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**uop**

**PENEX PROCESS**

**HYDROGEN ONCE THROUGH**

**GENERAL OPERATING MANUAL**

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# UOP PENEX PROCESS

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# I. INTRODUCTION

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# I. INTRODUCTION

## A. THE PENEX PROCESS

The Penex Process is a proprietary process developed by UOP LLC specifically designed for the continuous catalytic isomerization of pentanes, hexanes, and mixtures thereof. This is accomplished by the catalytic isomerization of pentanes and hexanes. The reactions take place in a hydrogen atmosphere, over a fixed bed of catalyst, and at operating conditions which promote isomerization and minimize undesirable side reactions such as hydrocracking.

The process is simple and straightforward in design and operation and trouble-free in performance, permitting a minimum of staffing and supervision. Operating conditions are not severe as reflected by moderate operating pressure, low temperature, high catalyst space velocity, and low hydrogen partial pressure requirements.

Except for normal hydrotreating, the Penex Process requires neither special feed pretreatment nor especially sharp or costly prefractionation for removal of C<sub>6</sub> cyclohexanes or C<sub>7+</sub>. The Penex Process affords the refiner considerable flexibility in the choice of feedstocks both at the time of design or after the unit is constructed, the latter being important as changes in the overall refinery processing scheme occur in response to changing market situations. To this end, the Penex Process can be configured to add fractionators either upstream or downstream of the unit in order to achieve optimum results for the refinery.

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 flowscheme).

Although not essential to the success of the process, the Penex process will normally employ two reactors in a series flow configuration with the total required catalyst loading being equally distributed between the two vessels. Valves and piping are provided which permit reversal of the processing positions of the vessels and the isolation of either for partial catalyst replacement. With time, the Penex isomerization catalyst will become deactivated mostly likely from oxygenates, in particular water, and not from hydrocarbon. Deactivation from water proceeds as a sharp front which moves down the bed in a piston-like fashion; catalyst downstream of the deactivation front normally remains unaffected. When catalyst in the Lead Reactor is deactivated, the reactor is taken off line for reloading. During the short period of time the reactor is out of service, the second reactor is capable of maintaining continuous operation at design throughput and yield; conversion may be moderately lower. After catalyst reloading is completed, the processing positions of the two reactors may be reversed. Freshly loaded catalyst is normally placed in the lag position.

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. Isomerization and benzene hydrogenation reactions are both exothermic and the temperature increases across both reactors. Equilibrium requires that the outlet temperature be as low as the activity of the catalyst permits. With a single reactor, this would lead to a low inlet temperature and low isomerization rates in part of the catalyst bed. The two-reactor system permits the imposition of an inverse temperature gradient by cooling between reactors through exchange against cold feed. The first reactor may, therefore, be operated at a higher temperature and achieve a higher reaction rate. This reduces the inventory of catalyst and the reactor size required. Most of the isomerization is thus accomplished at high rate in the first reactor and the final isomerization reaction is performed at a lower temperature to take advantage of the more favorable equilibrium.

In certain cases, due to the specific design of the unit, a three-reactor design is employed.

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.

Ideally, the isomerization catalyst would convert the feed paraffins to the highest octane number branched structure, i.e., normal pentane to iso-pentane and normal hexane to 2,2-dimethylbutane or 2,3-dimethylbutane. However, the isomerization reaction, while generally favored by low reaction temperatures, is equilibrium limited.

The C<sub>5</sub> paraffin equilibrium mixture will consist of essentially normal and iso-pentane. The C<sub>6</sub> isomer equilibrium distribution is split approximately 50/50 between the higher octane dimethylbutane and lower octane methylpentane.

Chloride promoter is added continuously with the feed and is converted to hydrogen chloride in the reactor. 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<sub>1</sub> through C<sub>4</sub>) 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.

The separation and recycle of unconverted C<sub>5</sub> and C<sub>6</sub> paraffins and low octane C<sub>6</sub> iso-paraffins back to the Penex reactors will produce higher octane product from the process. 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<sub>5</sub> fraction and C<sub>6</sub> 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<sub>6</sub> 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 ( $\text{NC}_5$  and  $\text{IC}_5$ ) 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  $\text{C}_5+$  octane obtained with the Penex/DIH process is in the 87-89 RONc range. Figure I - 54 represents the Penex/DIH flowscheme. The actual octane upgrade over once-through operation is a function of the relative  $\text{C}_5/\text{C}_6$  concentration in the isomerization feedstock (Figure I - 68) 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  $\text{C}_6$ , 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  $\text{C}_6$ . This flowscheme provides the highest product octane number; all the normal pentane ( $\text{NC}_5$ ) and low octane  $\text{C}_6$  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  $\text{C}_6$  sidcut 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  $\text{C}_5+$  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<sup>TM</sup> 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<sub>5</sub>+ 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<sub>5</sub>s than C<sub>6</sub>s (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<sub>6</sub> in the feeds and choice of hydrocarbon recycle flowscheme. The selection of the Penex unit configuration is dependent upon feed composition and octane targets.

## B. 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. Its low octane was compensated for by its excellent lead susceptibility (i.e. the octane number increase affected by the addition of lead). This placed the C<sub>5</sub>/C<sub>6</sub> 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.

As the petroleum industry moved toward marketing fuels with lower lead levels, it became increasingly difficult to use light straight run naphtha in the gasoline pool. Conversion of the low octane C<sub>5</sub>/C<sub>6</sub> normal paraffins to their corresponding branched isomers in order to increase their octane number is recognized as a logical and necessary step in a lead reduction program.

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<sub>5</sub>/C<sub>6</sub> 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<sub>5</sub>/C<sub>6</sub> 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<sub>5</sub>/C<sub>6</sub> or increasing the reforming severity to compensate for the octane numbers lost from the C<sub>5</sub>/C<sub>6</sub> 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 States 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<sub>5</sub>/C<sub>6</sub> to enter the gasoline pool at a clear Motor octane number at least as high as that of a 98 to 100 Research clear reformatte.
3. Non-Aromaticity – The aromaticity of the gasoline, at the same pool octane numbers, will tend to be higher without C<sub>5</sub>/C<sub>6</sub> 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.

## C. CATALYSTS

### 1. ALUMINUM CHLORIDE CATALYSTS

The isomerization catalysts employed during World War II were all of the Friedel-Crafts type. Those, which contained aluminum chloride only, were either a hydrocarbon/aluminum chloride complex (the so-called sludge process) or they were manufactured in-situ by deposition onto a support such as alumina or bauxite. They were intended to operate at very low temperatures [49-129°C (120-265°F)] and to approach the very favorable equilibrium composition characteristic of these temperatures.

The catalyst tended to consume itself by reaction with the feedstock and/or product. When temperature was raised a little in an effort to compensate for loss of catalyst and to speed the reaction to effect more isomerization, light fragments were formed by cracking and these, when vented, caused an excessive loss of the HCl promoter.

Corrosion of downstream equipment was also commonplace, due to the solubility of aluminum chloride in hydrocarbon, to its relatively high volatility and to the difficulty of removing it from the product by caustic washing. Aluminum chloride deposition in and plugging of reboiler tubes was not uncommon.

The process faced problems in sludge disposal, which were considered onerous even before the present acute awareness of environmental factors developed. The fixed bed process sometimes experienced unpredictable amounts of isomerization.

## 2. HYDRO-ISOMERIZATION CATALYSTS [ABOVE 199°C (390°F)]

The operational problems which had characterized the wartime Friedel-Crafts type isomerization plants, the advent of catalytic reforming which not only made hydrogen generally available in refineries but also demonstrated the practicality of using noble metal containing catalysts on a large scale, and the octane number race which postwar high compression engines initiated all combined in the 1950's to spawn a spate of hydro-isomerization processes. These catalysts generally contained a noble metal and some halide, operated at temperatures between about 299°C (560°F) and temperatures approaching those characteristic of catalytic reforming, employed recycle hydrogen to prevent catalyst carbonization and utilized either no promoter or traces at most. In general, they did not require an especially dry feedstock but did benefit from a low sulfur content feedstock. Most achieved a close approach to the equilibrium characteristic of their particular operating temperature.

Because of their high operating temperatures and their necessarily low conversions to iso-paraffins, these high temperature catalysts were quickly replaced with the advent of the "third generation" low temperature catalysts.

## 3. HYDRO-ISOMERIZATION CATALYSTS [BELOW 199°C (390°F)]

"Low temperature" is considered rather arbitrarily for catalyst classification purposes as anything below 199°C (390°F) operating temperature. Typically these are fixed bed catalysts containing a supported noble metal and a component to provide acidity in the catalytic sense. They operate in a hydrogen atmosphere and may employ a catalyst promoter whose concentration in the reactor may range from parts per million to substantially higher levels. They generally all require a dry, low sulfur feedstock; however, they may differ importantly in their tolerance of certain types and molecular weights of hydrocarbons. Hydrocracking to light gases is generally slight, so liquid product 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.

## 4. 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, 420-600°F (220-315°C) And 200-450 psig (14-31.5 kg/cm<sup>2</sup>g). The advantage of this system was no 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<sub>2</sub>:HCBN), the laydown of coke requires periodic regeneration, and the high temperature limits the conversion due to the lower equilibrium.

## 5. 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.

## D. 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<sub>6</sub> 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 blending; the bottoms material can be sent to gasoline blending or to a Naphtha Splitter. There is a sidedraw, comprised mostly of methylpentane (2MP + 3MP) and normal hexane (NC<sub>6</sub>) that is recycled to the reactors for further processing. An upper sidedraw can sometimes be employed to further segregate C<sub>6</sub> iso-paraffins.
7. **Deisopentanizer (DIP)** – A fractionator that separates isopentane from light straight naphtha, typically an 80-tray column. The overhead material, mostly IC<sub>5</sub>, is sent to gasoline blending. The bottoms material NC<sub>5</sub> and heavier material are sent to the Penex unit for processing.
8. **Delta Temperature (T)** – The Delta "T" (or DT or  $\Delta T$ ) 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 (C7<sup>+</sup>). 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<sub>7+</sub> material from C<sub>6</sub> 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<sub>2</sub>/HC ratios favor heavies formation. It is speculated that C<sub>6</sub> naphthenes not only tends to ring open (hydrocrack), but can also alkylate to form heavier C<sub>7</sub> 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 (C<sub>4</sub> and lighter) due to the cracking of heavier material under high temperature conditions.
14. **Hydrogen:Hydrocarbon Ratio (H<sub>2</sub>/HC)** – The hydrogen to hydrocarbon ratio is a ratio of the moles of hydrogen flowing across the reactor section to the moles of C<sub>5+</sub> hydrocarbon in the reactor feedstock. The H<sub>2</sub>/HC ratio at the reactor outlet will typically be maintained between 0.05 and 0.10. In addition, an inlet H<sub>2</sub>/HC ratio indicator is supplied. The makeup gas flowrate is adjusted to ensure a 0.05 H<sub>2</sub>/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.

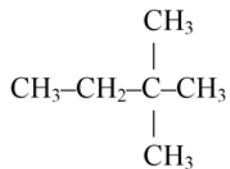
18. **Isomerate** – Stabilized product from the Penex unit. Depending on the specific flowscheme, the isomerate comprises the stabilizer bottoms or a combination of column overhead and bottom material.
19. **Isomerization** – Isomerization is the principal reaction which takes place in the Penex Isomerization 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<sub>5</sub>/C<sub>5</sub>P, 2-2 DMB/ C<sub>6</sub>P and 2-3 DMB/ C<sub>6</sub>P of the reactor feed, lead reactor effluent and stabilizer bottoms are usually tracked and monitored. Sometimes abbreviated to **Iso-Ratios**.
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. In practice, therefore, the product ratio will be less than the equilibrium product ratio. Any attempt to exceed equilibrium product ratio with the idea of producing more iso-paraffins would only result in less iso-paraffin yield and an increase in propane and lighter yield. 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<sub>5+</sub> reactor liquid feed over the catalyst per hour per volume of catalyst.
25. **Naphthenes** – Any of several cycloalkane hydrocarbons having the general formula C<sub>n</sub>H<sub>2n</sub> 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<sub>5</sub>/C<sub>5</sub>P + 2-2 DMB/C<sub>6</sub>P + 2-3 DMB/C<sub>6</sub>P), 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<sub>2</sub> 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.

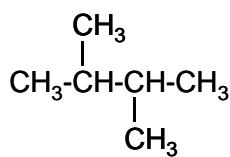
32. **Temporary Poisons** – A temporary poison, such as sulfur, has the effect of decreasing the catalyst activity while it is in the presence of the catalyst. It makes it necessary that higher temperatures are applied to the catalyst for the same product ratio while they are present. Upon removal of temporary poisons the catalyst has a tendency to regain its temporarily lost activity.

## E. ABBREVIATIONS

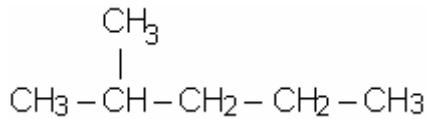
1. **2-2 DMB (2,2-dimethylbutane)** – a branched 6-carbon chain isomer of hexane with 2 methyl groups attached to the second carbon; the resulting chemical structure is :



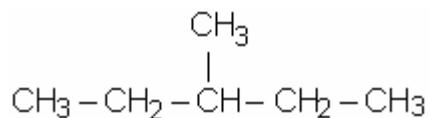
2. **2-2 DMB / C<sub>6</sub> P** = 2-2 DMB / (2-2 DMB + 2-3 DMB + 2MP + 3MP + NC<sub>6</sub>) \* 100, normally in weight or mole percent; product isomer ratio of 2-2 DMB.
3. **2-3 DMB / C<sub>6</sub> P** = 2-3 DMB / (2-2 DMB + 2-3 DMB + 2MP + 3MP + NC<sub>6</sub>) \* 100, normally in weight or mole percent; 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 :



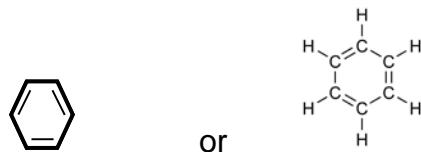
5. **2 MP (2 methylpentane)** – a branched 6-carbon chain isomer of hexane with a methyl group (-CH<sub>3</sub>) attached to the second carbon; the resulting chemical structure is :



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



7. **Bz (Benzene)** – an aromatic compound ring structure with the molecular formula C<sub>6</sub>H<sub>6</sub>; the resulting chemical structure is :

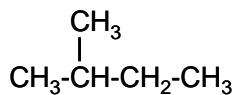


8. **C<sub>7</sub><sup>+</sup> (C7 Plus)** – Feed material heavier than heptane, including normal heptane
9. **CH (Cyclohexane)** – a cycloalkane with the molecular formula C<sub>6</sub>H<sub>12</sub>; the resulting chemical structure is :

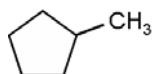


10. **DIH** –A fractionator that separates the C<sub>6</sub> isomers from light naphtha, typically an 80-tray column. The overhead material, mostly dimethylbutanes (2-2 DMB + 2-3 DMB) are sent to gasoline blending; the bottoms material can be sent to gasoline blending or to a Naphtha Splitter. There is a sidedraw, comprised mostly of methylpentanes (2MP + 3MP) and normal hexane (NC<sub>6</sub>) that is recycled to the reactors for further processing. An upper sidedraw can sometimes be employed to further segregate C<sub>6</sub> isoparaffins.

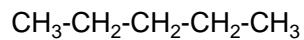
11. **DIP** – A fractionator that separates isopentane from light straight naphtha, typically an 80-tray column. The overhead material, mostly IC<sub>5</sub>, is sent to gasoline blending. The bottoms material NC<sub>5</sub> and heavier material are sent to the Penex unit for processing.
12. **DMB or 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 reaction is an equilibrium reaction, an equilibrium of iso- and normal-paraffins will be reached at the reactor effluent. When this equilibrium is reached, maximum product ratio or equilibrium product ratio will be obtained. Any attempt to exceed equilibrium product ratio with the idea of producing more isoparaffins in the reactor effluent would only result in less iso-paraffins yield and an increase in propane and lighter yield.
14. **IC<sub>5</sub> (Isopentane)** – a branched chain alkane with 5 carbon atoms; an isomer of normal pentane; the resulting chemical structure is :



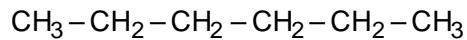
15. **IC<sub>5</sub> / C<sub>5</sub>P** = IC<sub>5</sub> / (IC<sub>5</sub> + NC<sub>5</sub>) \* 100, normally in weight or mole percent; product isomer ratio of IC<sub>5</sub>.
16. **MCP – Methylcyclopentane** – a chemical compound with an alkyl group attached to a 5-ring carbon compound. The molecular formula is (C<sub>5</sub>H<sub>10</sub>)-CH<sub>3</sub>; the resulting chemical structure is :



17. **MONc (Motor Octane Number clear)** – Octane ratings are ratings used to represent the anti-knock performance of petroleum-based fuels. One type of octane rating is the Motor Octane Number. Clear is an indication that there are no lead additives in the stream.
18. **MP or Methylpentanes** – 2MP and 3MP are collectively known as MPs or methylpentanes. Refer to 2MP and 3MP.
19. **NC<sub>5</sub> – Normal Pentane** – a straight chain alkane with 5 carbon atoms; the resulting chemical structure is :

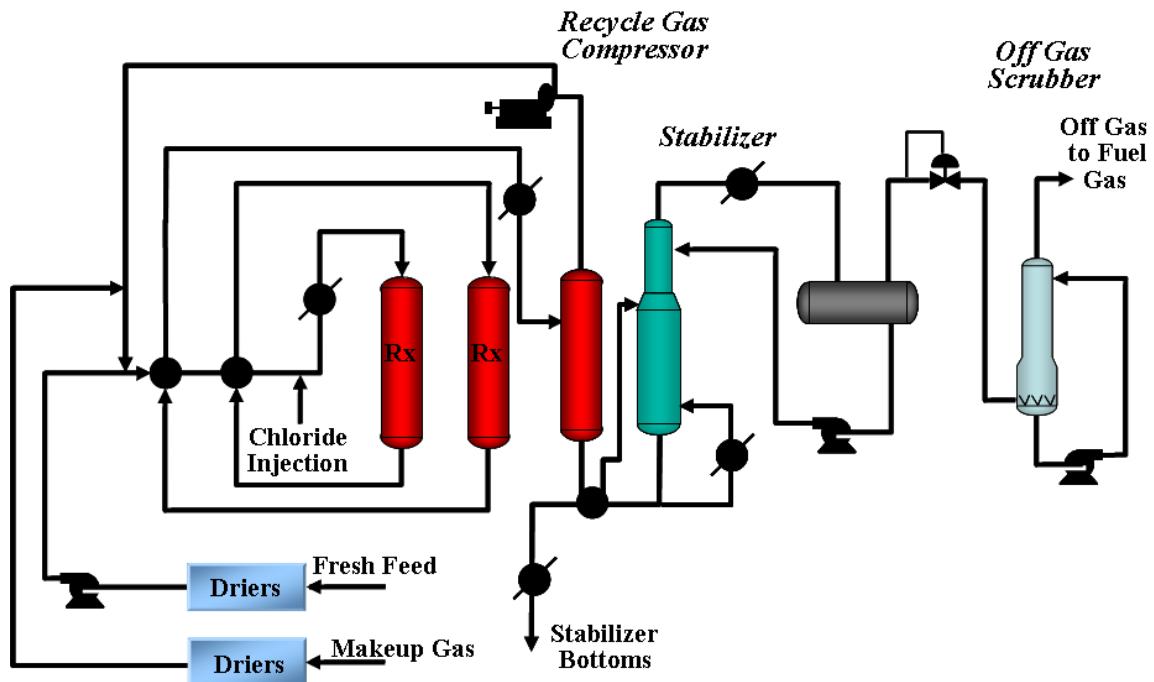


20. **NC<sub>6</sub> – Normal Hexane** – a straight chain alkane with 6 carbon atoms; the resulting chemical structure is :

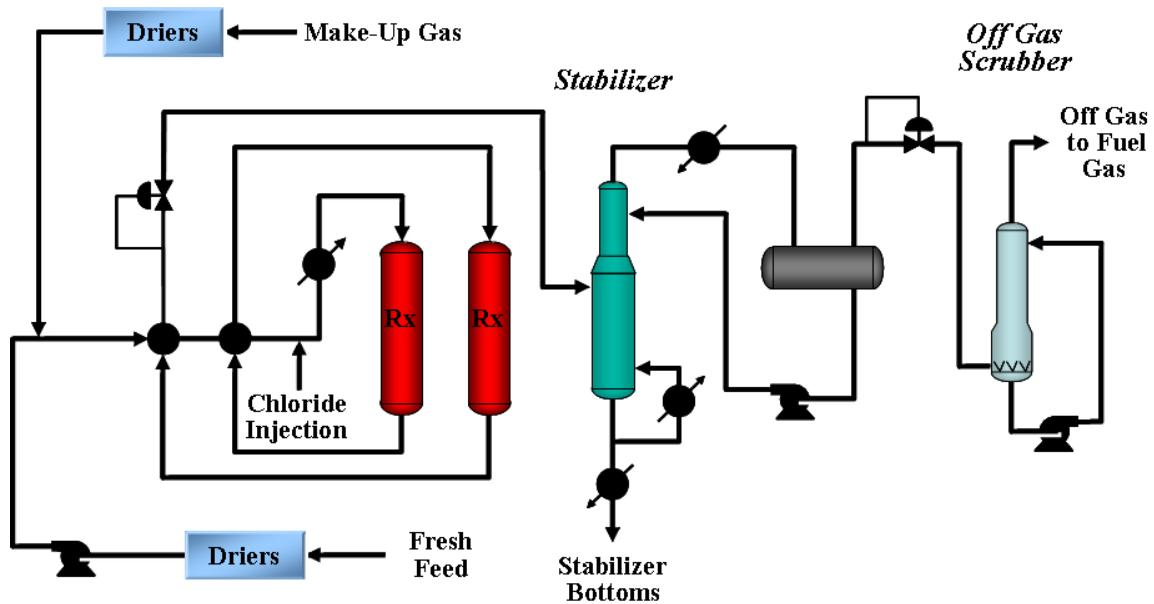


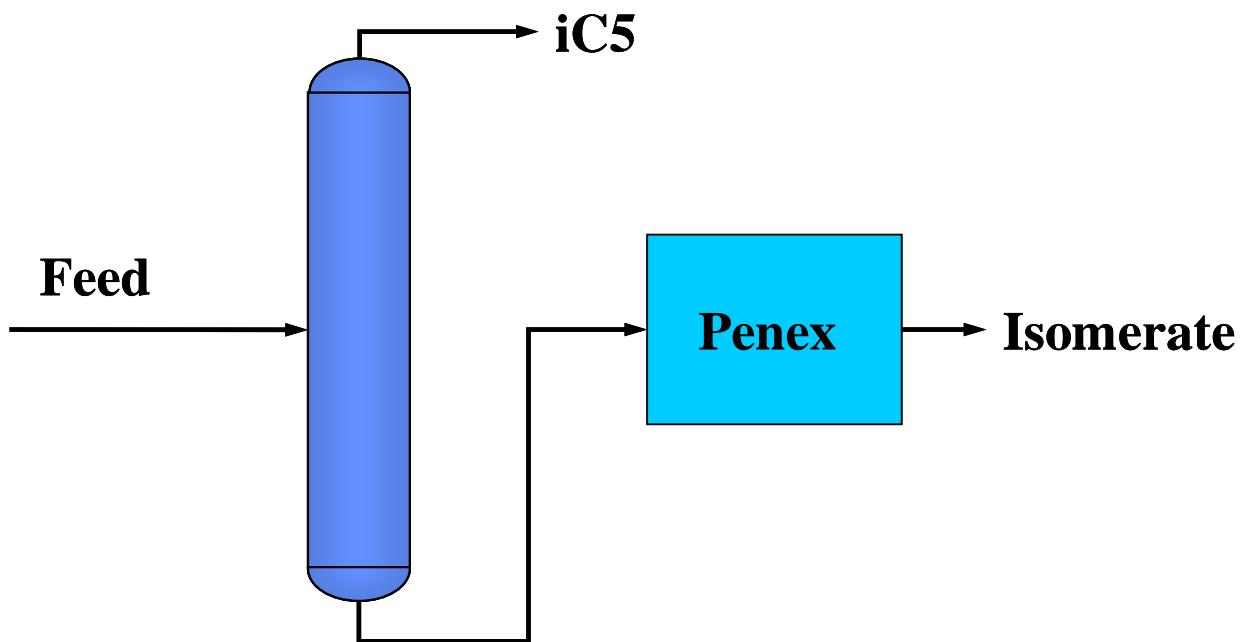
21. **Pickling** – Refer to Acidizing
22. **Product Ratio** – The product ratio is a term used to define the degree of isomerization taking place in the reactors. It is the weight or mol percent of isoparaffins in the total paraffins found in the reactor effluents.
23. **RONc (Research Octane Number clear)** – Octane ratings are ratings used to represent the anti-knock performance of petroleum-based fuels. The most common type of octane rating worldwide is the Research Octane Number. Clear is an indication that there are no lead additives in the stream.

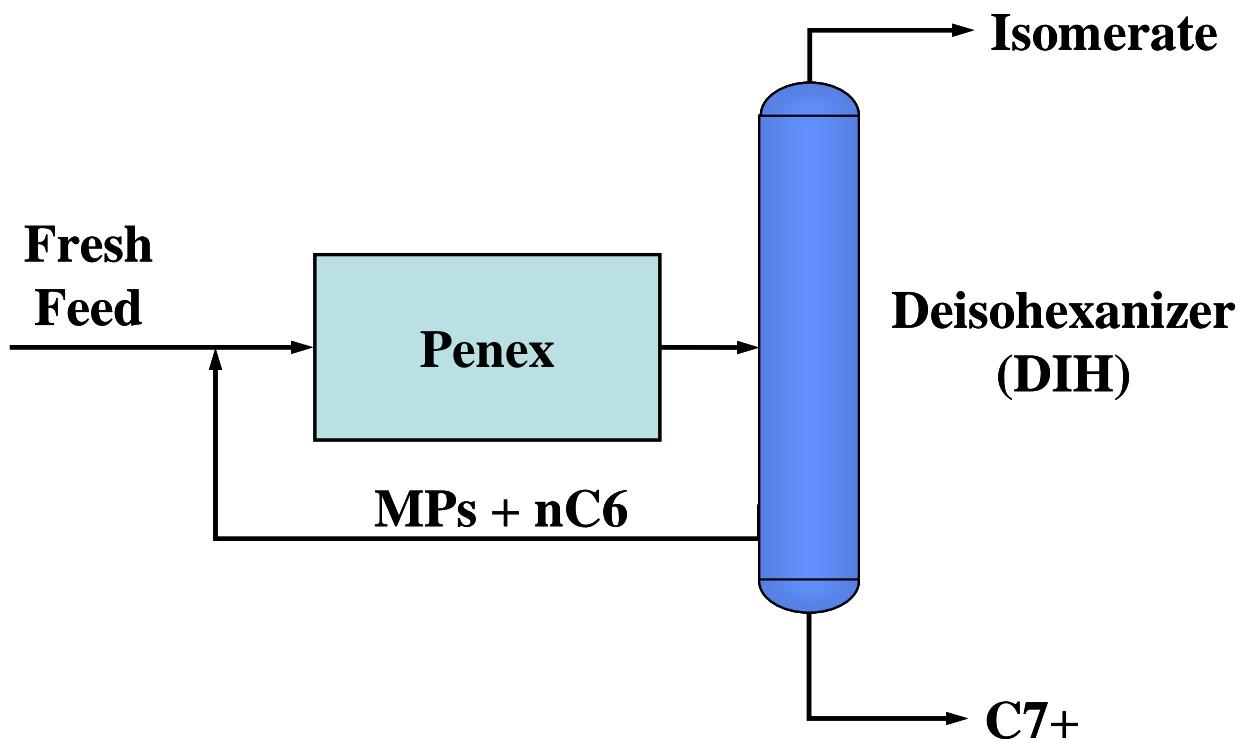
**Figure I - 1 (RECYCLE GAS) PENEX PROCESS**

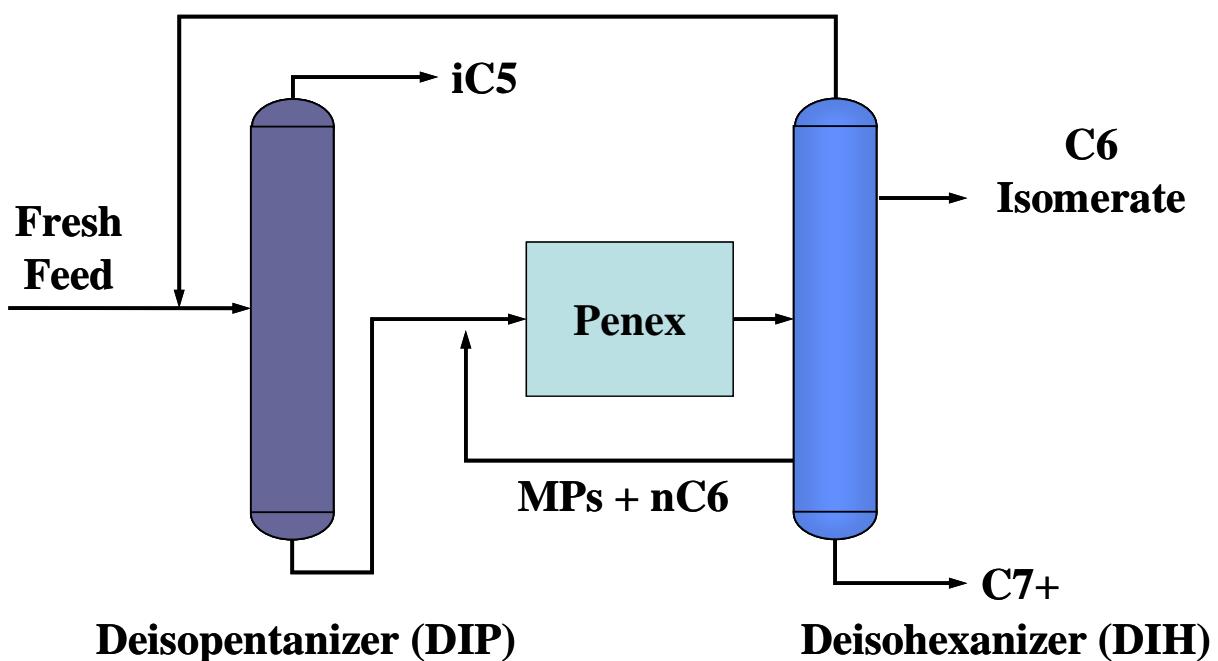


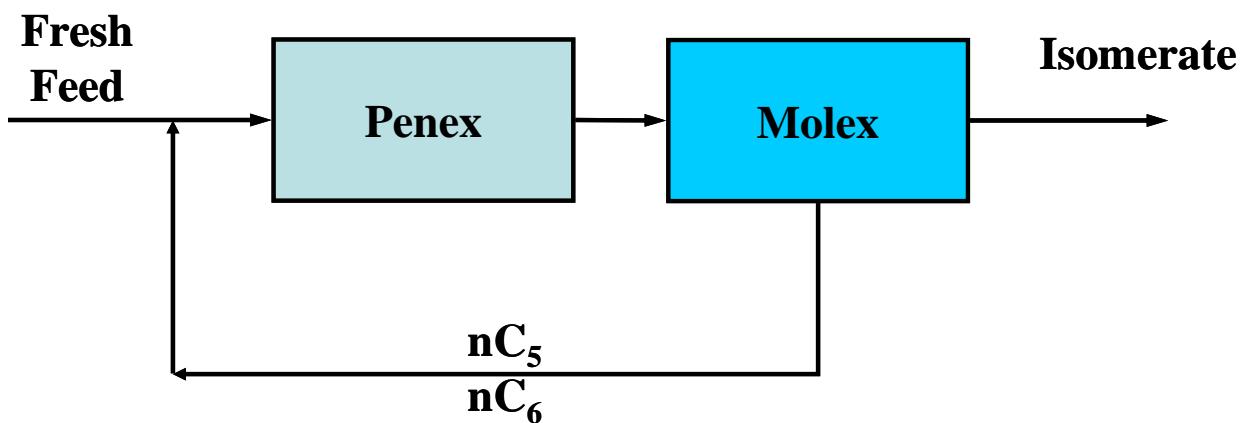
## Figure I - 2 (HYDROGEN ONCE THROUGH) HOT PENEX PROCESS



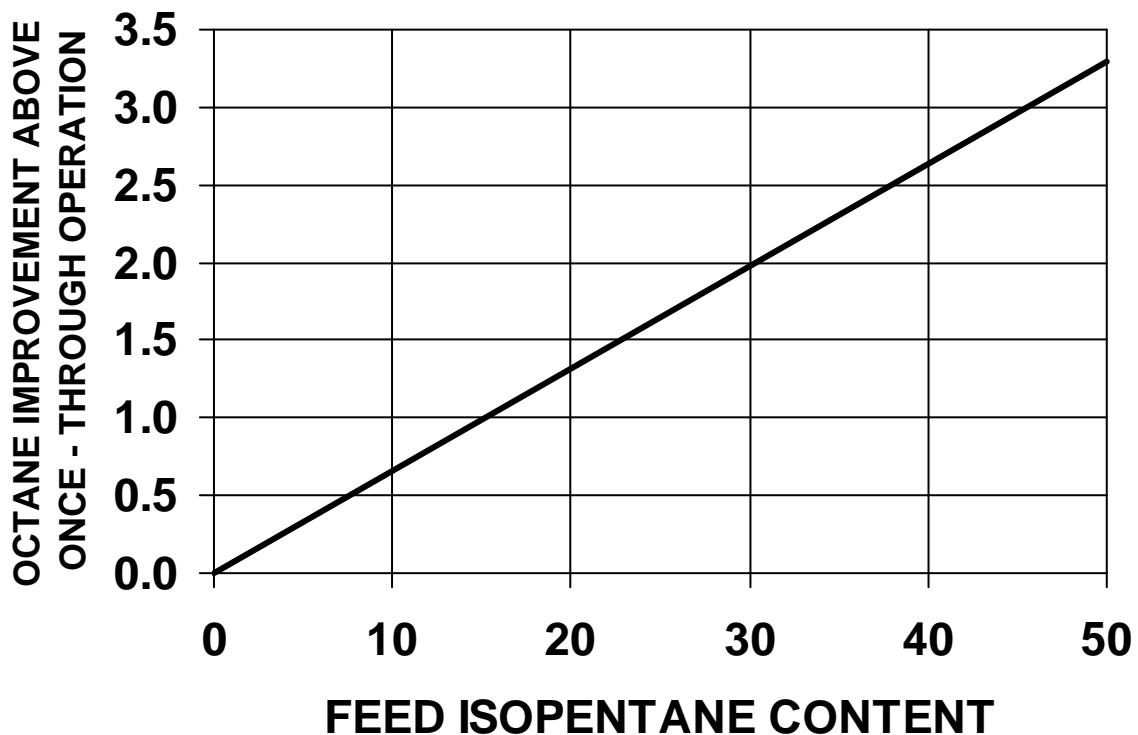
**Figure I - 3 DIP / PENEX FLOWSCHEME****Deisopentanizer (DIP)**

**Figure I - 4 PENEX / DIH FLOWSCHEME**

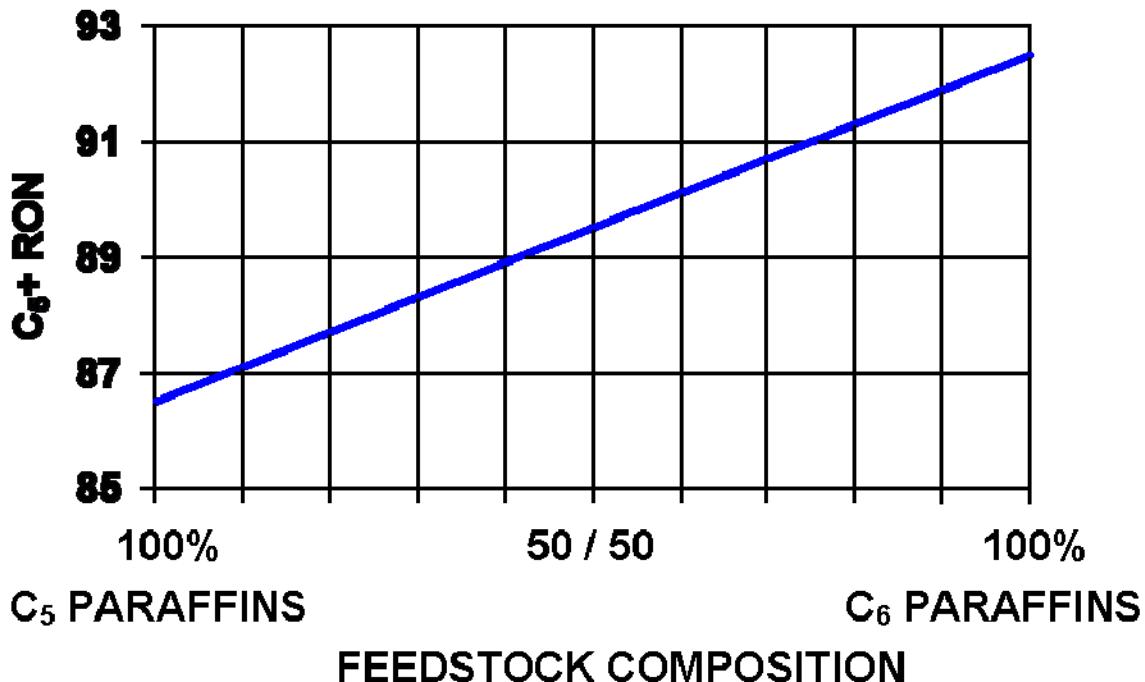
**Figure I - 5 DIP / PENEX / (SUPER) DIH FLOWSCHEME**

**Figure I - 6 PENEX / MOLEX FLOWSCHEME**

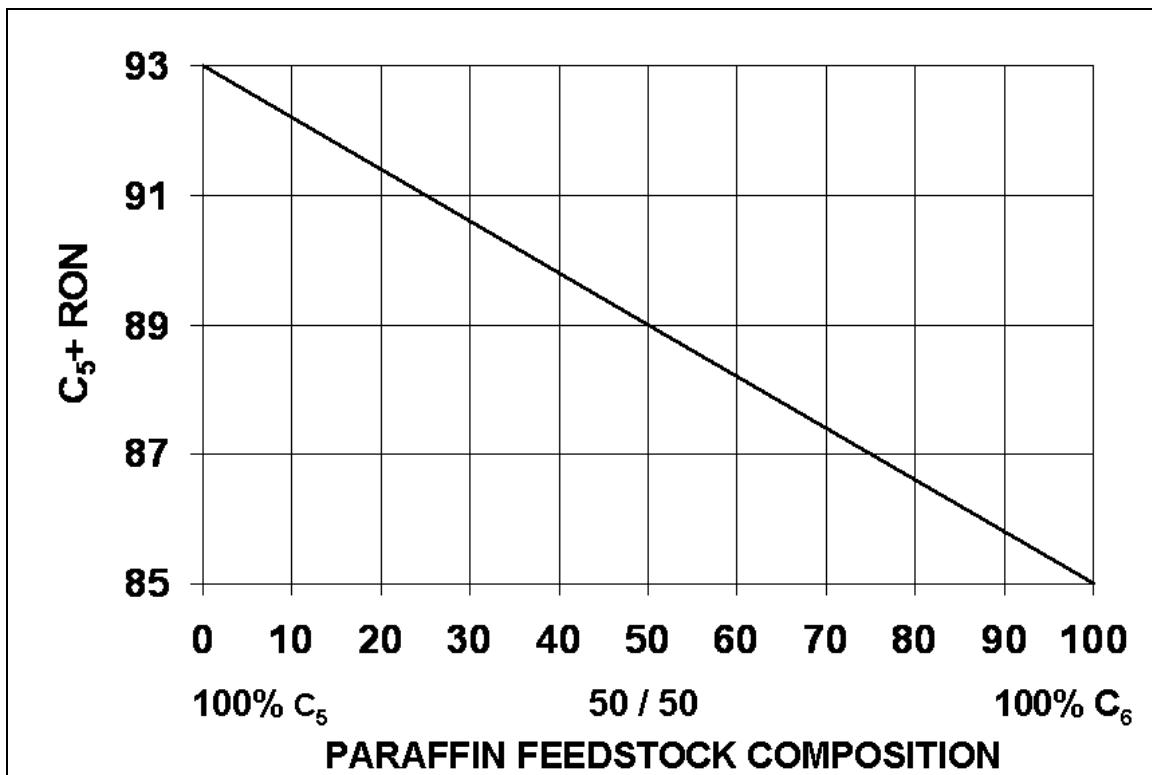
**Figure I - 7 DEISOPENTANIZER OCTANE INCREASE  
VERSUS  
FEED ISOPENTANE CONTENT**



