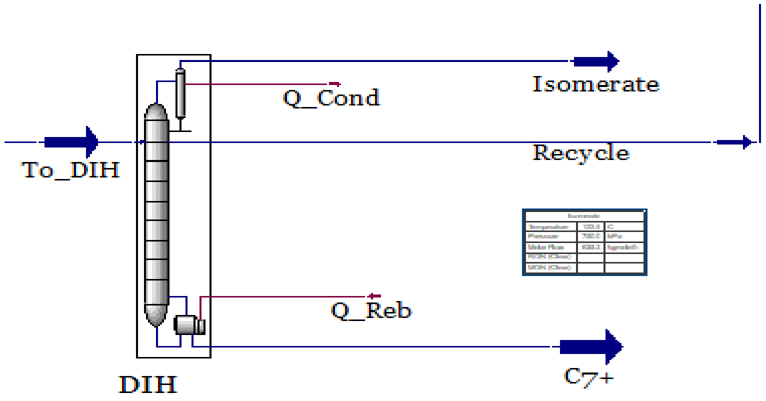


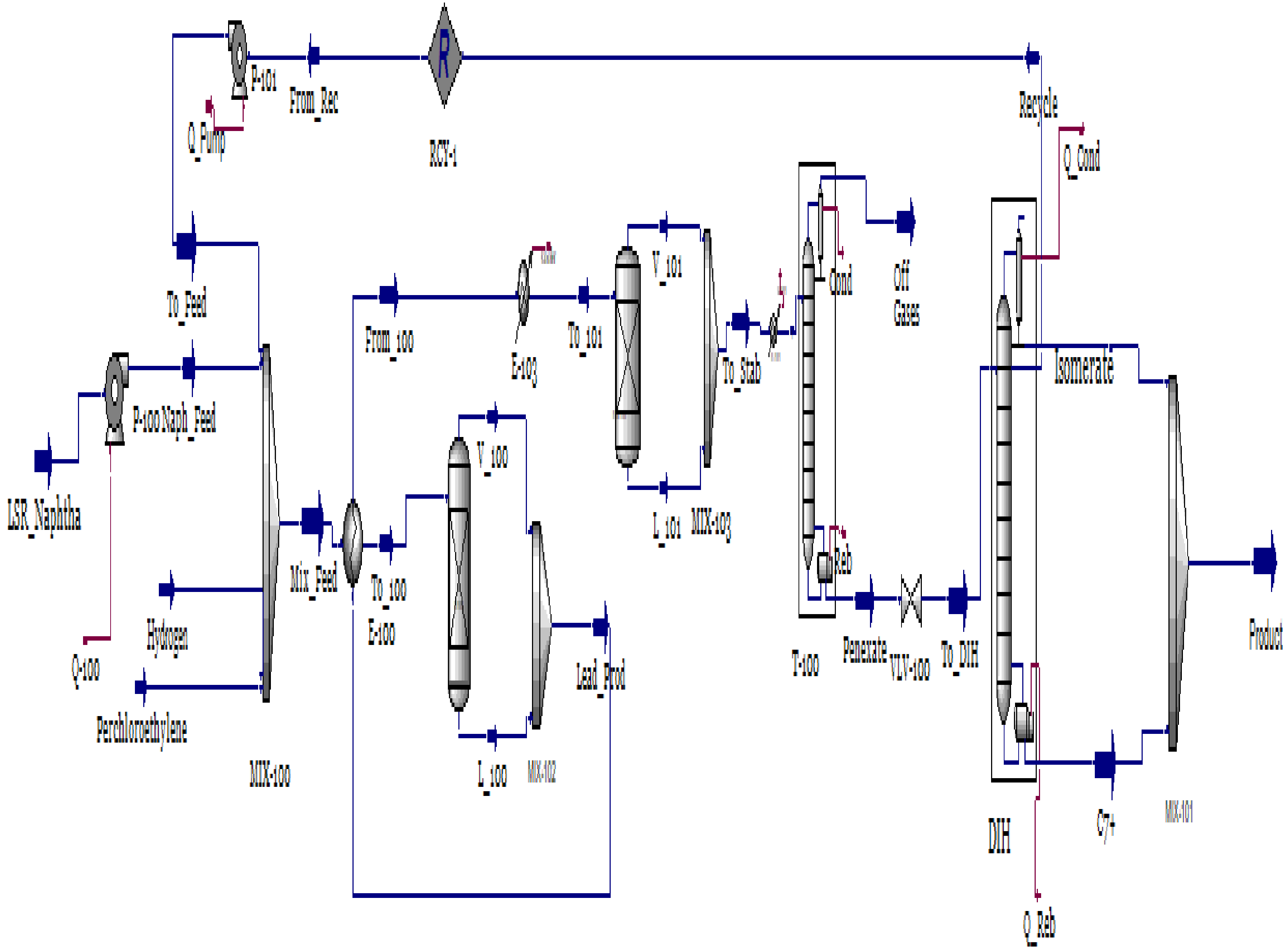
Table 22 Mass Balance Around DIH

Mass Flow In	**Mass Flow Out**
1.561×10^5 lb/hr	5.564×10^4 lb/hr
----------	2.311×10^4 lb/hr
----------	7.644×10^4 lb/hr
Total=1.561×10^5 lb/hr	Total=1.552×10^5 lb/hr

Table 23 Energy Balance Around DIH

Mass Flow In	**Mass Enthalpy In**	**Heat Duty In**
1.561×10^5 lb/hr	8919 Btu/lb	126.65×10^6 Btu/hr
Mass Flow In	**Mass Enthalpy In**	**Heat Duty In**
5.564×10^4 lb/hr	1081 Btu/lb	60.14×10^6 Btu/hr
2.311×10^4 lb/hr	1019 Btu/lb	23.54×10^6 Btu/hr
7.644×10^4 lb/hr	979.3 Btu/lb	74.85×10^6 Btu/hr
Total	--------------------	158.53×10^6 Btu/hr

Simulation


P-101
From_Rec
RCY-1
Recycle
Q_Pump
Q_Cond
To_Feed
LSR_Naphtha
P-100
Naph_Feed
Q-100
Hydrogen
Perchloroethylene
MIX-100
Mix_Feed
From_100
E-100
To_100
V_100
L_100
MIX-102
Lead_Prod
E-103
To_101
V_101
L_101
MIX-103
To_Stab
Cond
Off Gases
Reb
T-100
Penexate
VLV-100
To_DIH
Isomerate
DIH
C7+
MIX-101
Q_Reb
Product

Chapter 4 Equipment Design

4.1 Heat Exchanger

Given:

Working for a 21 ¼ in ID exchanger having 200 tubes with 1 in dia, 13 BWG, 16’ 0’’ long and pitch 1 ¼ in. Two tube passes, baffle spacing 5 in.

Tube side inlet T = tin = 145^o C = 293^o F

Tube side outlet T = tout = 116^o C = 241^o F

Shell side inlet T = tin = 58^o C = 136^o F

Shell side outlet T = tout = 100^o C = 212^o F

Solution:

Lead Product stream cp = 0.7005

From 100 stream cp = 0.6686

Mixed Feed stream cp = 0.5809

To 100 stream cp = 0.6354

Tube side cp = 0.68455 shell side cp = 0.60815

M = 1.580 x 10^5 lb/hr

Qhot = (1.58 x 10^5)(0.68455)(293-241) = lb/hr x Btu/lb.^{o}F x ^{o}F =5624262.8 Btu/hr

	HOT FLUID		COLD FLUID	
	T1=293	high T	t2=212	Δt2= 81
	T2=241	low T	t1=136	Δt1= 105
Diff	T1-T2=52		t2-t1=92.482	