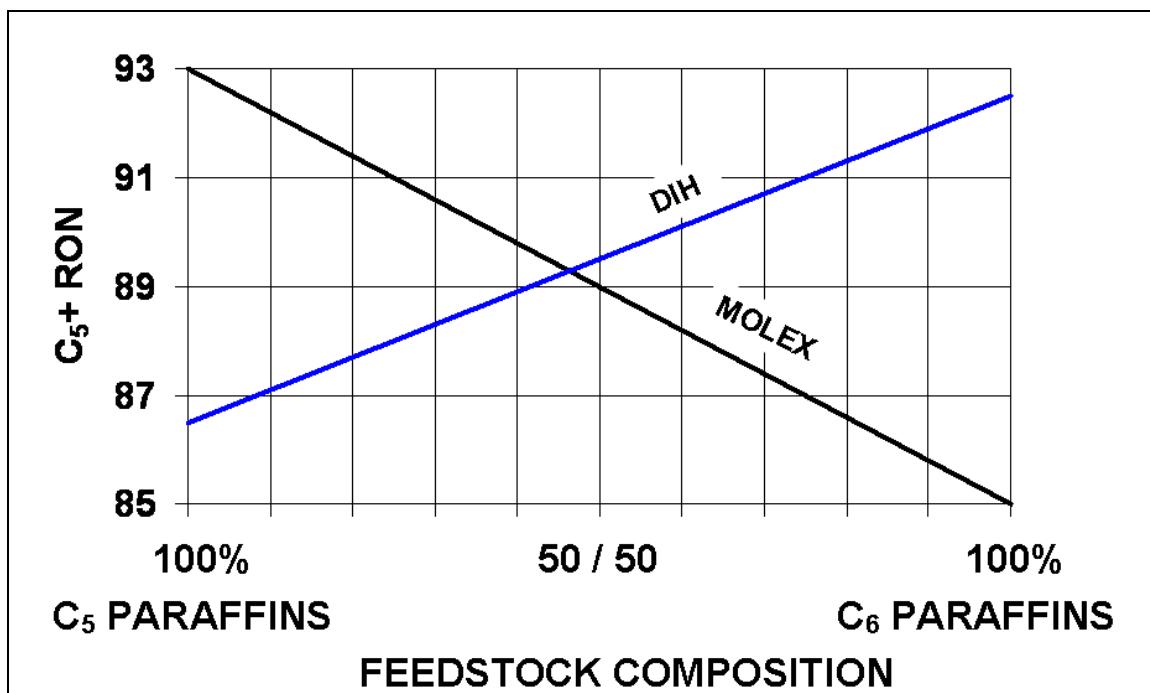
**Figure I - 8 DEISOHEXANIZER OCTANE  
VERSUS  
ISOMERIZATION FEED COMPOSITION  
BASIS: C<sub>5</sub>/C<sub>6</sub> PARAFFIN ISOMERIZATION FEED**



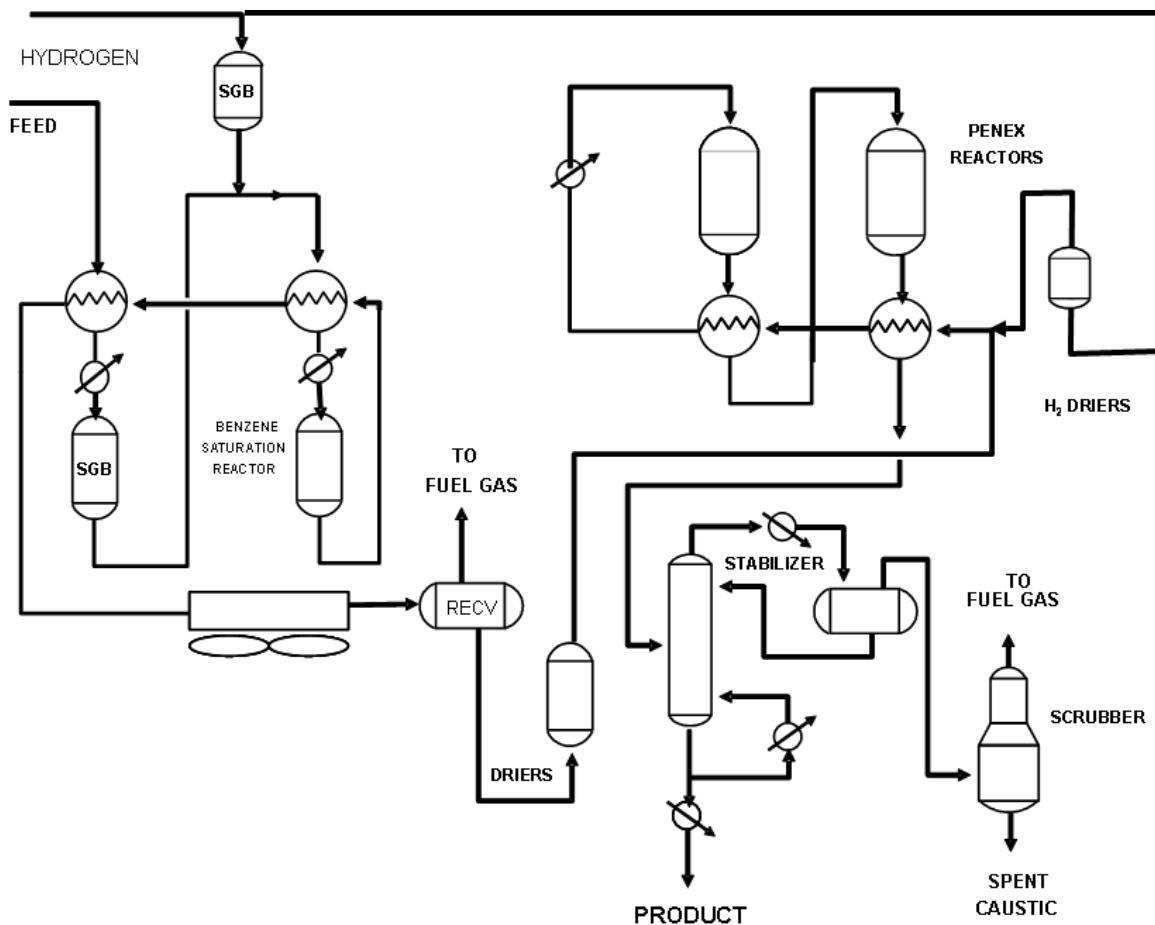
**Figure I - 9 PENEX / MOLEX OCTANE  
VERSUS  
FEED COMPOSITION**  
**BASIS: C<sub>5</sub>/C<sub>6</sub> PARAFFIN ISOMERIZATION FEED**



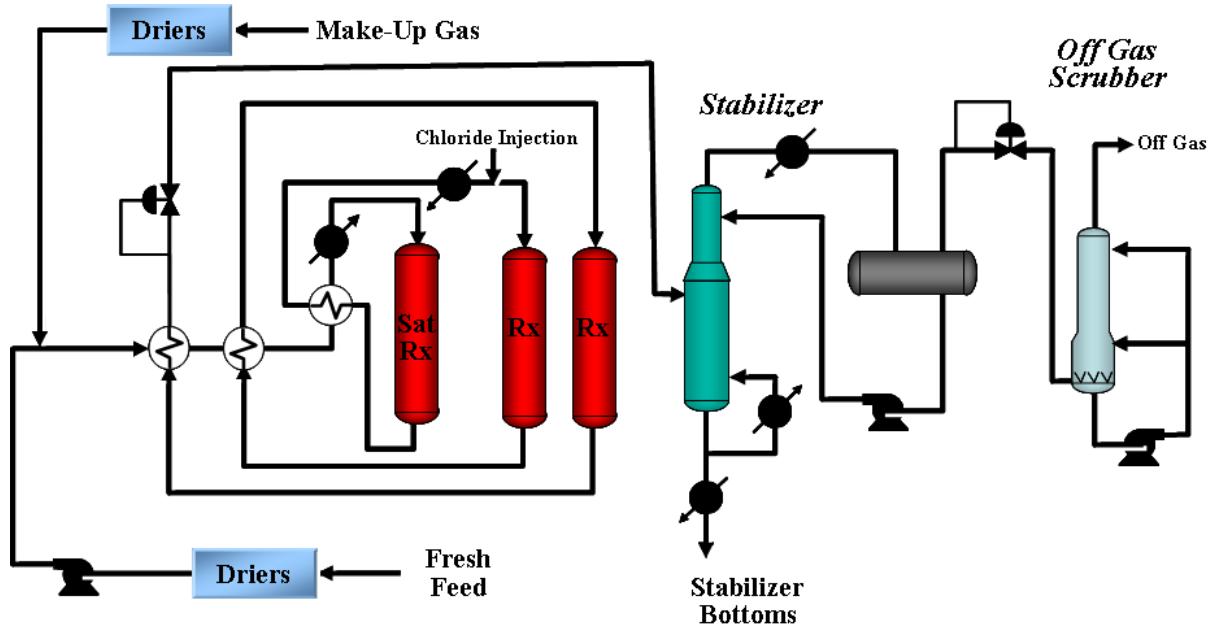
**Figure I - 10 OCTANE VERSUS FEED COMPOSITION  
PENEX / MOLEX VERSUS PENEX/DEISOHEXANIZER  
BASIS: C<sub>5</sub>/C<sub>6</sub> PARAFFIN ISOMERIZATION FEED**

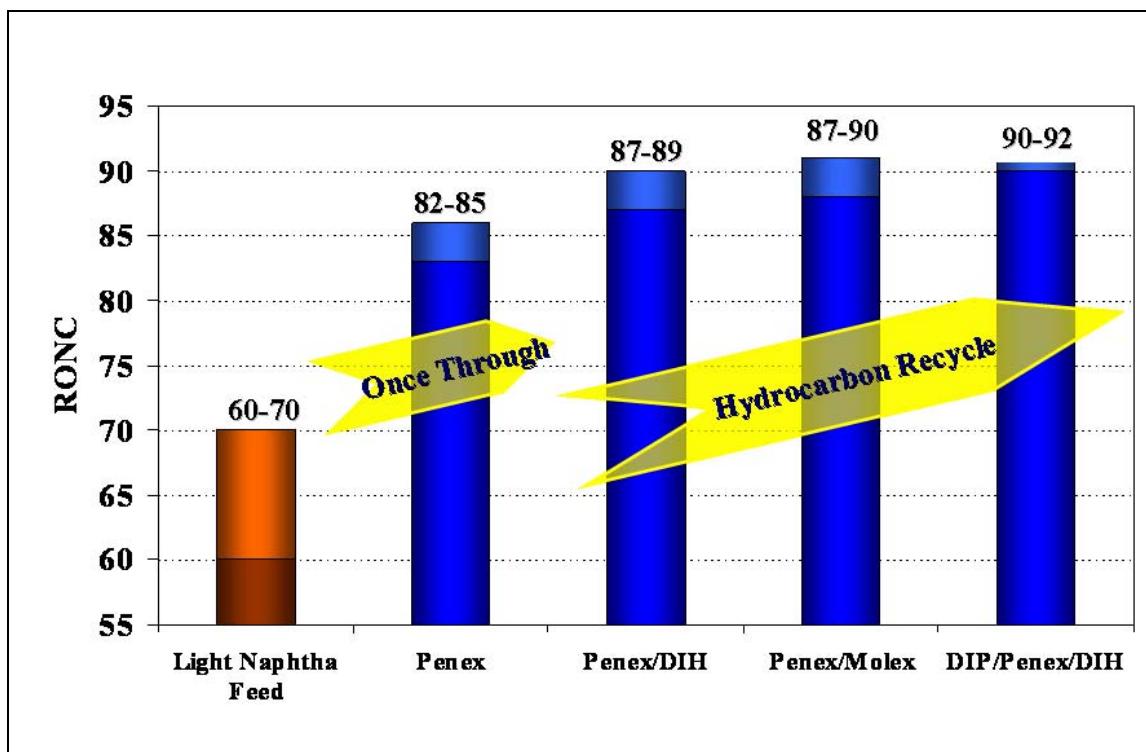


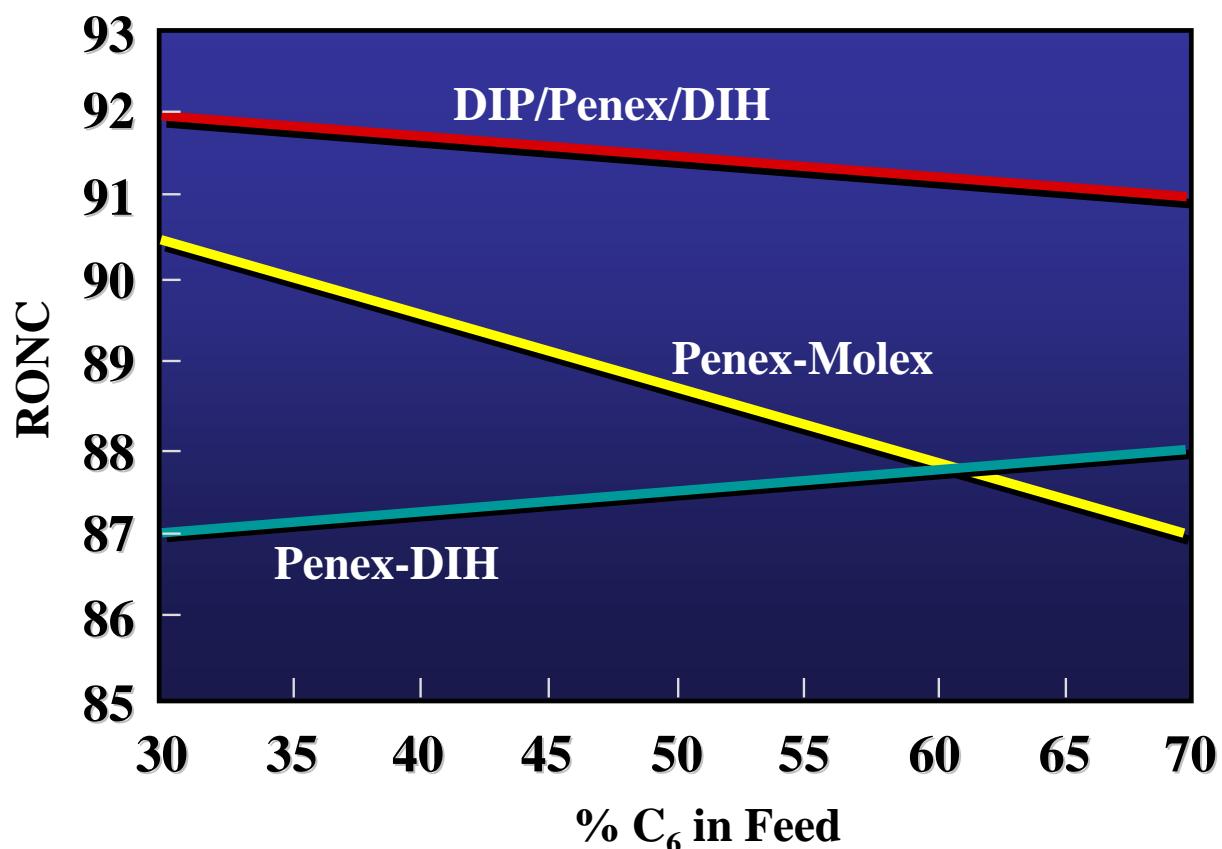
**Figure I - 11 CONVENTIONAL PENEX-PLUS FLOWSCHEM**



**Figure I - 12 INTEGRATED PENEX-PLUS FLOWSCHEM**



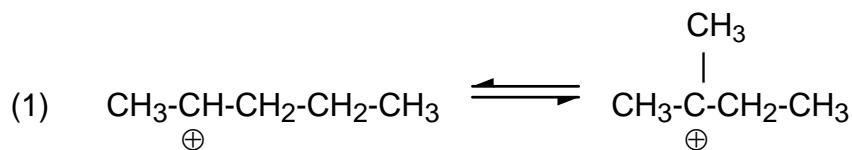
**Figure I - 13 PENEX PROCESSES OCTANE PORTFOLIO**

**Figure I - 14 SELECTING A RECYCLE FLOWSCHEME**

## II. PROCESS PRINCIPLES

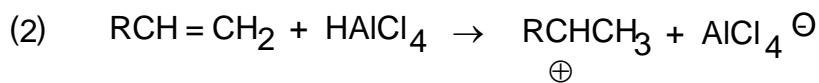
### A. REACTION MECHANISMS

Paraffin isomerization catalysts fall mainly into either of two principal categories: (1) those based on Friedel-Crafts catalysts as classically typified by 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:

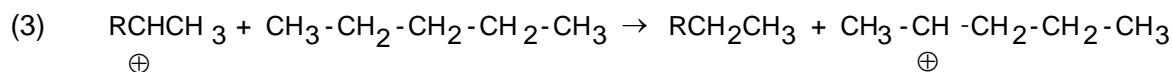


There appear to be two schools of thought regarding the Friedel-Crafts mechanism. Perhaps each mechanism is operative and the disagreement is merely over their relative importance under specific circumstances.

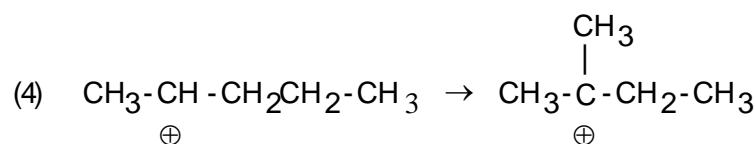
Friedel-Crafts isomerization is believed by some to require the presence of traces of olefins or alkyl halides as carbonium ion initiators, with the reaction thereafter proceeding through chain propagation. The initiator ion, which needs to be present in small amounts only, may be formed by the addition of HCl or  $\text{HAICl}_4$  to an olefin, which is present in the paraffin as an impurity or which is formed by cracking of the paraffin:



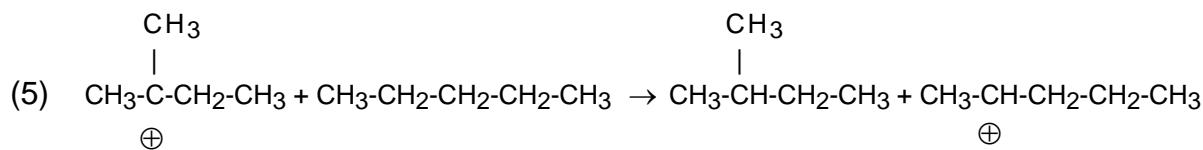
The initiator then forms a carbonium ion from the paraffin to be isomerized:



Skeletal rearrangement then occurs:

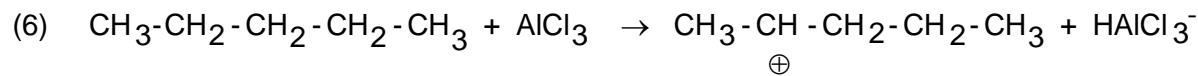


Isopentane is then formed and the chain propagated by the generation of a new normal carbonium ion:

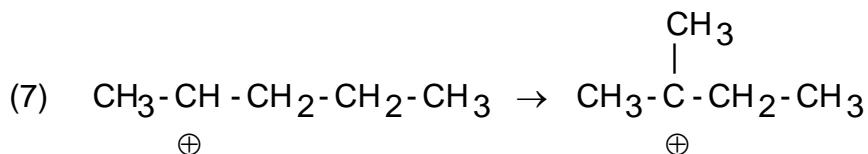


Naturally, the same sequence could have been illustrated starting with isopentane and ending with n-pentane and an iso-carbonium ion to propagate the chain, i.e., reactions (3), (4), and (5) are reversible, as are all of the reactions to be shown later. The composition of the final mixture is, of course,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

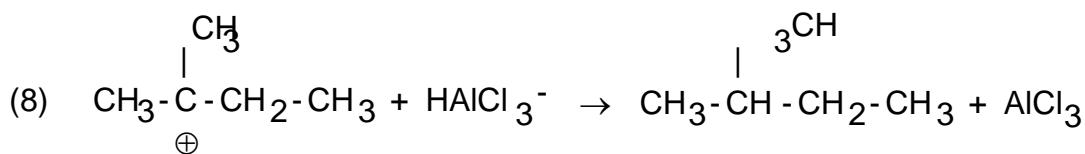
Another Friedel-Crafts route which has been suggested is direct hydride ion abstraction:



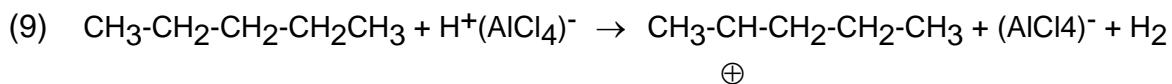
The carbonium ion, as before, rearranges



Finally, iso-pentane is formed:

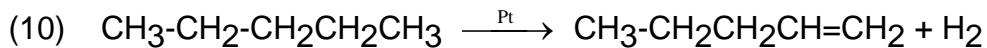


Abstraction of the hydride ion is energetically favored by the fact that the aluminum atom can thereby complete its electron octet. Since there is always some hydrogen chloride present, either by design or from hydrolysis of aluminum chloride by traces of water, a Bronsted (protic) acid could have been shown for Reactions (6) and (8) instead of a Lewis acid:



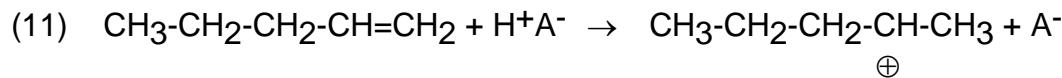
$\oplus$

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, assumed for illustration purposes to be platinum:

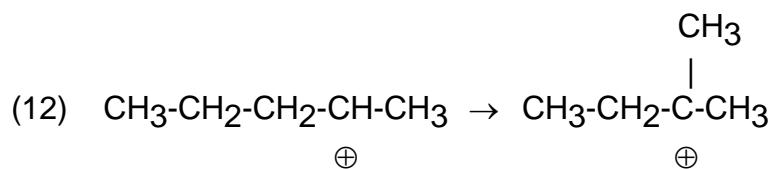


This reaction is, of course, reversible and, since these catalysts are employed under substantial hydrogen pressure, the equilibrium is far to the left. However, the acid function of the catalyst consumes the olefin by formation of a carbonium ion and thus permits more olefin to form despite the unfavorable equilibrium. This step

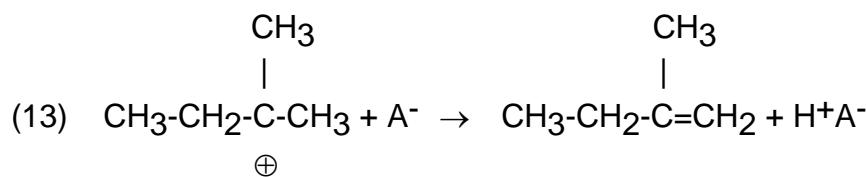
is entirely analogous to Reaction (2) shown for Friedel-Crafts, except that it is better to denote the acid function by a more general “ $H^+A^-$ .”



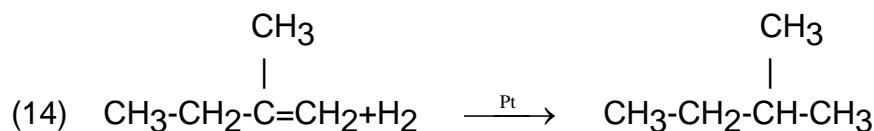
The usual rearrangement ensues:



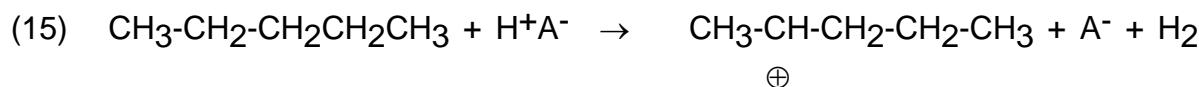
The iso-olefin is then formed by the reverse analog of (11):

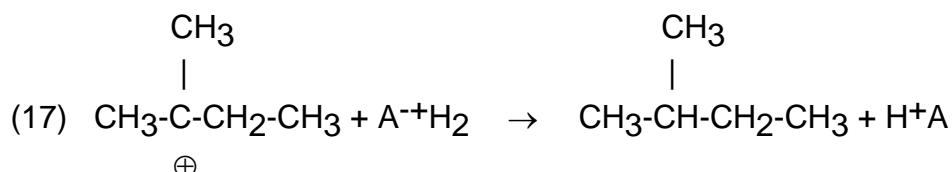
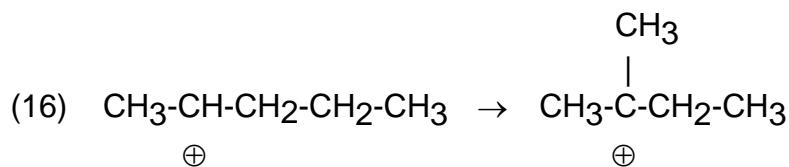


The iso-paraffin is finally created by hydrogenation:



Those dual-functional hydro-isomerization catalysts which operate at very low temperatures have stronger acid sites than those which require higher temperatures. In this case it is possible that the necessary carbonium ion is formed by direct hydride ion abstraction from the paraffin by the acid function of the catalyst:





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.

## B. ALUMINUM CHLORIDE

The isomerization catalysts employed during World War II were all of the Friedel-Crafts type. Those which contained aluminum chloride only were either a hydrocarbon/aluminum chloride complex (the so-called sludge process) or they were manufactured in-situ by deposition onto a support such as alumina or bauxite. They were intended to operate at very low temperatures [49-129°C (120-265°F)] and to approach the very favorable equilibrium composition characteristic of these temperatures.

The catalyst tended to consume itself by reaction with the feedstock and/or product. When temperature was raised a little in an effort to compensate for loss of catalyst and to speed the reaction to effect more isomerization, light fragments were formed by cracking and these, when vented, caused an excessive loss of the HCl promoter.

Corrosion of downstream equipment was also commonplace, due to the solubility of aluminum chloride in hydrocarbon, to its relatively high volatility and to the difficulty of removing it from the product by caustic washing. Aluminum chloride deposition in and plugging of reboiler tubes was not uncommon.

The process faced problems in sludge disposal which were considered onerous even before the present acute awareness of environmental factors developed. The fixed bed process sometimes experienced unpredictable amounts of isomerization.

### C. HYDRO-ISOMERIZATION CATALYSTS [ABOVE 199°C (390°F)]

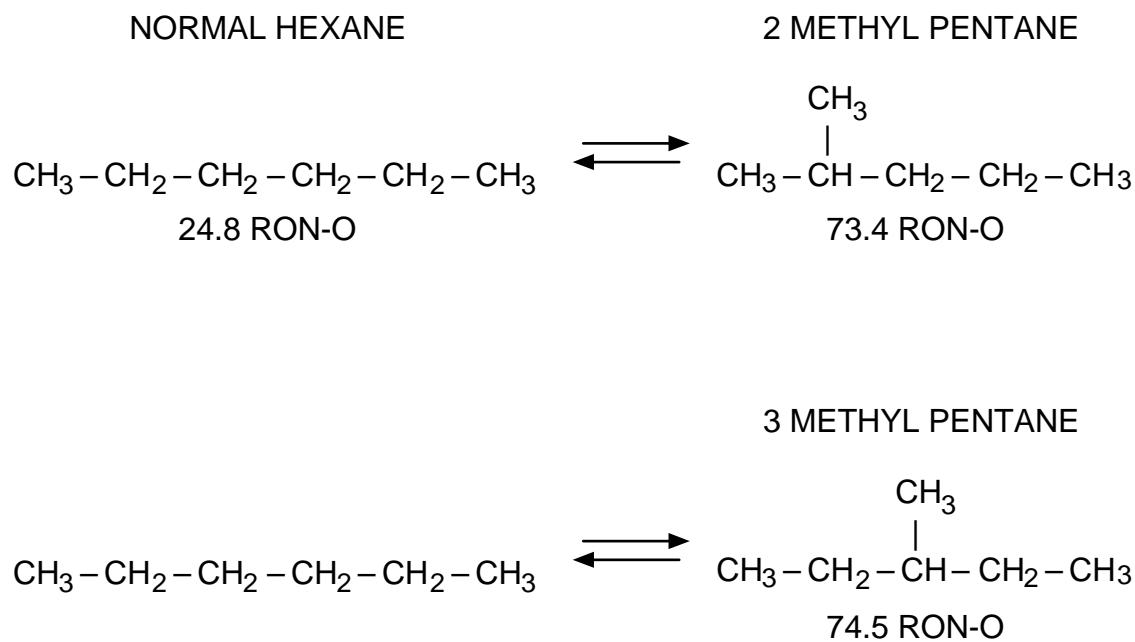
The operational problems which had characterized the wartime Friedel-Crafts type isomerization plants, the advent of catalytic reforming which not only made hydrogen generally available in refineries but also demonstrated the practicality of using noble metal containing catalysts on a large scale, and the octane number race which postwar high compression engines initiated all combined in the 1950's to spawn a spate of hydro-isomerization processes. These catalysts generally contained a noble metal and some halide, operated at temperatures between about 299°C (560°F) and temperatures approaching those characteristic of catalytic reforming, employed recycle hydrogen to prevent catalyst carbonization and utilized either no promoter or traces at most. In general, they did not require an especially dry feedstock but did benefit from a low sulfur content feedstock. Most achieved a close approach to the equilibrium characteristic of their particular operating temperature.

Because of their high operating temperatures and their necessarily low conversions to iso-paraffins, these high temperature catalysts were quickly replaced with the advent of the "third generation" low temperature catalysts.

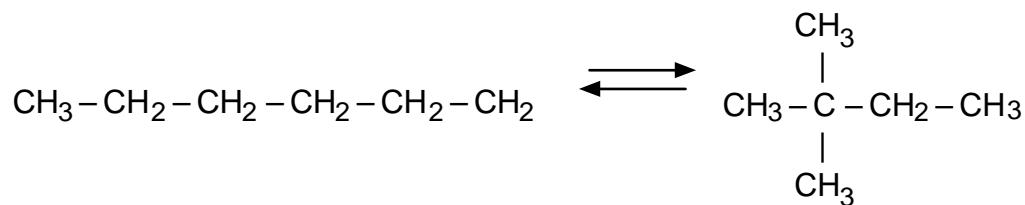
## D. HYDRO-ISOMERIZATION CATALYSTS [BELOW 199°C (390°F)]

"Low temperature" is considered rather arbitrarily for catalyst classification purposes as anything below 199°C (390°F) operating temperature. Typically these are fixed bed catalysts containing a supported noble metal and a component to provide acidity in the catalytic sense. They operate in a hydrogen atmosphere and may employ a catalyst promoter whose concentration in the reactor may range from parts per million to substantially higher levels. They generally all require a dry, low sulfur feedstock; however, they may differ importantly in their tolerance of certain types and molecular weights of hydrocarbons. Hydrocracking to light gases is generally slight, so liquid product yields are high. The type of catalyst used in the Penex unit is of this type.

The C<sub>5</sub>/C<sub>6</sub> paraffin isomerization reactions which occur in the Penex unit are shown below. The octanes presented in this section are for pure components. Blending octanes are presented in Table III-2.

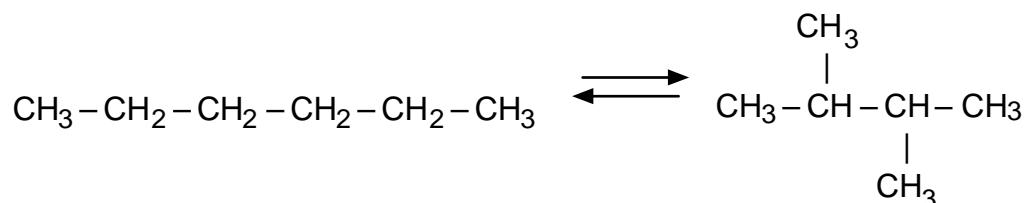


## 2-2 DIMETHYL BUTANE



91.8 RON-O

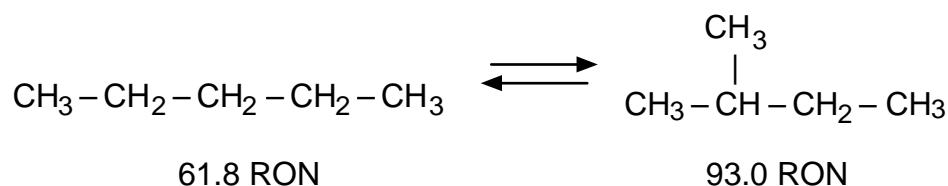
## 2-3 DIMETHYL BUTANE



104.3 RON-O

## ISO PENTANE

## NORMAL PENTANE



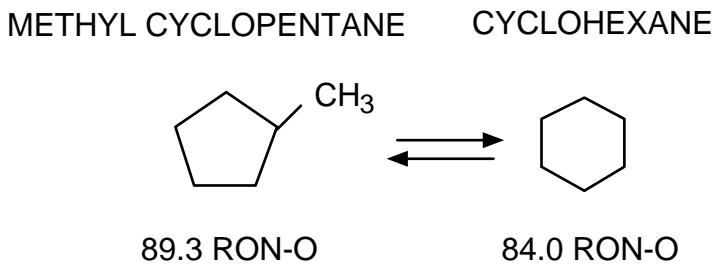
## E. OTHER REACTIONS

Apart from the paraffin isomerization reactions which were discussed in detail in the proceeding pages, there are several other important reactions including:

1. **Naphthene ring opening.**
2. **Naphthene isomerization.**
3. **Benzene saturation.**
4. **Hydrocracking.**

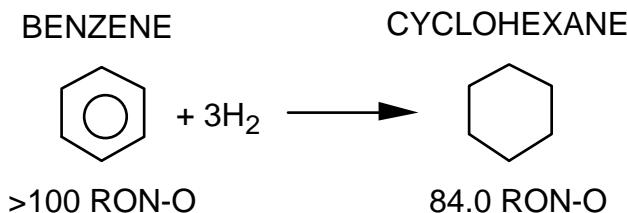
**Ring Opening:** The three naphthenes which are typically present in Penex feed are cyclopentane (CP), methyl cyclopentane (MCP) and cyclohexane (CH). The naphthene rings will hydrogenate to form paraffins. This ring opening reaction increases with increasing reactor temperature. At typical isomerization reactor conditions, the conversion of naphthene rings to paraffins will be on the order of 20-40 percent.

**Naphthene Isomerization:** The naphthenes MCP and CH exist in equilibrium. Naphthene isomerization will shift towards MCP production as temperature is increased.

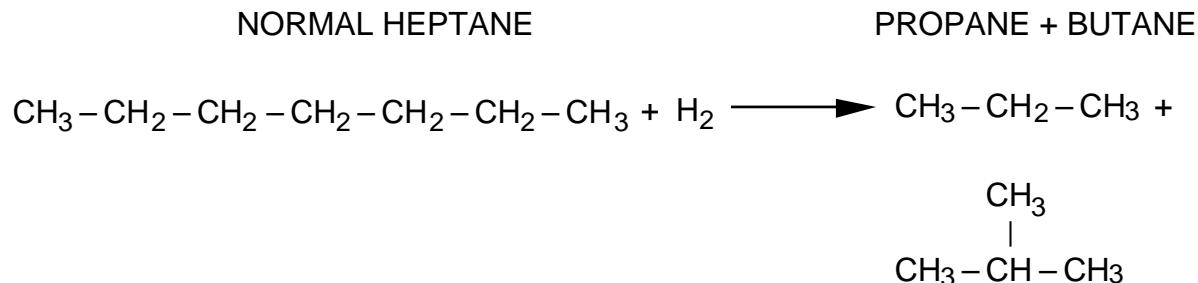


**Benzene Saturation:** The isomerization section is generally designed for 2 LV% benzene. The Penex catalyst will saturate benzene to cyclohexane. This reaction proceeds very quickly and is achieved at very low temperatures. Saturation of benzene is not equilibrium limited at the isomerization reactor conditions and conversion should be 100%. The amount of heat generated by the saturation of

benzene limits the amount of benzene which can be tolerated in the Penex feed. The isomerization section feed can contain up to 5% benzene. The platinum function on the isomerization catalyst is responsible for benzene saturation.

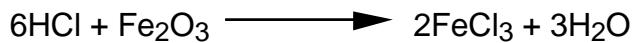
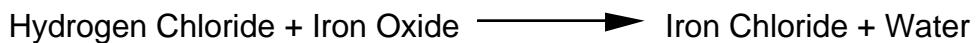


**Hydrocracking:** Hydrocracking occurs in the Penex reactors to a degree which depends on the feed quality and severity of operation. Large molecules such as C<sub>7</sub>'s tend to hydrocrack more easily than smaller molecules. C<sub>5</sub> and C<sub>6</sub> paraffins will also hydrocrack to a certain extent. As C<sub>5</sub>/C<sub>6</sub> paraffin isomerization approaches equilibrium, the extent of hydrocracking increases. If isomerization is pushed too hard, hydrocracking will reduce the liquid yield and increase heat production. Methane, ethane, propane and butane are produced as a result of hydrocracking.



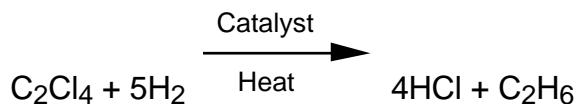
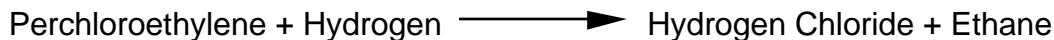
## ACIDIZING

During the initial commissioning period, hydrogen chloride (HCl) is injected into the process stream where it reacts with iron oxide ( $\text{Fe}_2\text{O}_3$ ) to form Iron Chloride ( $\text{FeCl}_3$ ) and water. This reaction will continue to take place until the rust present in the unit is depleted. The absence of  $\text{H}_2\text{O}$  in the unit, as detected by the moisture analyzers, will signify that the reaction has gone to completion.



## CHLORIDE PROMOTER

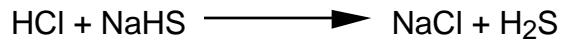
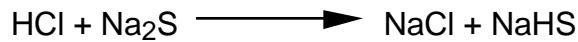
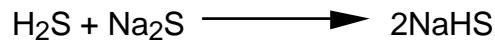
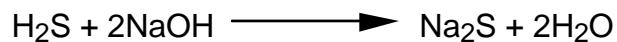
The addition of the chloride promoter (perchloroethylene  $\text{C}_2\text{Cl}_4$ ) to the process stream is intended to maintain the acid function of the catalyst with chloride atoms (Cl). At a reactor temperature of 105°C (220°F) or higher, the organic chloride will decompose to HCl in the presence of the Penex catalyst.

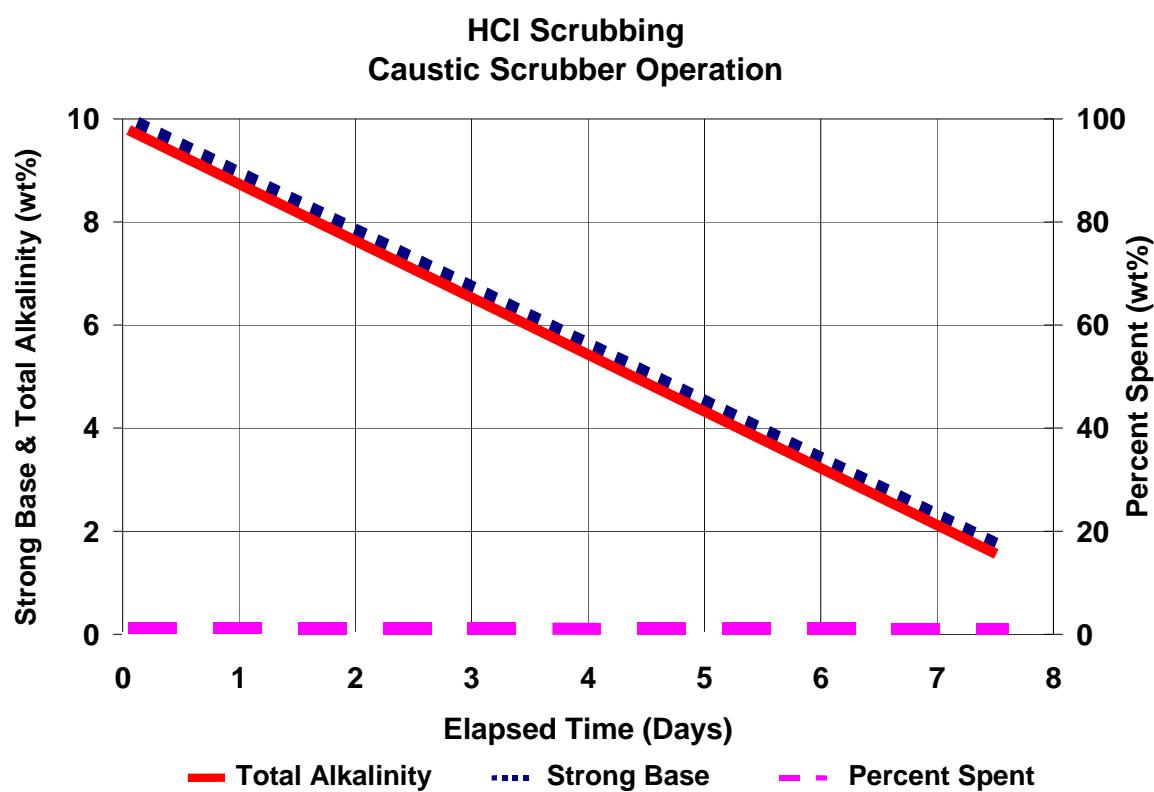


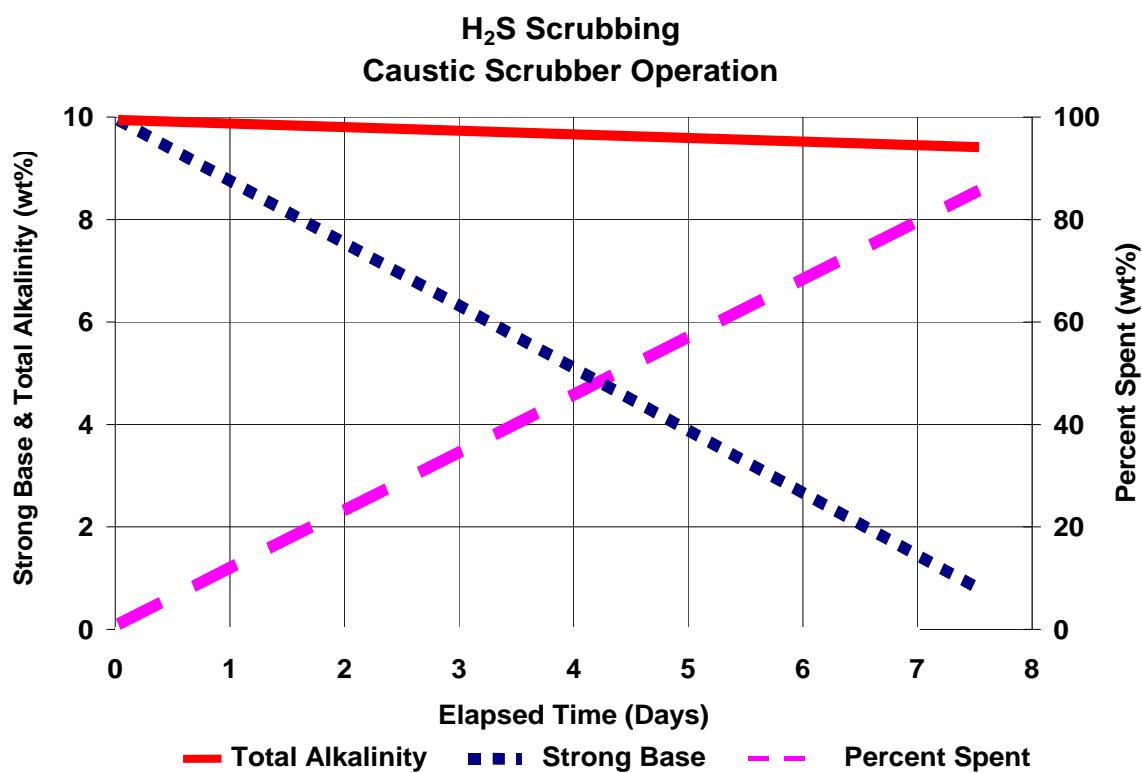
## CAUSTIC SCRUBBING

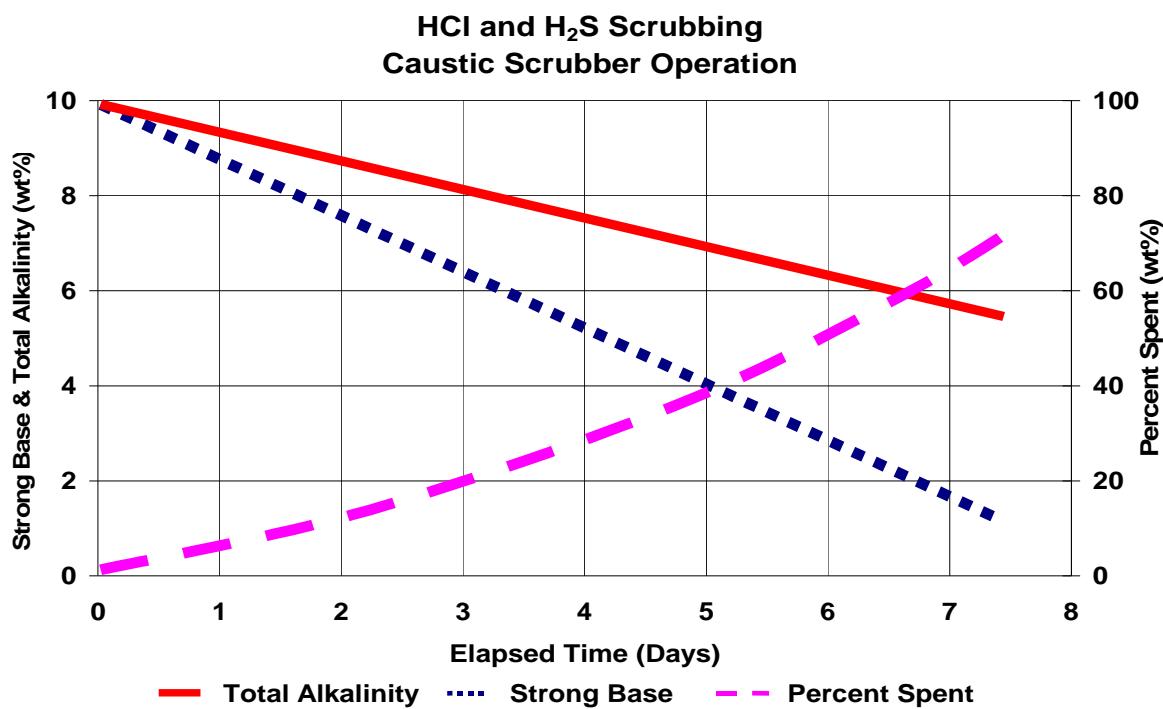
The hydrogen chloride formed in the isomerization reactors is neutralized in the Stabilizer Net Gas Scrubber, by means of an acid-base reaction between sodium hydroxide ( $\text{NaOH}$ ) and hydrogen chloride (HCl). The result of this neutralization reaction is sodium chloride ( $\text{NaCl}$ ) and water. A diagram of the caustic scrubbing operation is shown in Figure II-1. The strength of the caustic should be monitored by determining the total alkalinity of the solution. Report the concentration of strong base as wt% NaOH.

If a hydrogen stripping operation is performed, hydrogen sulfide ( $\text{H}_2\text{S}$ ) will be present in the stabilizer off gas and will react with sodium hydroxide to form sodium sulfide ( $\text{Na}_2\text{S}$ ), sodium bisulfide ( $\text{NaHS}$ ) 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. Report the concentration of strong base as wt% NaOH.



**FIGURE II-1**

**FIGURE II-2**

**FIGURE II-3**

## III. PROCESS VARIABLES

In the normal operation of a Penex Unit, having once set the operating pressure, fresh feed rate and makeup hydrogen flows, it is usually only necessary to adjust the reactor inlet temperatures. 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.

Once the catalyst has been loaded into the unit, the manner in which the catalyst is placed in service and the treatment it receives when in service will to a large extent influence its effectiveness for making quality product as well as the length of service it will give. In making any changes to the operation, the welfare of the catalyst must be given prime consideration for it can be regarded as the heart of the operation on which the quality of the results obtained will depend.

In the discussion which follows, the "product isomer ratio" refers to the weight percentage ratio of isopentane to total C<sub>5</sub> aliphatic paraffins, or the weight percentage ratio of 2,2 and 2,3 dimethyl butane in the total C<sub>6</sub> aliphatic paraffins in the stabilizer bottoms stream. The term "Liquid feed, reactor charge, and "combined feed," refer to the C<sub>5</sub>/C<sub>6</sub> charge to the liquid feed driers of the unit, the effluent from the liquid feed driers, and the reactor charge plus makeup hydrogen, respectively.

### A. REACTOR TEMPERATURE

In general, reactor temperature is the main process control. A definite upper limit exists for the amount of iso-paraffins which can exist in the reactor product at any given outlet temperature, as shown in Figures III-1, III-2 and III-3. This is the equilibrium imposed by thermodynamics, and it can be reached only after an infinite length of time, i.e. with an infinitely large reactor. In practice, therefore, the product will contain less than this equilibrium concentration of iso-paraffins. As reactor temperature is raised to increase the rate of isomerization, the equilibrium composition will be approached more closely. At excessively high temperatures, the

concentration of iso-paraffins in the product will actually decrease because of the downward shift in the equilibrium curve, even though the high temperature gives a higher reaction 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.

The use of temperatures higher than necessary to achieve a reasonably close approach to equilibrium accomplishes nothing other than to increase the amount of hydrocracking. Extremely high temperatures may lead to an increased rate of carbon laydown on the catalyst; however, the carbon forming propensity of the catalyst is inherently so low that excessive hydrocracking would normally be encountered before carbon formation problems would develop. It is recommended, however, that UOP be consulted before temperatures above about 204°C (400°F) are employed.

A typical C<sub>5</sub>/C<sub>6</sub> Penex Unit has two series reactors with provision for independent temperature control. The first reactor system affects the bulk of the isomerization, so long as most of the catalyst therein is still active. Any benzene in the feed is hydrogenated in the first reactor, even when the catalyst therein has lost its activity with respect to paraffin isomerization. Some conversion, ring opening, of cyclohexane and methyl cyclopentane to hexanes also occurs, as does some hydrocracking of C<sub>7</sub> to C<sub>3</sub> and C<sub>4</sub>. These three reactions (benzene hydrogenation, naphthene ring opening to hexane, and C<sub>7</sub> hydrocracking) are exothermic and, for a typical feed stock contribute more to the temperature rise in the first reactor than does paraffin isomerization, which is also exothermic.

Normally, the first reactor system will be operated at such a temperature as to maximize the concentration of isopentane and 2,2 dimethyl butane in its effluent. The concentrations attainable and the required outlet temperature will be influenced by the amount of active catalyst present and by the amount of C<sub>6</sub> cyclic and C<sub>7+</sub> components present in the feed, higher the temperatures being required with high concentrations of these components in the feed. By this procedure, the required operating temperature on the second reactor system is reduced and it is possible to operate under conditions where the equilibrium is more favorable.

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<sub>6</sub> cyclics. Since these materials tend to reduce the rate of paraffin isomerization, it may be beneficial with very C<sub>6</sub> 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.

## B. LIQUID HOURLY SPACE VELOCITY

This term, commonly shortened to LHSV, is defined as the volumetric hourly flow of reactor charge divided by the volume of catalyst contained in the reactors in consistent units. The design LHSV for C<sub>5</sub>/C<sub>6</sub> Penex operation is normally between 1 and 2. Increasing the LHSV beyond this will lead to lower product isomer ratios.

In order to avoid excessive reactor severity, the H.O.T. Penex reactor LHSV should always be maintained above 0.5 Hr.<sup>-1</sup> overall or 1.0 LHSV minimum per reactor.

## C. HYDROGEN TO HYDROCARBON MOL RATIO

This ratio is defined as the number of mols hydrogen at the reactor outlet per mol of reactor charge passing over the catalyst, and is specified at 0.05 mols H<sub>2</sub>/mol HCBN. The primary purpose of maintaining the ratio at or above the design is to avoid carbon deposition on the catalyst and maintain enough H<sub>2</sub> for the reactions to proceed. If necessary, the reactor charge rate is to be reduced to maintain the design hydrogen to hydrocarbon ratio. The H<sub>2</sub>/HCBN ratio is determined by measuring the total mols of hydrogen in the stabilizer overhead gas and dividing by the total moles of fresh feedstock.

## D. PRESSURE

C<sub>5</sub>/C<sub>6</sub> Penex Units are normally designed to operate at 31.6 kg/cm<sup>2</sup>g (450 psig) at the reactor outlet. Methylcyclopentane and cyclohexane appear to adsorb on the catalyst and reduce the rate of isomerization reactions. Higher pressure helps to offset this effect of the C<sub>6</sub> cyclic compounds. Lowering the unit pressure or operating at a slightly lower level would not affect the catalyst life but the extent of isomerization would be influenced.

## E. CATALYST PROMOTER

To sustain catalyst activity, the addition of chloride is necessary. At no time should the plant be operated for longer than six hours without the injection of chloride. Whenever there is a catalyst chloride deficiency, the product isomer ratios will decrease (although not necessarily instantaneously), other things being equal. Restarting the injection of chloride will tend to return the activity of the catalyst to its previous level, but it is possible that full activity will not be restored if a decline in activity as a result no chloride injection has been observed. Isomerization grade perchloroethylene ( $C_2Cl_4$ ) is UOP's recommended source of chloride.

## F. 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.  $C_7+$  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.

## **G. CONTAMINANTS**

### **1. Sulfur**

The presence of sulfur in the combined feed will decrease 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. 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.

### **3. Nitrogen Compounds**

These compounds normally react with the chloride in the catalyst or the HCl to form salts which can deactivate the catalyst permanently by coating the catalyst active sites, loss of chloride or maldistribution due to salt deposits.

### **4. Fluoride Compounds**

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

Although the Penex Process will tolerate certain hydrocarbon components, they should be minimized in the feedstock to assure optimum unit performance.

## **H. UNDESIRABLE HYDROCARBONS**

### **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<sub>5</sub>/C<sub>6</sub> fraction from a catalytic reformate are acceptable, but highly olefinic streams of thermal or FCC origin cannot be handled without prior hydrogenation to saturate the compounds. The adverse effect of appreciable quantities of olefins is thought to be due to their physically coating the catalyst following polymerization.

### **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<sub>6</sub> naphthenes are converted to C<sub>6</sub> 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<sub>6</sub> cyclics will result also in an exclusion in part of the normal hexane. Special fractionation facilities are not required for the UOP Penex Process.

### **3. C<sub>7+</sub> Hydrocarbons**

It is preferable to restrict the C<sub>7+</sub> content of the feedstock to the UOP Penex Process to 2 or 3%. C<sub>7</sub> paraffins hydrocrack quite readily to C<sub>3</sub> and C<sub>4</sub>, and those which do not hydrocrack will be isomerized to a mixture having a lower octane number than the C<sub>5</sub> or C<sub>6</sub> produce and will thus degrade the overall product octane number. C<sub>7</sub> naphthenes have the same adverse effect as the C<sub>6</sub> naphthenes described above, but to an even greater degree. Of course, the levels of the cyclic and C<sub>7</sub> hydrocarbons above mentioned are not normally expected unless there are plant upsets on the prefractionation equipment upstream of the Penex unit.

### **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 III-1**  
**TYPICAL LIMITS ON STREAM IMPURITIES**

**PENEX REACTOR CHARGE**

<b>Impurity</b>	<b>Typical Limit</b>	<b>Laboratory Method</b>
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**

<b>Impurity</b>	<b>Typical Limit</b>	<b>Laboratory Method</b>
Hydrogen Sulfide	1 mole-ppm	Detector Tube
NH <sub>3</sub>	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 III-2**  
**PROPERTIES USEFUL IN PREDICTING**  
**ISOMERATE PRODUCT QUALITY**

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 <sub>7+</sub> (Feed)	0.6915	1.97	100.198	55.0	78.0	55.0	79.0
C <sub>7+</sub> (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.

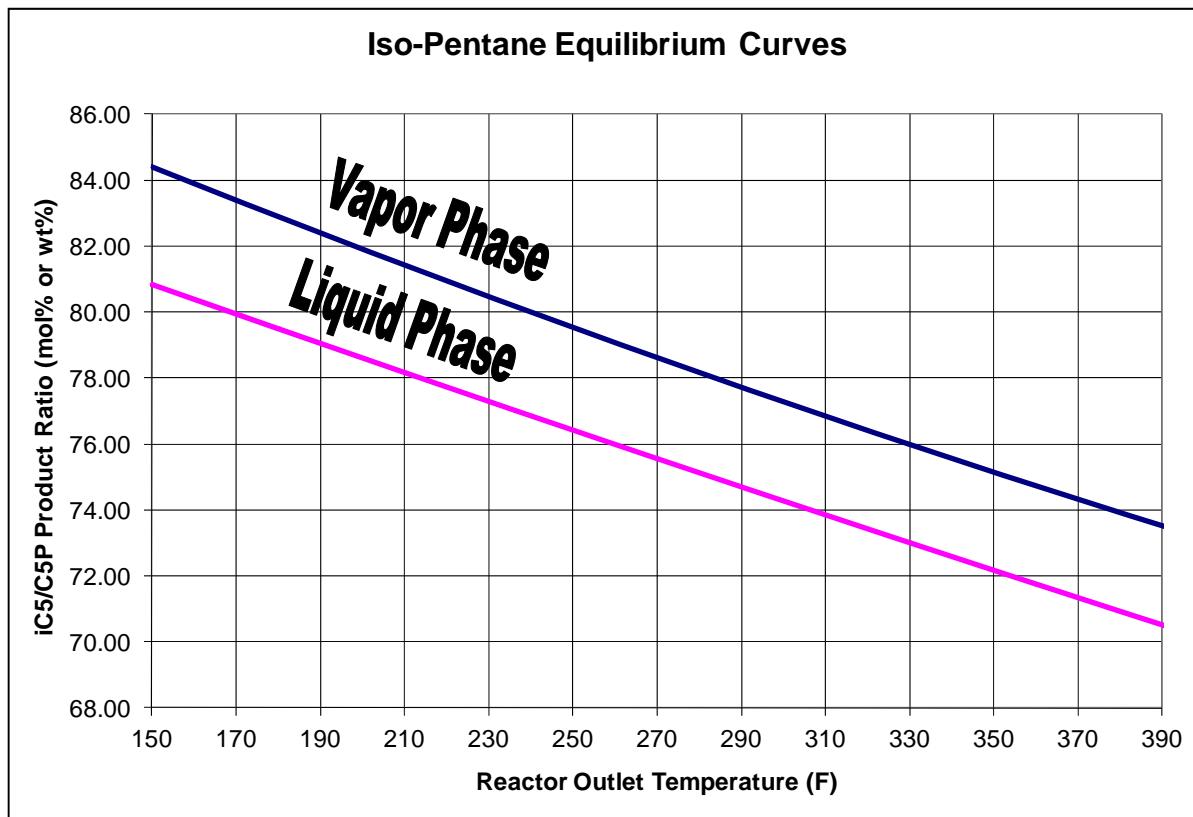
**TABLE III-3**  
**NAPHTHA FRACTIONATION**

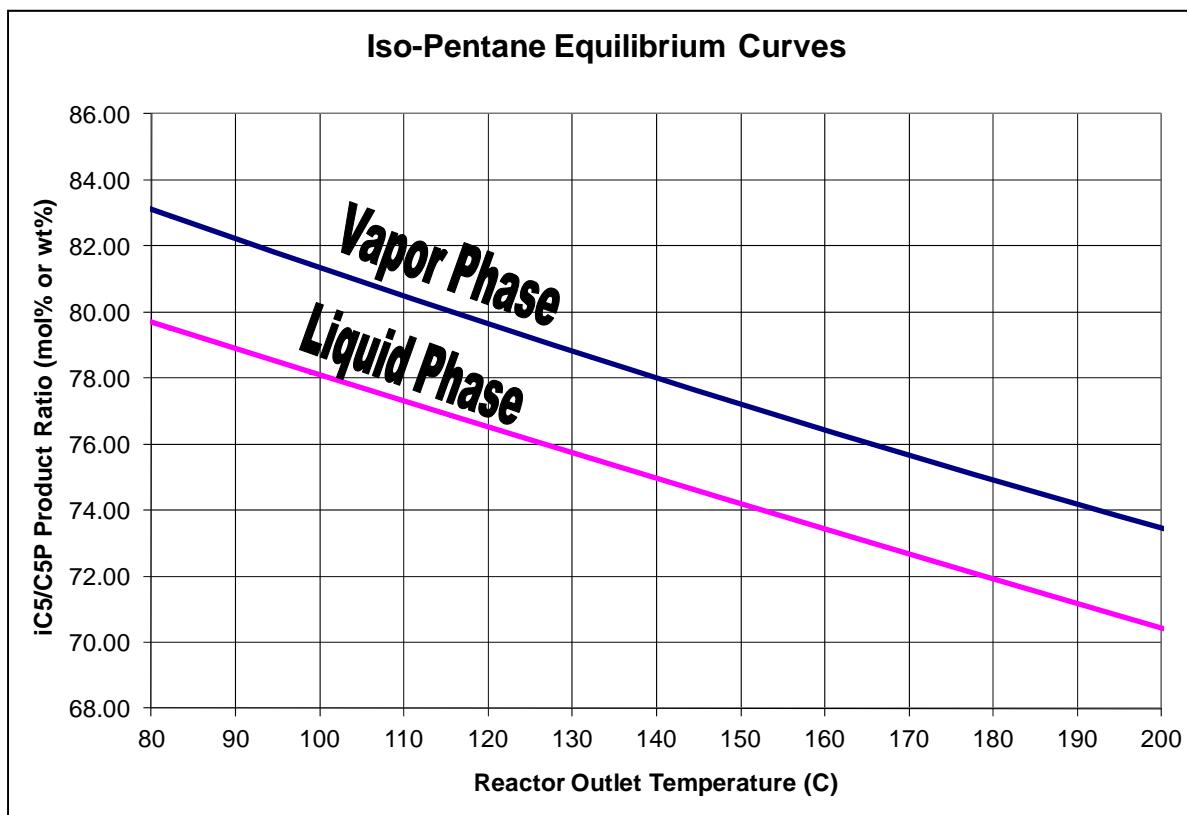
<b>Component</b>	<b>Boiling Point (F)</b>	<b>Boiling Point (C)</b>	<b>Relative Volatility</b>
Isopentane	82	28	3.18
n-Pentane	97	36	2.71
2,2 Dimethylbutane	122	50	1.90
2,3 Dimethylbutane	136	58	1.59
2 Methylpentane	140	60	1.53
3 Methylpentane	146	63	1.42
n-Hexane	156	69	1.26
Methylcyclopentane	161	72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

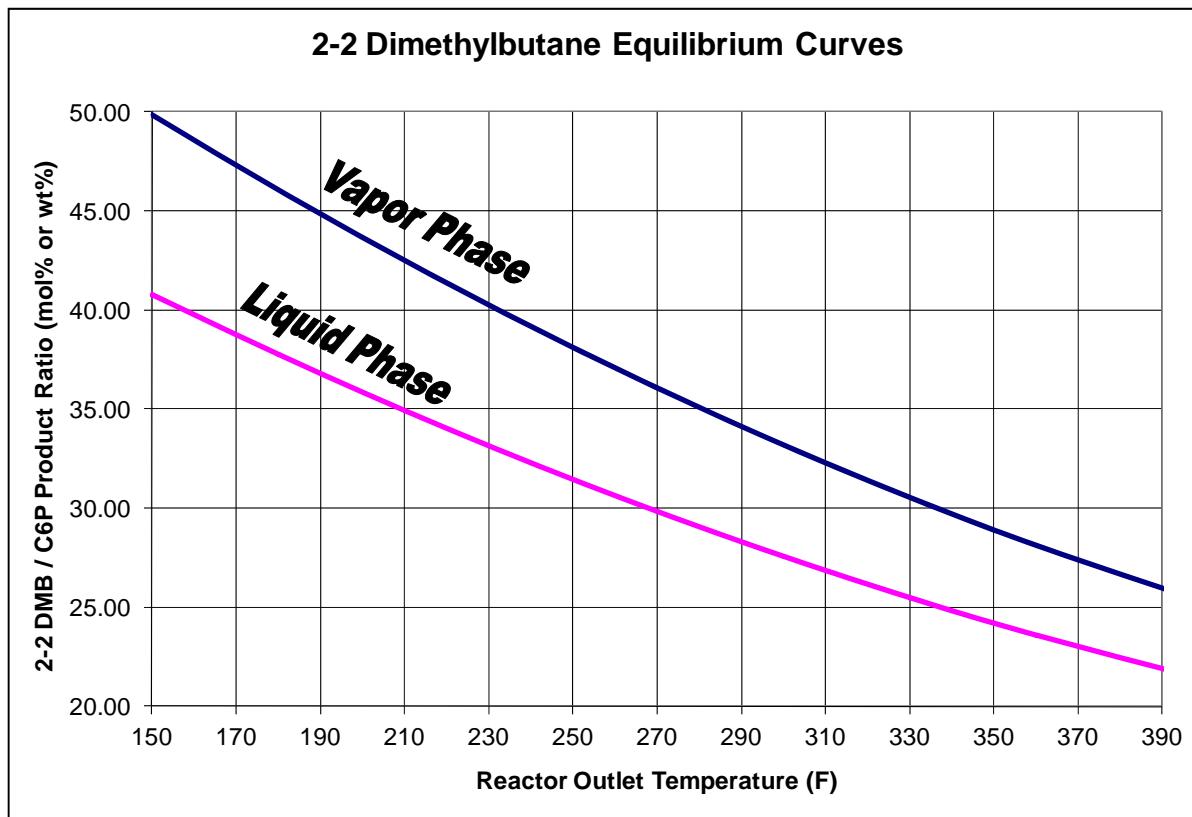
**TABLE III-4**  
**PROPERTIES OF Perchloroethylene**

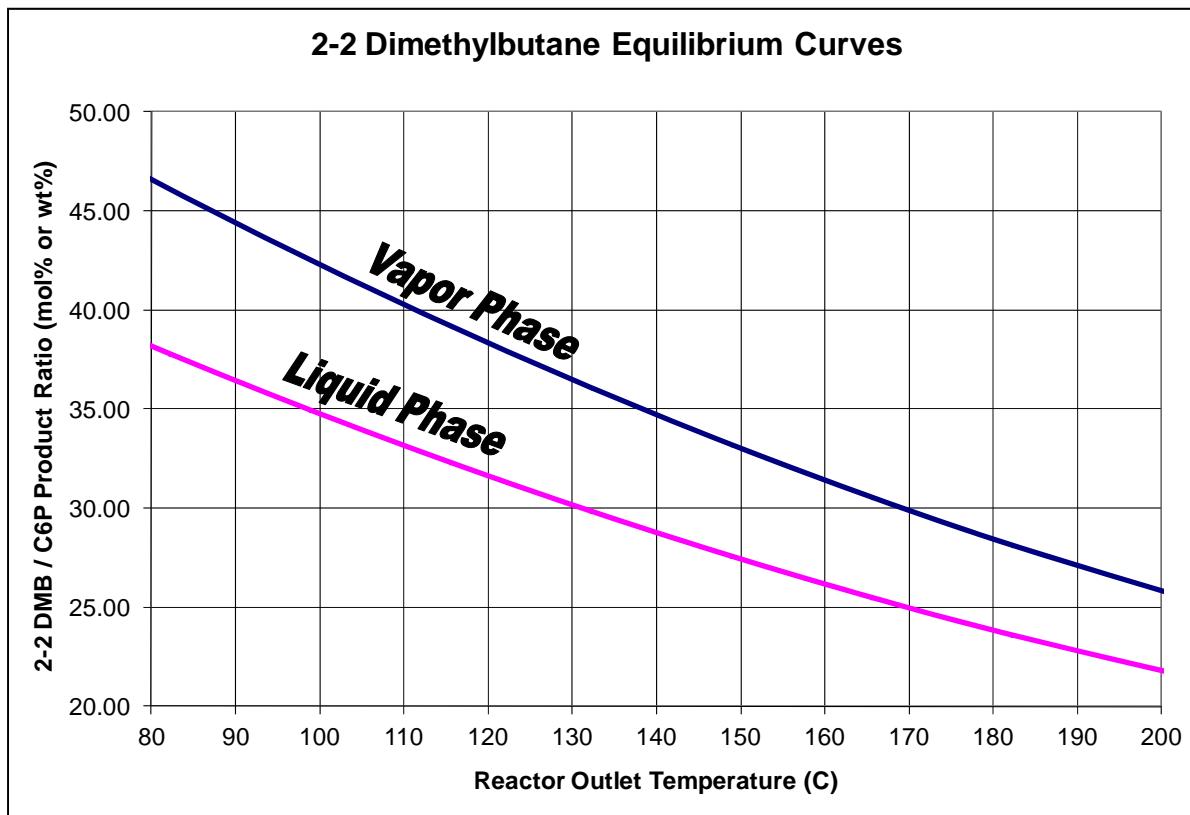
**Perchloroethylene**

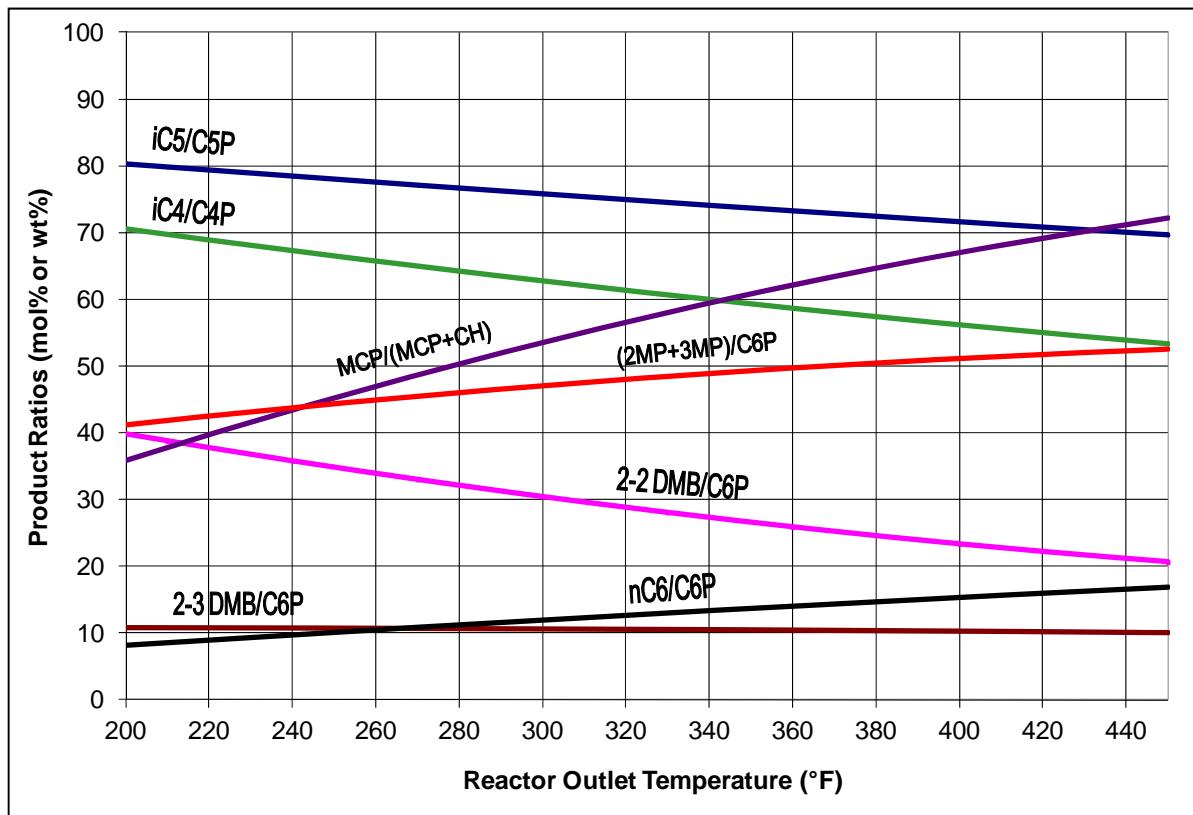
Formula	C <sub>2</sub> Cl <sub>4</sub>
Molecular Weight	165.8
Boiling Point	121°C (250°F)
Melting Point	-23°C (-9°F)
Specific Gravity (20/20°C)	1.62
Chloride Content, wt%	85.5

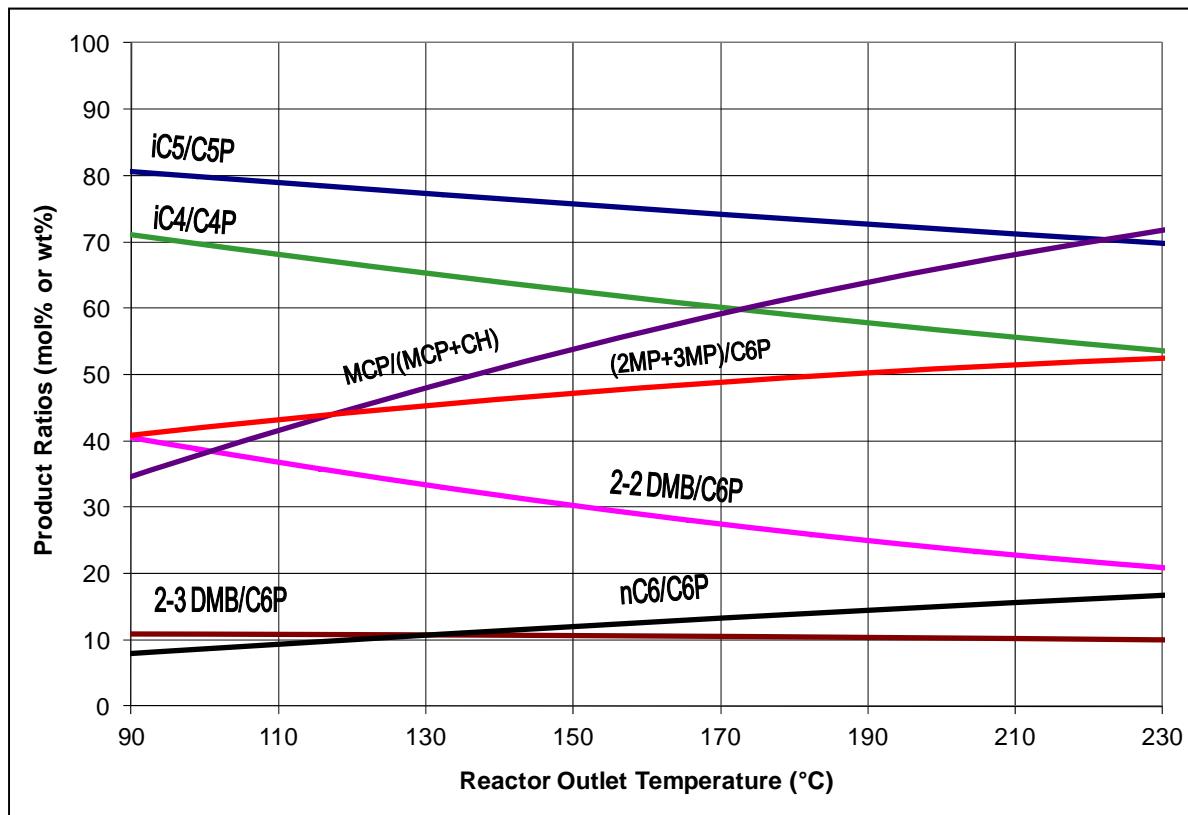
**FIGURE III-1**

**FIGURE III-1M**

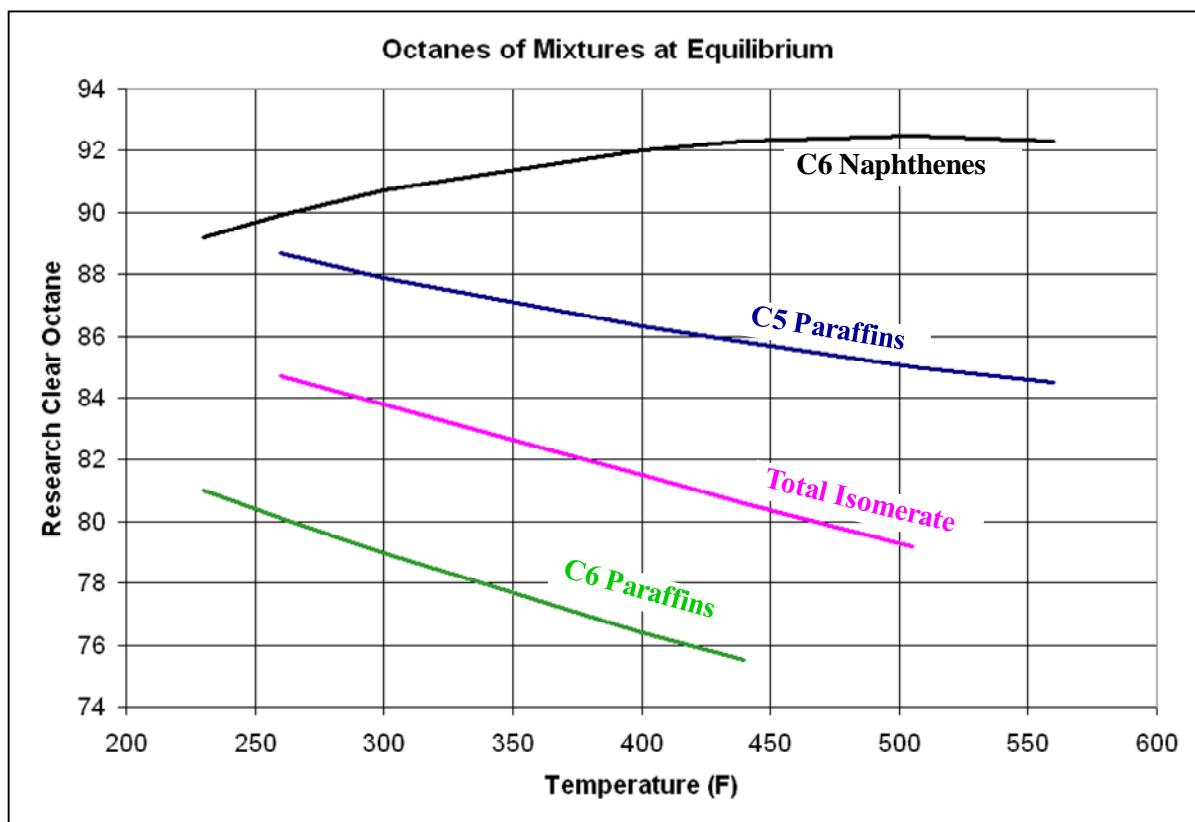
**FIGURE III-2**

**FIGURE III-2M**

**FIGURE III-3****Penex Process  
Equilibrium Curves**

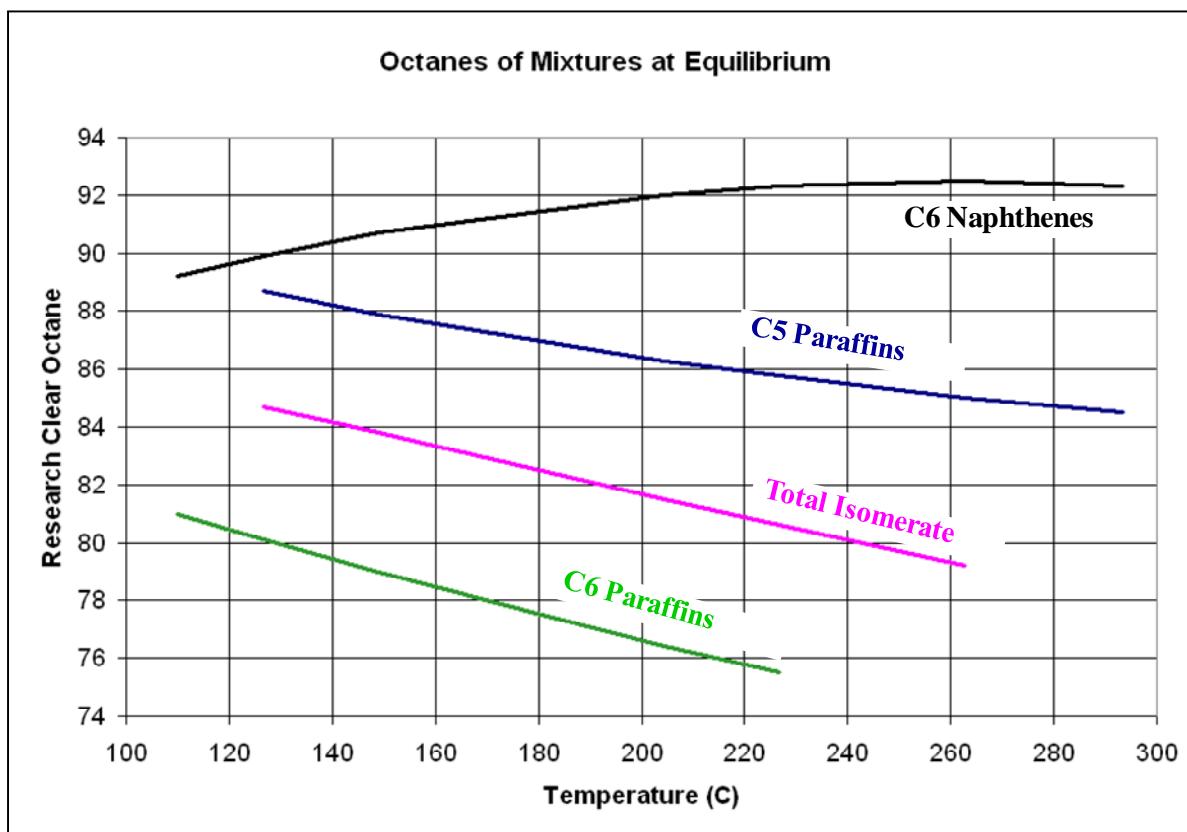
**FIGURE III-3M****Penex Process  
Equilibrium Curves**

**FIGURE III-4**  
**Penex Process**  
**Octanes of Mixtures at Equilibrium**



**FIGURE III-4M**

**Penex Process**  
**Octanes of Mixtures at Equilibrium**



**PIN**

**P**araffin

**I**somerization

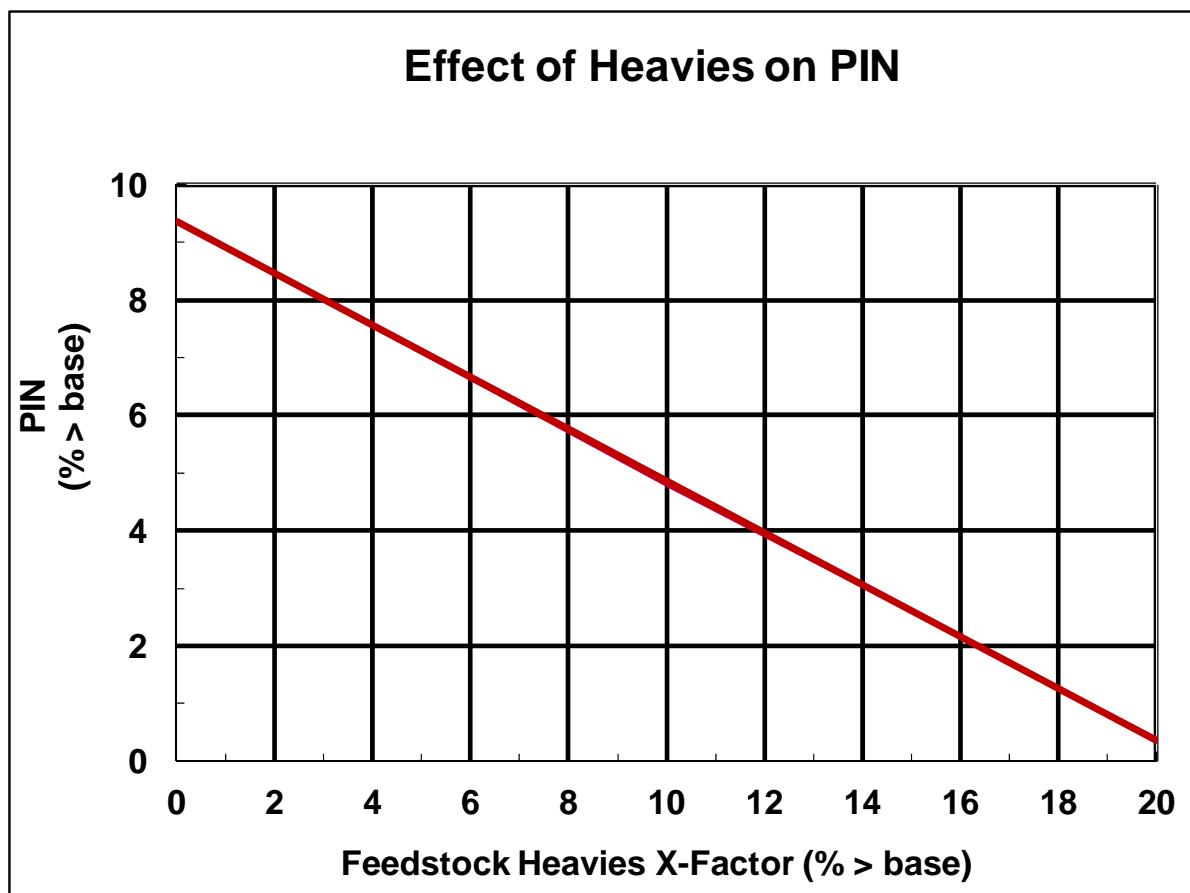
**N**umber

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

# X-Factor

Summation of:

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

**FIGURE III-5**

## IV. 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.

### A. SULFUR GUARD BED

The purpose of the sulfur guard bed is to protect the Penex catalyst from sulfur in the liquid feed. The hydrotreater will remove most of the sulfur in the Penex feed. The guard bed reduces the sulfur to a safe level for H.O.T. Penex operation and serves as protection in the event of upsets in the NHT which could result in higher than normal levels 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 required 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.