LMTD= -24/ln(81/105) = 92.482

R = 52/16 = 0.648 S = 76/156= 0.4841

FT=0.935

Δt= 0.935 x 92.482 = 86.471^{o}F

As Δtc/th = 1.296

For 42 API crude, kc = 0.12 and Fc = 0.49 Tc= T2 + Fc (T1-T2) = 241 + (0.49)(52) = 267^0F

tc = t1 + Fc (t2-t1) = 136 + (0.49)(76) = 173.24^0F

Hot fluid, tube side

Flow area = at’ = 0.515 in^2

at = Nt * at’/144n

=(200)(0.515)/144x2

=0.3576ft^2

Ga= w/at = 1.58x10^5/0.3576

Ga=441834.45 lb/hr.ft^2

Assuming viscosity at tc, 8.7 lb/ft.hr lb/ft.hr

Re = DeGe/μ

D= 0.81/12 = 0.0675 ft

Re= (0.0675)(441834.45)/8.7

=3428.026

L/D= 16/0.0675 = 237

Cold fluid, shell side

as= 1 D X C’B/144 Pt

=21.25 x 0.25 x5/144 x 1.25 =0.1476

Ga = w/as = 1.58 x 10^5/0.1476 =1070460.71 lb/hr.ft^2

Assuming viscosity at tc, 0.978

Re = DeGe/μ

D= 0.99/12=0.0825 ft

Re= (0.0825)(1070460.71)/0.97 =91044.3387

jH= 110

jH= 9	At Tc = 267^oF
At tc = 173^oF	
C= 0.52 Btu/lb.^{o}F	C= 0.58 Btu/lb.^{o}F
k = 0.078	k=0.076
hi/Qt = jH x k/D x (cμ/k)$^{1/3}$	hi/Qs = jH x k/D x (cμ/k)$^{1/3}$

= 9 x 0.078/0.0675 x (0.52x8.7/0.078)$^{1/3}$ =110 x 0.076/0.0825 x (0.58x0.97/0.076)$^{1/3}$

hs/at=40.257 hi/Qs=197.49

hi/at x 1D / OD = 40.257 x 0.87/1

hi/Qt = 32.61

As tw = tc + (ho/Qs)/(hi/Qt + ho/Qs) x (Tc – tc)

= 173.24 + (197.49\32.61 + 197.49) x 93.76

Tw = 253.24°F = 254°F

At 254°F , µws = 1.12 and µwt = 3.12

Qs = (µ/µw)$^{0.14}$ Qt = (µ/µw)$^{0.14}$

= (0.97/1.12)$^{0.14}$ = (8.7/3.12)$^{0.14}$

= 0.98 = 1.154

hio/Qt x Qt = 32.62 x 1.154 =38

ho/Qs x Qs = 197.49 x 0.98 =193

As Uc = hio ho/ hio + ho = (38 x 193) /(38 +193) = 31.74 lb/hr.ft

As at'' = 0.2618 ft^2/lb.ft

Total surface area = 200 x 16' 0'' x 0.2618 =

837.76 ft^2 And as

UD = Q/ A∆t Assuming equimolar heat transfer from tube hot fluid to shell fluid UD

= 5624262/837.76 x 86.47

UD = 77.76 Btu/hr.ft^2 °F

Now for Rd,

As Rd = Uc –UD / Uc UD = (77.76-31.74/ 77.76 x 31.74)

Rd= 0.0186 > given Rd

Pressure Drop

Tube side(hot fluid)

For Re = 3428.028

f = 0.0034 ft^2

s= 0.078

$\Delta Pt = (f.Gt^2.L.n)/(5.22 \times 10^{10} . Ds.Qt)$

$$\frac{(0.0034)(441834.45)2(16)(2)}{(5.22 * 1010.0.0675 \times 0.078 \times 1.154)} = 6.69 \text{ psi}$$

As Gt= 441834.45

$\Delta Pr = 4n/s. v^2/2g$

=4(8)/0.078 x 0.022

=2.256 psi

$\Delta PT = \Delta Pt + \Delta Pr$

6.69 + 8.256 psi

= 8.95 psi < 10 ps

Shell side(cold fluid)

For Re = 91044.3387

f = 0.00016

s = 0.79

Ds = 21.25/12 = 1.77 ft

No. of crosses= N=12 x 16/5 = 39

$\Delta Ps = 3.79 \text{ psi} < 10 \text{ psi}$

4.2 Reactor Design(R-100)

Pressure= 2386KPa

Temperature= 443K

Compressibility factor Z= 0.8392

Gas Constant R= 8.314 KPa/KmolK

Molar Flow rate F_O= 1302Kgmol/hr

Volume flow rate= 733.7 m^3/hr

Overall concentration= 1774.57mol/dm^3

Component	Mole fracti	Molar Flo	Volumetric Fl	Concentration CA	Conversion
n-butane	0.0168	21.8736	12.32616	29.8128	0.7
n-pentane	0.1904	247.9008	139.6965	33.7878	0.89
n-hexane	0.1269	165.1393	21.4760	225.1929	0.875

Reaction	n-Butane	n-Pentane	n-Hexane
k	8.5	7.9	6.7
k_N	1.12	1.2	1.6
K_I	13	11	9

Design Equation:

$$\frac{W}{FAo} = \int_0^{xi} dxi/-ra$$

$$W_i = \frac{\int (ZRT + K\mathrm{NCio}(1-\mathrm{X}) + \mathrm{KiXCiodx})}{\int kCio(1-X)}$$

For Butane=

W_B = 340.0912986Kg

X=0.7

For Pentane=

W_p= 6824.3748Kg

For Hexane=

$$W_i = \frac{\int (ZRT + K\mathrm{NCio}(1-\mathrm{X}) + \mathrm{KiXCiodx})}{\int kCio(1-X)}$$

W_H = 1005.673Kg

Total Weight = 8170.139099kgs

Volume of bed

$$\text{Volume of catalyst} = \frac{W}{Bulk\ density\ of\ catalyst}$$

Bulk density of catalyst = 760kg/m^3

= 8170.139/760

=10.75m^3

Bed porosity= 0.35

Volume of bed= volume of catalyst/(1- bed porosity)

Volume of bed= 16.54m^3

Height and diameter of bed

$$\text{Height of bed} = \frac{volume\ of\ bed}{\pi D^2/4}$$

D^3= 4v_{bed}/3π

D^3= 4(16.54)/3π

= 7.0198

Dia of bed= 1.9147m

Height of bed= 5.744m

Height and volume of reactor

15% clearance from bed height to obtain height of reactor

Height of reactor= height if bed + 0.15(height of bed)

H_R= 5.744 + 0.15(5.744)

Height of reactor = 6.6056m

Volume of reactor=19.02m^3

Space time and space velocity

Space time= volume of reactor/volumetric flow rate

= $19.02m^3/733.7m^3/hr$

Space time= 0.026hr

Space velocity = 1/ space time

Space velocity= $38.46hr^{-1}$

Pressure drop

Ergun equation for pressure drop

$$\frac{dP}{Hbed}= \frac{(1-E)}{E\text{^}3}\mathrm{G/dpg_cP_L}\frac{150(1-E)\mu G+1.75G)}{dp}$$

E= 0.30

dP= 0.0014m

g_c= $9.8m/s^2$

G= $12kg/m^3s$

P= 73.56kg/m

Ω= 8.320*10^-6 ib/fts

H_{bed}= 5.744m

Dp= 43Kpa

4.3 Pump design: P-101

Inlet pressure P1 = 185.9KPa

Outlet pressure P2= 2386KPa

Temperature T= 54.42C^0

Density p= 596.2Kg/m^3

Viscosity μ= 0.64Kg/m^3

Mass flow m= 1.048*10^4 Kg/h

Molar Flow F= 140.3 Kgmol/hr

Volumetric flow Q= 16.56 m^3/h

Vapour Pressure P_v= 110.4KPa

From the graph/chart between flowrate and diameter

We have

D= 0.034m

Velocity of fluid through pump is

$$V=\frac{4Q}{\pi D^2}$$

V= 18237.12223m/hr

V=5.07m/s

We find the work done through Bernoulli equation

dW= $\frac{dp}{p}$ + $\frac{dpf}{p}$ + dV/2g

dW= (2386*10^3)Pa-(185.9*10^3)Pa/596.2kg/m^3 + dPf/596.2kg/m^3 + 0

dW= 3690.204629Pa + dPf/596.2 Kg/m^3

Pressure drop by friction is given by using darcys equation

dP_f = 8fLV^{2}p/2D

where relative roughness= 0.046m

friction factor= 0.002

Assuming L= 100m from pump outlet to next exit

DP_F= 8*0.002*100*(5.07)^2*596.2kg/m^3/2*0.034m

DP_f= 360594.3854Pa

Putting back in equation of dW

So,

dW= 4295.03J

Total work is obtained by using efficiency of pump

$$\eta_p = 0.75$$

W= dW*m/ η_p

W= 4295.03*10480/0.75*3600

W= 16.67KW

NPSH available= Psaction- PVaporizing*(1000/pg)

NPSH available = (185.9-110.4)*(1000/596.2*9.8)

NPSH available= 12.92m

4.4 Pump design P-100

Inlet pressure P1 = 300KPa

Outlet pressure P2= 3204KPa

Team T= $62C^0$

Density p= $618.35Kg/m^3$

Viscosity µ= $0.71424Kg/m^3$

Mass flow m= 5.905*10^4 Kg/h

Molar Flow F= 750 Kgmol/hr

Volumetric flow Q= 89.43 m^3/h

Vapour Pressure P_v= 81.66KPa

From the graph or chart

Doptimum = 0.1023m

$$\text{Velocity of the fluid} = V=\frac{4Q}{\pi D^2}$$

V= 10880.33036m/hr

V= 3.022m/s

Work done by Bernoulli's equation

$$dW= \frac{dp}{p} + \frac{dpf}{p} + dV/2g$$

dW= 29040000/618.35 + dP_f/618.35

$dW = 4696.36937 + Dp_f/618.36$

pressure drop by friction is given by dP_f

$Dp_f = 8fLV^2p/2D$

Relative roughness= 0.046m

Friction factor f = 0.002

Assuming L=100

<u>$dP_f = 44160.8718 N/m^2$</u>

$dW = 4696.36937 + 44160.8718/618.35$

$dW = 4767.79 N/m^2$

Total work is given by taking effeciency of pump = 0.7

W= dW*m/effeciency

W= 4767.79*59050/0.7*3600

W= 111.72KW

NPSH actual = (200-81.66)*1000/618.35*9.8

NPSH actual = 36m

4.5 Cooler Design

We are employing NTU (Number of Transfer Units) method here. It is used to calculate the rate of heat transfer in heat exchangers when there is insufficient info to find LMTD. This method I also called effectiveness (ε) method.

E-101

To define ε, we need to find maximum possible heat transfer that can be hypothetically achieved in a counter flow heat exchanger. We start off by calculating C_p for hot and cold fluids respectively.

Hot Fluid In

Mass flowrate in= ṁ = 71660 kg/h = 19.91 kg/s

Mass specific heat capacity = Cp = 2.764 KJ/Kg-^{0}C = 2764 J/ Kg-^{0}C

C_{min}= C_c = (mC_p)c

Cc = 19.91 * 2764 = 55031.24 W/K

Cold Fluid Out

Mass flowrate in= ṁ = 71660 kg/h = 19.91 kg/s

Mass specific heat capacity = Cp = 2.322 KJ/Kg-^{0}C = 2322 J/ Kg-^{0}C

C_h = 19.91 * 2322 = 46231.02 W/K

For a given geometry, ε is found using C_p ratio.

$$C_r = \frac{C_{min}}{C_{max}}$$

$= \frac{24800}{46231.02}$

=0.54

Now, as ε is ration between actual heat transfer and maximum possible hea transfer,

$\varepsilon = \frac{q}{q_{max}}$ where q= Ch(Thi- Tci) = Cc(Tco-Tci)

As Thi = 126 oC , Tci = 50 oC and Tco= $\frac{50+126}{2}$ = 88 oC

So, $\varepsilon = \frac{T_{co}-T_{ci}}{T_{hi}-T_{ci}}$

$= \frac{88-50}{126-50}$

=0.5

Calculate qmax using equation

qmax= Cmin(Thi – Tci)

qmax= 462310.02 * (126-50)

qmax=3.51 * 105 KJ/h

qmax=97500 W

Now using

$$\text{NTU} = \frac{-\ln[(1-\varepsilon*(1+C_r)]}{1+C_r}$$

$=\frac{-ln[1-0.5(1+0.54)]}{1+0.54}$

=0.95

And now, the overall heat transfer coefficient U, can be found from table 6.2 from Richardson & Coulson.

As our system is light oil before stabilizer, and for cooler, U is between 350 and 900 W/m2-K.

So, taking U=625 W/m2-K where U= $\frac{350+900}{2}$ = 625 W/m2-K

Calculating Area

$$A=\frac{\boldsymbol{NTU*C_{min}}}{\boldsymbol{U}}$$

$= \frac{\mathbf{0.95*46231.02}}{\mathbf{625}}$

=70.27 m2

E-103

Hot Fluid In

Mass flowrate in= ṁ = 71660 kg/h = 19.91 kg/s

Mass specific heat capacity = Cp = 2.1 KJ/Kg-^{0}C = 2100 J/ Kg-^{0}C

C_{min}= C_c = $(mC_p)c$

Cc = 19.91 * 2100 = 41811 W/K

Cold Fluid Out

Mass flowrate in= ṁ = 71660 kg/h = 19.91 kg/s

Mass specific heat capacity = Cp = 2.824 KJ/Kg-^{0}C = 2824 J/ Kg-^{0}C

C_h = 19.91 * 2824 = 56226 W/K

For a given geometry, ε is found using C_p ratio.

$C_r= \frac{C_{min}}{C_{max}}$

$= \frac{41811}{56226}$

=0.74

Now, as ε is ration between actual heat transfer and maximum possible hea transfer,

$\varepsilon = \frac{q}{q_{max}}$ where q= $C_h(T_{hi}- T_{ci}) = C_c(T_{co}-T_{ci})$

As T_{hi} = 120 ^oC , T_{ci} = 115.9 ^oC and $T_{co}= \frac{120+115.9}{2}$ = 118 ^oC

So, $\varepsilon= \frac{T_{co}-T_{ci}}{T_{hi}-T_{ci}}$

$= \frac{118-115.9}{120-115.9}$

=0.51

Calculate q_{max} using equation

$q_{max}= C_{min}(T_{hi} - T_{ci})$

q_{max}= 41811 * (120-115.9)

q_{max}=1.7 * 10^5 KJ/h

q_{max}=47618.08 W

Now using

NTU = $\frac{-\ln[(1-\varepsilon*(1+C_r)]}{1+C_r}$

$=\frac{-ln[1-0.51(1+0.74)]}{1+0.74}$

=0.91

And now, the overall heat transfer coefficient U, can be found from table 6.2 from Richardson & Coulson.

As our system is light oil before stabilizer, and for cooler, U is between 350 and 900 W/m^2-K.

So, taking U=625 W/m^2-K where U= $\frac{350+900}{2}$ = 625 W/m^2-K

Calculating Area

$A=\frac{\boldsymbol{NTU*C_{min}}}{\boldsymbol{U}}$

$= \frac{\mathbf{0.91}*41811}{\mathbf{625}}$

=60.87 m2

4.6 DIH Column design

Height of column

Total number of trays = 76

We have divided the column in three parts

From tray 1-26

Effective no of trays = 26

Tray spacing= 0.55m

Height can be calculated using formula

Column height = Neh *tray spacing

H= 26*0.55

= 14.3m

From tray 26-50

Effective no of trays = Neff = 34

Tray spacing = 0.42m

H= 34*0.42 = 14.28m

From tray 60-76

Neff = 16

Tray spacing = 0.37m

H3= 16*0.37

= 5.92m

Assuming top clearance = 0.5m

Bottom clearance = 0.5m

According to US tray standards of gauge 18

Tray thickness = 4.75m/plate

= 0.4655m

Therefore the net height is calculated using following equation

Total height= H1-26 + H26-60 + Top clearance + bottom clearance + Tray thickness

= 35.96m

Diameter of a DIH column (C-factor method)

1) From tray 0-26

Assuming appropriate values based on system requirements for following parametres for diameter calculation

D_H= hole diameter= 0.343in= 0.0275ft

S= tray spacing = 0.55m= 1.804ft

Assuming hct = clear liquid height (transition from froth to spray of liquid)

H_{CT} = 2in = 0.166ft

Now we will calculate C-factor using following

Kester and has correlation which is

C_{sb} = 0.144*(dh^2 *6/p)^0.125 * (P_G/p)^0.1 *(s/H_{CT})^2

Where

6 = surface tension

P_L = density of liquid

P_G = density of vapors

Surface tension= 12.22 dyne/cm

Density of liquid = 595kg/m3 = 595+2.2/3.283 = 37.095Ib/ft3

Density of vapors = 8.474 kg/m3 = 8.474*2.2/3.28^3 = 0.49IB/ft^3

C_{SB} = 0.096ft

Flood velocity calculation

This is the velocity of upward vapor at which liquid droplets are uspende

We will use

Flood velocity = C_{SB} * $(P_l\text{-}P_v/P_v)^{0.5}$

U_N = 0.096 *$(P_l\text{-}P_v/P_v)^{0.5}$

U_N = 0.83 Ft/s

Net area calculation:

This represents the smallest area available for vapor flow in inter tray spacing

Assuming 80% flooding

AS = CFS/SF* FF*U_N

Where CFS= vapor flow rate

SF= derating factor

FF= flooding factor (80%) In this case

Downcomer Area Calculation :

As

A_D = Q_L/ v_{CL}

Where Q_L = Liquid flow rate= Vol flow rate of isomertae

Q_L = 41.72 m3/hr

Value of V_{CL} = from table 6.1

No derating factor required here as V_{CL} values here taken care of framing

V_{CL} = 0.3(Clear liquid velocity in downcomer for a tray spacing of 18 inches)

A_D = 0.4089/0.3

A_D = 1.363 f^2

Tower Diameter Calculation

Tower Area = $A_T = A_D + A_N$

= 442 ft^2

Calculating tower diameter by

$D_{T} = \sqrt{\frac{4*At}{3.14}\wedge 2}$

D_T= 23.7 ft

From Tray 26-60 :

Assuming appropriate values based on system requirements for following parametres for diameter calculation

D_H= hole diameter= 0.343in= 0.0275ft

S= tray spacing = 0.42m= 1.3776ft

Assuming h_{CT} = clear liquid height (transition from froth to spray of liquid)

H_{CT} = 2in = 0.166ft

Now as surface tension = 14.01 dyne/cm

Density of liquid = 614.8 kg/m^3

= 38.28 Ib/ft^3

Density of vapors = 8.833 kg/m^3

= 0.551 Ib/ft^3

Using kisher and Haas correlation again to find C_{SB}

C_{SB} = 0.0962Ft

Flood Velocity Calculation :

As

$$U_N = 0.0962 * \sqrt{Pl - PV/PV}$$

U_n = 0.796 Ft/sec

Net Area Calculation

As

G= vapor mass flow rate = 2560 kg/hr

P= vapor density = 8.833 kg/m^3

G = Density* Velocity* Area

$Q = V*A$

Vapors Volumetric flow rate = 2903 m^3/h

= 28.46 ft^3/s

Assumptions:

SF= 1

FF= 0.8

Flooding factor = 80%

As

A_S= CFS/ SF* FF* U_N

Where

CFS = Vapor flow rate

SF = derating factor

FF = Flooding factor (80% in this case)

Downcomer area calculation:

We will use

$$A_D = \frac{QL}{VCL}$$

Where Q_L = liquid flow rate = 0.16 ft^3/s

Value of Vcl from table 6.1 in thesis

A_D = 0.168/0.3

= 0.56 ft^2

Tower Diameter calculation :

$$\text{Total tower area(At)} = A_D + A_{CT}$$

= 180ft^2 + 0.56ft^2

A_t = 181 ft^2

Calculate tower dia by

$D_{T} = \sqrt{\frac{4*At}{3.14}}$^2

D_T= 4.65m

From Tray 60 to 76:

Tray Area:

Assuming appropriate values based on system requirements for following parameters for diameter calculation

D_H= hole diameter= 0.343in= 0.0275ft

S= tray spacing = 0.37m= 1.2136ft

Assuming h_{CT} = clear liquid height (transition from froth to spray of liquid)

H_{CT} = 2in = 0.166ft

Now as surface tension = 12.08 dyne/cm

Density of liquid = 599.2 kg/m^3

= 37.357 Ib/ft^3

Density of vapors = 7.658 kg/m^3

= 0.4774 Ib/ft^3

Using kisher and Haas correlation again to find C_{SB}

$$C_{SB} = 0.144 * \sqrt[0.125]{0.02755^2 * \frac{12.08}{37.357}} * \sqrt[0.1]{\frac{0.4774}{37.357}} * \sqrt[2]{0.37 * \frac{3.28}{0.166}}$$

C_{SB}= 0.0867Ft

Flood Velocity Calculation:

We will use

$$U_N = C_{SB} * \sqrt{Pl - PV/PV}$$

U_N = 0.762

Net area Calculation:

As

G= vapor mass flow rate = 34670 kg/hr

P= vapor density = 7.658 kg/m^3

G = Density* Velocity* Area

Q = V*A

Vapors Volumetric flow rate = 4527.28 m^3/h

= 44.37 ft^3/s

Assumptions:

SF= 1

FF= 0.8

Flooding factor = 80%

As

A_S= CFS/ SF* FF* U_N

A_S = 180Ft^2

Downcomer area calculation :

We will use

$A_D = \frac{QL}{VCL}$

Where Q_L = liquid flow rate = 0.5672 ft^3/s

Value of Vcl from table 6.1 in thesis

A_D = 0.5672/0.3

= 1.9ft^2

Tower Diameter Calculation :

Total tower area(At) = $A_D + A_{CT}$

= 180ft^2 + 1.9ft^2

A_t = 182 ft^2

Calculate tower dia by

$$D_T = \sqrt{\frac{4*At}{3.14}}\wedge 2$$

D_T= 4.87m

4.7 Stabilizer

For calculation of Theoretical plates = Underwood & Gilly’s method

For Minimum reflux ratio = Underwood’s Equation

operating Load = 85% of designed load

Component	Feed(mole Fraction)	Distillate(mole fraction)	Bottoms(mole fraction)	Relative Volatility(α)= K_i/K_{hk}	K_i
H2(HK)	0.1678	0.8700	0.0093	1(α_{HK})	1
i-Butane	0.0032	0	0.0039	0.242	2.6
n-Butane	0.0194	0	0.0240	0.17235	2
i-Pentane	0.3328	0	0.4115	0.06815	1.5
n-Pentane	0.0685	0	0.0847	0.052	0.85
22-MP	0.0005	0.0078	0.0005	0.011638	0.93
22-MB(LK)	0.1380	0	0.1707	0.03285(α_{LK})	0.47
23MB	0.0381	0	0.0381	0.024742	0.44
2MP	0.0834	0	0.1031	0.0225	0.31
3MP	0.0355	0	0.0439	0.020441	0.20
n-Hexane	0.0693	0	0.0856	0.0165	0.53
CH4	0.0201	0.1051	0	16.6667	6.3
HCl	0.0002	0.0007	0	0.00677	1.73
Propane	0.0075	0	0.0093	0.06288	5
C7i*	0.0045	0	0.055	0.0093	0.42
Ethane	0.0112	0.0164	0.089	2.6667	5.7

Component	X_D	X_B
H2 (HK)	0.8700	0.0093
22MP(LK)	0.0078	0.0005

Minimum Number of Plates

NM = Log((XLK/XHK)D*(XHK/XLK)B)/ Log(αLK) = NM

= Log((0.0078/0.8700)D*(0.0093/0.0005)B)/ Log(0.93)

Nm = 24.68

Minimum number of plates =Nm= 25

Minimum Reflux

Q= 1 (Feed is entering at boiling point)

Using Equation -> 1-q = ∑(αi*Xif/ αi-Θ) = 0 (Putting q=1)

Assume Θ = 0.95

Component	**α_i*X_{if}**	**α_i*X_{if}/ α_i-Θ**
H2	0.8700	17.4
22MP	7.25e-4	-0.3627
CH4	0.66213	0.12376
HCl	1.211e-3	1.5526e-3
Ethane	0.09348	0.01968
∑(α_i*X_{if}/ α_i-Θ)=17.1823		

Now,

Rm+1 = = ∑(αi*Xif/ αi-Θ)

Rm+1 = 17.1823

Rm = 16.1823

We will calculate actual reflux ratio R now

R = 1.5 * Rm = 1.5 * 16.1823 = 24.27

R = 24.27

Proceeding Further,

X = (R-Rm/R+1) ----------------------------

-- > X= 0.32

Y=1-X0.32 ------------------------------------

--- > Y=0.306

N=(Nm+Y)/(1-Y) ---------------------------

-- > N= 36.46

NACTUAL = 36 Stages

Height of Column

Stage Spacing = C = 0.6

Using Equation -> Ht = (NACTUAL-1)*C + (0.10C * NACTUAL)