Once sulfur breakthrough occurs, normally after one year or so of operation, the Sulfur Guard Bed is taken off line and reloaded with fresh adsorbent. The Penex

Unit need not be shut down during the short period of time required to reload the guard bed so long as the NHT is performing properly.

## B. FEED DRIERS

The purpose of the liquid feed driers is to ensure that the hydrocarbon stream from the treating section is dry before entering the Penex Unit.

The driers are operated in series except when they are in the regeneration mode when at that time only one will be in service.

The hydrotreated C<sub>5</sub>/C<sub>6</sub> stream is introduced to the liquid feed drier at the bottom and passes upflow through the molecular sieve desiccant and exits at the top. The flow is then routed through one of the drier crossovers to the other liquid feed drier. The flow through the liquid feed drier is also in the upflow pattern. The dried hydrocarbon is then routed to feed surge drum. Over a period of time, the drier in the lead position will become spent as indicated by the moisture analyzer located between the two driers. At this time, it will become necessary to regenerate this drier. The driers should be regenerated on a schedule frequent enough to avoid moisture breakthrough. The spent drier is taken out of service by closing the appropriate block valves. The second series drier is now alone in service as the only drier drying the feed. The moisture analyzer tap is switched to monitor this in-service drier. After the drier regeneration has been completed, it is now ready for service. A switch is made such that the regenerated drier takes the tail position with the in-service drier remaining as the lead drier. Over a period of time the lead drier will become spent and is now set up for regeneration with the tail drier now being the only one in service. This will be the manner in which these driers will be lined up for process flow. The regeneration procedure for the liquid driers is detailed in Section VIII Normal Operations.

## C. MAKEUP GAS DRIERS

Makeup gas must be dried in order to protect the Penex catalyst. The two Makeup Gas Driers operate in the same manner as the Feed Driers. The driers operate upflow, in series. The dried hydrogen is then sent to the reactor circuit on flow control. The hydrogen is also used for pressure control in the Feed Surge Drum and, for startup, in the Stabilizer. The regeneration procedure for the gas driers is detailed in Section VIII. Normal Operations.

## D. FEED SURGE DRUM

The purpose of this drum is to provide liquid feed surge capacity for the Penex Unit. Dried feed from the liquid feed driers is routed to this drum.

The Feed Surge Drum is blanketed with dry hydrogen gas originating from the outlet of the Makeup Gas Driers with the Feed Surge Drum pressure being controlled by a PRC.

## E. REACTOR EXCHANGER CIRCUIT

The dried liquid feed from the Feed Surge Drum is pumped by either of the two reactor charge pumps through the reactor exchanger circuit on flow control. The reactor exchanger circuit consists of the cold combined feed exchanger, the hot combined feed exchanger, and the reactor charge heater.

Prior to the entry of the liquid hydrocarbon into the Cold Combined Feed Exchanger, it combines with the makeup hydrogen stream. After combining, the mixed hydrocarbon-hydrogen stream passes through the exchanger circuit in the order previously mentioned.

The Cold Combined Feed Exchanger is equipped with a bypass which can be used to regulate the amount of combined feed preheat. The bypass is regulated with a board mounted control valve to maintain reactor charge heater control. The

combined feed is further preheated by exchange with a portion of the lead reactor effluent in the hot combined feed exchanger.

A small quantity of catalyst promoter (perchloroethylene) is added upstream of the reactor charge heater. This promoter is pumped into the process by either of the two injection pumps. The catalyst promoter is stored in a nitrogen blanketed storage drum.

The combined feed is finally brought up to the desired temperature in the reactor charge heater by a temperature controller which resets the exchangers heating medium flow. The charge heater is equipped with an automatic shutdown which is activated by low feed or low makeup gas flow.

After exiting the reactor charge heater, the heated combined stream then flows to the first reactor.

## F. PENEX REACTORS

The Penex Reactors are the heart of the process. The operation of them is such that a reactor will be placed in series with the other reactor. At various times throughout the unit's history it will be possible to have either reactor in the lead or tail position. A single reactor bypass allows operation of one reactor only during startup or partial catalyst replacement. Thermocouples are inserted into the catalyst bed of each reactor to monitor the activity of the catalyst in conjunction with product ratios.

After exiting the Charge Heater, the heated combined stream then flows to the first reactor. Upon exiting the first reactor, the stream then passes to the Hot Combined Feed Exchanger where the first reactor's heat of reaction is partially removed. The degree of temperature removal can be achieved by adjusting the amount of exchanger by-passing with a temperature controller. This temperature controller fixes the lag reactor's inlet temperature.

The partially cooled stream is then routed to the second reactor where the final process reactions are completed.

The reactors are equipped with hydrogen purge lines which are located at the inlet of each reactor. The hydrogen purge is used to remove hydrocarbon from a reactor which is to be unloaded or to pressurize a reactor. A hydrogen quench line is located at the lead reactor inlet header to aid in cooling the catalyst during a temperature excursion as well as removing hydrocarbon. The quench is controlled by an HIC with flow indication.

In case of a high reactor temperature emergency, the reactors are equipped with depressuring lines to the flare system. The reactors are depressured from the outlet of the lag reactor. The depressuring line is equipped with two motorized or pneumatically operated valves which can be operated from the control room once the reactors have been isolated from the charge heater and stabilizer.

After exiting the second reactor, the stream is then routed to the tube side of the cold combined feed exchanger.

The Cold Combined Feed Exchanger tube side effluent is then routed to the Stabilizer on pressure control.

## G. STABILIZER

The purpose of this column is to separate any dissolved hydrogen, HCl and cracked gases (C<sub>1</sub>, C<sub>2</sub>, and C<sub>3</sub>'s) from the isomerate.

The feed to this column is routed hot directly from the cold CFX before entering the stabilizer.

The column is reboiled by either steam or hot oil. The reboiler heat input is controlled by an FRC on the heating medium. The amount of heat input is adjusted to maintain sufficient reflux to adequately strip the HCl and light ends from the

stabilizer bottoms material. The typical design external reflux to feed ratio is approximately 0.5 on a volume basis and is recommended as a starting point.

The Stabilizer column overhead vapor, consisting of the light hydrocarbon components of the column's feed, is routed to an air or water cooled condenser and then to the stabilizer receiver. To maintain pressure control on the column, gas is vented on pressure control to the Net Gas Scrubber. Liquid is pumped from the receiver on level control with the Stabilizer reflux pump. All liquid from the Stabilizer Overhead Receiver is refluxed to the column on tray No. 1.

Bottoms product is routed to storage on level control after first being cooled in the Stabilizer bottoms cooler. If the Stabilizer bottoms is sent to a Deisohexanizer it is not cooled, but is charged hot to the column. Part of the stabilizer bottoms is used for regenerating the driers.

## H. NET GAS SCRUBBER

The Stabilizer off gas flows upflow through the Net Gas Scrubber to remove hydrogen chloride. The scrubbed gas leaves the top of the vessel and typically goes to fuel gas on back pressure control. The hydrogen purity is monitored on the scrubbed off gas to determine the moles of H<sub>2</sub> leaving the system for the H<sub>2</sub>/HCBN determination.

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 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 flow rate of the circulating caustic can be monitored by a local flow indicator.

Periodically (about once per week) a portion of the caustic is withdrawn to the refinery spent caustic facilities as spent caustic. The caustic level in the scrubber is maintained about 1-2 feet below the distributor under the packed section.

Several units are equipped with circulating water wash sections above the caustic circulation to remove entrained caustic in the net gas.

## I. DEISOHEXANIZER (DIH)

The purpose of this vessel is to recover product isohexane and pentanes from the stabilized reactor products. Generally, the feed to this column is the stabilizer bottoms stream. Stabilizer bottoms is fed to the deisohexanizer on level control.

Heat input to the column is provided by a steam reboiler, generally serviced by low pressure steam on condensate flow control. The reboiler heat input is adjusted to generate adequate reflux.

Overhead vapor is totally condensed in an air fin type exchanger. 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<sup>2</sup>g (10 psig).

The overhead product which is mainly C<sub>5</sub>'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.

Overhead product is generally sent directly to storage. Very often part of the overhead liquid is used for drier regeneration. After service in the drier, the product joins the material sent to storage.

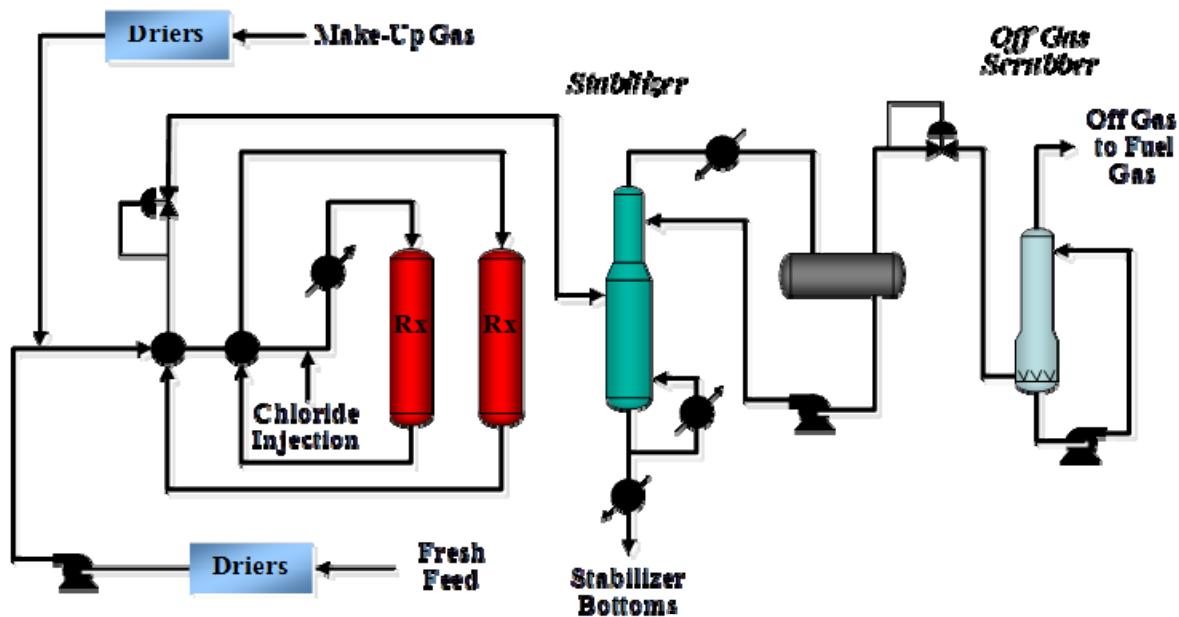
Bottoms from the DIH column is sent to storage with the overhead product or may be charged to a reforming unit.

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 overhead 3 methylpentane content. The composition of the overhead is set by the TRC setpoint. Heat is provided to the column at a rate which optimizes reflux while keeping the overhead methylpentane content at its normal level. The column pressure should be controlled at its design value. The DIH recycle stream is taken off as a lower sidecut. The lower sidecut is pumped back to the Penex liquid feed driers on flow control. The flow controller is typically re-set by a temperature controller in the lower portion of the tower. 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<sub>7+</sub> material should be rejected out the bottom of the tower. As the temperature in the bottom of the tower increases, this is an indication that the composition is getting heavier. The TRC below the sidecut draw will then cause the sidecut flow to be reduced. An increase in the bottoms drag will then be required to reject the heavies and control the bottoms level. The octane of the overhead product is set by two independent variables.

1. The pentane composition of the overhead. The total amount of pentane in this stream is set by the feedstock composition. The iso-pentane content is then set by the degree of C<sub>5</sub> isomerization in the reactors. For a given feedstock composition the octane of the overhead is improved by maximizing the IC<sub>5</sub>/C<sub>5</sub>P ratio in the overhead product. Since the pentanes in the product are processed “once through,” the higher the concentration of pentanes in the feedstock, the lower the product octane will be.

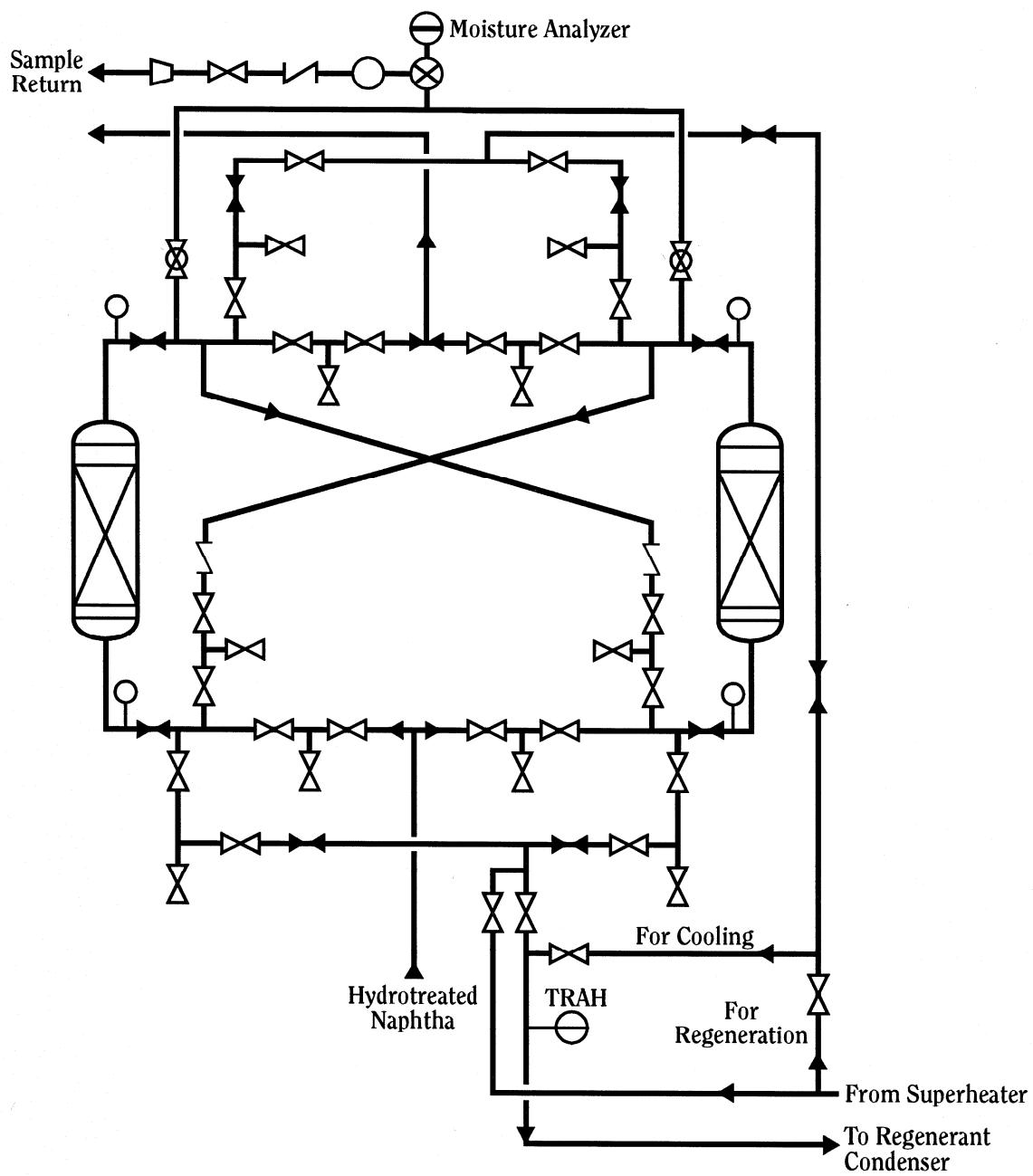
2. The amount of 2-methylpentane and 3-methylpentane in the overhead. Since these components have an octane blending value of about 75, the higher their concentration in the overhead product, the lower the octane will be. Since eliminating all of the methylpentanes would required; a) more trays, b) more reflux, and c) more recycle to the reactor section, an economic compromise must be made to adjust the product octane vs. utility consumption.

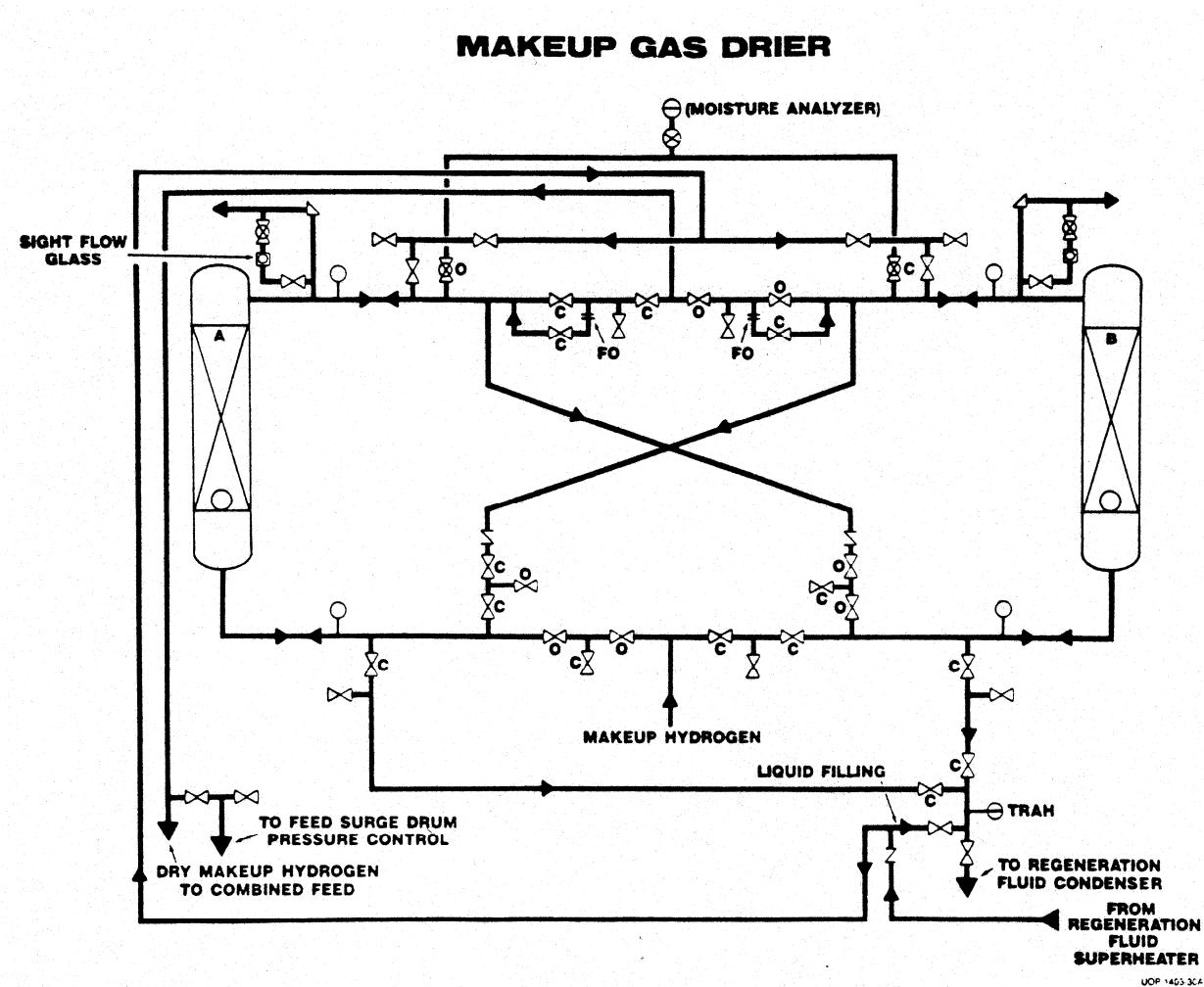
Generally, about 80 percent of the methylpentanes are recovered in the recycle stream back to the reactor section. If a higher octane product is required then the tower reflux should be increased, the overhead rate decreased and the liquid recycle to the Penex driers increased.

**FIGURE IV-1****UOP PENEX PROCESS  
(ONCE THROUGH)**

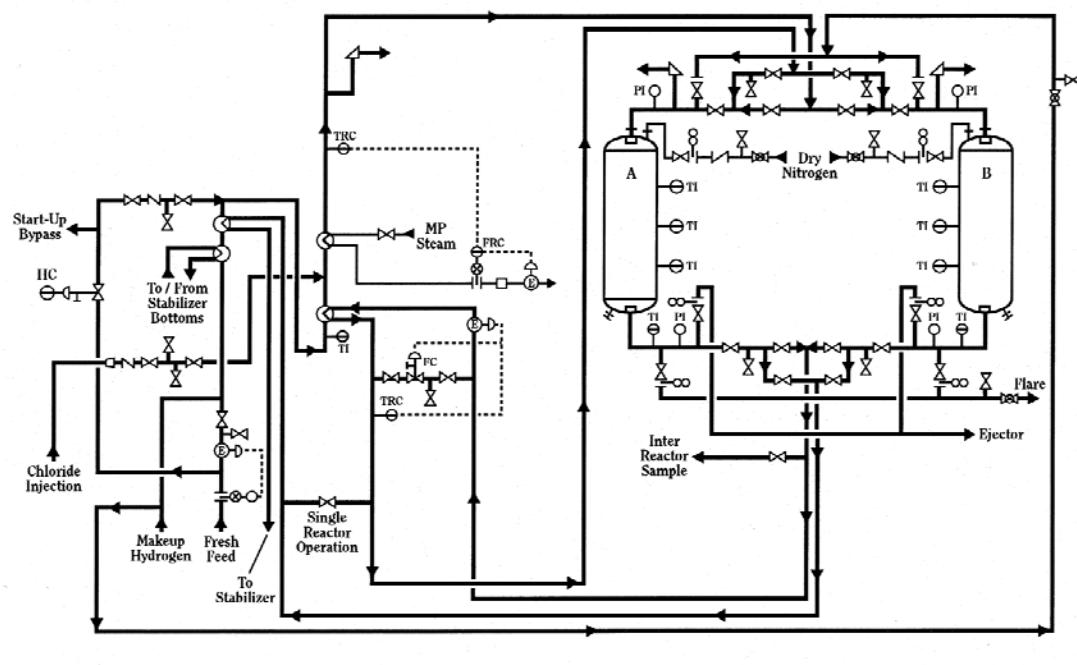
**Figure IV-2**  
**Liquid Feed Drier**

**Series Flow Drier Operation**



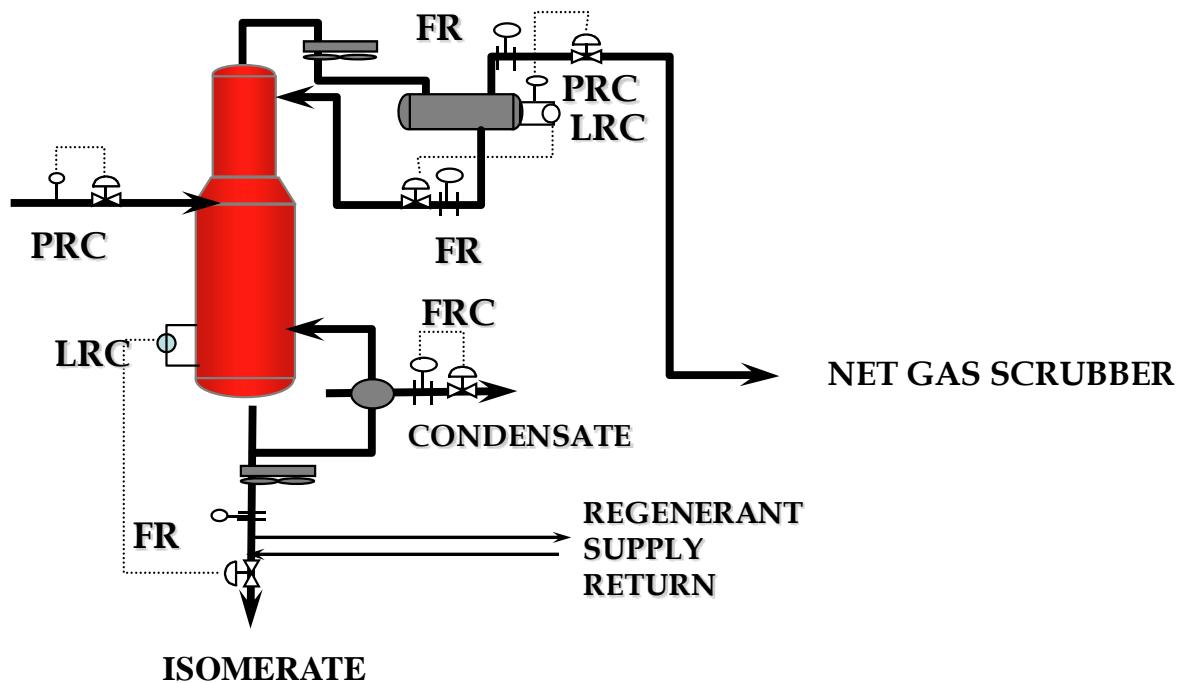
**FIGURE IV-3**

**Figure IV-4**  
**Reactor Section**

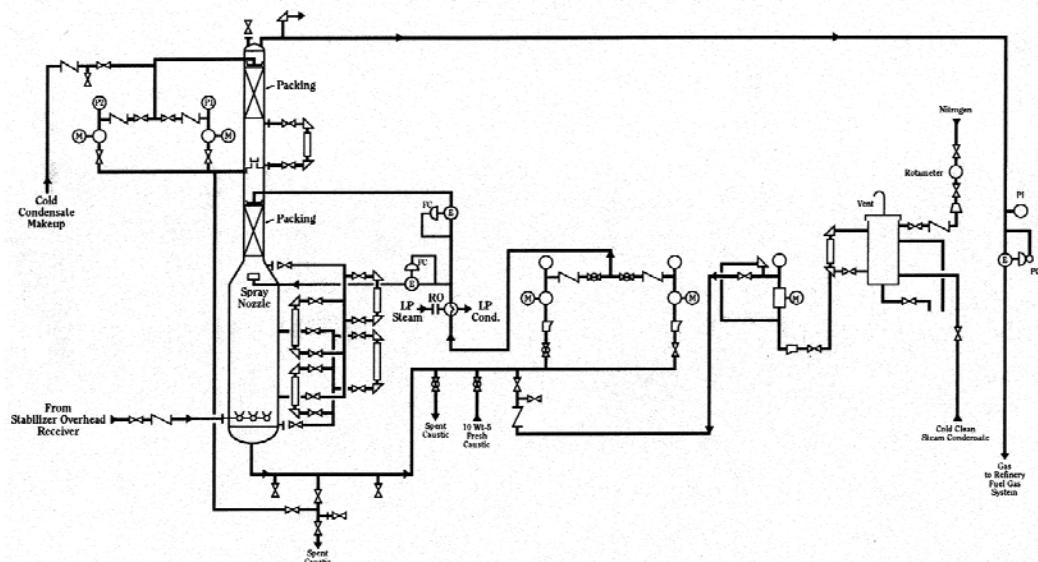


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**Figure IV-5**  
**Stabilizer Section**



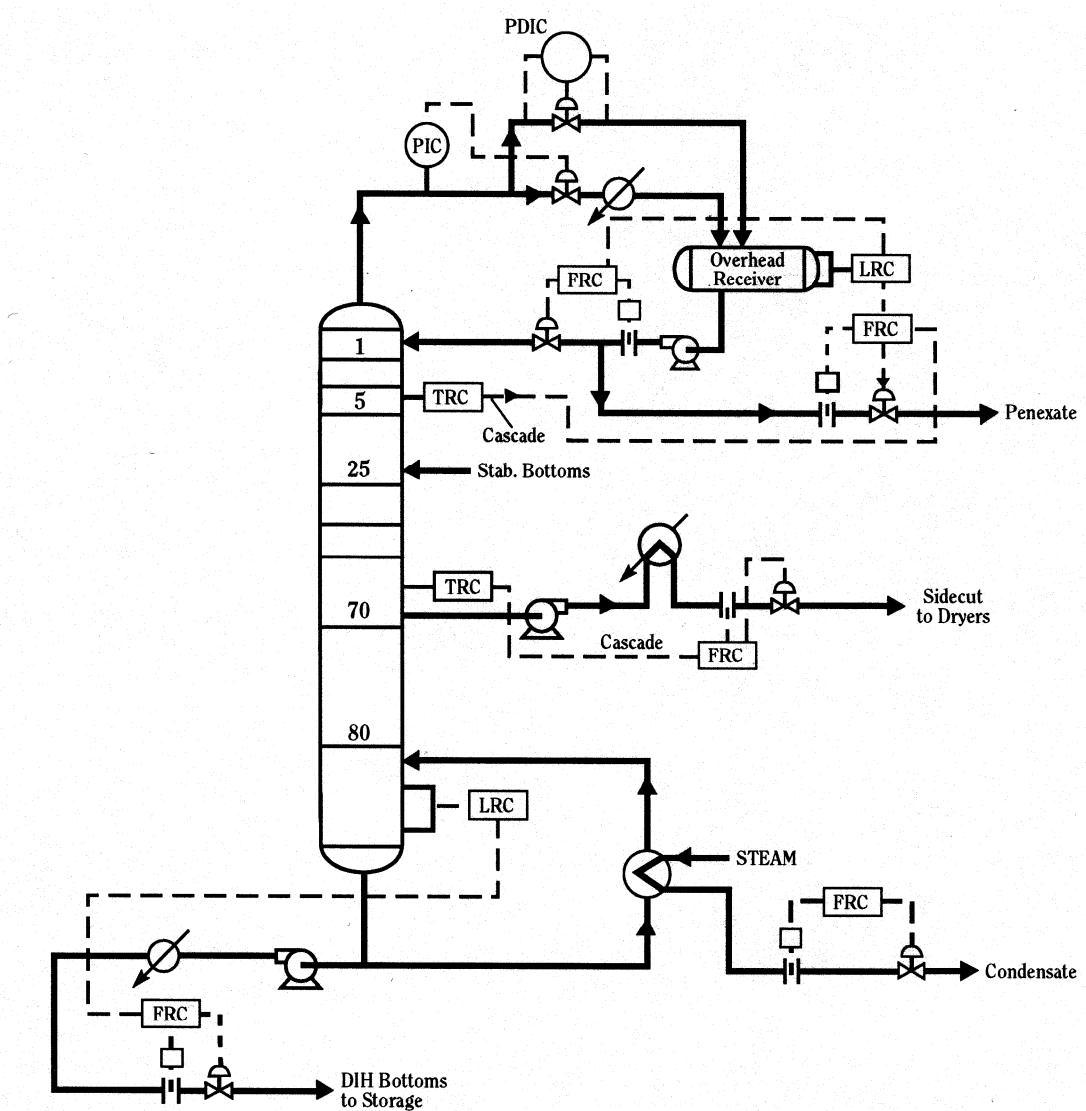
**Figure IV-6  
Caustic Scrubber**



PNX-R00-40

**Figure IV-7**

## DIH Column



## V. 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.

### A. SULFUR GUARD BED

The purpose of the Sulfur Guard Bed is to protect the Penex catalyst from sulfur in the liquid feed. The Naphtha Hydrotreater (NHT) will remove most of the sulfur in the Penex feed. The Sulfur Guard Bed reduces the sulfur to a safe level for H.O.T. Penex operation and serves as protection against upsets in the NHT which could result in higher than normal levels of sulfur in the feed.

The Sulfur Guard Bed is loaded with either UOP ADS-11L (nickel) or ADS-12/ADS-120 (copper) adsorbent designed to chemisorb sulfur from the liquid feed. The feedstock is heated to the required temperature for sulfur removal, usually between 121°C (250°F) to 150°C (300°F), and passed downflow over the adsorbent.

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.

## B. 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-2 for a diagram of the Feed Surge Drum.

## C. 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 Feed Driers typically are loaded with UOP Molsiv Adsorbent HPG-250 or HPG-429 for the removal of water and trace levels of oxygenates or sulfur compounds. 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 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 and alumina 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 provide bed stability.

Refer to Figures V-3 and V-4 for example loading diagrams of the Feed Drier and Makeup Gas Drier, respectively.

## D. HEAT EXCHANGERS

### Reactor Section Heat Exchangers

The Penex Reactors have combined feed/reactor effluent heat exchangers. These exchangers are shell and tube type, and allow heat transfer from the hot effluent of each reactor outlet stream to the incoming feed stream to the first reactor. 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-5) in order to minimize the potential for leakage.

### Regenerant Vaporizer

The regenerant vaporizer uses low pressure steam to heat the regenerant stream before it reaches the electric superheater. The vaporizer, shown in Figure V-6, is an upright heat exchanger which uses bayonet type tubes that have been strength welded and fully rolled. This heat exchanger is equipped with a level indicator and a high level alarm, and is designed to operate with the top portion of the tubes uncovered. Low pressure steam on the inside of the bayonet tubes transfers heat to the regenerant on the outside of the bayonet tubes. This arrangement allows hot steam in the tip of the bayonet tube to transfer heat to the vaporized regenerant stream, giving it several degrees of superheat. This prevents the regenerant from condensing which could damage the electric bundles in the superheater when operating. Refer to Figure V-6 for a diagram of the Regenerant Vaporizer.

## E. REGENERANT SUPERHEATER

The regenerant superheater, shown in Figure V-7, raises the temperature of the vaporized regenerant to a temperature of 315°C (600°F). The regenerant stream is heated by Inconel electric elements, which are capable of reaching temperatures of over 600°C (1112°F). The regenerant entering the Regenerant Superheater must

be in the vapor phase to avoid damaging the electric bundles when power is applied to the superheater.

## F. REACTORS

The reactors in the Penex Unit contain the isomerization catalyst. They are constructed of killed carbon steel. The process stream which consists of a naphtha feed and hydrogen mixture enters the reactor vessel top through an inlet distributor and leaves at the bottom. There is a vapor liquid distributor tray installed, above the catalyst bed, to ensure even distribution of the hydrocarbon stream over the catalyst. Refer to Figures V-8 and V-9.

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. There are catalyst unloading nozzles located in the bottom head. The nozzles extend through the catalyst support material to allow catalyst removal without disturbing the support material. The nozzles are blind flanged during normal operation. The bottom head of the reactor is filled with 19 mm (3/4") diameter ceramic balls to a level 450 mm (18") above the top of the outlet basket. A layer of 6 mm (1/4") and a layer of 3 mm (1/8") ceramic balls are placed directly on top of the 19 mm (3/4") ceramic balls as shown in the UOP Project Specifications.

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-10 for a diagram of the bottom head of the Penex Reactors.

## G. STABILIZER COLUMN

The purpose of the Stabilizer Column is to remove hydrogen chloride, hydrogen, and light hydrocarbons ( $C_1$  through  $C_3$  or  $C_4$ ) from the product stream. The Bottoms

stream contains normal and isoparaffins and may be sent to a deisohexanizer for further fractionation, or directly to storage for gasoline blending.

The top half of the Stabilizer Column is narrower 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-11 for a diagram of the Stabilizer.

## H. NET GAS SCRUBBER

The function of the Stabilizer Net Gas Scrubber is to neutralize the hydrogen chloride present in the Stabilizer Off Gas prior to its entry into the fuel gas system or the flare header. The HCl is formed in the reactor section and then vented off through the Stabilizer Overhead Receiver, to the Stabilizer Net Gas Scrubber. In this vessel, the off gas from the Stabilizer Receiver is contacted through a liquid level and later with a counter current flow of caustic solution (10 wt% NaOH) which reacts with HCl to form sodium chloride and water. The entry point for the offgas is located at the bottom of the scrubber, and consists of a monel distributor with small holes to allow even gas distribution. The bottom distributor and the inlet flange are both made of monel to prevent corrosion, resulting from contact with high concentrations of HCl in an aqueous environment. The vessel is constructed of killed carbon steel.

The top portion of the vessel is filled with 25 mm (1") Carbon Raschig Rings, which provide a good contact area for the interaction of the liquid caustic and the acidic overhead gas. The packing in the scrubbing section is held in place by a support grating on the bottom and a hold down grating on the top.

The incoming gas is contacted with the caustic in the bottom portion of the scrubber or "reservoir" section. This is where most of the HCl is removed before it reaches the top portion or the scrubbing section of the column. A high level of caustic

solution is usually kept in the reservoir section of the column to ensure that there is always an ample supply of caustic for circulation. A pump is used to circulate the caustic to the two injection points on the scrubber column. One injection point is located at the top of the packed section (a spray nozzle or slot type distributor) and the other is located just below the packed section (a spray nozzle or ring type distributor). The purpose of the lower spray distributor is to direct the caustic flow to the conical walls of the scrubber to keep the walls wetted with caustic. The design flow of caustic should be continuously maintained to each distributor to ensure good flow distribution.

A water wash section may be included above the circulating caustic to remove entrained caustic from the net gas. Circulating water monitored by an FI is passed over a bed of 25 mm (1") Carbon Raschig Rings at design rate. Makeup water is added to overflow a chimney trap tray which replaces water lost to saturating the dry gas in the caustic inventory section. The water is typically changed out if the caustic strength reaches 2 wt% NaOH in the circulating water or if caustic entrainment is observed.

## I. DEISOHEXANIZER (DIH)

The purpose of this vessel is to recover product isohexane and pentanes from the stabilized reactor products. Generally, the feed to this column is the stabilizer bottoms stream. Stabilizer bottoms is fed to the deisohexanizer on level control.

Heat input to the column is provided by a steam reboiler, generally serviced by low pressure steam on condensate flow control. The reboiler heat input is adjusted to generate adequate reflux.

Overhead vapor is totally condensed in an air fin type exchanger. 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<sup>2</sup>g (10 psig).

The overhead product which is mainly C<sub>5</sub>'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.

Overhead product is generally sent directly to storage. Very often part of the overhead liquid is used for drier regeneration. After service in the drier, the product joins the material sent to storage.

Bottoms from the DIH column is sent to storage with the overhead product or may be charged to the Platforming unit.

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 overhead 3 methylpentane content. The composition of the overhead is set by the TRC setpoint. Heat is provided to the column at a rate which optimizes reflux while keeping the overhead methylpentane content at its normal level. The column pressure should be controlled at its design value. The DIH recycle stream is taken off as a lower sidecut. The lower sidecut is pumped back to the Penex liquid feed driers on flow control. The flow controller is typically re-set by a temperature controller in the lower portion of the tower. 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<sub>7+</sub> material should be rejected out the bottom of the tower. As the temperature in the bottom of the tower increases, this is an indication that the composition is getting heavier. The TRC

below the sidecut draw will then cause the sidecut flow to be reduced. An increase in the bottoms drag will then be required to reject the heavies and control the bottoms level. The octane of the overhead product is set by two independent variables.

1. The pentane composition of the overhead. The total amount of pentane in this stream is set by the feedstock composition. The iso-pentane content is then set by the degree of C<sub>5</sub> isomerization in the reactors. For a given feedstock composition the octane of the overhead is improved by maximizing the IC<sub>5</sub>/C<sub>5</sub>P ratio in the overhead product. Since the pentanes in the product are processed “once through,” the higher the concentration of pentanes in the feedstock, the lower the product octane will be.
2. The amount of 2-methylpentane and 3-methylpentane in the overhead. Since these components have an octane blending value of about 75, the higher their concentration in the overhead product, the lower the octane will be. Since eliminating all of the methylpentanes would require; a) more trays, b) more reflux, and c) more recycle to the reactor section (higher CFR), an economic compromise must be made to adjust the product octane vs. utility consumption.

Generally, about 80 percent of the methylpentanes are recovered in the recycle stream back to the reactor section. If a higher octane product is required then the tower reflux should be increased, the overhead rate decreased and the liquid recycle to the Penex driers increased.

Refer to Figure V-12 for a diagram of the DIH.

## J. PUMPS

Centrifugal pumps are used for several applications in the Penex Unit. Common applications for the centrifugal pumps are for reactor charge pumps, reflux pumps for the fractionation columns, and caustic recirculation pumps. Proportioning pumps

are used for chloride injection into the feed stream and makeup water to the net gas scrubber.