Ht – 0.1 Ht = (35*0.6) + (0.06*36)

Ht = 25.73m ==26m

Feed Flow Rate = F = 7.16e04 kg/hr

Top Flow Rate = D = 857.5 kg/hr

Bottom Flow Rate = B = 7.080e04 Kg/hr

proceeding further ,

Vapour Rate At Tops = D(1+RACTUAL) = 21169.05 kg/hr

Liquid Rate at Tops= LT = D*RACTUAL = 20811.525 Kg/hr

Liquid Rate at Bottom = LB = F + LT = 92411.525 kg/hr

Vapour Rate at Bottom = VB= B(1+RACTUAL) = 1789116

kg/hr Now,

(L/V)TOP= 0.96

(LV)BOTTOM = 0.052

Diameter of Column

By Assuming Constant Density at top and bottom section

At Top ,

ρv = 3.67 kg/m3 ; ρL = 738 kg/m3

At Bottom,

$\rho V = 2.16$ kg/m3 ; $\rho L = 578$ kg/m3

Now, let us calculate Flow factors

-Flow Factor = $Lw/VW * (\rho v/ \rho L)^{½}$

Top Flow Factor = $0.96*(3.67/7738)^{½} = 0.068$

Top Flow Factor = 0.068

Bottom Flow Factor = $0.052 * (2.16/578)^{½} = 0.0032$

Bottom Flow Factor = 0.0032

Now,

Flooding Velocity = VF = KT OR B *$((\rho L- \rho v)/ \rho v)^{½}$ KT = 0.18 while KB = 0.16

Flooding velocity at Top = $0.18*((738-3.67)/3.67)^{½} = 2.546$ m/s

(VF)T = 2.546 m

At Bottoms,

(VF)B= $0.16* ((578-2.16)/2.16)^{½} = 2.61$ m/s

(VF)B = 2.61 m/s

So, our calculations are correct as operating velocity is 85% of flooding velocity.

Volumetric Flow Rates

At Top = (21669.025kg/hr / 3.67kg/m3) * 1hr/3600sec

VTOP = 1.64 m3/s

At Bottom = (21169.025kg/hr/ 2.16kg/m3) * 1hr/3600sec

VBOTTOM = 2.787m3/sec

Area at Top = (1.64m3/s) / (2.546m/s) = 0.36m2

ATOP = 0.36m2

Similarly,

ABOTTOMS = (2.787m3/s)/(2.2185m/s) = 1.25m2

ABOTTOMS = 1.25m2

Area of Cross-Section

Top = 0.76/0.88 = 0.86m2

Top Cross Section = 0.86m2

Chapter 5 Economic Analysis

5.1 STORAGE TANK

Capacity= S =14000 Barrels = 2225.82 m^3

Design Pressure = 25 psig

Material of construction = Carbon Steel

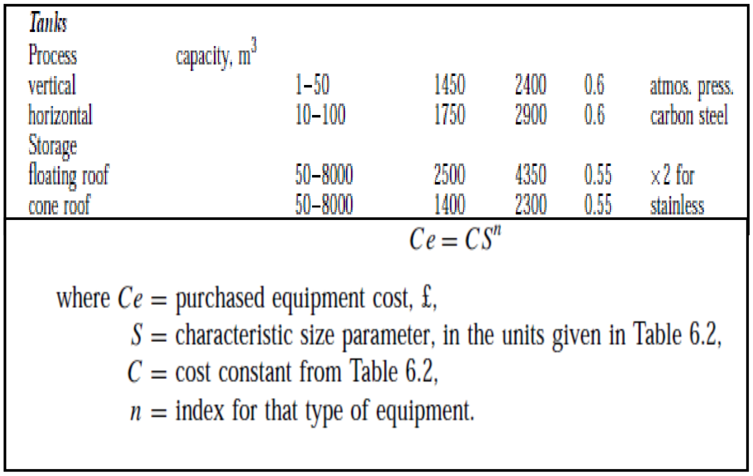
C_e= C*S^n

From table 6.2

C=cost constant=$4350

n=0.55

Storage Tank Cost = $301,723



Tanks					
Process	capacity, m^3				
vertical	1–50	1450	2400	0.6	atmos. press.
horizontal	10–100	1750	2900	0.6	carbon steel
Storage					
floating roof	50–8000	2500	4350	0.55	×2 for
cone roof	50–8000	1400	2300	0.55	stainless

$$Ce = CS^n$$

where Ce = purchased equipment cost, £,

S = characteristic size parameter, in the units given in Table 6.2,

C = cost constant from Table 6.2,

n = index for that type of equipment.

5.2 STABILIZER COLUMN

Height = 26m

Operating Pressure = 24bar

Column Diameter= 1.35m

Construction Material = Carbon Steel

Cost of Column = Bare Cost*Material Factor*Pressure factor

Cost of Column=$70,000*1*1.4=$98,000 (in 2004)

Inflation Rate till 2019=1.86

Cost of column in 2019=$182280

Types of Tray = Bubble Cap

Material of trays = Carbon Steel

Diameter of Trays= Diameter of Column = 1.35m

Number of Trays = 36

Total Tray Cost = 36*1000$ = 36,000$

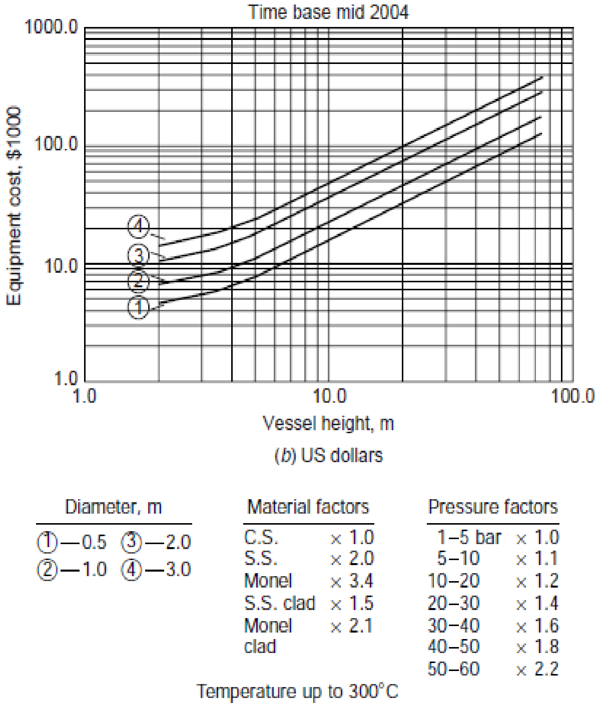


Figure 6.5*a*, *b*. Vertical pressure vessels. Time base mid-2004. Purchased cost = (bare cost from figure) × Material factor × Pressure factor

Total Tray Cost in 2019=$36,000*1.86 = $66960

Total Stabilizer Column Cost = $249,240

5.3 DIH COLUMN

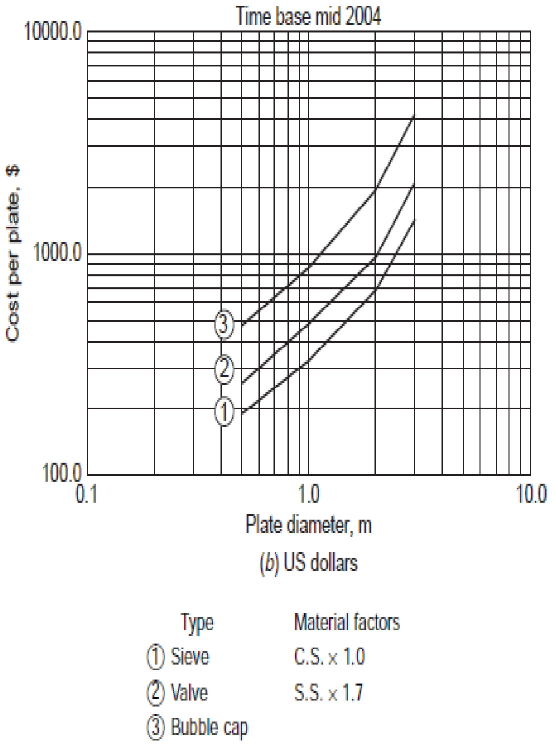


Figure 6.7a, b. Column plates. Time base mid-2004 (for column costs see Figure 6.4)
Installed cost = (cost from figure) × Material factor