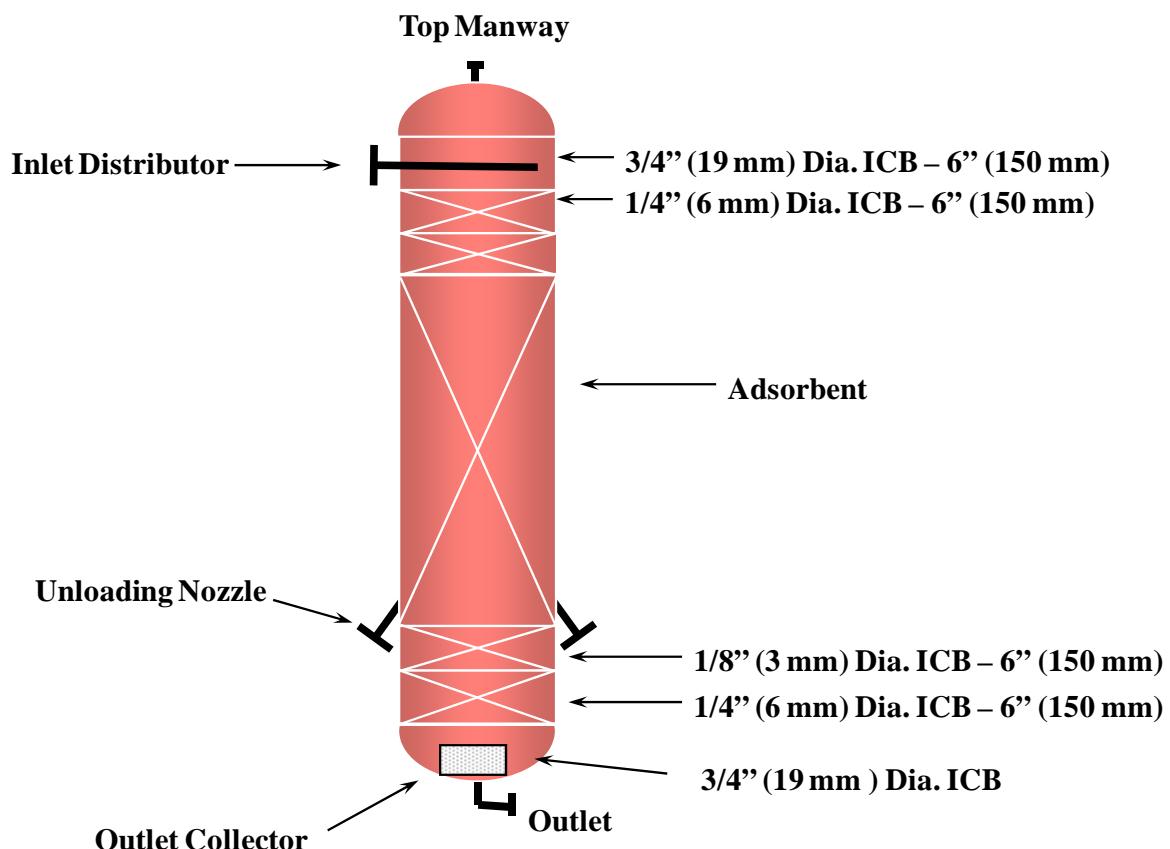
Pumps used in hydrocarbon service use tandem seals with API 52 seal plans. In this application the seal oil circulation is established by way of a siphon. The seal oil is contained in a reservoir where it can be pumped to and from the pump seal. The oil is continuously pumped between the two seals. In the event of a seal failure, hydrocarbon will leak into the oil system and cause a pressure increase in the reservoir. The seal oil reservoir is equipped with a pressure alarm and pressure gauge to alert the operator to a seal failure. The reservoir is usually vented to flare through an orifice plate.

## K. FIN-FAN HEAT EXCHANGERS

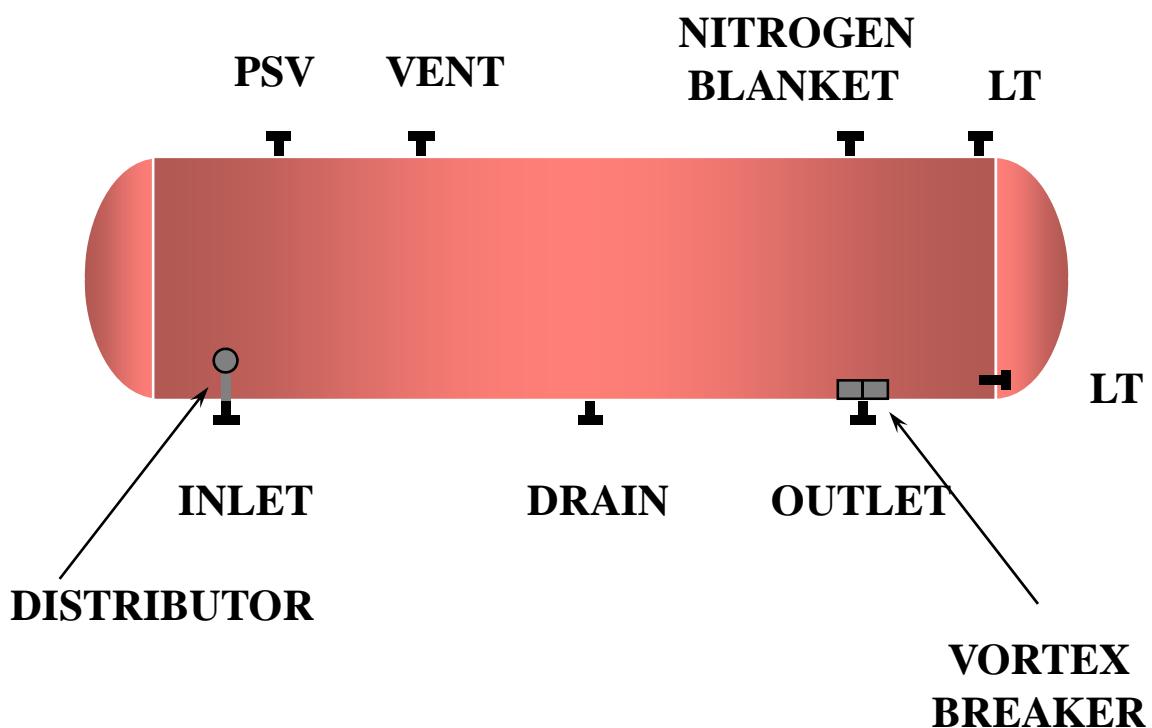
An air fin exchanger consists of a fan with one or more heat transfer sections mounted horizontally on a frame. The heat transfer sections consist of finned tubes fixed between header boxes. Allowance for thermal expansion of the tubes is accomplished by anchoring only one header box and permitting the other 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.

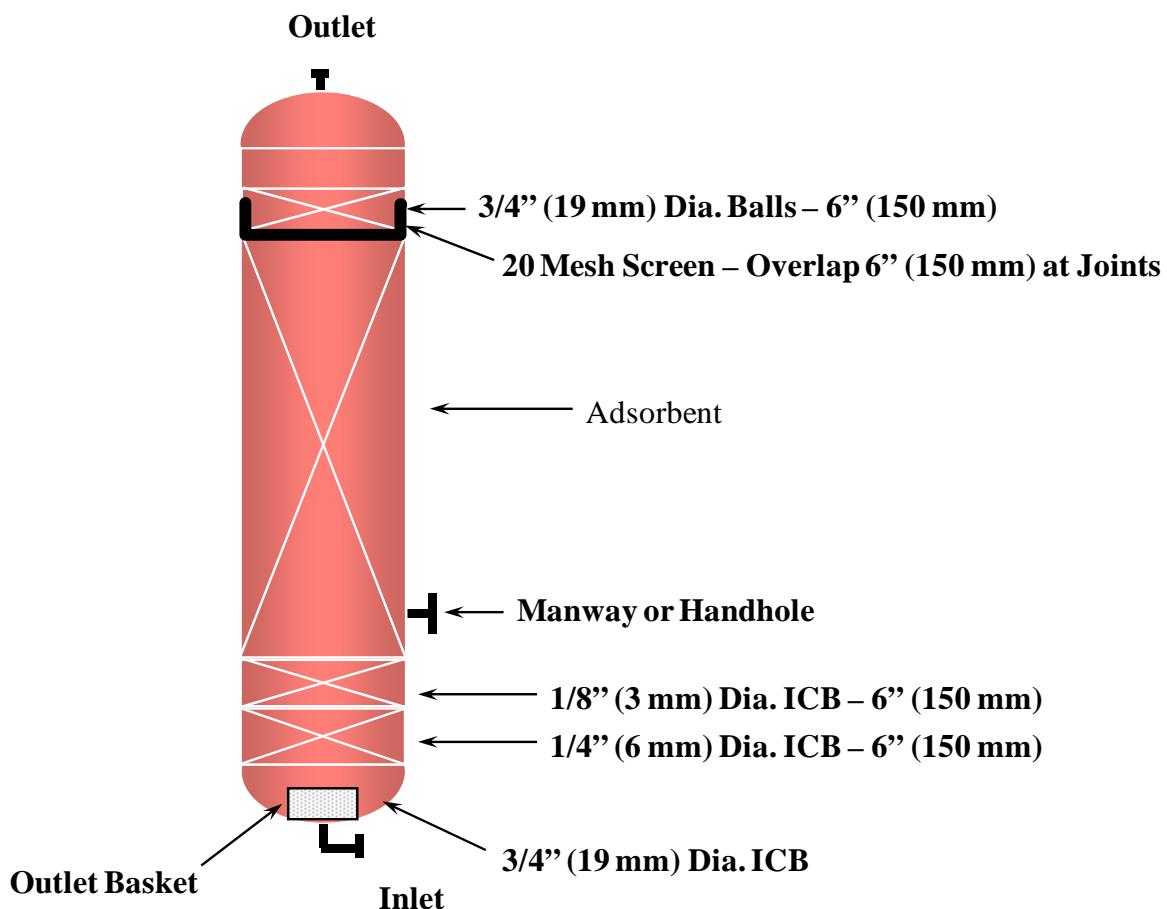
## FIGURE V-1 Sulfur Guard Bed



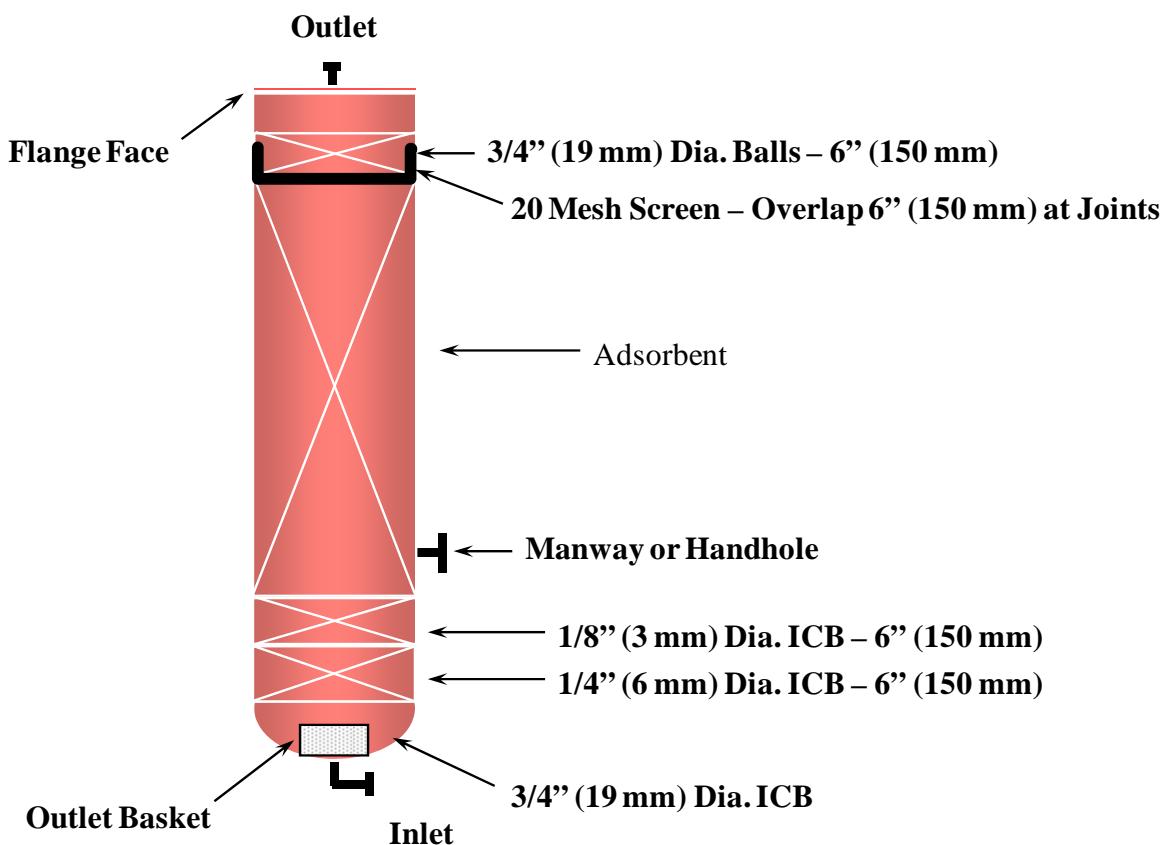
**FIGURE V-2**  
**Feed Surge Drum**



## FIGURE V-3 Feed Drier

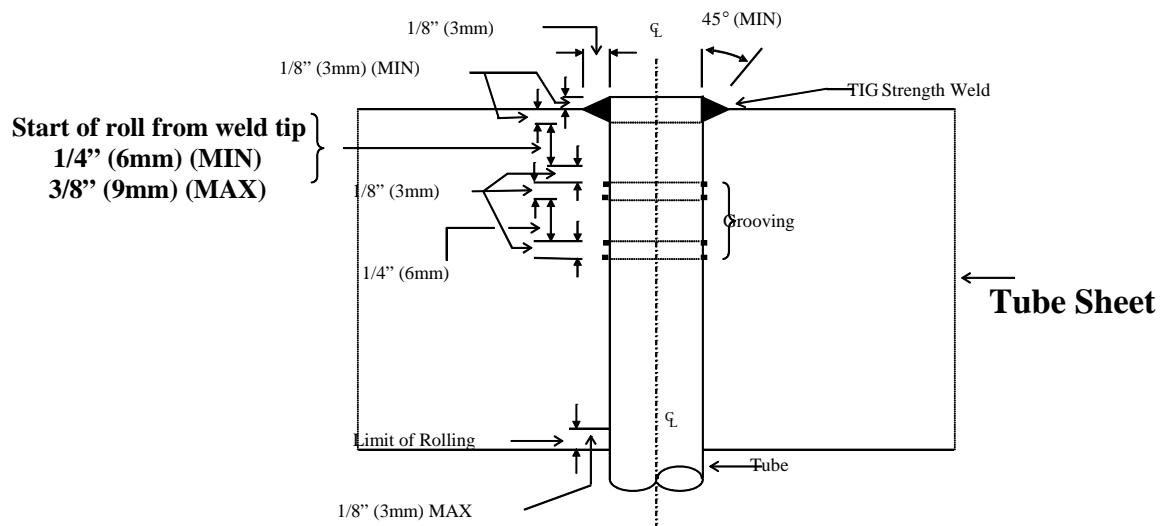


## FIGURE V-4 Makeup Gas Drier

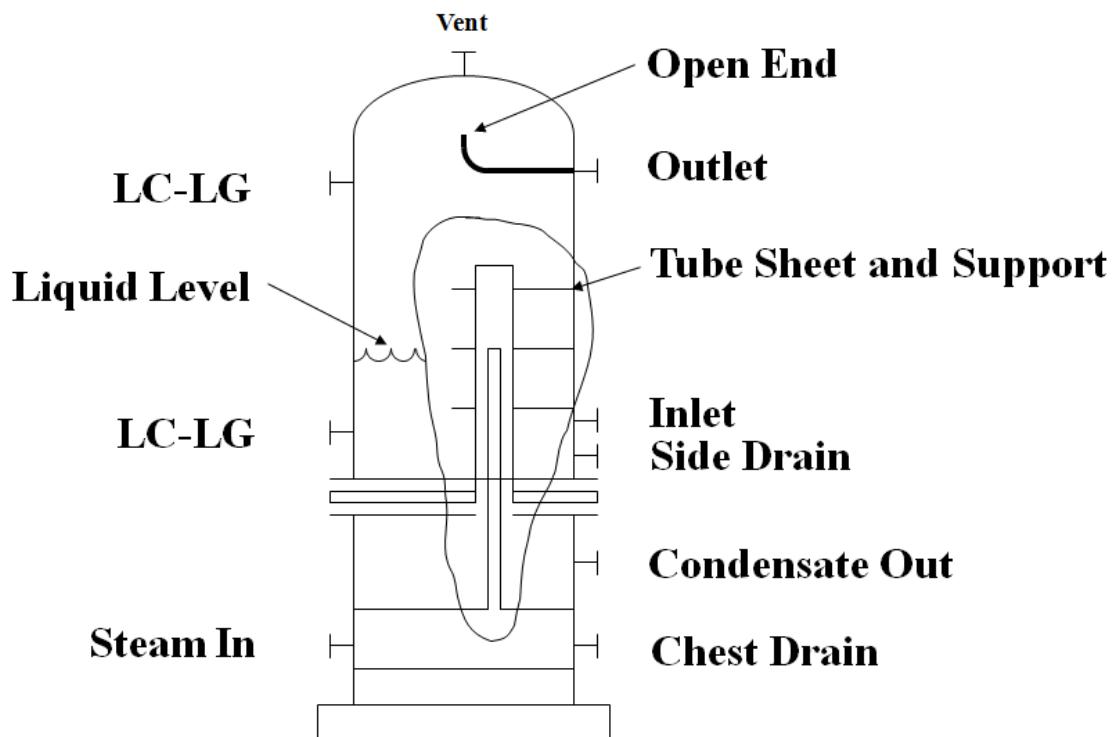


## FIGURE V-5

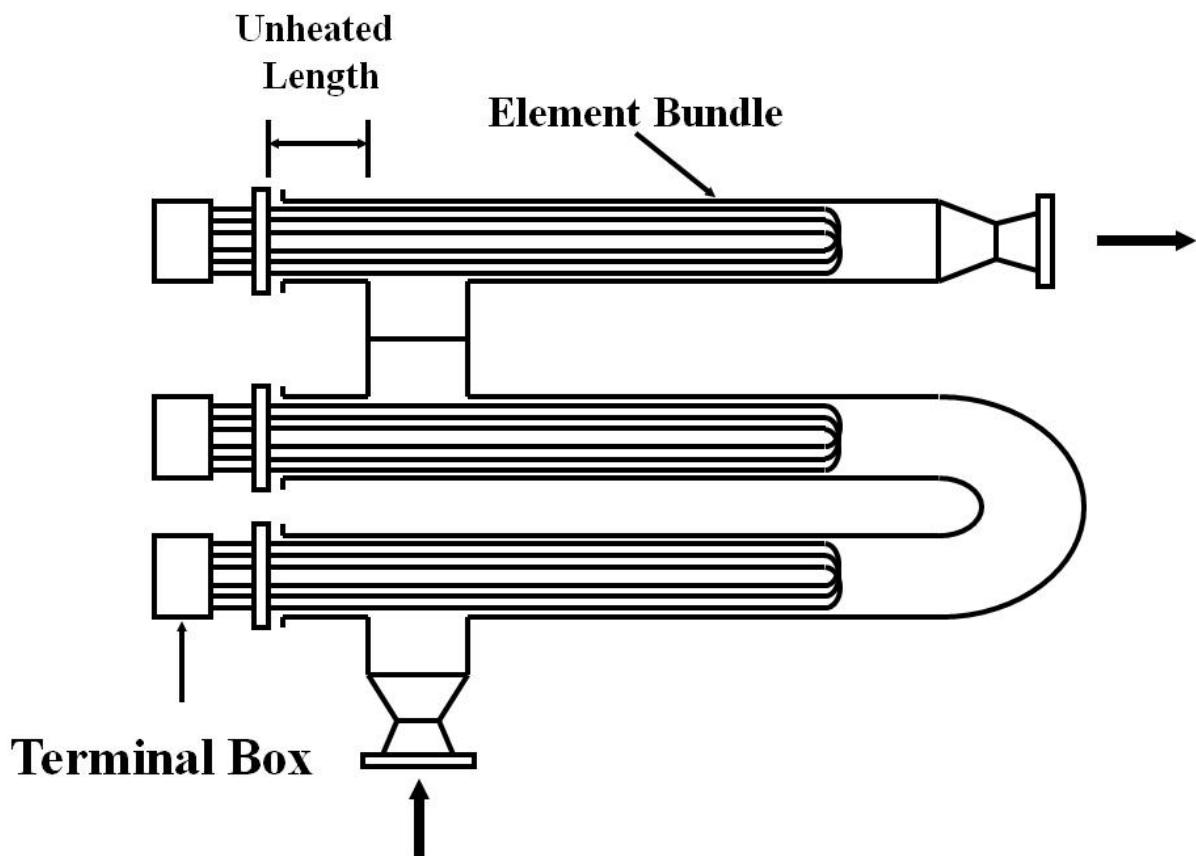
### Strength-Weld Plus Full Rolled Tube Joint Requirements



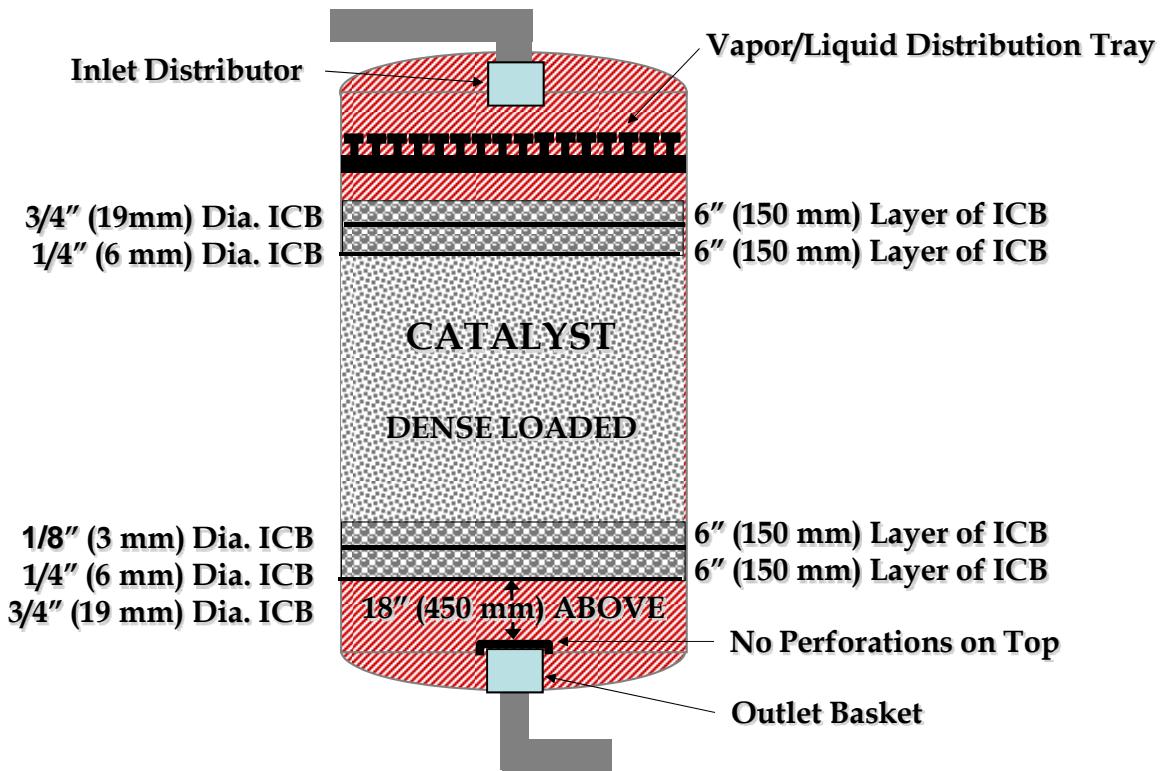
**FIGURE V-6**  
**Regenerator Vaporizer**



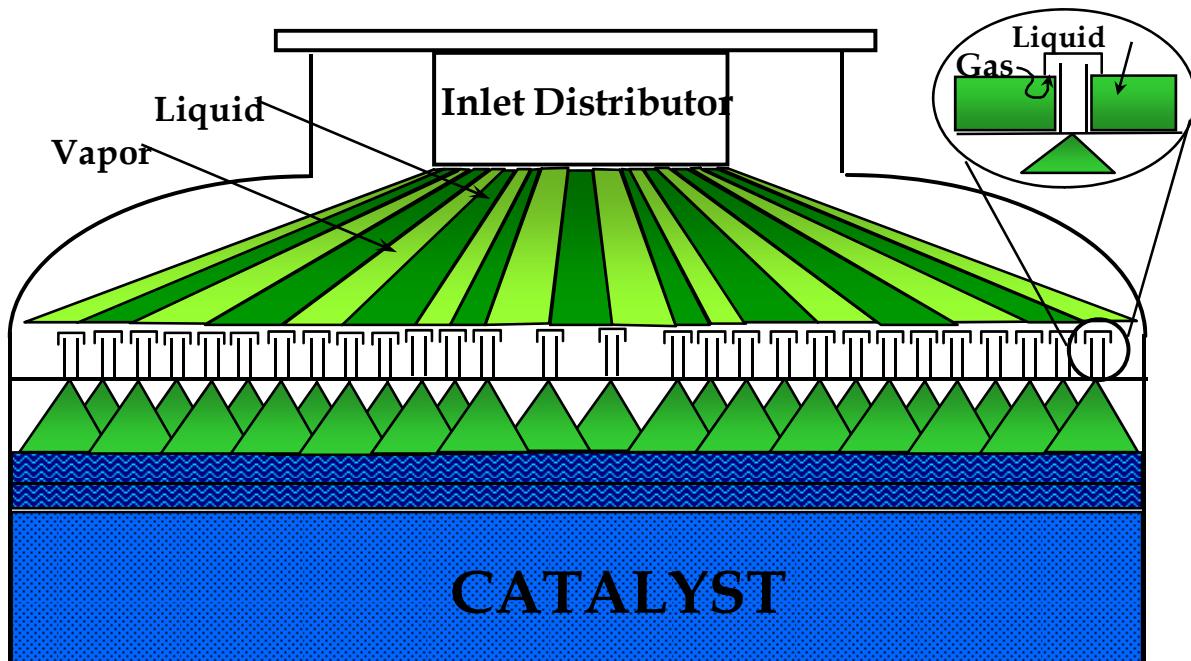
**FIGURE V-7**  
**Regenerator Superheater**



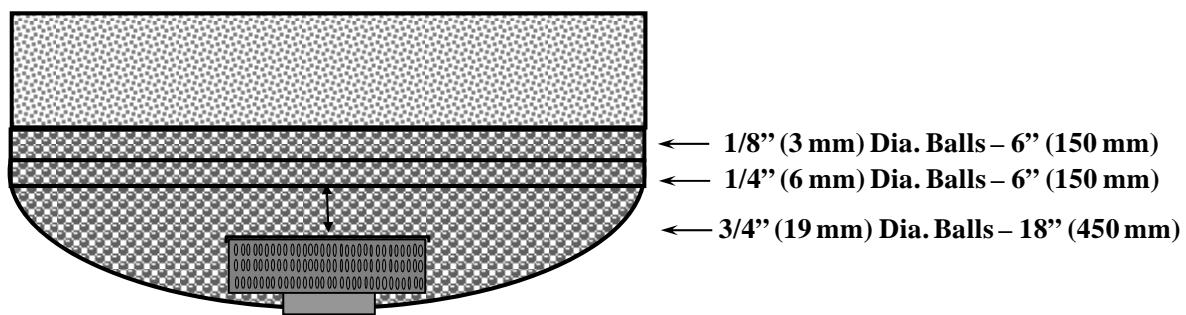
**FIGURE V-8**  
**Mixed Phase Penex Reactor**



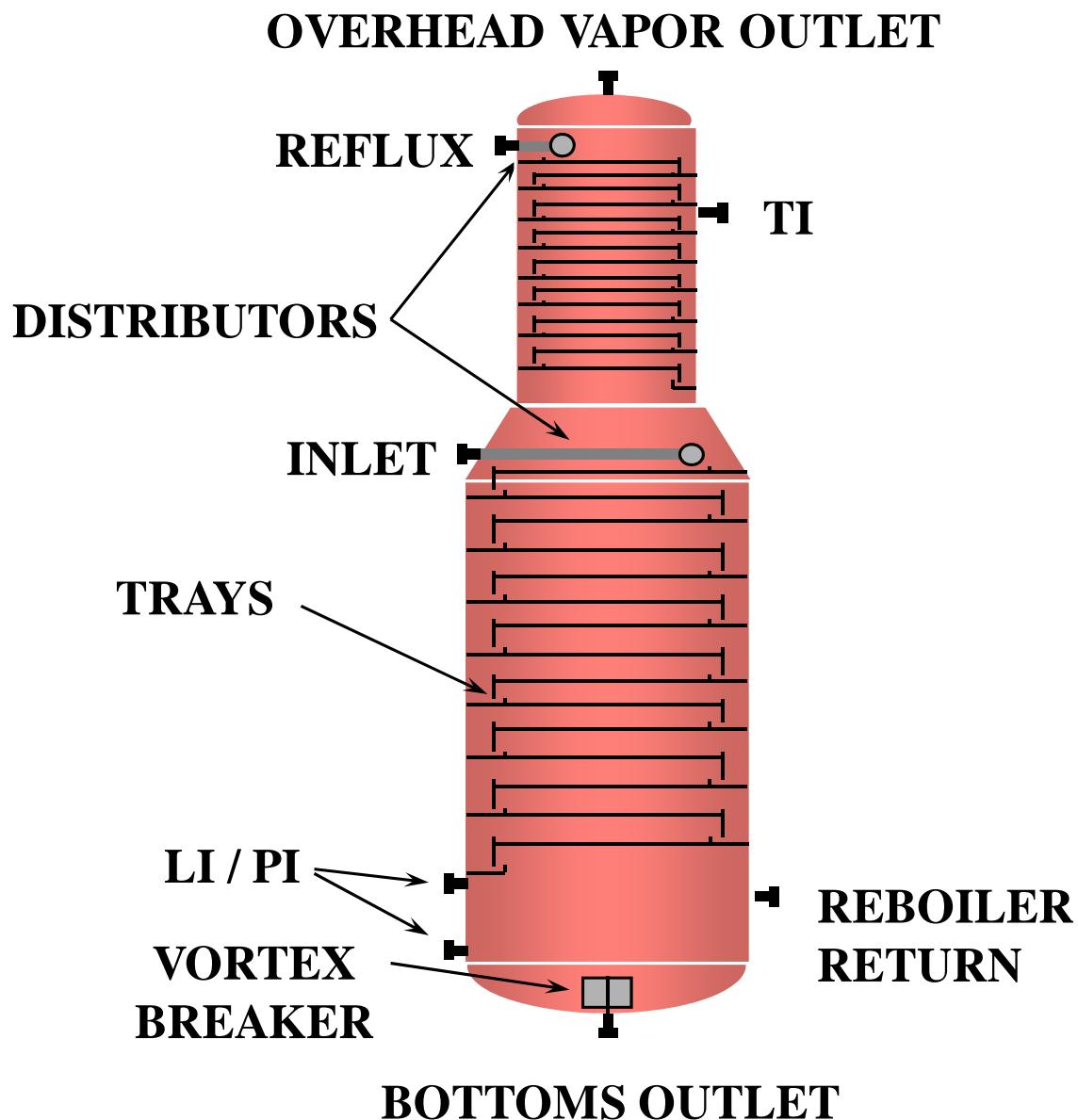
**FIGURE V-9**  
**Reactor Inlet Vapor Liquid Distribution Tray**



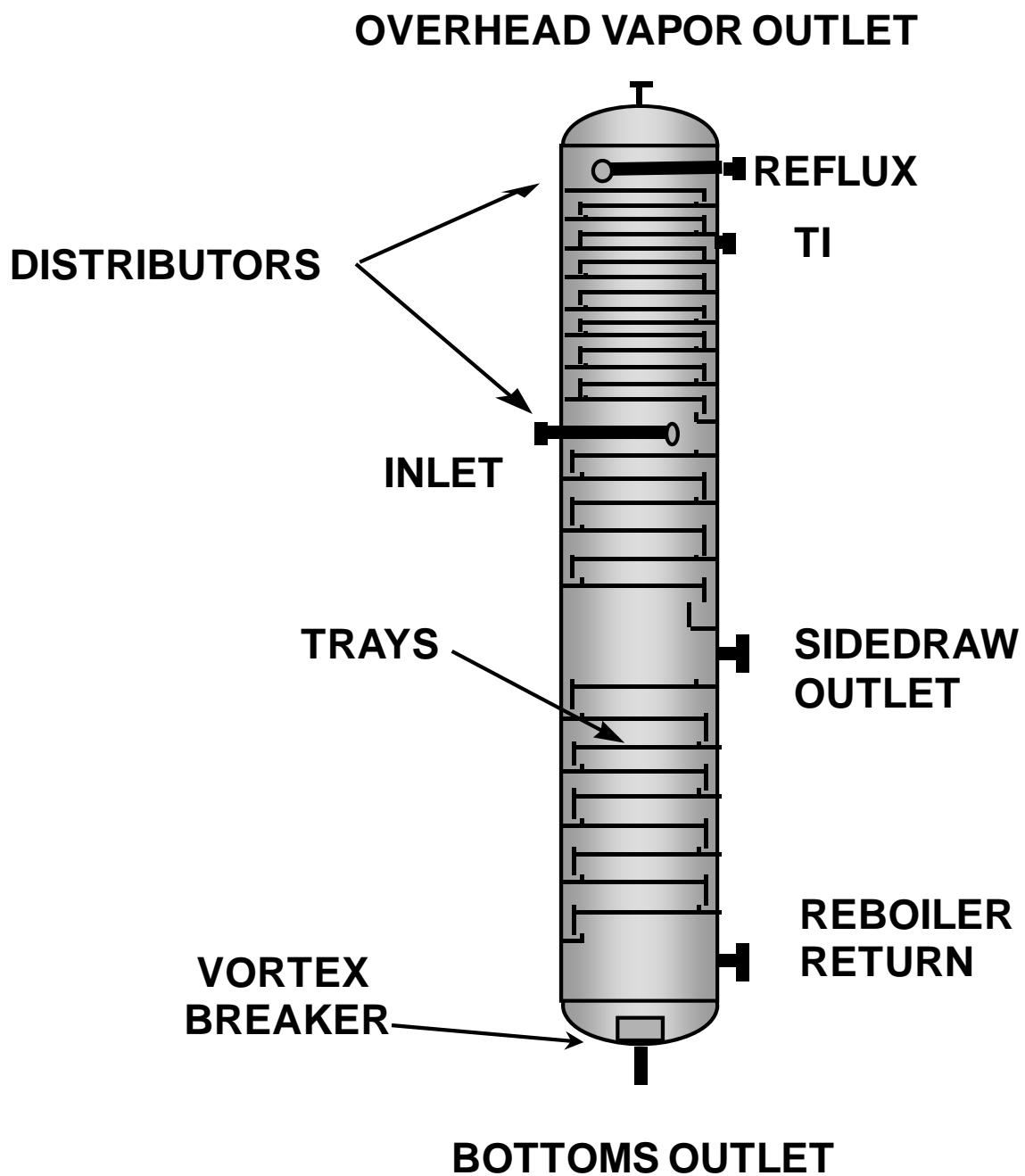
**FIGURE V-10**  
**Reactor Outlet Basket**



**FIGURE V-11**  
**Stabilizer**



**FIGURE V-12**  
**Deisohexanizer**



## VI. COMMISSIONING

The following section will discuss the various aspects associated with the commissioning of the Penex Unit. The section contains information about the precommissioning and initial startup of the unit. The precommissioning procedures ensure that the unit is safe, operable, and constructed as specified by thorough inspection and testing. The initial startup subsection includes guidelines for vessel loadings, unit dryout, and other procedures used for commissioning the unit.

### **PRECOMMISSIONING ACTIVITIES**

During the final stages of construction and on completion of construction, there is a large amount of detailed preparatory work which should be done by operating personnel in cooperation with others at the job site. The primary purpose of this work is to acquaint the operators with the equipment, to inspect the equipment to make certain the construction was done exactly as shown on the piping and instrument diagrams, to insure the equipment is free of debris and construction trash, to "run in" pumps and drivers, and to commission all utilities and supporting facilities so these will be ready for the startup of the process equipment.

This subsection covers the work required in preparing the unit for operation. This work (such as testing and cleaning), is generally carried out during final stages of construction and on the whole, is generally carried out only once; however, it may be necessary to repeat some procedures after major turnarounds. Careful and thorough preparation is a requisite for satisfactory performance and will eliminate much trouble and delays during the startup. An outline is presented for a general method of cleaning and flushing lines and equipment. The outline for checking pumps, after installation and prior to operation, is applicable on all startups. Much of the work noted in this section is performed by construction personnel. No attempt is made herein to designate the personnel performing this preparatory work. There are some phases of the preparation, such as run-in of pumps during water circulation for line cleaning, which are best completed by the refiner's operating personnel. Much valuable experience can be obtained in this manner.

## A. CLEAN AND SERVICE UTILITY SYSTEM

For ease of operation the utility system should be put into service as soon as possible. The various lines must be tested for leakage and washed free of debris and construction trash. Steam lines should be warmed up slowly to prevent damage by water hammer. All steam traps and control valves in the system are to be placed in service for purposes of testing. Likewise the control system for air, water and fuel gas should be tested for operability.

## B. CHECK UNIT AGAINST PIPING AND INSTRUMENT DIAGRAMS

Following construction it is necessary that a careful inspection be made of the equipment to ascertain that the construction was performed exactly as indicated on the piping and instrument diagrams. This can best be accomplished by covering every line and every notation with print marking pencils as the check is made. Particular attention should be paid to the details where errors in construction are most likely to occur. Any deviations from design are to be brought to the attention of those concerned for special consideration.

## C. INSPECTION OF VESSELS

Before all vessels are closed and final bolting of manways done, they should be inspected for completeness and cleanliness. A suggested general check list follows:

1. Make sure the tray installation is complete and that all inspection plates where used are in place. If perforated trays or sieve trays are used, verify that all openings are clear. If side-to-side draw type are used with trap trays, make sure these are clear and properly installed. Test where required.
2. Make sure all internal distributors for all of the towers are installed as the design case specifies. Verify that the openings and the sizings of the distributors are as specified.

3. Where internal drawoff piping is installed off the bottom of the towers or vessels, make sure that these installations are as specified.
4. Verify the location and length of all the thermowells.
5. Determine that the location and range of level instrument internal floats, external type displacement tube cages or differential pressure type nozzles are as specified. Verify that all orifice plates are available to be installed in their proper locations and are properly sized. Prior to hydrostatic testing, make sure that all lead lines to and from orifice tap flanges are shut off.

## D. HYDROSTATIC TESTING

1. Hydrostatic tests are made on new or repaired equipment to prove strength of materials and welds. This test is made by completely water filling the equipment to be tested and increasing the pressure to the specified pressure. Normally, a portable positive displacement pump will be used to raise the pressure. This test should not be confused with other less severe tests generally carried out before a startup to check tightness of connections.
2. The hydrostatic testing is ordinarily done by construction personnel. If for any reason it should become necessary for the operators to carry out such a test, the specified hydrostatic test pressure is normally 1.5 times design operating pressure. Equipment to be tested is generally divided into groups of similar test pressures and isolated from other sections by installing suitable blinds.
3. Screens should be placed in the suction lines of all pumps before any liquid is allowed to pass through them from newly constructed lines. If this is not done, scale, weld metal or slag, stones, etc., may freeze or damage the impellers of the centrifugal pumps. The screens also act to trap such dirt in a location where it can be conveniently removed. Screens should be placed in a flange between the suction valve and the pump so that the screen may be removed

without depressuring any vessels. The flow through the screen should preferably be downward or horizontal. Precautions should be taken to place screens in a location where the dirt particles will not drop into an inaccessible place in the line when the flow through the pump stops. If this should happen, it would not be possible to remove the dirt upon removal of its screen.

An air pressure test can be placed on the sections of the unit prior to a water test so that any open lines or flanges discovered and taken care of before liquid is admitted. However, a water hydrostatic test is considered necessary for final testing and the location of all leaks. It should be remembered that in pressure testing all vessels and towers, the test gauge should be placed at the bottom of the vessel so that the liquid head will be taken into account. Before introducing water into a tower vessel, vents should be opened. After the test, reduce the pressure developed during the hydrostatic test very slowly.

4. Some further suggestions which should be followed prior to and during the hydrostatic test period are as follows:
  - a. Relief valves or rupture discs must be removed, blinded or gagged.
  - b. All items under test must be liquid filled and all air vented.
  - c. Internals such as level ball floats, which are not designed for the test pressure, must be removed.
  - d. Items, such as connecting piping to a vessel under test, which are capable of withstanding the test, may be subjected to the test.
  - e. Items, such as vessels connected to piping under test, which are not capable of withstanding the test, must be isolated by blinding.
  - f. A water filled system must be vented while draining to avoid collapsing equipment not designed for vacuum.

- g. The minimum temperature at which hydrotesting can be conducted is 15.6°C (60°F).
- h. All relief valves (PSV's) must be bench tested and set before final installation. This testing and setting may be done while hydrostatic testing is in progress.

## E. FLUSHING OF LINES

- 1. All piping should be thoroughly cleaned of debris and scale. Generally, fluid handling lines are flushed with water and thoroughly drained. Where practical, clean water should be supplied to the vessels and the contiguous lines be flushed away from the vessel. Do not flush debris into equipment.
- 2. Water flushed lines which do not drain freely should be blown clear with air.
- 3. Gas-handling piping may be either water flushed or air blown. Water should be blown from the gas lines on completion of flushing. Gas piping to compressors must be free of water.
- 4. Instrument air lines should be thoroughly blown with clean dry air.
- 5. In all cleaning by flushing, whether with water, steam or air, maximum volume and velocity should be used for thorough cleaning.
- 6. Care must be taken to avoid a vacuum condition when draining any pieces of equipment. When flushing from a vessel or other equipment, adequate venting must be provided.

7. Following is a guide for flushing:

- a. Orifice plates must not be installed prior to flushing.
- b. Control valves and special drier circuit valves should be removed or rolled out. Flexitallic gaskets cannot be reused so they should not be put in until final installation. Temporary gaskets can be used for initial installation.
- c. Instrument lines should be closed off or disconnected.
- d. Flush pump intake and discharge piping while disconnected.
- e. Supply and exhaust steam lines to turbines are cleaned by blowing while disconnected.
- f. Flush through open end lines. Do not restrict flow.
- g. Regulate rate of flushing medium from source. For example, water from a tower, regulate at the tower; and steam, at the valve in the supply to the line being blown.
- h. Flush through all drains and vents.
- i. Where possible, flush downward or horizontally.
- j. First, flush or blow each lateral header from the source to end.
- k. Second, flush or blow each lateral header from the main to end.
- l. Third, flush or blow each lateral header from the main to end.
- m. Always flush through bypass to an open end before flushing through equipment.

- n. For steam systems flush well through dirt leg drains and steam trap bypasses before placing the trap in service.
  - o. Disconnect lines at exchangers and flush to open end lines.
8. Upon completion of line flushing of any system, carefully check that all temporary breaks are reconnected, control valves replaced, and pump alignments are normal.

## F. INITIAL RUN-IN OF PUMPS AND DRIVERS

During precommissioning the only equipment that may be run in on clean wash water are the caustic circulation pumps. If wash water circulation pumps, and the water addition pump are present, they too may be run in on clean wash water. The drivers on the reactor charge pumps and stabilizer reflux pumps should be checked uncoupled. All the fin-fans should have been checked for amperage load and vibrational problems.

1. Proper installation and operation of pumps and drivers is essential for trouble-free performance. The pumps and drivers should receive careful handling during initial run-in. The initial run-in of pumps is generally done by circulating water through the new equipment. Temporary strainers are installed in the intake of the pumps. During run-in of pumps, the strainers may cause some restriction of flow, as debris collects in the strainers, and the flow to the pump will fall off. In this event, it will be necessary to limit the flow of centrifugal pumps by throttling the discharge valve. Avoid restricting the discharge to the extent that it will cause internal slippage and excessive heat generation. The pump must not be permitted to cavitate, i.e., "losing suction," which may cause damage to the pump. In starting a centrifugal pump, the rotation should be brought up to speed as rapidly as possible. An operating speed is attained rapidly and automatically with motor drive pumps and the usual motor starting control.

2. The development of discharge pressure is essential to flush and lubricate the wearing rings. Subsequently, it is advisable, where practical, to close the pump discharge immediately prior to shutting down a centrifugal pump, to maintain maximum flush through wearing rings.
3. The discharge valve, of an operating positive displacement type pump, rotating or reciprocating, should not be closed as this will cause overpressuring.
4. Pumps in hot service must be gradually warmed to near operating temperature before placing in service. Uneven expansion of the internals and casing may cause seizure and damage when starting.
5. Following is a check list for prior-to-run-in:
  - a. The manufacturer's operating instructions should be reviewed for any specific precautions that should be observed.
  - b. Check that the overall installation is complete.
  - c. Verify that the pump and driver have been aligned for cold operation. There must be no undue strain on the pump or driver by the piping.
  - d. Check the water piping. Verify that the water piping is connected, where required, to bearing jackets, pedestals, stuffing boxes, etc.
  - e. Check the steam piping. Verify that the steam piping, where required, is complete.
  - f. Check the seal or gland oil piping. Conventionally packed pumps in hot service are generally furnished with gland oil: verify that this installation is correct and complete. When a pump is furnished with mechanical seals, verify that all of the components of the flushing system, such as strainers, separator, restriction orifices and coolers, when required, have been correctly installed and are clean. It is very important that the flush system

be clean since the loss of flush or dirty flush can cause the loss of seals.

- g. Verify that packing or seals are installed.
  - h. Check that temporary strainers in suction piping, when required, have been installed.
  - i. Verify that bearings and shafts have been cleaned prior to final lubrication.
  - j. Check that the pump and driver are lubricated according to the vendor's lubrication instructions.
  - k. Check the rotation of electric motor drivers uncoupled from the pump. Run-in uncoupled, verifying operability.
  - l. Run-in, uncoupled from pump, the other non-electric drivers. During run-in of the driver, overspeed trip bearings, controls, vibration, etc., are all satisfactorily checked to confirm operability. Abnormal conditions must be corrected before coupling to the pump.
6. The pumps are normally delivering a material of lighter weight than the water circulated during initial run-in. The pump driver is sized for the normal pumping fluid, consequently while pumping water, the electric motors are easily overloaded. To avoid overloading the motor driving a centrifugal pump, the flow must be limited by throttling the pump discharge valve. If possible, check the amp usage against the design.
7. The following list is for operating the pumps during run-in:
- a. Rotate pump and driver by hand, verifying that they roll freely.
  - b. Check that the water supply and delivery circuits are properly lined up.

- c. Open the pump suction valves fully, venting air from the piping and pump, completely filling it with liquid.
- d. Establish cooling water flow, where required.
- e. Check that the pump lubrication is satisfactory.
- f. Make sure that electric power is available from the switch gear to the starter of the electric motor drivers. For steam turbine drivers, the turbine is warmed by slowly opening the exhaust valve back-in steam while draining water from the casing. The exhaust valve is always fully opened before starting. Where the exhaust system is under vacuum, the case must be warmed by gradually introducing the driving steam, after opening the exhaust valve. In vacuum exhaust systems, sealing steam to the turbine shaft labyrinth must be admitted to avoid loss of vacuum.
- g. Barely open the discharge valve of a centrifugal pump and fully open the discharge valve of a positive displacement pump before starting.
- h. Start the pump and bring it up to speed immediately, observing the discharge pressure. If the pressure does not build immediately, stop the pump and find the cause. Refill the pump and restart when the previous difficulty is corrected.
- i. When the discharge pressure of a centrifugal pump has increased satisfactorily after starting, gradually open the discharge valve to obtain the desired flow rate.
- j. In the event of unusual noise, vibration, overheating or other abnormal conditions, shut the pump down immediately. Correct the cause before resuming operation. Continue checking for abnormal conditions as these may occur after prolonged operation.

- k. Check safety sealing. Mechanical seals should show no leakage. Conventionally packed stuffing boxes must always be permitted to leak slightly, to provide some lubrication and prevent overheating. Stuffing box gland nuts are generally only finger tight. A mechanical seal may show some leakage on startup. After the pump has been started and stopped a few times, the leakage should stop. If the seal leakage persists, then steps are to be taken to correct the problem.
- l. Operate the pump, directing flows through all suction and discharge piping circuits.
- m. Inspect and clean screens as required.
- n. Recheck and realign if required, after any disturbance of piping, such as after suction screen inspection or cleaning.
- o. In shutting down a centrifugal pump, close the discharge valve first, thereby maintaining discharge pressure while the pump rolls to a stop. This also prevents valve leaks. Positive displacement pump discharge valves must not be closed until the pump is shut down and rolling stops.
- p. After all lines available to the pump have had suitable flushing, the temporary suction strainer may be removed only after showing itself to be free of debris on two successive examinations. The permanent strainers may then be installed where required.
- q. Packing, in conventionally packed pumps normally not in water service, must be replaced upon completion of run-in and screen removal.

## G. INSTRUMENT CHECKING

Prior to initial startup, instrumentation must be completed and checked out. Following is the required check list:

1. Testing and setting of all safety valves complete prior to operation.
2. Checking out all transmission systems of each instrument after installation.
3. Testing of air system to all control valves. Control valves are removed while line flushing; when replaced, this section of the air system should be retested
4. Checking of control valve operability, i.e., stem travel, action on air failure, etc.
5. Calibration of all pressure and temperature gauges.
6. Testing all instrument lead lines for leaks.
7. Checking sealing fluid, where required.
8. Calibrate all instruments and synchronize the transmitter and receiver readings for each instrument.
9. Installation of meter factor cards.
10. After line flushing, calibrate and install all orifice plates. Check the orifice plates for plate direction, weep hole orientation and tag accuracy.
11. Check all instrumentation for correct metallurgy.

## H. HOT OIL SYSTEM

If a hot oil system is used, the following procedure is to be used in commissioning it:

1. After the hot oil heater is dried (as per heater vendor's guidelines), and the heater has been shut down, all equipment in this system is to be drained and nitrogen purged.
2. The reboiler oil surge drum is first filled with heating oil to the middle of the gauge glass.
3. If the system has not yet been thoroughly cleaned, the screens in the suction lines of the pumps should be left in place until the initial circulation is complete.
4. After any water in the surge drum has been drained, the oil system is lined up through the pump, heater, bypass valve to the return header, and back to the surge drum. Circulate the system for a short period of time.
5. The hot oil surge drum is then again checked for water and drained if necessary.
6. Open the valves to one reboiler at a time and start the circulating pump circulating at high velocity through a reboiler control valve and then through the control valve bypass. Take all excess through the bypass at the end of the header in order to stay slightly above the minimum flow recommended for the circulating pump. As the level drops in the surge drum, add fresh makeup oil. Circulate through each reboiler in turn until all reboilers have been circulated. At this time the oil level in the surge drum should be in the bottom of the glass to allow for expansion when the oil is heated.
7. Drain any water from the hot oil surge drum.
8. Purge the heater with steam and start a small fire in the heater as recommended in the heater startup procedure. Put the heater on temperature

control at about 204°C (400°F), with all reboilers closed in, until heat is required for drying out.

## I. FIN-FAN HEAT EXCHANGERS

An air fin exchanger consists of a fan with one or more heat transfer sections mounted horizontally on a frame. The heat transfer sections consist of finned tubes fixed between header boxes. Allowance for thermal expansion of the tubes is accomplished by anchoring only one header box and permitting the other 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.

The fin-fan heat exchangers should be installed and commissioned with manufacturer's recommendations. Special attention should be given to:

1. Check on condition of fins and remove any debris that might be left such as wool, insulating scraps, etc.
2. Alignment and coupling of motor.
3. Check free rotation by hand.
4. Belt tension on fin-fan drive pulleys.
5. Check guards - must be safe.
6. Check bearings - clean and lubricate only if necessary - check for oil leaks.
7. Proper motor-fan rotation.

8. Check earthing.
9. Check amperage to insure proper pitch setting.
10. Check on metallurgy and pressure/temperature ratings.
11. Vibration switches - check for vibration during startup and load runs.
12. Check that the louvers above fin-fans are greased sufficiently to prevent rusting.
13. Vents and drains where applicable.

## **INITIAL STARTUP PROCEDURES**

The following procedures describe the method for placing the Penex Unit in operation. Some variations in the following startup procedure are possible due to different refinery practices. Also as experience is gained by the operating crew, it is expected that improvements or other changes may be possible.

### **A. PRELIMINARY**

Before proceeding with the startup, the following preliminary items should be checked to insure that a safe and orderly commissioning of the unit can be effected:

#### **1. Safety**

All safety equipment which will be required for hydrocarbon addition to the unit is to be on-site and operable. Check that:

- a. All portable fire equipment is in place
- b. The fire hydrant system is in service

- c. Miscellaneous safety equipment is available
- d. The area is reasonably free from obstructions
- e. Necessary warning signs are posted
- f. All relief valve keys are removed
- g. Adequate lighting is available for night operations (night time review)

## **2. Activate Utility Headers**

Commissioning utility systems is a routine refinery operation and as such will not be discussed in detail. In general, the main utility headers will be lined up with all vents and drains closed and the sub-headers isolated. All other plants which may be affected will be advised before the main header is slowly pressurized up, after which the subheaders will be commissioned. All steam systems and all traps will be placed in service, and then regularly checked to insure that they are operating. Air headers must be checked for water, and gas headers for water and condensate.

In the case of electrical power to instruments, the operator should witness a simulated power failure to check that the auxiliary power system takes over within five seconds. He should also witness a simulated automatic transfer from the voltage regular transformer to the standby isolating transformer.

## **3. Blind List**

The blind list must always be current, and it is good practice to double check not only that the list is accurate but that all blinds necessary for the safety of the plant are in place.

## **4. Mechanical Equipment**

Any mechanical equipment which did not function properly during the precommissioning equipment run-in period must be ready for operation at this time.

## 5. Instruments

All instrument loop checking must be completed by this time with the instruments ready for service.

## 6. Inter-Departmental Coordination

Notification should be given to the other departments of the refinery concerned with the startup. These areas would include offsites, other process units integrated with the Penex Unit, the utility, maintenance, and instrument departments and the laboratory. During the startup phase additional manpower should be made available from the operating, maintenance, and instrument departments to assist in unit coverage. Also the final laboratory schedule should be posted and the laboratory alerted so that the required quality control tests can be carried out when required.

## 7. Steam and Electrical Tracing

Verify that all steam and electrical tracing is turned on and is functioning properly.

## 8. Chemical Cleaning

On any revamped Penex Units that have had their origin as another type of process unit, it is highly suggested that the equipment in the reactor circuit be chemically cleaned prior to the normal Penex drying and anhydrous HCl cleaning. The existing equipment could have appreciable quantities of sulfur or iron scale and its presence could delay the startup. Chemical cleaning is also specified on piping around reciprocating compressors. The general conditions for this type of acid cleaning appear in the unit's project specification under "Mill Scale Removal."

**IF THIS CHEMICAL CLEANING ROUTE IS FOLLOWED, IT MUST BE REMEMBERED THAT THE GASES LIBERATED DURING THIS OPERATION CAN CONTAIN APPRECIABLE QUANTITIES OF H<sub>2</sub>S AND H<sub>2</sub>. THESE GASES MUST BE DISPOSED OF PROPERLY AS THEY CONSTITUTE A SAFETY HAZARD.**

## 9. Sand-blasting

After the pressure testing has been completed and the chemical cleaning operation (revamped unit only) has been finished, the reactors, and other vessels specified in the project specification are to be sand-blasted to remove scale and rust, since any iron oxide liberates water on contact with HCl. The water thus formed will extend the unit drydown period. Immediately following sand-blasting, a light coat of mineral oil is to be applied to the sand-blasted surfaces to prevent oxidation. The compressors and heat exchangers are not to be sand-blasted.

## 10. Vessel Loading

When the sulfur guard bed, hydrogen and liquid feed driers are hydrotested, dried, and cleaned they may be loaded. Procedures for loading the driers and the Off Gas Scrubber are given in XIII. Special Procedures.

The loading of the reactors will take place in two distinct stages. The first is the installation of the catalyst support material before the unit is dried and the second is the actual catalyst loading after the unit has finally been dried. After the completion of the sand-blasting and oil coating, the reactors are ready for the installation of the catalyst support material. Refer to XIII. Special Procedures for the “Loading Reactor Support Material” procedure.

## 11. Air Test

A plant fitness test using air should be conducted to insure that all lines and process equipment (excluding the process pumps and the compressor) are “tight” prior to steam purging and gas blanketing.

The basic procedure for this step consists of pressuring the vessels and lines in the appropriate circuit to either their maximum operating pressure or 3.5 kg/cm<sup>2</sup>g (50 psig) (WHICHEVER IS LESS) and then conducting the fitness test. The test

pressure should be held for a minimum of one hour, while every flange and joint in the system is closely examined for leaks.

## 12. Purging and Gas Blanketing

It must be remembered that oil or flammable gas should never be charged into process lines or vessels indiscriminately. The unit must be purged before admitting hydrocarbons. There are many ways to purge the unit and ambient conditions may dictate the procedure to be followed :

Nitrogen or inert gas purging.

Evacuating the equipment followed by nitrogen blanketing.

Steaming followed by fuel gas blanketing. Steaming followed by fuel gas blanketing is generally the most common technique used for air freeing the fractionation section of the Penex Unit. Thus, the following steps will briefly outline this method.

- a. Potential problems or hazards which could develop during the steam purge are as follows:
  - (1) Collapse Due to Vacuum: Some of the vessels are not designed for vacuum. This equipment must not be allowed to stand blocked in with steam since the condensation of the steam will develop a vacuum. Thus, the vessel must be vented during steaming and then immediately followed up with an inert fuel gas purge at the conclusion of the steamout.
  - (2) Flange and Gasket Leaks: Thermal expansion and stress during warmup of equipment along with dirty flange faces can cause small leaks at flanges and gasketed joints. These must be corrected at this time.
  - (3) Water Hammering: Care must be taken to prevent “water hammering” when steam purging the unit. Severe equipment damage can result from water hammering.

- b. Block in the cooling water to all coolers and condensers. Shut down fans on Fin-Fan coolers and condensers.
- c. Open high point vents and low point drains on the vessels to be steam purged.
- d. Start introducing steam into the bottom of the columns, towers, and at low points of the various vessels in the fractionation circuit. It may be necessary to make up additional steam connections to properly purge some piping which may be “dead-ended.”
- e. Thoroughly purge all equipment and associated piping of air. The progress of the steam purge can be followed by marking up a P&I diagram to indicate the lines purged. Verify that sufficient drains are open to drain the condensate which will collect in low spots in the unit.
- f. When the steam purging is completed, start to close all the vents and drains. Immediately start to introduce fuel gas into all vessels and then cut back the steam flow until it is stopped. Regulate the fuel gas flow and the reduction of steam so that a vacuum due to condensing steam is not created in any vessel or that the refinery fuel gas system pressure is not appreciably reduced. Some additional fuel gas connections may have to be made up to assist in the gas blanketing of the Penex Unit. Pressure the Penex Unit up to approximately 10 psig (.7 kg/cm<sup>2</sup>) with fuel gas.
- g. Drain any residual condensate from the Penex Unit.

Evacuating and nitrogen blanketing is normally the manner in which the reactor section is freed of oxygen. For this section, the following guides are suggested:

- (1) Test the ejector to make sure that it will work.
- (2) Make sure the gas flow will be in the same direction as the normal flow. This applies to both the evacuation as well as the subsequent filling with nitrogen.

- (3) Use a compound pressure gauge located as far as possible from the ejector.
- (4) Following the final evacuation and fill, a portable combustibles analyzer should be used to confirm that an explosive mixture does not exist.
- (5) Do not evacuate any pumps or compressors. They are to be nitrogen purged separately.

The liquid feed driers, the feed surge drum, the interconnecting lines, the make-up hydrogen dryers and its associated equipment can be purged with nitrogen until free of air. Leave this equipment under a slight positive pressure ( $N_2$ ) when the purging has been completed.

During all purging and/or depressuring, drain all low points of any water.

## B. HYDROCARBON CIRCULATION AND INITIAL DRYDOWN

With all of the process equipment purged of oxygen as verified by the refinery safety department and under an inert gas blanket the first phase of drying down the unit (initial drydown) can begin.

### 1. Reactor and Line Switching

During this “Dry Out” and the subsequent “Acidizing” period it will be necessary to change the flow pattern through all of the reactors and associated piping to ensure that all lines are used. In addition any “dead” lines in the reactor circuit, e.g. control valve bypasses should have flow established through them for a short time, also instrument lead lines are to be purged. An operator is to be stationed at the CV bypass and instruments during this operation. This line and reactor switching is done to ensure that no pockets of water (initial drydown) or rust (acidizing) will remain in the system.

Initially line-up the reactors for series flow operation. Then, every eight hours after hydrocarbon circulation has been established switch the flow pattern as follows:

- Reactor A single operation
- Reactor B single operation
- Reactor A to Reactor B series operation
- Reactor B to Reactor A series operation

When switching make sure that flow through the system is always maintained and do not proceed to the next step before completely opening or closing the valves listed in each step.

## 2. Hydrogen Addition

Introduce sweet hydrogen to the unit. The process flow will be lined up such that the hydrogen will be routed to the make-up compressor suction drum, bypassing the make-up gas compressor, through the make-up gas cooler, through the make-up gas driers in series and to the reactor preheat exchange train. During this initial fill of the reactor section with hydrogen, care should be exercised such that the rate of filling of the Penex unit does not disrupt the source unit operation. Leak checks of discreet sections of the plant should be performed as hydrogen is introduced in a stepwise manner.

The rate of filling can be monitored by a FR on the hydrogen feed line to the make-up compressor suction drum. Also check that the liquid accumulation in the make-up compressor suction drum does not become excessive. If a high level is noticed then drain this hydrocarbon to the fuel gas system or typical destination.

Pressure up the Penex reactor section to about 19 kg/cm<sup>2</sup>g (275 psig) (or to a pressure level consistent with the make-up H<sub>2</sub> pressure) as indicated by the PRC located at the outlet of the cold combined feed exchanger.

With the reactor system at 19 kg/cm<sup>2</sup>g (275 psig) slowly open the hydrogen pressuring line to pressure up the stabilizer column. Increase the Stabilizer

pressure to 17.5 kg/cm<sup>2</sup>g (250 psig) or to the normal operating pressure by design. Adjust the pressuring gas flow rate to minimum. Add sufficient hydrogen to the reactor circuit to maintain it at 19 kg/cm<sup>2</sup>g (275 psig). Note that gas exiting the reactor section can also be used to hold pressure on the stabilizer. Place the stabilizer pressure controller in service at this time with flow from it routed through the net gas scrubber and then to either fuel gas or flare.

### **3. Hydrocarbon Addition**

The initial period of this step will be carried out on a batch type basis until the liquid feed driers are liquid full and an operating level established in the feed surge drum.

Purge the hydrotreated feed slowly through the liquid feed driers and into the feed surge drum. Displace and vent off whatever blanketing gas is necessary. Establish pressure control on the feed surge drum by admitting hydrogen to the drum. This hydrogen originates from the outlet of the make-up gas driers.

Once the liquid feed driers are liquid full they are to be lined up for series flow.

When an operating level is established in the feed surge drum start one of the reactor charge pumps.

Charge the feed to the stabilizer via the startup bypass line which bypasses the reactor section and ties into a point downstream of the reactor pressure control valve. The level in the feed surge drum should be watched in order to prevent losing suction on the charge pumps.

When a level appears in the stabilizer column bottoms start a flow of steam to the reboiler. Raise the heat input to the reboiler.

Route any excess column bottoms to storage on column bottoms level control. After eight hours the stabilizer bottoms material may be routed back to the fresh feed driers via the startup bypass line. When material is available in the overhead

receiver, start reflux to the column and commission the overhead receiver level control.

Establish stable operations at 50% of the design reactor charge rate and 100% of the design hydrogen flowrate.

Initiate drier regenerations. Information relating to this topic can be found in the Normal Operating Procedures of this manual.

Calibrate the moisture analyzers in the unit and commission them to monitor drier performance.

#### **4. Reactor Circuit Circulation**

Start the make-up compressor and start to raise the reactor circuit pressure to approximately 28 kg/cm<sup>2</sup>g (400 psig) or to about 3.5 kg/cm<sup>2</sup>g (50 psig) below the normal operating pressure by design. Place the reactor section PRC on control. Establish the make-up compressor spillback to the make-up compressor suction drum.

Establish the design hydrogen flow through the reactor section.

Once hydrogen flow has been established, the reactors will be heated up for preliminary drying. Start a flow of steam to the charge heater via the condensate FRC and raise the temperature to 121°C (250°F) as indicated by the TRC. Place these instruments on cascade.

With pressure and temperature control established on the system, slowly reroute the liquid feed, which is flowing through the startup bypass, so that it enters the reactor section through the normal charge line, and then slowly close the startup bypass. Do this quickly to simulate how the reactor section bypass must be used once catalyst is loaded into the unit. There will be a period of time where the reactor section will be inventoried with hydrocarbon and feed is lost to the stabilizer. Pressure upsets are expected in the reactor section and stabilizer; therefore, just

prior to the feed being routed to the reactor section, reduce stabilizer heat input in anticipation of the temporary loss of feed to the stabilizer.

Route the liquid feed to the stabilizer on pressure control. At this point the entire unit will be in operation at about 50% of design HCBN flow and 100 percent of design H<sub>2</sub> flow, with no catalyst in the reactors. Raise the reactor pressure to the normal operating pressure by design. The liquid leaving the reactor section to the stabilizer contains the H<sub>2</sub> makeup gas which will increase the pressure on the stabilizer. Establish pressure control on the stabilizer at the design pressure. The stabilizer pressuring gas flow can be discontinued at this time.

With both reactors in service hold the reactor inlet temperatures at a minimum of 177°C (350°F) (and higher if possible, up to 204°C (400°F)). The reactor intercooler, i.e. hot combined feed exchanger control system should be commissioned and tested at this time.

The flow of liquid feed through the reactor section will remove the film of oil placed there after sandblasting. Drier regeneration and/or cooling should be completed before flowing through the reactors and then discontinued for the first eight hours after liquid feed flow has been established in the reactors by shutting down the regeneration system and stopping the flow. The timing of the initial liquid feed drying should be adjusted to fall between regeneration cycles to avoid placing any of the oil contaminated liquid feed from the reactor circuit over the sieves. The oil will flow out in the stabilizer column bottoms and all of it should be routed to storage.

A moisture analyzer probe is installed on the inter-reactor sample pot to measure the water content of the reactor effluent during startup. Flush through the inter-reactor sample system and lines well to obtain accurate moisture readings of the reactor section.

During this hydrocarbon circulation it will be necessary to alter the flow through the reactors and reactor circuit piping as outlined previously. The sulfur stripping lines and hydrogen quench lines should also be dried out during this period.

Continue drying until the water content of the liquid leaving the reactor section is below 10 wt ppm.

## C. ACIDIZING AND FINAL DRYDOWN

When the water content in the system has been reduced to the level previously outlined, injection of anhydrous HCl will be initiated to remove any iron oxide not removed by the sandblasting.

1. Drain any liquid water that may have accumulated in the stabilizer overhead receiver. During the acidizing period with HCl it will be necessary to check and drain this point on a frequent basis as a highly acidic liquid could be present.
2. Inventory the stabilizer off gas scrubber with 10 wt % caustic and establish circulation.
3. Connect up the cylinder of anhydrous HCl to the inlet of the cold combined feed exchanger. The cylinder of HCl should be mounted on a scale such that an injection rate determination can be made.
4. During the acidizing period it will be necessary to temporarily block in the moisture analyzer on the inter-reactor sample pot during the HCl injection as the highly acidic environment could damage the analyzer probe. After HCl has been injected, an hour period will be allowed to lapse and then the analyzer will be recommissioned if the HCl content of the gas from the inter-reactor sample pot is less than 10 ppmv.
5. With hydrogen and hydrocarbon flow established in the unit and drier regenerations being performed frequently, the following will outline the acidizing and final drydown steps.

- a. Block in the moisture analyzer probe that is monitoring the reactor effluent.
  - b. Inject 5 kgs (10 lbs) of HCl to the system over a 10 minute period of time.
  - c. Wait one hour with unit circulation continuing or until the reactor effluent sample pot vapor contains less than 10 ppmv of HCl.
  - d. Reconnect the moisture analyzer and obtain a reading on the sample pot liquid.
  - e. Continue injecting HCl (repeat steps “a” through “d”) until the moisture in the reactor effluent liquid reaches a maximum and starts down. During this period continue draining low points, purging instrument lead lines, flushing by-passes around control valves and switching the reactor flow pattern. The sulfur stripping lines and hydrogen quench line should also be acidized during this period during a shift.
  - f. When no further unit response to HCl addition is noted by the moisture analyzer, have the instrument department verify that the readings are correct. Add another 12 kgs (25 lbs) of HCl over a half hour period. Again re-check the moisture content of the effluent stream. If no response is noted, discontinue HCl injection and dry the unit down (continue unit circulation) until the reactor effluent is 1 wt ppm. If a response to this last HCl addition is noted then return to step 5a.
  - g. It is typical to inject the design quantity of HCl. If no iron oxide is present, additional injection of HCl consumes the HCl and caustic; however, unit final drydown is initiated which does not impact the overall startup schedule.
6. It will be required to run the chloride injection pumps at this time and carry out the injection pump calibration if it has not been done before.

7. Reduce and eventually stop the flow of steam to the charge heater. Continue liquid feed and hydrogen flow through the reactor circuit until the reactors have been cooled to 121°C (250°F).
8. When the reactors have been cooled to 121°C (250°F), again route the liquid feed through the startup bypass.
9. Continue makeup gas H<sub>2</sub> flow to the unit such that the pressure on the stabilizer can be temporarily maintained.
10. Sweep the entire reactor circuit with the hydrogen to purge all of the hydrocarbon over to the stabilizer.
11. Cool the reactor circuit to 49°C (120°F).
12. Discontinue make-up hydrogen addition and keep pressure on the reactor section.
13. Block in each of the reactors, inlet and outlet, and blind the reactors.
14. If liquid feed circulation becomes unstable at this time (i.e., loss of pressure on the stabilizer) it might be advantageous to discontinue it.
15. Depressurize, evacuate and purge each reactor. Use dry nitrogen containing less than 10 ppm of water for the purge. If this is in doubt, route the nitrogen through a freshly regenerated, properly purged hydrogen drier. Clean temporary piping will be needed for this operation. No refinery hoses will be used. Perform the evacuation and purging operation twice. Maintain a positive nitrogen pressure on the reactors.
16. Maintain hydrogen pressure on the balance of the reactor circuit.
17. The isomerization reactors are now ready for loading. Proceed to the I-8 Catalyst Loading Procedure in Section XIII of this manual.

## D. STARTUP PROCEDURE

Upon completion of the catalyst loading operation the reactors can be prepared for startup. Initially only one reactor will be placed on line.

When feed is first introduced to a reactor, particularly when the catalyst is fresh, it is important that the severity of operation be minimized to prevent hydrocracking and the resulting high reactor temperatures. It is very important that the procedure be followed exactly as detailed below. No alterations will be accepted by UOP.

### 1. Initial Operation

- a. Slowly pressure the two reactors up with hydrogen to approximately 28 kg/cm<sup>2</sup>g (400 psig). This “pressure up” is accomplished by opening the appropriate line that originates from the makeup hydrogen gas line and terminates at the reactor inlet. There is a restriction orifice or globe valve in this “pressure up” line to control the rate of “pressure-up.” Pressure test the reactors, then the rest of the reactor circuit.
- b. Once the reactor circuit has been pressure tested, line up the lead reactor for operation. The lead reactor effluent will be lined up to completely bypass the hot combined feed exchanger. The lag reactor will be bypassed using the “single reactor operation” bypass.
- c. Pressure up the stabilizer to 17.5 kg/cm<sup>2</sup>g (250 psig) or to the normal operating pressure. Use the pressuring line from the hydrogen driers to the stabilizer. Excess stabilizer off gas is to be routed through the net gas scrubber which should be in operation.
- d. Establish hydrocarbon circulation as outlined in Section VI item B-2. However, route all stabilizer bottoms to off-spec storage. Verify that the liquid feed driers are functioning, i.e., the moisture analyzer reads below 0.1 wt ppm H<sub>2</sub>O. On

startup, the feed will be introduced to the reactor at least 50% of design. The reactors should never be operated at less than 50% of design feedrate.

- e. Start the make-up compressor, and if not already done, raise the reactor circuit pressure to 28 kg/cm<sup>2</sup>g (400 psig) or to about 3.5 kg/cm<sup>2</sup>g (50 psig) below the normal operating pressure and establish reactor effluent pressure control. Establish the make-up compressor spillback to the make-up compressor suction drum. Verify that the make-up dryers are functioning, i.e. the moisture analyzer reads below 0.1 vppm H<sub>2</sub>O.
- f. Establish a flow of H<sub>2</sub> makeup gas and increase the flow to design. It is very important that the makeup gas flow be at least design at the time feed is introduced to the reactor.
- g. Commission the charge heater to ensure that it is operational. A very small flow of steam to the heater should be maintained to ensure operability. Feed will be introduced to the reactor cold. The heater is being commissioned at this point, rather than after feed is cut in, to ensure that the heater functions properly. If the heater does not function properly, when feed is introduced, overheating of feed may result and a reactor temperature excursion could occur.
- h. With makeup gas flow and reactor pressure control established, prepare to introduce feed to the reactor. FEED SHOULD NOT BE INTRODUCED TO THE REACTOR IF ANY TEMPERATURE IN THE REACTOR IS OVER 65°C (150°F). Introduce feed to the reactor by opening the control valve to the reactor circuit and closing the startup bypass. Ensure that the feed is introduced, at a rate of at least 50% of design. This should be done as quickly as possible.

Do not try to maintain flow through the startup bypass with feed going to the reactor. The stabilizer can operate on total reflux for the period of time that it takes to inventory the reactor circuit.

- i. When feed enters the reactor, there will be an exothermic reaction which will increase the reactor temperature quickly. This phenomenon will be short in duration. The extent of the temperature increase will depend on the feed quality, however, the rise should not pose a problem if the feed introduction temperature is lower than 65°C (150°F). Under no circumstances should the feed be removed from the reactor during this initial startup period unless the reactor temperatures increase above 232°C (450°F). This will result in over-conversion of the feed and hydrocracking. If the temperature gets over 232°C (450°F) the “High Reactor Temperature Differential Emergency” procedure should be followed. (See Section XI. Emergency Procedures.)
- j. Route the liquid feed to the stabilizer on pressure control. At this point, the entire unit will be in operation at about 50% of design HCBN flow and 100% of design hydrogen flow.
- k. After stabilizing the operation, slowly increase the reactor inlet temperature to 121°C (250°F). Raise the temperature at a rate of 11-17°C (20-30°F) per hour. When the temperature reaches 105°C (220°F), start the C<sub>2</sub>Cl<sub>4</sub> injection. Inject C<sub>2</sub>Cl<sub>4</sub> at 300 wt ppm (as chloride) based on reactor liquid charge. When the first reactor stops consuming chloride, as determined by stabilizer off gas chloride analysis, the chloride injection rate can be reduced to 150 wt ppm. Chloride breakthrough is typically observed within 24-36 hours of initial startup on fresh catalyst.
- l. Raise the reactor effluent pressure to 31.6 kg/cm<sup>2</sup>g (450 psig) or to the normal operating pressure.
- m. Route stabilizer bottoms to product storage. The liquid leaving the reactor section to the stabilizer contains hydrogen and light ends which will increase the pressure on the stabilizer. Establish pressure control on the stabilizer at the design pressure. Discontinue flow of pressurizing gas from the makeup gas driers to the stabilizer.
- n. Continue lining out flow rates, temperatures, pressures, etc., through-out the unit.

- o. Adjust the reactor temperatures to give the desired product ratio of approximately 70 IC<sub>5</sub>/C<sub>5</sub>P.
- p. The hydrogen analyzer on the scrubber off-gas should be commissioned. This signal is used to manually adjust the make up gas rate such that a minimum of 0.05 H<sub>2</sub>/HCBN ratio is maintained at the lag reactor outlet.

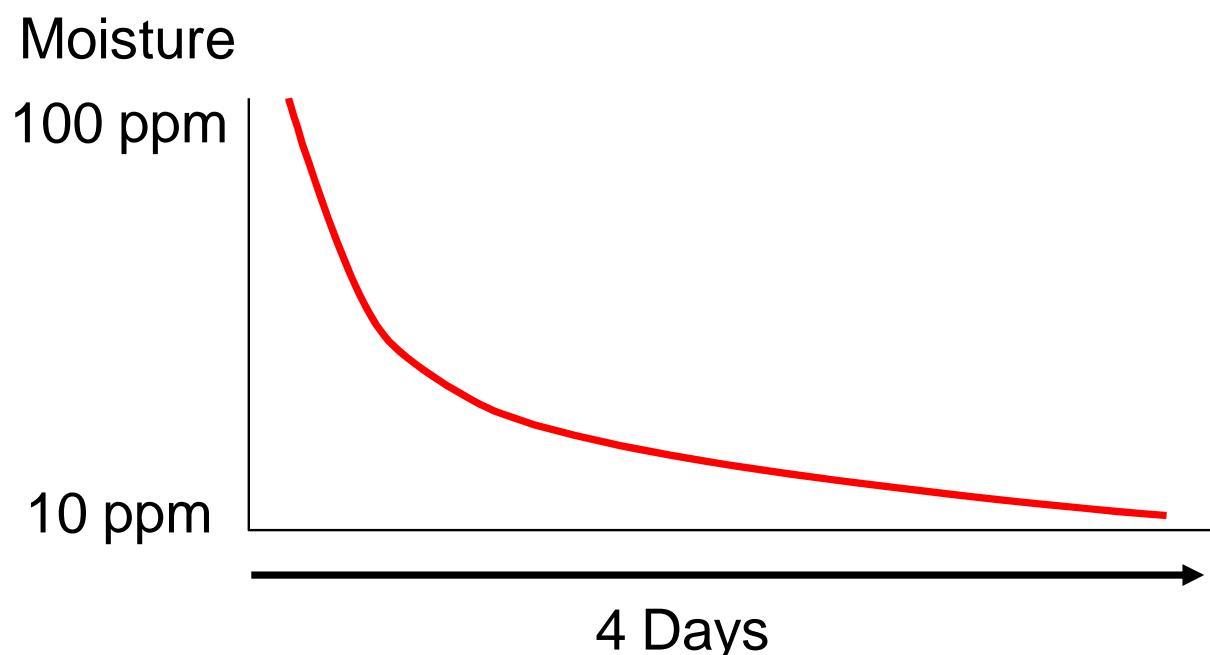
## 2. Series Flow Operation

The first reactor should run for at least 2 days and stable normal operation verified before the second reactor is put on line. The second reactor will be lined up such that it is in series with the first reactor.

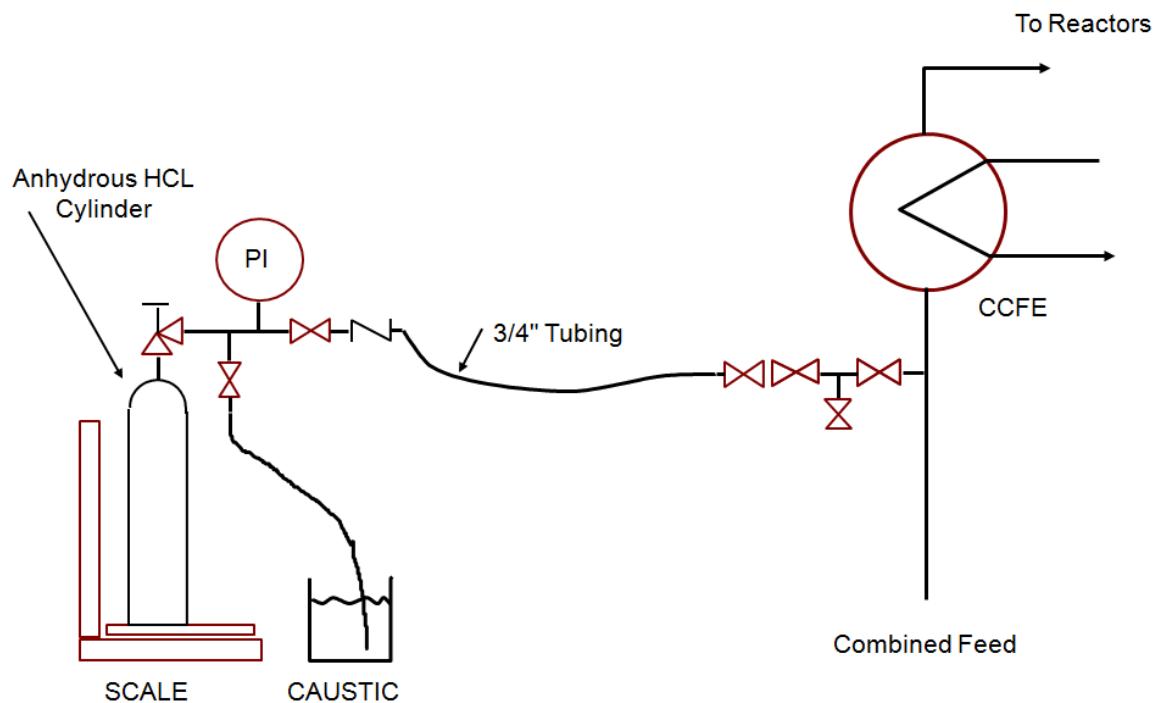
- a. Pressure up the other reactor in the same manner that was used for the on-stream reactor, i.e. via the “pressuring up” line.
- b. The second reactor should be put on line with at least 50% of design feed to the first reactor.
- c. Reduce the reactor system pressure to 28 kg/cm<sup>2</sup>g (400 psig).
- d. Reduce the lead reactor outlet temperature to 121°C (250°C).
- e. Establish flow of lead reactor effluent through the hot combined feed exchanger and cool the feed to the lag reactor as much as possible.
- f. Open the off line reactor’s inlet valves.
- g. Open the off line reactor’s outlet valves.
- h. Establish flow through the reactor by closing the “single reactor operation” bypass and commissioning the TRC which regulates flow through the hot

combined feed exchanger. Keep the lag reactor as cool as possible until the reactor has inventoried and operations are stable.

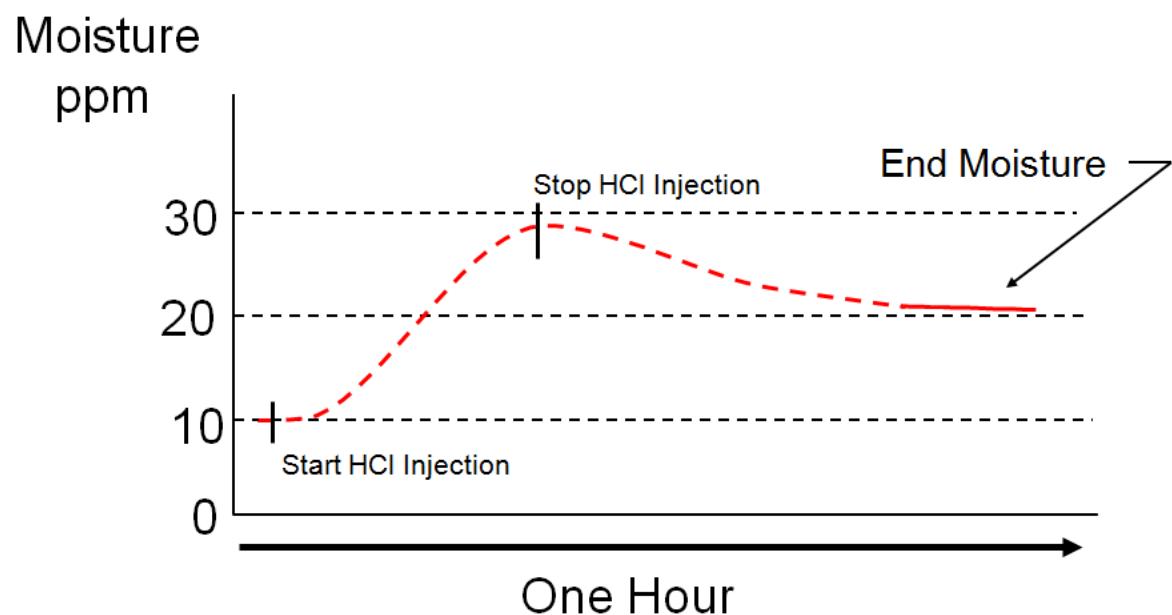
- i. When the second reactor is commissioned, the fresh catalyst will consume chloride for a period of time. The chloride injection rate should be increased to 300 wt ppm chloride based on feed in the same manner as for the first reactor. Reduce the chloride injection to 150 wt ppm based on feed after the chloride level in the stabilizer off gas levels off.