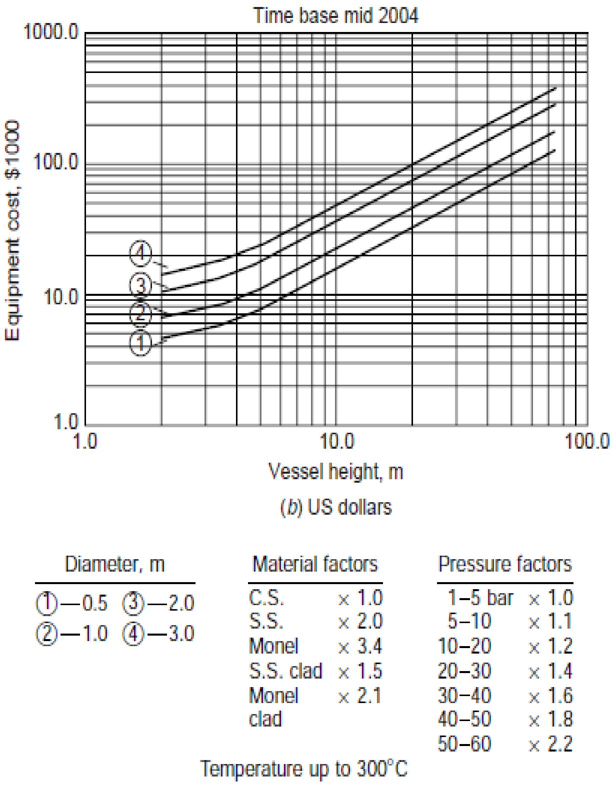


Figure 6.5a, b. Vertical pressure vessels. Time base mid-2004.
Purchased cost = (bare cost from figure) × Material factor × Pressure factor

Types of Tray= Sieve Trays

Number of Trays = 76

Material of Trays = Carbon Steel

Operating Pressure = 10.5 bar

Diameter of Column = 3m

Plate Diameter = 3m

Height of column = 36m

Material of Column=Carbon Steel

Cost of Column = $180000*1*1.2 =$216000

Inflation Rate=1.86

Cost of column in 2019 = $401760

Cost of Trays = $4000/plate

Total Tray Cost = $4000*76*1.86 =$565440

Total Cost = $40176 + $565440 = $967200

5.4 Reactor R-100

Volume of Reactor = S = 19.02 m^3

Material of Construction = Carbon Steel

Cost Constant = C = $15,000

Index= n = 0.40

$C_e = C * S^n$

$C_e = \$15,000(19.02)^{0.40}$

C_e=$48727.65

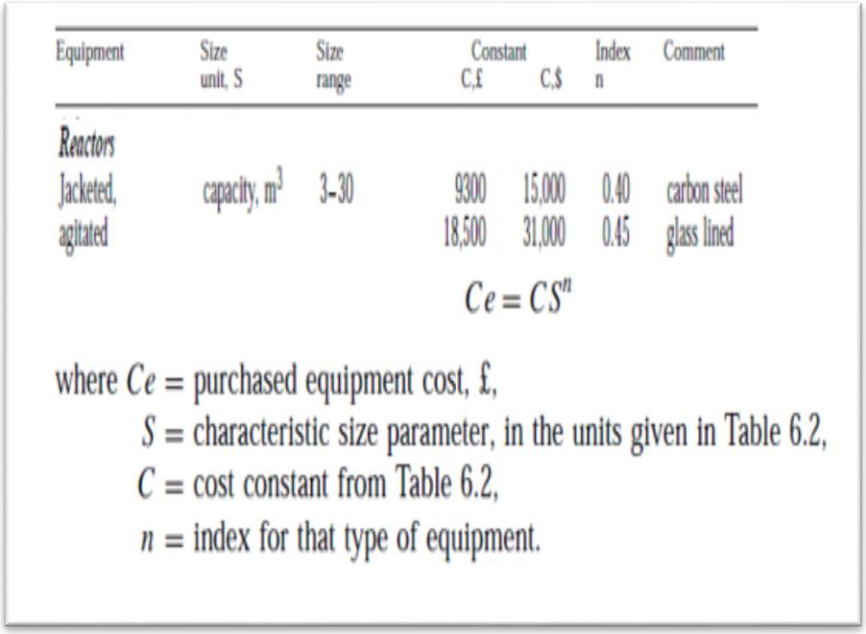
Inflation Rate = 1.86

Cost of reactor vessel =$48727.65 * 1.86 = $90633.43

Weight of the catalyst = 8170.14 kg

Cost of Catalyst/kg = $175/kg

Total Cost of catalyst =$1429774



Equipment	Size unit, S	Size range	Constant C,£	C,$	Index n	Comment
Reactors						
Jacketed, agitated	capacity, m^3	3–30	9300	15,000	0.40	carbon steel
			18,500	31,000	0.45	glass lined

$$Ce = CS^n$$

where Ce = purchased equipment cost, £,
S = characteristic size parameter, in the units given in Table 6.2,
C = cost constant from Table 6.2,
n = index for that type of equipment.

Total cost of reactor = $1429774.5 + $90633.43 = $1520408

5.5 PUMP P-100 & PUMP P-101

Volumetric Flow rate =89.43 m^3/hour

=393.74844 gallons/min

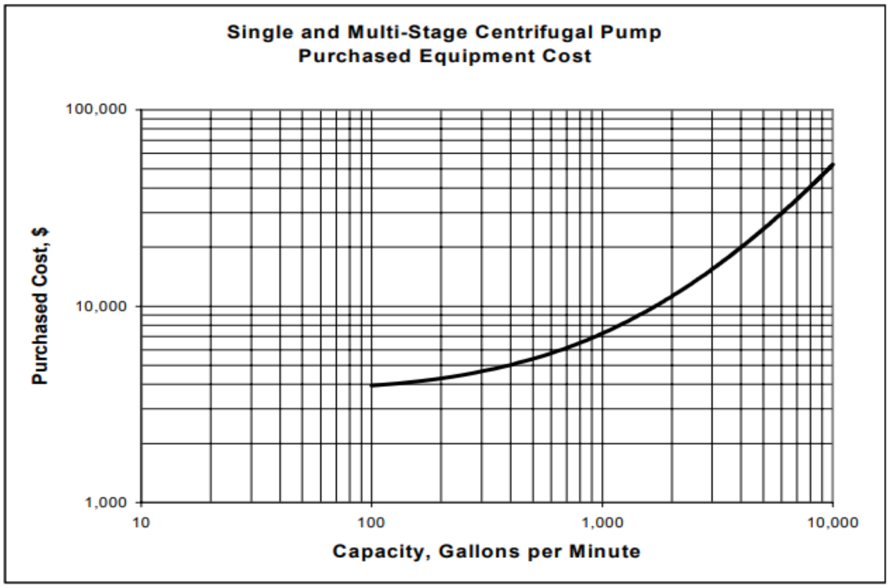
Material of pump = Carbon Steel

Cost of pump= $5000

Volumetric Flowrate = 22.7125 m^3/hour=100 gallons/min

Material of pump = Carbon Steel

Cost of pump = $ 4000



5.6 HEAT EXCHANGER E-100

Heat transfer Area = 77.87 m^2

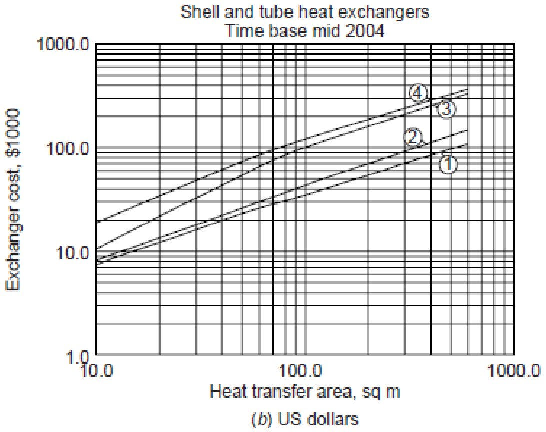
Shell & Tube Heat Exchanger Material = Carbon Steel