**FIGURE IV-1 INITIAL DRYDOWN**

## FIGURE IV-2 ACIDIZING EQUIPMENT

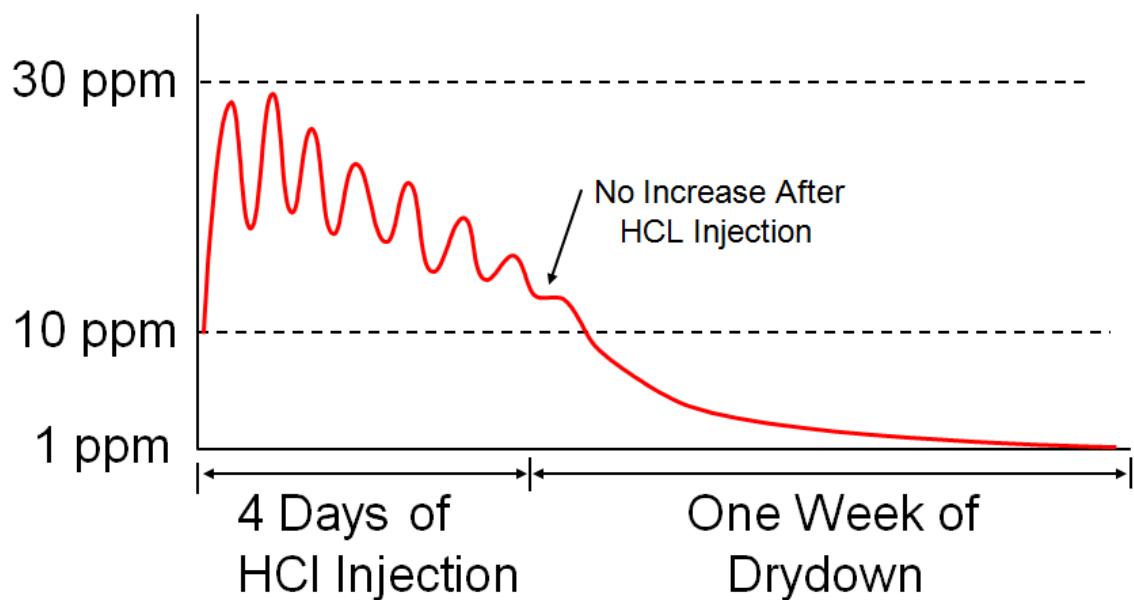


## FIGURE IV-3 HCL INJECTIONS



**FIGURE IV-4 ACIDIZING AND FINAL DRYDOWN**

Reactor Outlet  
Moisture



## VII. NORMAL STARTUP

The following procedures may be used to start up the unit provided moisture and/or air was kept out of the reactor section while shut down. If air or moisture contaminated or is suspected to have contaminated the reactor section, the dryout and acidizing procedures should be followed as provided in the Initial Startup Procedures in Section VI.

Two startup procedures are given below. If the entire unit was shutdown then procedure "A" should be used. If one reactor is in operation and the other reactor has just been loaded with fresh I-8 catalyst, procedure "B" should be used. Procedure B can also be used to bring the second reactor on stream if one reactor was shut down for a reason other than catalyst changeout.

### A. STARTUP AFTER TOTAL UNIT SHUTDOWN

At this point it is assumed that the unit is shut down and under a slight positive pressure of H<sub>2</sub> or dry N<sub>2</sub>.

- a. Slowly pressure the two reactors up with hydrogen to approximately 28 kg/cm<sup>2</sup>g (400 psig). This “pressure up” is accomplished by opening the appropriate line that originates from the makeup hydrogen gas line and terminates at the reactor inlet. There is a restriction orifice or globe valve in this “pressure up” line to control the rate of “pressure-up.” Pressure test the reactors, then the rest of the reactor circuit.
  
- b. Once the reactor circuit has been pressure tested, line up the lead reactor for operation. The lead reactor effluent will be lined up to completely bypass the hot combined feed exchanger. The lag reactor will be bypassed using the “single reactor operation” bypass.

- c. Pressure up the stabilizer to 18 kg/cm<sup>2</sup>g (250 psig) or to the normal operating pressure. Use the pressuring line to a point upstream of the stabilizer column's pressure controller. Excess stabilizer off gas is to be routed through the off gas scrubber which should be in operation.
- d. Establish hydrocarbon circulation as outlined in Section VI item B-2. However, route all stabilizer bottoms to off-spec storage. Verify that the liquid feed driers are functioning, i.e., the moisture analyzer reads below 0.1 wt ppm H<sub>2</sub>O. On startup, the feed will be introduced to the reactor at least 50% of design. The reactors should never be operated at less than 50% of design feedrate.
- e. Start the make-up compressor, and if not already done, raise the reactor circuit pressure to 28 kg/cm<sup>2</sup>g (400 psig) or to about 3.5 kg/cm<sup>2</sup>g (50 psig) below the normal operating pressure and establish reactor effluent pressure control. Establish the make-up compressor spillback to the make-up compressor suction drum. Verify that the make-up dryers are functioning, i.e. the moisture analyzer reads below 0.1 vppm H<sub>2</sub>O.
- f. Establish a flow of H<sub>2</sub> makeup gas and increase the flow to design. It is very important that the makeup gas flow be at least design at the time feed is introduced to the reactor.
- g. Commission the charge heater to ensure that it is operational. A very small flow of steam to the heater should be maintained to ensure operability. Feed will be introduced to the reactor cold. The heater is being commissioned at this point, rather than after feed is cut in, to ensure that the heater functions properly. If the heater does not function properly, when feed is introduced, overheating of feed may result and a reactor temperature excursion could occur.
- h. With makeup gas flow and reactor pressure control established, prepare to introduce feed to the reactor. FEED SHOULD NOT BE INTRODUCED TO THE REACTOR IF ANY TEMPERATURE IN THE REACTOR IS OVER

65°C (150°F). Introduce feed to the reactor by opening the control valve to the reactor circuit and closing the startup bypass. Ensure that the feed is introduced, at a rate of at least 50% of design. This should be done as quickly as possible.

Do not try to maintain flow through the startup bypass with feed going to the reactor. The stabilizer can operate on total reflux for the period of time that it takes to inventory the reactor circuit.

- i. When feed enters the reactor, there will be an exothermic reaction which will increase the reactor temperature quickly. This phenomenon will be short in duration. The extent of the temperature increase will depend on the feed quality, however, the rise should not pose a problem if the feed introduction temperature is lower than 65°C (150°F). Under no circumstances should the feed be removed from the reactor during this initial startup period unless the reactor temperatures increase above 232°C (450°F). This will result in over-conversion of the feed and hydrocracking. If the temperature gets over 232°C (450°F) the “High Reactor Temperature differential Emergency” procedure should be followed. (See Section XII. Emergency Procedures.)
- j. Route the liquid feed to the stabilizer on pressure control. At this point, the entire unit will be in operation at about 50% of design HCBN flow and 100% of design hydrogen flow.
- k. After stabilizing the operation, slowly increase the reactor inlet temperature to 121°C (250°F). Raise the temperature at a rate of 11-17°C (20-30°F) per hour. When the temperature reaches 105°C (220°F), start the C<sub>2</sub>Cl<sub>4</sub> injection. Inject C<sub>2</sub>Cl<sub>4</sub> at 300 wt ppm (as chloride) based on reactor liquid charge. When the first reactor stops consuming chloride, as determined by stabilizer off gas chloride analysis, the chloride injection rate can be reduced to 150 wt ppm.
- l. Raise the reactor effluent pressure to 31.6 kg/cm<sup>2</sup>g (450 psig) or to the normal operating pressure.

- m. Route stabilizer bottoms to product storage. The liquid leaving the reactor section to the stabilizer contains hydrogen and light ends which will increase the pressure on the stabilizer. Establish pressure control on the stabilizer at the design pressure. Discontinue flow of pressurizing gas from the makeup gas driers to the stabilizer.
- n. Continue lining out flow rates, temperatures, pressures, etc., through-out the unit.
- o. Adjust the reactor temperatures to give the desired product ratio of approximately 70 IC5/C5P.
- p. The hydrogen analyzer on the scrubber off-gas should be commissioned. This signal is used to manually adjust the make up gas flowrate such that a minimum of 0.05 H<sub>2</sub>/HCBN ratio is maintained at the lag reactor outlet.

## B. STARTUP AFTER CATALYST CHANGEOUT

The first reactor should run for at least 2 days and stable normal operation verified before the second reactor is put on line. The second reactor will be lined up such that it is in series with the first reactor.

- a. Pressure up the other reactor in the same manner that was used for the on-stream reactor, i.e. via the “pressuring up” line.
- b. The second reactor should be put on line with at least 50% of design feed to the first reactor.
- c. Reduce the reactor system pressure to 28 kg/cm<sup>2</sup>g (400 psig).
- d. Reduce the lead reactor outlet temperature to 121°C (250°F).

- e. Establish flow of lead reactor effluent through the hot combined feed exchanger and cool the feed to the lag reactor as much as possible.
- f. Open the off line reactor's inlet valves.
- g. Open the off line reactor's outlet valves.
- h. Establish flow through the reactor by closing the “single reactor operation” bypass and commissioning the TRC which regulates flow through the hot combined feed exchanger. Keep the lag reactor as cool as possible until the reactor has inventoried and operations are stable.
- i. When the second reactor is commissioned, the fresh catalyst will consume chloride for a period of time. The chloride injection rate should be increased to 300 wt ppm chloride based on reactor liquid charge in the same manner as for the first reactor. Reduce the chloride injection to 150 wt ppm based on feed after the chloride level in the stabilizer off gas levels off.

## VIII. NORMAL OPERATIONS

As in any chemical process this unit has many operating variables which influence product purity, yields, utility consumption, etc. The process specification for this unit is used only as a guide as reduced rates, equipment design variations, and other factors can and will cause a change in these process conditions. It is, therefore, up to the unit operators, supervisors, and the other personnel involved in the startup and subsequent operation of the unit to see that the unit is being operated at maximum efficiency.

The most useful tool for detecting operational difficulties is the log sheet and listed readings. The board operator must be careful to list each reading correctly at the appointed time. It is then important to review all of the readings to determine what and if any changes have occurred. No changes are to be overlooked until a reason is discovered and corrective measures, if necessary, are taken.

The outside operator should review the process equipment operation during his routine duties and report any abnormalities (leak, noise, etc.) to the control room personnel. Proper coordination between the board operator and the outside operators is essential for good operation. The following sections will highlight each major piece of equipment and its operation.

A. FEED DRIERS.....	2
B. MAKEUP GAS DRIERS.....	2
C. REACTOR OPERATIONS .....	3
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3. Hydrogen to Hydrocarbon Ratio .....	4
D. STABILIZER .....	4
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H. OPERATIONS DATA SUMMARY SHEETS .....	6

## A. FEED DRIERS

The Feed Driers are sized by UOP to operate 24 hours each before requiring regeneration. This assumes that the feed is water saturated at 38°C (100°F) and design operating pressure, and no other contaminants in the feed. Free water should not be charged to the Feed Driers, as free water can damage the molecular sieve.

The driers are operated such that one drier is in the lead position and the other is in the lag position, or is being regenerated.

The lead drier must be regenerated before its effluent indicates more than 1 wt-ppm water. As operating experience is gained, and providing a water breakthrough is not observed, the drying periods may be extended. However, even if the moisture content in the lead drier effluent does not increase from the baseline value, the drier must be regenerated at least once a week for optimum catalyst protection.

The guidelines for taking the lead Feed Drier offline, regenerating it, and placing it onstream in the lag position are detailed in the following section:

Section XIII. Special Procedures

F. Drier Regeneration

1. Feed Drier Regeneration.

## B. MAKEUP GAS DRIERS

Similarly, as the Feed Driers, the Makeup Gas Driers in the unit are generally sized to operate for 24 hours each before requiring regeneration. This assumes that the makeup gas is water saturated at design operating conditions, nominally 38°C (100°F) and 38.6 kg/cm<sup>2</sup> (550 psig) and no other contaminants in the makeup gas. Free water should not be charged to the Makeup Gas Driers, as free water can damage the molecular sieve.

The driers are operated such that one drier is in the lead position and the other is in the lag position, or is being regenerated.

The lead drier must be regenerated before its effluent indicates more than 1 ppm water or if available, the CO/CO<sub>2</sub> analyzer indicates CO<sub>2</sub> breakthrough. As operating experience is gained, and providing a water breakthrough is not observed, the drying periods may be extended. However, even if the moisture content in the lead drier effluent does not increase from the baseline value, the drier must be regenerated at least once a week for optimum catalyst protection.

The guidelines for taking the lead Makeup Gas Drier offline, regenerating it, and placing it onstream in the lag position are detailed in the following section:

### Section XIII. Special Procedures

#### F. Drier Regeneration

##### 2. Makeup Gas Drier Regeneration.

## C. REACTOR OPERATIONS

The reactor system is typically designed to operate at a minimum pressure of 31.6 kg/cm<sup>2</sup>g (450 psig). Lead inlet temperatures typically range from 121°C (250°F) to 177°C (350°F), and lag reactor inlet temperatures typically range from about 110°C (230°F) to 149°C (300°F).

### 1. Penex Reactor Temperatures

As the catalyst ages in the first reactor it will be necessary to increase the first reactor inlet temperature to obtain the maximum benefit from the catalyst. The temperature should be adjusted to maximize the isomerization reactions in the first reactor and then adjust the second reactor inlet temperature to maintain the desired product octane number. Lower reactor temperatures favor higher equilibrium ratios of the iso-compounds in the product.

## 2. Lead Reactor Effluent Sample

A lead reactor effluent sample should be obtained by condensing the sample stream at a pressure as close as possible to the plant operating pressure. The performance of the catalyst in the lead stage is determined by evaluating the composition and iso-ratios of this stream. This sample should be taken on a weekly basis at a minimum to provide information on the lead reactor catalyst activity and history. This sample will contain levels of HCl which should be communicated to the laboratory.

## 3. Hydrogen to Hydrocarbon Ratio

For the Penex unit, the design H<sub>2</sub>/HCBN ratio is 0.05 moles hydrogen at the reactor outlet per mole of charge. Operating with too low H<sub>2</sub> in the reactors can result in increased coking or flow maldistribution in the reactors. The H<sub>2</sub>/HCBN ratio is calculated by determining the total molar flowrate of hydrogen in the caustic scrubber off gas and dividing this by the total molar flowrate of the reactor liquid charge.

If it is determined that the H<sub>2</sub>/HCBN ratio is below 0.05, the makeup gas flowrate should be increased to increase the ratio. Hydrogen analyzers are provided on both the makeup gas and scrubber off gas to aid in this determination.

## D. STABILIZER

The stabilizer is designed to remove HCl and light ends, C4-, from the isomerate product. Periodic laboratory tests should also be made to verify that essentially no chloride is exiting with the Isomerate. If HCl is found in the bottoms stream, an increase in the column reflux rate is recommended. Since stabilizer bottoms is used to regenerate the driers, it is important that the regenerant be free of HCl.

## E. NET GAS SCRUBBER

The gases from the unit containing HCl are scrubbed with a 10 wt% caustic solution in the Net Gas Scrubber. This is accomplished by contacting the rising acidic gases counter-currently with caustic.

The caustic level in the scrubber is to be held at a point 300-600 mm (1-2 Ft.) below the caustic distributor just below the packed section.

The caustic is to be changed out before it falls below 2 wt% NaOH. The temperature of the scrubber should be maintained close to the same temperature of the stabilizer overhead receiver in order to avoid forming a liquid hydrocarbon phase which can cause foaming and operating problems with the scrubber.

Scrubbers equipped with water wash sections will require checking the circulating water for pH and wt% NaOH. Consider changing out the circulating water if the sodium hydroxide concentration exceeds 2 wt% NaOH or if the water wash should ever go acidic.

## F. SULFUR GUARD BED

The sulfur guard bed requires very little attention. The temperature should be monitored to ensure that the design value is maintained (usually 121°C (250°F) to 150°C (300°F)). Samples of the inlet and outlet stream should be analyzed for sulfur. The guard bed can hold approximately 8% of its weight in sulfur. Once saturated the guard bed is reloaded.

## G. PREVENTIVE MAINTENANCE

Below are several items to remain conscious of to help ensure maximum life from the Penex catalyst.

1. Valves on both the makeup gas and liquid feed driers should be checked, repaired, and replaced, if necessary, to insure a positive shutoff when required. Testing of valves on both the liquid feed and makeup gas driers for leaks should be carried out at least once per month; refer to the "Drier Manifold Leak Testing Procedure" in Section XIII of this manual.
2. The organic chloride injection pump should be kept in an operable state, i.e. leakage at the plunger.
3. Consider replacement of the drier sieves after 250-300 regeneration cycles. The sieve vendor can verify the condition of the sieves.
4. The moisture analyzers should be verified frequently for response and accuracy.
5. Routine analyses for feed contaminants and compositions should be performed.

## H. OPERATIONS DATA SUMMARY SHEETS

Operating data to be collected are shown in the following pages.

<b>UOP</b> a Honeywell Company	<b>TABLE VIII-1</b>					Page 1 of 5
<b>TECHNOLOGY SERVICES DEPARTMENT</b>	<b>H.O.T. PENEX OPERATIONS SUMMARY</b>					
REFINER:	UNIT TYPE:					
LOCATION:	CATALYST:					
<b>DATE:</b>						
DAYS ON STREAM	WT%					
CUMULATIVE CHARGE	MM <sup>3</sup> (BBL)					
REACTOR A CATALYST LIFE	M <sup>3</sup> Kg(BPP)					
RX A CAT LIFE IN LEAD POSITION	M <sup>3</sup> Kg(BPP)					
REACTOR B CATALYST LIFE	M <sup>3</sup> Kg(BPP)					
WEIGHT RECOVERY	WT%					
PRODUCT YIELD	WT%					
PRODUCT YIELD	LV%					
ADJ. C5+PRODUCT YIELD	WT%					
ADJ. C5+PRODUCT YIELD	WT%					
LHSV	HR <sup>-1</sup>					
RX INLET H <sub>2</sub> /HC RATIO	MOL/MOL					
RX OUTLET H <sub>2</sub> /HC RATIO	MOL/MOL					
H <sub>2</sub> CONSUMED	NM <sup>3</sup> M <sup>3</sup> (SCFB)					
STABILIZER OFFGAS YIELD	NM <sup>3</sup> M <sup>3</sup> (SCFB)					
STABILIZER R/F RATIO	VOL/VOL					
CHLORIDE INJECTION,PPM OF FF	WT PPM					
LEAD REACTOR OUTLET TEMP	°C (°F)					
LAG REACTOR OUTLET TEMP	°C (°F)					
<b>PRODUCT PROPERTIES</b>						
PIN RATIO	WT%					
IC5/(IC5+NC5)	WT%					
2-2 DMB/C6P	WT%					
2-3 DMB/C6P	WT%					
2MP/C6P	WT%					
3MP/C6P	WT%					
NC6/C6P	WT%					
TOTAL C4's	WT%					
TOTAL C5's	WT%					
TOTAL C6's	WT%					
TOTAL C7's	WT%					
RON-O, ENGINE	RONC					
MON-O, ENGINE	MONC					
C4+ RON-O, CALCULATED	RONC					
C5+ RON-O, CALCULATED	RONC					
C4+ MON-O, CALCULATED	MONC					
C5+ MON-O, CALCULATED	MONC					
LABORATORY R.V.P.	KG/CM <sup>2</sup> A(PSIA)					
CALCULATED R.V.P.	KG/CM <sup>2</sup> A(PSIA)					
<b>CHARGE STOCK PROPERTIES</b>						
X-FACTOR(MCP+CH+BZ+C7+)	WT%					
TOTAL C4's	WT%					
TOTAL C5's	WT%					
C6 PARAFFINS	WT%					
BENZENE	WT%					
TOTAL C7+	WT%					
C5+ RON-O, CALCULATED	RONC					

<b>UOP</b> a Honeywell Company							Page 2 of 5
<b>TECHNOLOGY SERVICES DEPARTMENT</b>	<b>H.O.T. PENEX OPERATIONS SUMMARY</b>						
REFINER:							UNIT TYPE:
LOCATION:							CATALYST:
DATE:							
<b>FLOWS</b>							
FRESH FEED RATE	M <sup>3</sup> /HR(BPD)						
COMBINED FEED RATE	M <sup>3</sup> /HR(BPD)						
PENEXATE RATE	M <sup>3</sup> /HR(BPD)						
STABILIZER REFLUX	M <sup>3</sup> /HR(BPD)						
STAB NET OVHD LIQUID	M <sup>3</sup> /HR(BPD)						
MAKEUP GAS	NM <sup>3</sup> /HR(SCFD)						
STABILIZER OFFGAS	NM <sup>3</sup> /HR(SCFD)						
<b>TEMPERATURES</b>							
LEAD REACTOR INLET	°C (°F)						
LEAD REACTOR DELTA T1	°C (°F)						
LEAD REACTOR DELTA T2	°C (°F)						
LEAD REACTOR DELTA T3	°C (°F)						
LEAD REACTOR DELTA T4	°C (°F)						
LEAD REACTOR OUTLET	°C (°F)						
LAG REACTOR INLET	°C (°F)						
LAG REACTOR DELTA T	°C (°F)						
SULFUR GUARD BED	°C (°F)						
LIQUID FEED AT DRIERS	°C (°F)						
MAKE-UP GAS AT DRIERS	°C (°F)						
STABILIZER OVHD	°C (°F)						
STABILIZER BTMS	°C (°F)						
STABILIZER FEED	°C (°F)						
STABILIZER OVHD RCVR	°C (°F)						
NET GAS SCRUBBER	°C (°F)						
<b>PRESURES</b>							
SULFUR GUARD BED	Kg/CM <sup>2</sup> (PSIG)						
REACTOR OUTLET	Kg/CM <sup>2</sup> (PSIG)						
MAKE-UP GAS TO REACTORS	Kg/CM <sup>2</sup> (PSIG)						
STABILIZER OVHD	Kg/CM <sup>2</sup> (PSIG)						
NET GAS SCRUBBER	Kg/CM <sup>2</sup> (PSIG)						
<b>LIQUID DRIER REGENERATION</b>							
REGENERANT FLOW	M <sup>3</sup> /HR(BPD)						
SUPERHEATER OUTLET	°C (°F)						
DRIER OUTLET	°C (°F)						
HEAT UP TIME	HOURS						
HOLD TIME	HOURS						
COOLDOWN TIME	HOURS						
DRIER OUTLET MOISTURE	WT PPM						
<b>GAS DRIER REGENERATION</b>							
REGENERANT FLOW	M <sup>3</sup> /HR(BPD)						
SUPERHEATER OUTLET	°C (°F)						
DRIER OUTLET	°C (°F)						
HEAT UP TIME	HOURS						
HOLD TIME	HOURS						
COOLDOWN TIME	HOURS						
DRIER OUTLET MOISTURE	VOL PPM						

<b>UOP</b> a Honeywell Company		Page 3 of 5					
<b>TECHNOLOGY SERVICES DEPARTMENT</b>		<b>H.O.T. PENEX OPERATIONS SUMMARY</b>					
REFINER:		UNIT TYPE: _____					
LOCATION:		CATALYST: _____					
DATE:							
<b>MISCELLANEOUS</b>							
TOTAL LOADED CATALYST VOLUME	M <sup>3</sup> (Ft <sup>3</sup> )						
TOTAL LOADED CATALYST WEIGHT	Kgs(LBS)						
CATALYST DISTRIBUTION RX-A	WT%						
CATALYST DISTRIBUTION RX-B	WT%						
CHARGE HEATER CONDENSATE FLOW	M <sup>3</sup> /HR(GPM)						
CAUSTIC CIRC.-UPPER SECTION	M <sup>3</sup> /HR(GPM)						
CAUSTIC CIRC.-LOWER SECTION	M <sup>3</sup> /HR(GPM)						
WASH WATER CIRCULATION	M <sup>3</sup> /HR(GPM)						
CAUSTIC STRENGTH	WT% NaOH						
<b>LABORATORY ANALYSES</b>							
<b>FEED COMPOSITION</b>							
SPECIFIC GRAVITY							
C3	WT%						
IC4	WT%						
NC4	WT%						
IC5	WT%						
NC5	WT%						
CP	WT%						
2-2 DMB	WT%						
2-3 DMB	WT%						
2 METHYL PENTANE	WT%						
3 METHYL PENTANE	WT%						
N HEXANE	WT%						
METHYL CYCLOPENTANE	WT%						
BENZENE	WT%						
CYCLOHEXANE	WT%						
C7+	WT%						
SULFUR	WT PPM						
NITROGEN	WT PPM						
MOLECULAR WEIGHT							
PIN RATIO	WT%						
IC5/(IC5+NC5)	WT%						
2-2 DMB/C6P	WT%						
2-3 DMB/C6P	WT%						
2MP/C6P	WT%						
3MP/C6P	WT%						
NC6/C6P	WT%						
RON-O, ENGINE	RONC						
MON-O, ENGINE	MONC						
C4+ RON-O, CALCULATED	RONC						
C5+ RON-O, CALCULATED	RONC						
C4+ MON-O, CALCULATED	MONC						
C5+ MON-O, CALCULATED	MONC						

<b>UOP</b> a Honeywell Company		Page 4 of 5					
TECHNOLOGY SERVICES DEPARTMENT		<b>H.O.T. PENEX OPERATIONS SUMMARY</b>					
REFINER:		UNIT TYPE: _____					
LOCATION:		CATALYST: _____					
DATE:							
<b>PRODUCT COMPOSITION</b>							
SPECIFIC GRAVITY							
C3	WT%						
IC4	WT%						
NC4	WT%						
IC5	WT%						
NC5	WT%						
CP	WT%						
2-2 DMB	WT%						
2-3 DMB	WT%						
2 METHYL PENTANE	WT%						
3 METHYL PENTANE	WT%						
N HEXANE	WT%						
METHYL CYCLOPENTANE	WT%						
BENZENE	WT%						
CYCLOHEXANE	WT%						
C7+	WT%						
PENEXATE R.V.P.	Kg/cm <sup>2</sup> (PSIA)						
<b>MAKE-UP GAS COMPOSITION</b>							
H2	MOL%						
C1	MOL%						
C2	MOL%						
C3	MOL%						
I-C4	MOL%						
n-C4	MOL%						
I-C5	MOL%						
N-C5	MOL%						
C6+	MOL%						
H2S	MOL PPM						
HCL	MOL PPM						
CO	MOL PPM						
CO2	MOL PPM						
<b>STABILIZER OFFGAS</b>							
H2	MOL%						
C1	MOL%						
C2	MOL%						
C3	MOL%						
I-C4	MOL%						
n-C4	MOL%						
I-C5	MOL%						
n-C5	MOL%						
C6+	MOL%						
H2S	MOL PPM						
HCL	MOL PPM						
MOLECULAR WEIGHT							



## IX. ANALYTICAL

The following topics will be discussed in this section.

A. SAMPLING .....	1
B. CLOSED FLOW-THROUGH SAMPLING (LIQUID OR GAS).....	2
C. CLOSED FLOW-THROUGH TO FLARE SAMPLING (GAS OR LPG) .....	3
D. REACTOR EFFLUENT SAMPLING PROCEDURE .....	4
E. LABORATORY TEST SCHEDULE.....	6
F. GENERAL GUIDELINES FOR SAMPLE SHIPMENTS TO UOP .....	8
G. SAMPLE CONTAINERS, PACKAGING, AND LABELING .....	21
H. SAMPLE CONTAMINATION – CONTAINER PROBLEMS .....	23
I. MINIMUM SAMPLE SIZE .....	24

The following figures are included in this section.

Figure IX - 1 Closed Flow-Through Sampling (Liquid or Gas) .....	25
Figure IX - 2 Closed Flow-Through Sampling to Flare (Gas or LPG).....	26
Figure IX - 3 Reactor Effluent Sampling.....	27

### A. SAMPLING

Sampling process streams normally requires some care in order to limit personnel exposure and prevent the release of potentially dangerous compounds into the environment. All streams should be sampled carefully. Even if the stream is thought to contain non-hazardous and non-toxic chemicals, good sampling techniques and care should be employed. Samples should be taken on a regularly scheduled basis by authorized personnel knowledgeable in the procedure.

Samples should be taken on a regularly scheduled basis by authorized personnel knowledgeable in the correct procedure. Personnel taking the samples must be protected by the required safety equipment, including rubber gloves and protective face shields.

Operator equipment required during sampling includes rubber gloves and protective face shields.

Sample cylinders used for gas and liquid samples should be received from the laboratory properly cleaned. The cylinders should be made of stainless steel, should have their pressure ratings stamped on them, and should be capable of safely holding 711 psig (50 kg/cm<sup>2</sup>g) pressure. As much as possible, always use the same cylinder for the same sample to avoid the chance of contamination.

All samples leaving the process area for the laboratory should be tagged with the following information: sample description, sample source, analyses requested, date and time sampled.

## B. CLOSED FLOW-THROUGH SAMPLING (LIQUID OR GAS)

Refer to Figure IX-1 for valve designation (by number) and use the following procedure for a closed flow-through sampling system.

1. Open valve 1 wide and 2 enough to have a good flow past the sample connection tap. If a sample cooler is located between valves 1 and 2, check to be sure that the flow is not so high that the sample temperature rises above 120°F (50°C).
2. Open valve 3 and 4 and after venting for at least 15 seconds, close the valves and attach the sample cylinder in a vertical position.
3. Open valves 5 and 6 wide. Then open valves 3 wide and 4 enough to have a good flow of sample out the top of the cylinder for at least half a minute.
4. Then slowly close valve 6 and let stand for 30 seconds. NOTE: Valve 2 can be closed at this stage if desired.
5. Close valves 5, 4, and 1 and disconnect the cylinder.
6. While holding the cylinder vertically, crack valve #5 of the cylinder and drain about half an ounce (10 cc) of liquid out of the cylinder.

**CAUTION:** When taking samples containing H<sub>2</sub>S, and air mask should be worn at all times; follow normal procedures for safety in handling H<sub>2</sub>S.

## C. CLOSED FLOW-THROUGH TO FLARE SAMPLING (GAS OR LPG)

Refer to Figure IX-2 for valve designation (by letter) and use the following procedure when sampling gas or high vapor pressure liquids such as LPG:

1. Cylinder should be cleaned, passivated and filled with nitrogen to 30 psig (2 kg/cm<sup>2</sup>g).
2. Place cylinder in clamp; be sure clamp is adjusted so that flexible hoses will not be bent more than 90 degrees.
3. Connect hoses at quick-connects B. Close valves C and E to flare.
4. Open  $\frac{3}{4}$ " gate valves to process line to full open.
5. Open both cylinder valves A. Crack inlet valve D pressure gauge at inlet should rise rapidly and outlet pressure gauge should follow quickly or the line is obstructed.
6. Open outlet valve D to full open: pressure gauge at outlet should drop to outlet pipe connection pressure.
7. Close outlet valve D. Continue to open inlet valve D allowing cylinder pressure to rise slowly.
8. Crack outlet valve D and slowly open until pressure gauge on outlet has slightly lower pressure reading than inlet pressure gauge. Let sample flow through cylinder for ten minutes or sufficient time for a representative sample..
9. Pinch outlet valve D until both pressure gauges have the same reading.

10. Close outlet valve D. Close inlet valve D. Close  $\frac{3}{4}$ " gate valves to process line.

**THE FOLLOWING IS IMPORTANT BEFORE DISCONNECTING CYLINDER:**

11. Close both valves A; slowly open both valves C and E to flare until pressure gauges read flare pressure. In all cases, the pressure gauges should read less than 250 psig (17.5 kg/cm<sup>2</sup>g) before disconnecting cylinder. For high vapor pressure liquid samples, crack bottom valve A to expel about a half an ounce (10 cc) of the liquid in the cylinder, then close.
12. Disconnect hoses at quick-connects B and remove cylinder from clamp.
13. After sample is taken, sample cylinder should be taken to laboratory and emptied as soon as possible. Care must be exercised in transportation and storage of full cylinder to avoid cylinder temperature increase that can result in a hazardous high internal cylinder temperature.

**CAUTION: When taking samples containing H<sub>2</sub>S, and air mask should be worn at all times; follow normal procedures for safety in handling H<sub>2</sub>S.**

## D. REACTOR EFFLUENT SAMPLING PROCEDURE

1. Start cooling water to the sample cooler. Refer to Figure IX-3 valve designation (by number).
2. Close bleed valves between 1 and 2, 3 and 11. Open the bottom outlet valves 4 and 5, the return valve 3, and gas valves 8 and 9 of the sample receiver. Crack open the inlet valves 1 and 2 to the sample cooler and purge the system for at least one minute to remove inert gas.
3. Close the bottoms outlet, return and flare valves 3, 4, 5, and 8 and pinch down the gas globe valve 9 and open common return valve 11 to build pressure on the receiver to near reactor pressure. Then fully open the inlet valve 1 and adjust sample flow using valve 2 to achieve a reasonable liquid level build-up

rate in the sample receiver. Crack open liquid return valve 3 if necessary for additional level control. Adjust flow to keep the sample receiver temperature below 120°F (50°C).

4. Once liquid level is seen on the level gauge, attach the sample cylinder in a vertical position to the sampling tap.
5. Open valves 5, 6, 7 wide and then partially open valve 10 to have a good flow of sample out the top of the cylinder for at least half a minute. Then slowly close valve 10 and let stand for 30 seconds.
6. Close valves 5 and 6. Then disconnect the cylinder.
7. While holding the bomb vertically, crack sample cylinder valve 6 and drain about half an ounce of liquid out of the cylinder.
8. Close sample feed valves 1 and 2 and gas return valve 9. Drain bleeder per refinery practice.
9. Pressure the liquid with nitrogen through return valves 3 and 11 back to the process until liquid level is not observed in the level glass. Close return valves 3 and 11. Drain bleeder per refinery practice
10. Depressurize the sample cooler and receiver to the flare through the flare valve 8. Thoroughly purge the sample apparatus with dry nitrogen to flare.
11. Close remaining valves 4, 5, and 10. The system is now in standby for the next sample. Note: the system can be kept in continuous operation. The negative consequence is the significant frequency that the sample receiver level must be checked and resulting adjustments made to the globe valves.

## E. LABORATORY TEST SCHEDULE

In order to fully evaluate the performance of any process unit it is necessary to maintain detailed analytical as well as operating records. All streams entering and exiting the Reformate Splitter should be routinely analyzed. The analyses conducted should be detailed and should include stream compositions, specific gravities, and other properties that are important from a process and catalyst protection standpoint. The stream compositions should indicate not only the major components but also certain minor components or contaminants. This is very important because even small concentrations of certain impurities can have an adverse impact on the overall process performance.

The laboratory staff and personnel should be thoroughly familiar with the various analytical test methods prescribed for the Reformate Splitter.

The following is a recommended schedule for analyzing the various streams. This is a fairly exhaustive schedule and may be modified as operating experience is gained. However, the UOP Chief Process Advisor on site for unit startup may at various points in time require more sample analyses to line out the unit and check its performance in the shortest period of time.

During initial startup, the UOP Chief Process Advisor may require more analyses as needed to assist in the startup of the unit.

### RECOMMENDED LABORATORY TEST SCHEDULE PENEX PROCESS UNIT

STREAM AND TEST	TEST METHOD	FREQUENCY
<b>Fresh Stock Charge</b>		
Composition, wt-%	UOP-690	Daily
Total Sulfur, wt-ppm	UOP-987	Daily
Total Nitrogen, wt-ppm	UOP-981	Weekly
Water, wt-ppm	UOP-481* or Analyzer	Weekly
Dissolved Oxygen, wt-ppm	UOP-678	Occas.
***Oxygenates		
Oxygenated Hydrocarbons	UOP-960	Occas.

Methanol, wt-ppm	UOP-569	Occas.
Peroxides, wt-ppm	ASTM D-2340	Occas.
Carbonyl, wt-ppm	UOP-624	Occas.
Arsenic, wt-ppb	UOP-992	Occas.
Lead, wt-ppb	UOP-952	Occas.
Copper, wt-ppb	UOP-962	Occas.
Fluoride, wt-ppm	UOP-991 or ASTM D7359	Occas.
Bromine Number	UOP 304 or ASTM D2710	Occas.
RON-clear	ASTM D-2699	Daily
MON-clear	ASTM D-2700	Occas.
<b>Makeup Gas</b>		
Composition, mol-%	UOP-539	Weekly
H <sub>2</sub> S, mol-ppm	Detector Tube	Daily
NH <sub>3</sub> , mol-ppm	Detector Tube	Daily
Water, mol-ppm	** Analyzer	Occas.
CO/CO <sub>2</sub> , mol-ppm	UOP-603	Occas.
HCl, mol-ppm	UOP-910 or UOP 930 or Detector Tube	Occas.
<b>Lead Reactor Effluent</b>		
Composition, wt-%	UOP-690	Weekly
<b>Stabilizer Off-Gas</b>		
Composition, mol-%	UOP-539	Daily
H <sub>2</sub> S, mol-ppm	Detector Tube	Weekly
HCl, mol-ppm	UOP-910 or UOP 930 or Detector Tube	3/D
<b>Net Gas Scrubber (to Fuel Gas)</b>		
HCl, mol-ppm	UOP-910 or UOP 930 or Detector Tube	Daily
<b>Circulating Caustic</b>		
NaOH, wt-%	UOP-209	Daily
<b>Circulating Water</b>		
NaOH, wt-%	UOP-209	Daily
<b>Stabilizer Bottoms</b>		
Composition, wt-%	UOP-690	Daily
****RON-Clear	ASTM D-2699	Daily
****MON-Clear	ASTM D-2700	Daily
RVP	ASTM D-323	Daily
HCl	UOP 588	Daily

**NOTES:**

- \* UOP-481 is used for fresh stock charge upstream of the Feed Driers.
- \*\* Check in field with portable moisture analyzer.
- \*\*\* Oxygenates other than water are to be determined individually based on the suspected compound.
- \*\*\*\* Samples for octane number must be taken in 1000 ml steel sample cylinders.

Items marked “occasionally” should be scheduled once a week or when requested by UOP for troubleshooting purposes.

## F. GENERAL GUIDELINES FOR SAMPLE SHIPMENTS TO UOP

Listed below are the general guidelines to use when sending samples(s) to UOP for analyses. Following these procedures will minimize delays and aid in quicker turnaround once the sample has been received.

**Revised December 1, 2009**

Please find attached the processing procedures revised for the date listed above as an example of how to send samples to UOP. UOP has a state of the art laboratory facility that serves the research and development that is ongoing at UOP. It is not an industrial laboratory and so does not have the typical quick turnaround time of an industrial laboratory. Please contact your Regional Service or Operating Technical Service Representatives to verify the current procedures prior to sending any samples to UOP.

### **Shipping Instructions for Domestic Samples (from within the USA)**

In order to ensure compliance with U.S. regulations on hazard communication and hazardous material transportation and to ensure samples are effectively processed, all chemical samples shipped to UOP LLC must meet the following requirements:

1. All samples must be classified in compliance with U.S. Dept. of Transportation Hazardous Materials Regulations. **All shipments classified as hazardous by DOT, must be marked, labeled and packaged in compliance with DOT Hazardous Material Regulations.**

2. Samples are to be placed in appropriate containers. A container must be selected based on the sample's DOT hazardous material classification, the sample compatibility with the container material and considerations to ensure the sample's quality is maintained. The use of inappropriate containers will cause your sample to be discarded.
3. Each individual sample container (each "inner container" for dual packaging systems), must be clearly labeled with a description of the sample, sample number and marked with any warnings necessary to communicate hazards in accordance with the OSHA Hazard Communications Standard. If possible, a Material Safety Data Sheet should accompany each hazardous chemical sample.
4. A Sample Requisition Form must accompany all samples (Attachment 1A and 1B; a blank and example). Please ensure that all fields on the form labeled "REQUIRED" are completed. Care should be taken to ensure that the sample numbers and descriptions on the requisition form correspond with the information on the individual sample labels.
5. Samples must be packed in such a way that they are secure in the package. The use of an adsorbent packing material is required for liquid samples to contain any spills that may occur if the sample container breaks or leaks during shipment. The use of packing peanuts or styrofoam is discouraged. The cover of the container must be secure, if in doubt, please use a strong tape to secure the cover.
6. All samples must be shipped with a Bill of Lading (also known as a *Master Airwaybill*) which includes vessel/flight information. If applicable, the Bill of Lading must meet shipping paper requirements of the U.S. DOT Hazardous Material regulations.
7. All Samples are to be shipped Pre-paid and sent to:

**UOP LLC**

**Sample Receiving  
200 East Algonquin Road  
Des Plaines, IL 60016  
Attn: Technology Services or Regional Services Representative**

8. **UOP recommends that samples be shipped by Federal Express or Emery.** US Mail may be used for non-hazardous samples when expedited service is not required.
9. **Hand carrying of samples to UOP without proper documentation is prohibited.** Therefore, UOP employees and customers are to refrain from transporting any samples by this method, from any refinery to any UOP laboratory or office.