Operating Pressure = 24 bar

Type of Shell & Tube Exchanger = U-tube

Cost in 2004 = $12000*1.25*0.85 = $12750

Cost in 2019 = $23715



Materials		Pressure factors		Type factors	
Shell	Tubes				
① Carbon steel	Carbon steel	1–10 bar	× 1.0	Floating head	× 1.0
② C.S.	Brass	10–20	× 1.1	Fixed tube sheet	× 0.8
③ C.S.	Stainless steel	20–30	× 1.25	U tube	× 0.85
④ S.S.	S.S.	30–50	× 1.3	Kettle	× 1.3
		50–70	× 1.5		

Figure 6.3*a*, *b*. Shell and tube heat exchangers. Time base mid-2004
Purchased cost = (bare cost from figure) × Type factor × Pressure factor

5.7 COOLER E-101 & COOLER E-103

Heat Transfer Area = 70.27 m^2

Type of material = Carbon Steel

Operating pressure = 24 bar

Cost in 2004 = $27000*1.25*0.85 = $28687.5

Cost in 2019 = $28687.5*1.86 = $53358.75

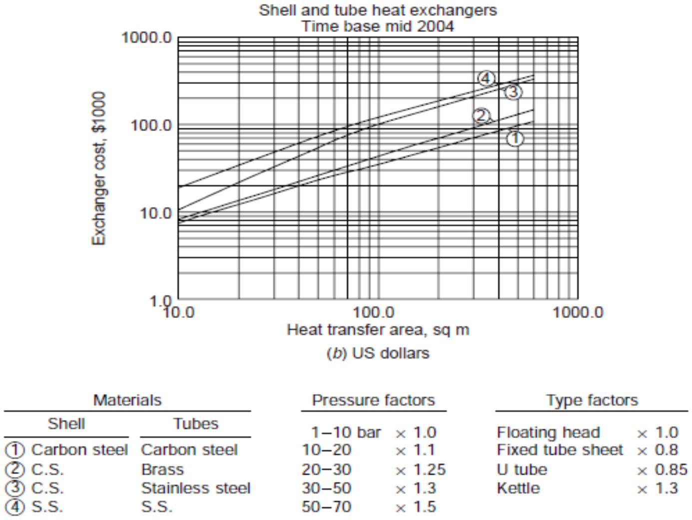
Heat Transfer Area = 60.87 m^3

Type of material = Carbon Steel

Operating Pressure = 24bar

Cost in 2004 =$24000*1.25*0.85 = $25500

Cost in 2019 = $47430



Materials		Pressure factors		Type factors	
Shell	Tubes				
① Carbon steel	Carbon steel	1–10 bar	× 1.0	Floating head	× 1.0
② C.S.	Brass	10–20	× 1.1	Fixed tube sheet	× 0.8
③ C.S.	Stainless steel	20–30	× 1.25	U tube	× 0.85
④ S.S.	S.S.	30–50	× 1.3	Kettle	× 1.3
		50–70	× 1.5		

Figure 6.3*a*, *b*. Shell and tube heat exchangers. Time base mid-2004
Purchased cost = (bare cost from figure) × Type factor × Pressure factor

Table 24 Purchased Cost Of Equipment (PCE)

Storage Tank	$561204
Stabilizer Column	$249,240
DIH Column	$967,200
Reactor R-100	$1520408
Pump P-100	$5000
Pump P-101	$4000
Heat Exchanger E-100	$23715
Cooler E-101	$53359
Cooler E-103	$47430

PCE	**$3431556.7**

Table 25 Physical Plant Cost (PPC)

Symbol	**Correction Factor**	**Value**
F1	Equipment Erection	0.40
F2	Piping	0.70
F3	Instrumentation	0.20
F4	Electrical	0.10

Physical Plant Cost (PPC) = PCE (1+0.40+0.70+0.20+0.10) = $8235737

PPC = $8235737

Table 26 Fixed & Working Capital

Factor Symbol	Correction Factor	Value
F10	Design & Engineering	0.30
F11	Contractor Fee	None
F12	Contingencies	0.10

Fixed Capital = PPC*(1+0.30+0.10) = $11530031.52

Fixed Capital = $11530031.52

Now, Working Capital = Fixed Capital * 0.05 =$576501.58

Working Capital = $576501.58

Total Investment = Working Capital + Fixed Capital

Total Investment = $12106533

Operating Cost = $ 6 Million

Payback Period = 2 years

Chapter 6 Hazop Analysis

Table 27 Hazop Analysis On Stabilizer Column

Guide Word	**Parameter**	**Deviation**	**Possible causes**	**Consequences**
No	Flow	No flow to stabilizer column	Blockage of pipeline Valve Failure occurred Failure of flow in previous units	High liquid holdup in the column V/L is lower than required
More		More flow to stabilizer column	LCV fails open Valve left open by operator	Flooding High pressure drop across column
Less		Less flow to stabilizer column	Leakage in pipe Valve partially open	V/L ratio is lower than required Inefficient separation
More	Pressure	High pressure of inlet stream	LCV closes while pump is running Malfunctioning of valve	Transfer line subjected to full pump delivery or surge pressure Breakage of the packing or bursting of column
Less		Low pressure of inlet stream	There is a malfunction of pressure regulating valve	Leads to abnormal pressure and temperature in column Leads to improper separation
More	Temperature	High temperature of inlet stream	Excess heat in column Disturbed rate of reaction	Increased pressure in column leading to excess heat Hydrocracking
Less		Low temperature of inlet stream	Low temperature in column	Incomplete separation Acid gases release to atmosphere

Table 28 Hazop Analysis On Reactor

Guide word	**Deviation**	**Consequences**	**Possible causes**
No	No H_2 flow	○ No product formed ○ Excess hydrocarbon in the reactor	○ Valve closed by operator ○ Line blockage ○ Pipe rupture
Less	Low H_2 flow than design intention	○ Unconverted reactants ○ Product specifications not met	○ Valve is partially closed ○ Leak in pipe
More	More H_2 flow than design intention	○ Hydrocracking may occur ○ Loss of Hydrogen, economic loss	○ Excessive pump speed ○ LCV fails open
Part of	Normal flow of decreased concentration of H_2	○ Excess hydrocarbons in reactor ○ Less concentration than normal can cause incomplete reaction	○ Vendor delivers wrong material or construction ○ Error in charging hydrogen supply tank
Other Than	Material flow other than H_2 in line	○ Depends on substituent nature ○ Product may be corroded if corrosive material	○ Wrong delivery from vendor ○ Judgement error in material choice

Chapter 7 Conclusion

Desired RON of the product according to the specifications have been achieved. The RON of this product is 89. The final Euro IV Mogas is produced for which desired RON of 95 has been achieved. A comprehensive calculation approach including the compositions of different fractions in isomerate and their respective RON has been shown in the table below. The final product RON is around approx. 89, which was desired.

Table 29 Isomerate RON

ISOMERATE	COMPOSITION	RONC	ISOMERATE RONC
i-Butane	0.00972	100.2	0.973944
n-Butane	0.05924	95	5.6278
i-Pentane	0.86493	93.5	80.870955
n-Pentane	0.01697	61.7	1.047049
22-Mpropane	0.0014	85.5	0.1197
22-Mbutane	0.00000059	94	0.00005546
23-Mbutane	1.7E-09	105	1.785E-07
2-Mpentane	7.2E-10	74.4	5.3568E-08
3-Mpentane	4.2E-11	75.5	3.171E-09
n-Hexane	1.9E-12	31	5.89E-11
Propane	0.001	110	0.11
C7+*	2.6E-25	82	2.132E-23
n-Heptane	4.2E-29	100	4.2E-27
Cyclohexane	9.5E-19	83	7.885E-17
Benzene	2.1E-26	120	2.52E-24
Mcyclopentan	6.5E-17	96	6.24E-15
Ethane	0	108	0
Cl4-C2=	0	0	0
ISOMERATE RONC OBTAINED			88.7495037

A similar table of calculations for the final product motor gasoline has been shown. As shown, after employing specified portions of blending components, gasoline RON desired value of 95 is achieved.

Table 30 Mogas RON

PENEX/DIH		
MOGAS BLENDING COMPONENTS	BLEND PERCENTAGES	RONC
Isomerate	30%	89
Heavy Naphtha	5%	54
Reformate	65%	101
MOGAS BLEND RONC		95.05

Glossary Of Terms

1. **Acidizing or Pickling** – Prior to startup the reactor circuit is internally acidized or pickled by injecting anhydrous hydrochloric acid. The purpose is to remove all iron oxide rust with the injection of HCl before catalyst is loaded into the reactors and the unit started. During the acidizing operation, iron oxide or rust is converted to iron chloride and water. The free water generated must be removed and drained from all low point drains in a normal drying process. If not, this water, if allowed to reach the catalyst would act as a permanent catalyst poison.

2. **Catalyst Activity** – The activity of the Penex catalyst is a measure of its ability to convert normal paraffins into iso-paraffins. As the Penex catalyst deactivates, the activity of the catalyst at the top of the bed decreases, and the necessary reactions will move down to a lower level in the catalyst bed where the activity of the catalyst is still at its peak. When the catalyst has finally lost all of its activity, it must be replaced with a new batch. The Penex catalyst has a very low tendency to form carbon. The activity will not drop due to carbon formation, unless there were operations with excessive temperatures, such as in the event of a temperature excursion.

3. **Catalyst Promoter** – The catalyst promoter is a chloride compound, nominally perchloroethylene, injected into the feed stream for the purpose of maintaining the proper chloride level of the Penex catalyst.

4. **Combined Feed (or Combined Charge)** – Reactor liquid feed and makeup gas.

5. **CSM** – Ceramic Support Material. Refer to UOP Standard Specifications 3- 37-1 Inert Ceramic Ball. ICB is used in the top and bottom of catalyst and adsorbent beds. Also referred to as ICB. See ICB in this section.

6. **Deisohexanizer (DIH) –** A fractionator that separates the C_6 isomers from light naphtha, typically an 80-tray column. The overhead material, mostly dimethylbutane (2-2 DMB and 2-3 DMB) are sent to gasoline blendingThere is a sidedraw, comprised mostly of methylpentane (2-MP + 3-MP) and normal hexane (NC_6) that is recycled to the reactors for further processing. An upper sidedraw can sometimes be employed to further segregate C_6 iso- paraffins.

7. **Deisopentanizer (DIP) –** A fractionator that separates isopentane from light straight naphtha, typically an 80-tray column. The overhead material, mostly IC_5, is sent to gasoline blending. The bottoms material NC_5

and heavier material are sent to the Penex unit for processing.

8. **Delta Temperature (T)** – The Delta “T” (or DT or ΔT) is a short-cut symbol used when referring to the temperature rise across the total catalyst bed or across sections of the catalyst bed. It is related to the exothermic reactions occurring across all catalyst beds or across section of catalyst beds. Since benzene saturation and hydrocracking are highly exothermic reactions, the Delta "T" increases with increasing amounts of benzene and heavy components in the reactor feed. The delta T from isomerization is relatively small in comparison.

9. **End of Run (EOR) Conditions** – The end of run conditions refer to the operating conditions when the catalyst in the isomerization lead reactor has finally lost enough isomerisation activity to necessitate a catalyst changeout.

10. **Feed X-Factor** – The sum of the wt% of benzene, cyclohexane, methylcyclopentane, and heavier components (C_7^+). This value is useful in measuring the degree of isomerization inhibition that occurs due to the cyclic and heavier components. Normally the X-Factor term is used in reference to the Isomerization Reactor feed characterization

11. **Fresh Feed** – Feed entering the unit from battery limits that has not been processed through the reactors.

12. **Heavies Formation** – The formation of C_7+ material from C_6 cyclic material across the reactors. This phenomenon across the Penex isomerization catalyst remains largely unexplored and the mechanism for the reactions is unknown. High X-Factor feeds, at high reactor temperatures, low pressure, and low H_2/HC ratios favor heavies formation. It is speculated that C_6 naphthenes not only tends to ring open (hydrocrack), but can also alkylate to form heavier C7 naphthenes.

13. **Hydrocracking** – Hydrocracking is a side reaction that also occurs in the Penex reactors. A symptom of hydrocracking is the formation of light gasses (C4 and lighter) due to the cracking of heavier material under high temperature conditions.

14. **Hydrogen:Hydrocarbon Ratio (H_2/HC)** – The hydrogen to hydrocarbon ratio is a ratio of the moles of hydrogen flowing across the reactor section to the moles of C_5+ hydrocarbon in the reactor feedstock. The H_2/HC ratio at the reactor outlet will typically be maintained between 0.05 and 0.10. In addition, an inlet

H_2/HC ratio indicator is supplied. The makeup gas flowrate is adjusted to ensure a 0.05 H_2/HC ratio or greater is maintained at the reactor outlet.

15. **Hydrogenation** – Hydrogenation is the addition of hydrogen bonds to unsaturated compounds such as olefins or aromatics. An example is the conversion of benzene to cyclohexane.

16. **ICB** – Inert Ceramic Balls. Refer to UOP Standard Specifications 3-37-1 Inert Ceramic Ball. ICB is used in the top and bottom of catalyst and adsorbent beds. Also referred to as CSM. See CSM in this section.

17. **Isomers -** Compounds that have the same molecular formula, but different structural formula or different arrangement of molecules.

18. **Isomerate** – Stabilized product from the Penex unit. Depending on the specific flowscheme, the isomerate comprises the stabilizer bottoms or a combination of column overhead and bottom material.

19. **Isomerization** – Isomerization is the principal reaction which takes place in the Penex Isomerization Reactors. It is the conversion of normal paraffins to iso-paraffins.

20. **Isomer Ratio (Actual)** – The product isomer ratio is a term used to define the degree of isomerization taking place in the reactors. It is the weight or mol percent of a specific iso-paraffin in the total paraffins found in the reactor feed, lead reactor effluent or isomerate product. The product isomer ratios of IC_5/C_5P, 2-2 DMB/ C_6P and 2-3 DMB/ C_6P of the reactor feed, lead reactor effluent and stabilizer bottoms are usually tracked and monitored. Sometimes abbreviated to **Iso-Ratio**s.

21. **Isomer Ratio (at Equilibrium)** – Since the isomerization reaction is an equilibrium reaction, a mixture approaching an equilibrium mixture of iso and normal paraffins will be reached at the reactor effluents. The equilibrium product ratio is the highest product ratio attainable at a given temperature. Achieving it would require an infinitely long reactor residence time . Isomer Ratio is sometimes abbreviated to **Iso- Ratios**.

22. **Isomerization** – Isomerization is the principal reaction occurring in the Penex reactors. It is the conversion of normal paraffins to iso-paraffins.

23. **Iso-Ratio** – Refer to Isomer Ratio (Actual or at Equilibrium)

24. **Liquid Hourly Space Velocity (LHSV)** – Liquid Hourly Space Velocity (LHSV) is a term which describes the feed rate over the catalyst with reference to the catalyst volume. The units are volumes of C_5+ reactor liquid feed over the catalyst per hour per volume of catalyst.

25. **Naphthenes –** Any of several cycloalkane hydrocarbons having the general formula C_nH_{2n} and found in various petroleums. Example : cyclohexane

26. **Paraffin Isomerization Number (PIN) –** Paraffin Isomerization Number (PIN) is a summation of the 3 product ratios (IC_5/C_5P + 2-2 DMB/C_6P + 2-3 DMB/C_6P), measured in wt%. PIN is a measure of the degree of isomerisation occurring across the reactors.

27. **Permanent Poisons** - Permanent poisons are compounds which permanently affect catalyst activity. Examples of permanent poisons water, nitrogen compounds, fluorine, oxygen, CO_2 and CO. The catalyst can tolerate only a fixed amount of these materials, after which it is deactivated and will therefore have to be replaced.

28. **Reactor Feed (or Reactor Charge)** – Liquid feed to the reactors, includes fresh feed and hydrocarbon liquid recycle. Makeup gas is not included.

29. **Reactor Temperature Profile** – The reactor temperature profile is a plot of the reactor temperature versus the number of feet into the catalyst below the top surface in the reactor. Several thermocouples in the reactors are provided for the purpose of reading the temperature level at various depths so that this plot can be made.

30. **Ring Opening** – The conversion of cyclics to paraffins across the reactors.

31. **Start of Run (SOR) Conditions** – The start of run conditions refer to the operating conditions when the catalyst is new and fresh.

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