**IF PAPERWORK IS NOT INCLUDED WITH THE SHIPMENT OF YOUR SAMPLES, YOUR SAMPLE WILL THEN GO INTO QUARANTINE UNTIL PROPER CLEARANCE CAN BE OBTAINED.**

**ATTACHMENT 1a****SHIP TO: UOP**

**DOMESTIC**  
**SAMPLE REQUISITION FORM**  
**UOP TECHNICAL SERVICES**

**SAMPLE RECEIVING DEPARTMENT**  
 200 E. Algonquin Road  
 Des Plaines, IL 60017  
 847-391-2943

To Name REQUIRED  
 Company Name REQUIRED  
 Street Address REQUIRED  
 City, State Zip Code REQUIRED  
 Customer ID REQUIRED

UOP CONTACT	UOP CONTACT PHONE #	SAMPLES SHIPPED VIA:	AIRWAY BILL NUMBER
REQUIRED	REQUIRED	REQUIRED	REQUIRED

SAMPLE #	PROCESS UNIT	PRODUCT	DATE/TIME SAMPLED	QUANTITY	DESCRIPTION OF SAMPLE
REQUIRED	REQUIRED	REQUIRED	REQUIRED	REQUIRED	REQUIRED

**ATTACHMENT****1b****SHIP TO: UOP**

A Honeywell Company

**DOMESTIC**  
**SAMPLE REQUISITION FORM**  
**UOP TECHNICAL SERVICES**

**SAMPLE RECEIVING DEPARTMENT**  
**200 E. Algonquin Road**  
**Des Plaines, IL 60017**  
**847-391-2943**

To JOES REFINERY  
 849 Thomas Drive  
 Bensenville, IL 60106  
 123-456-7890  
 Customer ID ABC12345

**EXAMPLE**

UOP CONTACT	UOP CONTACT PHONE #	SAMPLES SHIPPED VIA:	AIRWAY BILL NUMBER
Mr. Joe UOP	847-555-1212	Expeditors Intl.	123-4567

SAMPLE #	PROCESS UNIT	PRODUCT	DATE/TIME SAMPLED	QUANTITY	DESCRIPTION OF SAMPLE
1	#1 CCR UNIT 217	R-234	01-02-08 01:00 HRS	4OZS	R-234 REGENERATED CATALYST CAT REGENERATED CYCLES = 421 SCHEDULED SAMPLE DATE OCTOBER 2006 ACTUAL DATE SAMPLE TAKEN 3-22-2007  R-234 SPENT CATALYST CAT REGENERATED CYCLES = 420 SCHEDULED AMPLIE DATE OCTOBER 2006 ACTUAL DATE SAMPLE TAKEN 3-21-2007
2	#1 CCR UNIT 217	R-234	01-02-08 15:30 HRS	4 OZS	

**EXAMPLE**

## **Shipping Instructions for International Customers (to be provided by UOP)**

In order to ensure compliance with governmental regulations on chemical control, hazard communication and hazardous material transportation and to ensure samples are effectively processed, all chemical samples shipped to UOP LLC must meet the following requirements:

- 1) All samples must be classified in compliance with international regulations for the Transport of Dangerous Goods. All shipments classified as dangerous for transport must be marked, labeled and packaged in compliance with either the International Air Transportation Association (IATA), if shipped by air, or International Maritime Organization (IMO) if shipped by sea.
- 2) Samples are to be placed in appropriate containers. A container must be selected based on the sample's dangerous goods classification, the sample compatibility with the container material and considerations to ensure the sample's quality is maintained. The use of inappropriate containers will cause your sample to be discarded.
- 3) Each individual sample container (each "inner container" for dual packaging systems), must be clearly labeled with a description of the sample, sample number and marked with any warnings necessary to communicate hazards in accordance with the US OSHA Hazard Communications Standard. If possible, a Material Safety Data Sheet should accompany each hazardous chemical sample.
- 4) Samples must be packed in such a way that they are secure in the package. The use of an adsorbent packing material is required for liquid samples to contain any spills that may occur if the sample container breaks or leaks during shipment. The use of packing peanuts or styrofoam is discouraged. The cover of the container must be secure, if in doubt, please use a strong tape to secure the cover.

- 5) The documentation listed below must accompany each sample shipment. A copy of all the documents must be included inside the package with the samples and in the customs pouch on the outside of the package.

Bill of Lading or Master Airwaybill which includes vessel/flight information. The Bill of Lading description field must include the words "TSCA Certified Chemical Sample." The Airwaybill should be marked "Broker Select" and indicate "Customs Clearance Through :

Expeditors International,  
849 Thomas Drive, Bensenville, IL 60106.

- b) Shipper's Declaration of Dangerous Goods form for all applicable shipments of dangerous goods
- c) **Pro forma Invoice** (See *attachments 1a and 1b: a blank form and example*). The information labeled "REQUIRED" must be filled out.
- d) **TSCA Certification** (See *attachment 3*) including the following information:
  - i. Sample description in English, UOP has provided this information.
  - ii. Date the sample is to be shipped, in English; this should be filled in by the customer.
  - iii. Signature by UOP LLC employee (this is included, please do not change).
- d) **Sample Requisition Form (Attachment 2A and 2B; a blank and example)** Please ensure that all fields on the form are completed. Care should be taken to ensure that the sample numbers and descriptions on the requisition form correspond with the information on the individual sample labels.

- 6) All Samples are to be shipped Pre-paid and should be routed through Chicago O'Hare International Airport, and addressed as follows:

UOP LLC  
Sample Receiving  
200 East Algonquin Road  
Des Plaines, IL 60016  
Attn: INCLUDE THE NAME OF YOUR UOP CONTACT PERSON

**IMPORTANT: Please use the following Honeywell Approved Freight Forwarder Carriers **only**:**

### **UPS**

Tim Burhenne  
502 485 2689 phone  
502 374 1612 fax  
[tburhenne@ups.com](mailto:tburhenne@ups.com)  
1930 Bishop Lane, Suite 200, Louisville KY 40215

### **EXPEDITORS**

Lynda Coughlin/Lydia Wrona  
630 616 2556 630 616 2305  
849 Thomas Drive  
Bensenville, IL 60106

- 7) An email must be sent prior to initiating the shipment to the UOP CUSTOMS CLEARANCE COORDINATOR ([Dorothy.Buikema@UOP.com](mailto:Dorothy.Buikema@UOP.com)). The email must contain a scanned copy of the Pro Forma Invoice, the Bill of Lading, TSCA Certificate Form, and the Analytical Requisition Form

Failure to send samples with the proper documentation and information will result in a delay of Customs clearance or refusal of the sample.

**Pro-Forma**  
**No Charge Invoice**  
**ATTACHMENT 1A**

**COSIGNEE/DELIVERY ADDRESS:**

UOP LLC Sample Receiving  
 200 E. Algonquin Rd, Des Plaines, IL 60017  
 Phone: 847-391-2943 fax: 847-391-2253  
 elena.crumbaugh@uop.com

**IMPORTER OF RECORD:**

UOP LLC  
 25 E. Algonquin Rd, Des Plaines, IL  
 60017  
 TERMS: Pro-Forma Invoice

**INTERNATIONAL SHIPPER/EXPORTER:**

Company Name - REQUIRED  
 Street Address - REQUIRED  
 City, State ZIP Code - REQUIRED  
 Country - REQUIRED  
 Phone - REQUIRED

INVOICE #: "INVOICE NUMBER" - REQUIRED  
 INVOICE DATE: "INVOICE DATE - REQUIRED  
 REFERENCE #: "REFERENCE NUMBER" - REQUIRED

UOP OTS CONTACT	# of packages	gross weight in kgs	country of origin
REQUIRED	REQUIRED	REQUIRED	REQUIRED

\*\*MARKET VALUE DECLARED FOR CUSTOMS CLEARANCE PURPOSES  
 ONLY\*\*

qty	description of samples (english only)	**amount (us\$)**
REQUIRED	REQUIRED	REQUIRED

I HEREBY CERTIFY THAT THIS INVOICE IS TRUE AND CORRECT

REFINERY REPRESENTATIVE NAME (PLEASE PRINT)	REFINERY REPRESENTATIVE SIGNATURE
REQUIRED	REQUIRED

**Pro-Forma**

**No Charge Invoice  
ATTACHMENT 1B  
EXAMPLE FORM**

**COSIGNEE/DELIVERY ADDRESS:**  
 UOP LLC Sample Receiving  
 200 E. Algonquin Rd, Des Plaines, IL 60017  
 Phone: 847-391-2943 fax: 847-391-2253  
 elena.crumbaugh@uop.com

**IMPORTER OF RECORD:**  
 UOP LLC  
 25 E. Algonquin Rd, Des Plaines, IL 60017  
  
**TERMS:** Pro-Forma Invoice

**INTERNATIONAL SHIPPER/EXPORTER:**  
 JOES REFINERY  
 849 Thomas Drive  
 Devonshire, The Moors QVC106  
 Disneyland  
 (056) 123-456-7890

**INVOICE #:** **11234456**  
**INVOICE DATE:** **01/12/2008**  
**REFERENCE #:** **987-227**

UOP OTS CONTACT	# of packages	gross weight in kgs	country of origin
MR. UOP HONEYWELL	1	3.5 kgs	Italy

**\*\*MARKET VALUE DECLAIRED FOR CUSTOMS CLEARANCE PURPOSES  
ONLY\*\***

QTY	DESCRIPTION OF SAMPLES	**AMOUNT (US\$)**
3 total	1 liter catalyst samples	100.00
2	Regenerated R-134 CCR Platforming Catalyst	
1	Coked R-134 CCR Platforming Catalyst	

**I HEREBY CERTIFY THAT THIS INVOICE IS TRUE AND CORRECT**

REFINERY REPRESENTATIVE NAME (PLEASE PRINT)	REFINERY REPRESENTATIVE SIGNATURE
Mark Sampletakar	X

## ATTACHMENT 2a

SHIP TO: UOP  
A Honeywell Company

INTERNATIONAL SAMPLE  
REQUISITION FORM  
UOP TECHNICAL SERVICES

SAMPLE RECEIVING  
200 E. Algonquin Road  
Des Plaines, IL 60017  
Phone 847-391-2943 Fax 847-391-2253  
elena.crumbaugh@uop.com

FROM: Contact Name  
Company/Refinery Name  
Street Address  
City, State Country ZIP Code  
Phone  
Customer e-mail

RS/TS uop contact	uop contact phone #	sample shipped via:	airway bill #

sample #	process unit	product	date/time sampled	quantity	description of sample
1					
2					
3					
4					

Thank you for your business!

## ATTACHMENT 2b EXAMPLE

**SHIP TO: UOP**  
A Honeywell Company

### INTERNATIONAL SAMPLE REQUISITION FORM UOP TECHNICAL SERVICES

**SAMPLE RECEIVING**  
200 E. Algonquin Road  
Des Plaines, IL 60017  
Phone 847-391-2943 Fax 847-391-2253  
elena.crumbaughf@uop.com

**FROM:** JOES REFINERY  
849 Thomas Drive  
Devonshire, The Moors QVC106  
Disneyland  
(056) 123-456-7890  
JOECUSTOMER@JR.COM

RS/TS uop contact	uop contact phone #	sample shipped via:	airway bill #
MR. UOP HONEYWELL	847-391-2000	EXPEDITORS 800-333-9090	123-355600

Sample #	process unit	Product	date/time sampled	quantity	description of sample
1	#1 CCR UNIT 217	R-234	01-02-08 01:00 HRS	4OZS	R-234 REGENERATED CATALYST CAT REGENERATED CYCLES = 421 SCHULED SAMPLE DATE OCTOBER 2006 ACTUAL DATE SAMPLE TAKEN 3-22-2007  R-234 SPENT CATALYST CAT REGENERATED CYCLES = 420 SCHEUDLED AMPLE DATE OCTOBER 2006 ACTUAL DATE SAMPLE TAKEN 3-21-2007
2	#1 CCR UNIT 217	R-234	01-02-08 15:30 HRS	4 OZS	

Thank you for your business!



TSCA CERTIFICATION FORM  
ATTACHMENT 3

Date:

To:  
Area Director of Customs

DESCRIPTION OF SAMPLE	QUANTITY

**( X ) TSCA Positive Certification**

I certify that all chemical substances in this shipment comply with all applicable rules or orders under TSCA and that I am not offering a chemical substance for entry in violation of TSCA or any applicable rule or order under TSCA.

SIGNATURE OF UOP LLC EMPLOYEE	PRINTED NAME OF UOP LLC EMPLOYEE

## G. SAMPLE CONTAINERS, PACKAGING, AND LABELING

### Specifications for Dangerous Goods/Hazardous Materials

As a first step in assessing the appropriate container, it must first be determined if the sample is classified as a dangerous good/hazardous material for transportation purposes. This determination must be completed by an individual certified in dangerous goods transportation regulations. If the sample meets any of the criteria for classification as a dangerous good/hazardous material, the shipper must utilize containers, packaging and labels in accordance with appropriate transportation regulations. References for classification, packaging and labeling of dangerous goods by air are the International Air Transport Association (IATA) Dangerous Goods Regulations. For shipments by sea, the references are the International Maritime Dangerous Goods Code (IMDG) by the International Maritime Organization (IMO). National Transportation Regulations should be referenced for ground shipments. In the U.S., the U.S. Department of Transportation Hazardous Materials Regulations (49 CFR Parts 171 – 180) should be utilized.

### Supplemental Quality Control Guidance for Sample Containers, Packaging and Labeling

Once it has been assessed whether the sample will be subject to shipment as a dangerous good/ hazardous material, the following additional guidelines should be considered to ensure integrity and quality of the sample.

Any person collecting and/or shipping a sample is encouraged to use the appropriate container for the type of sample. All containers must be sealed in such a way as to prevent contamination and spillage during shipping. The containers should be packed in such a way that they will not shift and neither spill nor break during the shipping process.

#### Liquid samples:

- Containers must be clean and dry before use. New containers are preferred.

- Glass or metal containers are best. Foil-lined caps are the most impermeable. Conical polyethylene-lined caps may be used. Paper-lined caps have been found to be permeable and should not be used.
- If trace levels of nitrogen, sulfur, chloride or other heteroatoms are to be analyzed, the appropriate container is glass, with a Teflon-lined, not foil lined, cap.
- If the sample containers are placed in plastic bags, use a separate plastic bag for each sample to minimize cross contamination.
- Liquid samples should be packed in an upright position and be packed with an adsorbent mat or other material that will hold the containers in position and contain any spillage that may occur. The use of non-adsorbent packing (e.g., foam peanuts) is not acceptable for liquid samples.
- Commercially available UN shipping containers must be used for samples classified as dangerous goods/hazardous materials and are also recommended for non-hazardous materials.

#### **Catalyst/solid samples:**

- Catalyst and solid samples must be packed in a rigid container (either a bottle, jar, or can) that is appropriate for the sample.
- The use of plastic bags as a primary container is not acceptable.
- The containers must be packed in such a way that they will not shift and neither spill nor break during the shipping process.

#### **Gas/LPG cylinders:**

- Cylinders must be shipped in wooden boxes or other sturdy containers that secure the cylinders from shifting in transit.
- Within the United States, unexpired DOT approved cylinders must be used. One-liter and larger cylinders expire 5 years from the date stamped on them. 500-mL and smaller cylinders have no expiration date.
- Cylinders must be checked for leaks before packaging.
- Cylinders containing samples to be analyzed for trace sulfur or other heteroatoms must be shipped in specially coated cylinders to minimize sample interaction with the cylinder walls. Such coated cylinders may be available on loan from UOP.

**Labeling:**

- Each container (inner container for combination packaging) must be properly marked with the customer/company name, location, specific type of sample and any additional information the shipper wants included.
- This information must be written directly on the container with a marker that will not wipe off, or be put on a label and attached with either tape or glue directly on the container, or securely tied to the container with wire or string.
- For single container shipments, the above information should be in addition to label requirements necessary for compliance with dangerous goods/hazardous materials transportation regulations and should not conflict with the transportation labels.

## H. SAMPLE CONTAMINATION – CONTAINER PROBLEMS

There have been found to be problems associated with the shipment of liquid samples shipped in standard laboratory vials with conical polyethylene caps. It has been found, through controlled tests, that samples cannot only permeate out of the containers in question, but that the samples can actually cross permeate between samples.

Tests were performed with the type of vials generally available in the laboratory using caps with liners of various materials. In a typical test, a vial containing only benzene and a vial containing only orthoxylene were placed together in a sealed jar for a period of time. The jars were heated to 40°C (104°F) (a very possible shipping temperature) to speed the permeation. Tests were done both with the vials in an upright position and with the vials lying on their side so that the liquid would contact the caps. The common conical polyethylene lined caps cross-permeated from 0.50 to 4.0% under these conditions. Paper lined caps produced terrible results. Corks and Teflon linings worked well until they were tipped over, at which point these containers also produced terrible results. The best caps found thus far are the foil lined caps. The aluminum foil lined caps cross-permeate only slightly and the tin foil lined caps do not cross-permeate at all.

The following recommendations are made: If possible, keep the samples cool. Temperature does affect the permeation rate through some materials. Use tin foil lined caps when available and keep the samples as far apart as possible so they will have less tendency to cross-permeate.

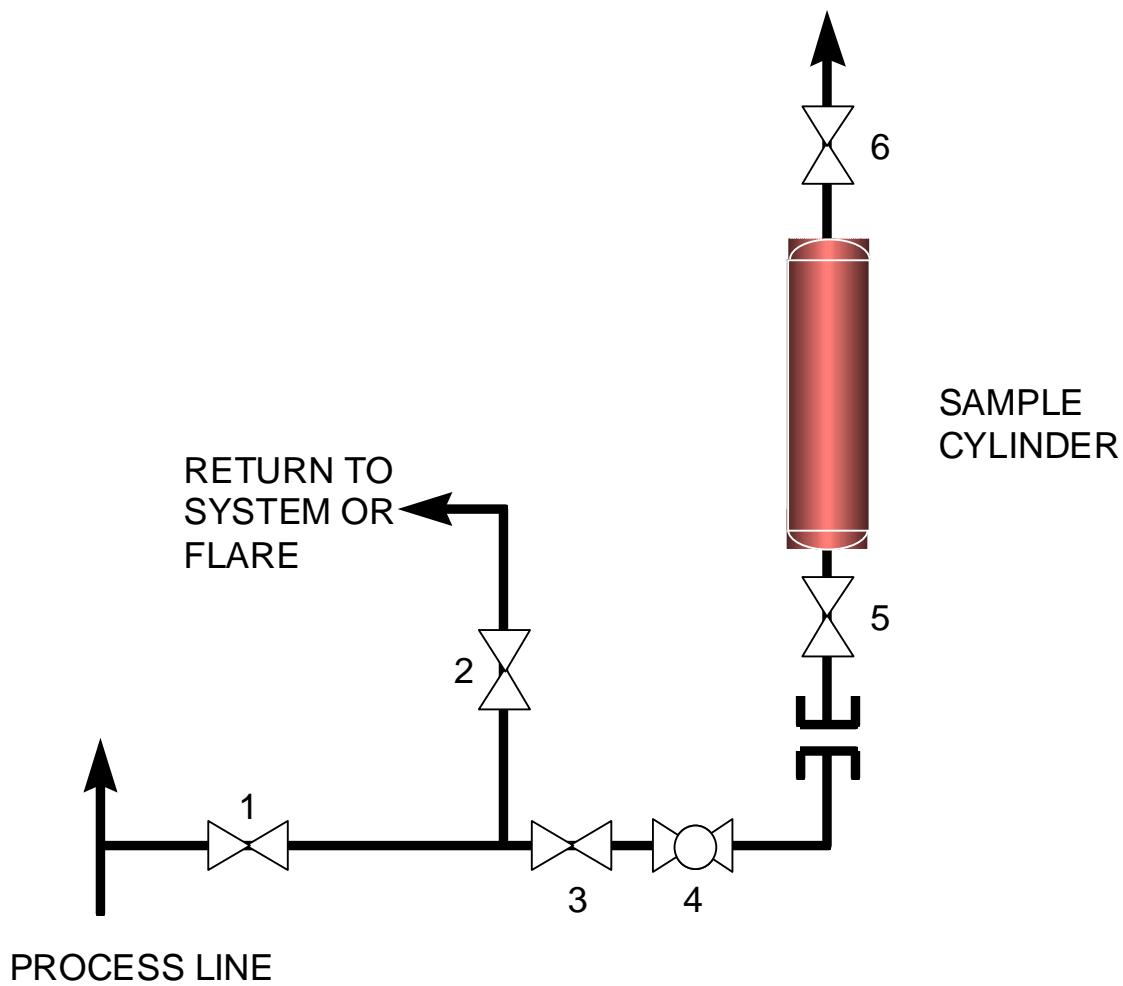
## I. MINIMUM SAMPLE SIZE

Analyses	Preferred Minimum (cm <sup>3</sup> )
Density	100
Distillation	210 <sup>(1)</sup>
Composition by GC	150
Sulfur, Microcoulometric	10
Nickel Reduction	100
Nitrogen, Kjeldahl	800
Microcoulometric	10
Chloride	100
All common analyses	2 liters

Note: (1) May also be used for density

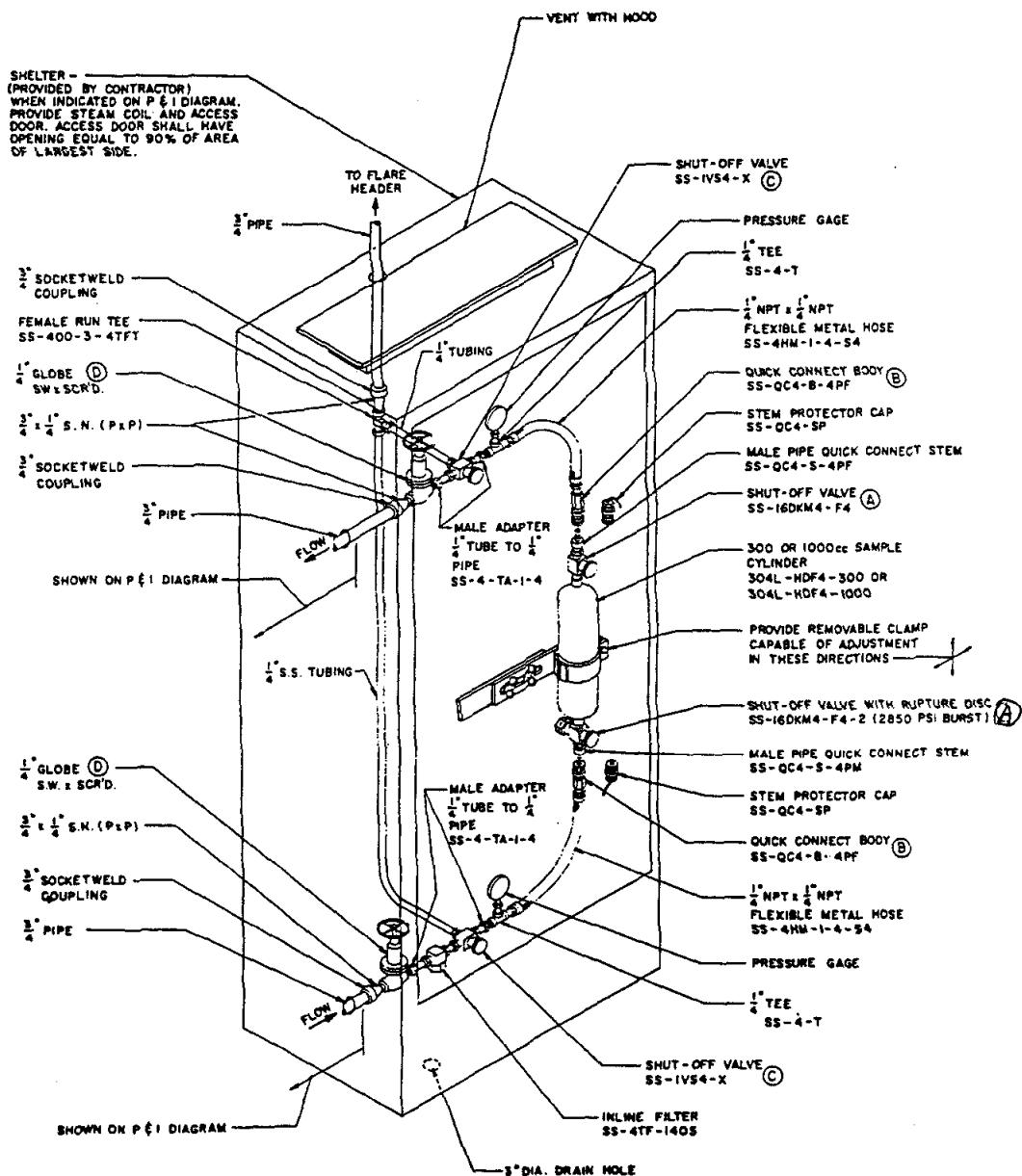
**Figure IX - 1 Closed Flow-Through Sampling (Liquid or Gas)**

# **HYDROCARBON SAMPLING PROCEDURE**



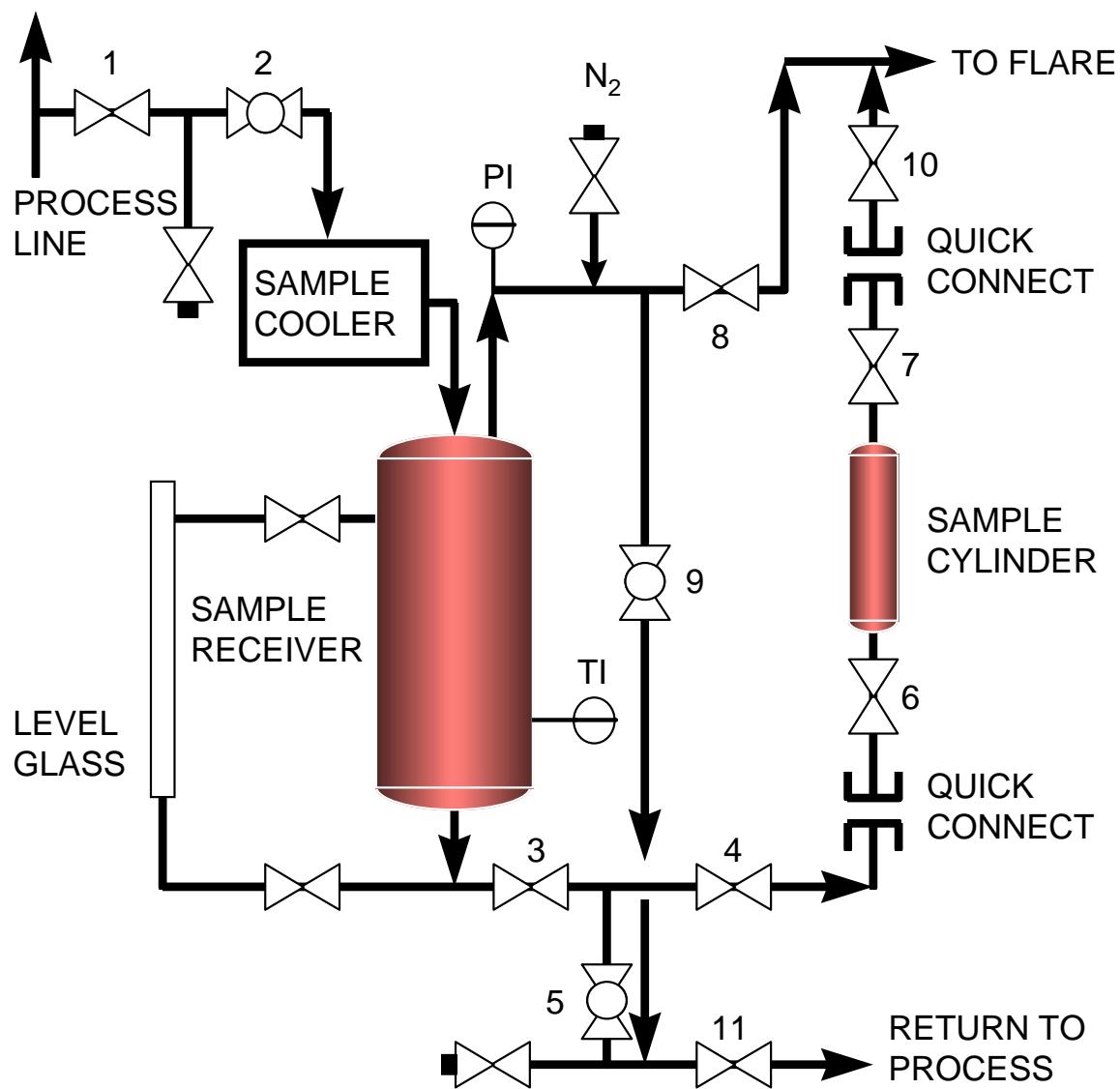
**Figure IX - 2 Closed Flow-Through Sampling to Flare (Gas or LPG)**

**CLOSED FLOW-THROUGH SAMPLING APPARATUS  
FOR GAS, TOXIC LIQUIDS OR HIGH VAPOR PRESSURE LIQUIDS  
(LIMITED TO MAXIMUM ALLOWABLE DESIGN PRESSURE OF 1500 PSIG )**



**Figure IX - 3 Reactor Effluent Sampling**

# **REACTOR EFFLUENT SAMPLING PROCEDURE**



## X. TROUBLESHOOTING

Troubleshooting of a Penex Unit, like any process unit, should be an ongoing part of normal operations. Daily logs of operations are recorded and should be reviewed to catch any changes before they become problems. Any unexplained changes should be followed-up on to identify their source and the necessary corrections should be made. Presented below are two tables which attempt to guide corrective actions for problems which are peculiar to Penex Units. Table X - I is a Penex Unit Troubleshooting Guide. Table X - II is a list of Penex Streams Contamination Limits and Performance Identifiers.

**TABLE X-1**  
**TROUBLESHOOTING GUIDE: PENEX**

<b>Problem</b>	<b>Possible Cause(s)</b>	<b>Solution(s)</b>
Low Product Octane	1. Feedstock Composition Change 2. High C <sub>6</sub> Paraffins in Feed 3. High C <sub>6</sub> Cyclics in Feed 4. Low Iso-Ratios 5. Cross Leakage 6. Contaminated Feed	1a. Check Iso-Ratios. 1b. Optimize for new feedstock. 2. Return to design feedstock. (See Equilibrium Octanes.) 3. Adjust splitter operation (Send 90% C <sub>6</sub> cyclicity to reformer). 4. See below. 5. Check for benzene in product. 6. Check for sulfur/other poisons.
Low Iso-Ratios	1. High LHSV 2. High H <sub>2</sub> /HC Ratio 3. High Benzene in Feed 4. High C <sub>7+</sub> in Feed 5. High C <sub>6</sub> Cyclics in Feed 6. Reactor Temperatures Either to High or to Low 7. Sulfur in Liquid Feed	1. Reduce feed rate to design. 2. Reduce recycle gas rate to design. 3a. Return to design feedstock 3b. Adjust reactor temperature to compensate for high delta T. 3c. Reduce LHSV. 4. Adjust splitter operation. 5a. Adjust splitter operation. (Send 90% of the cyclohexane to the reformer.) 5b. Increase the lead reactor temperature to optimize C <sub>6</sub> ring opening. 6. Optimize reactor temperatures. 7a. Correct NHT operations. 7b. Check for combined feed exchanger leaks in the NHT. 7c. Correct stripper operations. 7d. Has feedstock source changed on the NHT?

<b>Problem</b>	<b>Possible Cause(s)</b>	<b>Solution(s)</b>
Low Iso-Ratios (continued)	8. H <sub>2</sub> S in Makeup Hydrogen	8a. Correct desulfurizer operations. 8b. Check for exchanger leaks. 8c. Remove H <sub>2</sub> S from reformer recycle gas. 8d. Check for benzene in reactor effluent. 8e. Check for H <sub>2</sub> S in stabilizer gas.
	9. H <sub>2</sub> O in Liquid Feed or Makeup Hydrogen	9a. Correct drier operations and regenerations. 9b. See problem: H <sub>2</sub> O Breakthrough from Driers. 9c. Purge equipment to remove air and water after maintenance before placing on line. 9d. Bypass reactors until problem solved.
	10. Erratic Feed Flow Rates	10a. Stabilize feed flow and optimize reactor temperatures. 10b. Check feed surge drum pressure controller. 10c. Check pump suction strainer. 10d. Check naphtha splitter operation.
	11. Deactivated or Dead Catalyst	11a. Check inter reactor sample. 11b. Determine type and source of catalyst poison. 11c. Perform sulfur strip if warranted. 11d. Replace catalyst.
	12. Inaccurate Lab Results	12a. Correct sampling procedure. 12b. Troubleshoot lab equipment. 12c. Verify lab is using correct test method.
	13. Faulty Thermocouples	13. Correct thermocouple and optimize reactor temperatures.
	14. Poor Drier Regeneration	14. See Problem: H <sub>2</sub> O Breakthrough from Driers.
	15. Feed Contamination	15a. Identify type of contaminant and eliminate. 15b. See Table II: Penex Streams Contamination Limits and Performance Identifiers.

<b>Problem</b>	<b>Possible Cause(s)</b>	<b>Solution(s)</b>
	16. Reactor Channeling	16a. Check proper reactor internals installed correctly. 16b. Check dense loading results.
H <sub>2</sub> O Break-through from Driers	1. Channeling - upset 2. HCl in stabilizer bottoms poisoning mol sieves 3. Insufficient Regeneration Frequency 4. Sieves Contaminated With Heavy Oil 5. Inaccurate Moisture Analyzer 6. Spent Drier Sieves 7. Leaking Valves 8. Excessively Long Regeneration Cycle 9. High Drier Temperatures	1. Check and reload driers sieves. 2. Correct stabilizer operations (verify reflux at design). 3a. Regenerate driers more often. 3b. Calibrate moisture analyzers. 4a. Identify and eliminate source of heavy oil. 4b. Replace drier sieves. 4c. Lubricated makeup gas compressors. 5. Troubleshoot moisture analyzer. Replace probe. 6a. Replace sieves after 500 regenerations. 6b. Have sieves activity checked. 7. Use double blocks and bleeds correctly. Repair seats. 8. See Problem: Long Drier Regeneration Cycle. 9. Check cooler on liquid feed or makeup gas.
Long Drier Regeneration Cycle	1. Low Regeneration Bed Temperature 2. Superheater Tripping Out	1a. Identify and replace leaking valves. 1b. Check regeneration flow data and pressure. Correct to design. 1c. Check vaporizer and superheater. 1d. Check thermocouples. 1e. Check insulation. 1f. Use double block and bleeds correctly. 2a. Check superheater element. 2b. Check fuse. 2c. Check regeneration flow rate, return to design.

<b>Problem</b>	<b>Possible Cause(s)</b>	<b>Solution(s)</b>
	3. Vaporizer Flooding	3a. Check vaporizer level controller. 3b. Return to design flow rate and pressure. 3c. Check steam trap. 3d. Check steam pressure.
Reactor Temperatures (or delta T's) Decreases	1. Regenerated Liquid Drier Put on Line 2. H <sub>2</sub> O Breakthrough from Driers 3. Sulfur or H <sub>2</sub> S Breakthrough from Driers 4. Feed Composition Changes 5. Feed Contamination 6. Increased Feed Rate 7. Charge Heater Upset (Loss of Heating (Medium)) 8. Loss of Organic Chloride Injection	1. No problem - temperatures will return to within one hour. 2a. See Problem: H <sub>2</sub> O breakthrough from driers. 2b. Bypass reactors and regenerate driers. 3a. Bypass reactors. 3b. Determine and eliminate source of high sulfur or H <sub>2</sub> S. 3c. Regenerate driers. 3d. Check for H <sub>2</sub> S in recycle gas and in stabilizer off-gas. 4a. Correct splitter operations. 4b. Optimize for new feedstock. 5a. Identify type of contaminate and eliminate. 5b. See Table I Penex Streams Contamination Limits. 6a. Stabilize operations at new feed rate. 6b. Check H <sub>2</sub> /HC ratio. 7. Check charge heater. 8a. Check organic chloride injection package. 8b. Inject only UOP approved organic chloride compounds.
Benzene in Lead Reactor Effluent	1. HC FX Leak 2. Sulfur Attenuation of Catalyst 3. Carbon Oxide Attenuation of Catalyst 4. Incorrect Lab Analysis	1. Fix leak. 2. Identify source of sulfur and eliminate. 3. Remove source of carbon oxides. 4. Recheck result.

<b>Problem</b>	<b>Possible Cause(s)</b>	<b>Solution(s)</b>
Benzene in Tail Reactor Effluent	1. CCFX Leak 2. Sulfur Attenuation of Catalyst 3. Carbon Oxide Attenuation of Catalyst	1. Fix leak. 2a. Identify source of sulfur and eliminate. 2b. Perform sulfur strip. 3. Remove source of carbon oxides.
High Temperatures Out of Water Coolers	1. Exchanger Fouling	1a. Correct cooling water problems problems. 1b. Clean exchanger.
Chlorides in Product	1. Poor Stabilizer Operation 2. Stabilizer Feed/Effluent Exchanger Leak	1. Correct stabilizer operation. Verify R/F is at design or higher. 2. Fix leak.
Chlorides in Scrubber Off-Gas	1. Weak Caustic 2. Inadequate Caustic Circulation 3. Erratic Gas Flow 4. Caustic Level Being Held Too Low 5. Contaminated Sample Lines	1. Charge-out spent caustic when 2 wt-% NaOH. Makeup fresh 10 wt-% NaOH. 2a. Clean pump suction strainer(s). 2b. Return to design circulation rate. 3. Check stabilizer and scrubber pressure controllers. 4. Hold level up in packed section Calibrate level indicators. 5. Use clean sample lines for detector tube connection.
Hydrocarbon Layer on Caustic in Scrubber	1. Make up Caustic Too Cold 2. Caustic Temperature Below Stabilizer Off-Gas Temperature 3. Poor Stabilizer Operations (heavy ends in overhead)	1. Use caustic heater during fresh caustic makeup. 2a. Use caustic heater to raise caustic temp. to 38-49°C (100-120°F). 2b. Check stabilizer overhead temperature. Return to design. 3. Correct stabilizer operations. Return reflux rate to design.

<b>Problem</b>	<b>Possible Cause(s)</b>	<b>Solution(s)</b>
High RVP in Product	1. Poor Stabilizer Operation 2. Butanes in Feedstock	1. Correct stabilizer operation; establish design reflux and overhead temperature 2. Verify feedstock is normal per GLC on feed.
Caustic Circulation Pumps Plugging	1. Dirty Makeup Caustic 2. High Wt-% NaOH	1. Use only fresh, clean caustic. 2a. Dilute caustic to 10 wt% NaOH. 2b. Correct condensate injection rate.
Caustic Carryover from Scrubber	1. Erratic Gas Flow Rate 2. Scrubber Plugged Due to Too Strong or Fouled Caustic 3. Foaming	1. Correct pressure controllers on stabilizer and scrubber. 2a. Dilute caustic to 10 wt%. 2b. Use only fresh, clean caustic for makeup. 2c. Replace rings in packed section. 2d. Shut down to clean vessel. 3. Contaminated caustic, liquid hydrocarbon layer.
Corrosion in Scrubber	1. Too High Caustic Temperature 2. Dry Areas in Scrubber 3. Improper Caustic Changeout Procedure	1a. Limit caustic strength to 10 wt-% limit temperature to less than 49°C (120°F) max. 1b. Do not steam out scrubber at shutdown. 1c. Do not put steam trap on caustic heater condensate to drain. 2a. If caustic level is kept in packed area, use the lower caustic spray nozzle during caustic changeout. 2b. If caustic level is kept below packed area, maintain lower spray ring flow continuously. 3a. 2 wt% min NaOH at changeout. 3b. Regularly scheduled changeout. 3c. Don't use pH as control use caustic strength as wt% NaOH.

<b>Problem</b>	<b>Possible Cause(s)</b>	<b>Solution(s)</b>
Corrosion in Regeneration Gas Cooler	<ol style="list-style-type: none"> <li>1. Chlorides in Regenerant</li> <li>2. Stabilizer Feed/Effluent Exchanger Leak Causing Chlorides in Regenerant</li> <li>3. HCl in Makeup Gas</li> <li>4. Moisture Buildup from Insufficient Drier Regenerations and HCl Present</li> </ol>	<ol style="list-style-type: none"> <li>1a. Correct stabilizer operation. Verify R/F is at design or higher.</li> <li>2a. Fix leak.</li> <li>3a. Eliminate HCl.</li> <li>4a. Minimum regeneration cycle of 1 regen per drier per week (i.e. 4 regenerations per week).</li> </ol>
Sulfur in Liquid Feed	<ol style="list-style-type: none"> <li>1. Too High Desulfurizer Temperature</li> <li>2. Combined Feed Exchanger Leaks in the NHT</li> <li>3. Desulfurizer Temperature Too Low</li> <li>4. Poor Stripper Operations</li> </ol>	<ol style="list-style-type: none"> <li>1. Lower desulfurizer reactor temperature and check for reduction in effluent sulfur.</li> <li>2. Repair leaks.</li> <li>3. Raise desulfurizer reactor temperature to check for reduction in effluent sulfur.</li> <li>4. Correct stripper operations. Establish a RIF of about 0.3.</li> </ol>
Sulfur in Liquid Feed (continued)	<ol style="list-style-type: none"> <li>5. Startup Bypass Valves Leaking</li> <li>6. Contaminated Gas Blanket on Feed Surge Drum</li> </ol>	<ol style="list-style-type: none"> <li>5. Blind-off all unnecessary lines and check double blocks and bleeds.</li> <li>6a. Use only dry makeup hydrogen for gas blanket.</li> <li>6b. Check for H<sub>2</sub>S breakthrough around makeup hydrogen driers.</li> </ol>
Oxygenates in Liquid Feed	<ol style="list-style-type: none"> <li>1. Feed Coming from Storage</li> <li>2. Feed Blanketed with Fuel or Natural Gas</li> </ol>	<ol style="list-style-type: none"> <li>1. Use only fresh feed. Route storage back through desulfurizer.</li> <li>2. Do not blanket liquid feed with CO/CO<sub>2</sub> containing gases.</li> </ol>
Insufficient Makeup Hydrogen	<ol style="list-style-type: none"> <li>1. Low Reformer Feed Rates or Temperatures</li> </ol>	<ol style="list-style-type: none"> <li>1. Reduce Penex feed rate until reformer back up to normal.</li> </ol>

<b>Problem</b>	<b>Possible Cause(s)</b>	<b>Solution(s)</b>
CO/CO <sub>2</sub> in Makeup Hydrogen	<ol style="list-style-type: none"> <li>1. Poor Methanator Operations</li> <li>2. Drier Needs Regeneration</li> <li>3. Cyclic Reforming Operations</li> <li>4. High Moisture Content in CCR Platforming Unit Recycle Gas</li> <li>5. Poor PSA Operations</li> <li>6. Cross-Contamination in Hydrogen Header</li> </ol>	<ol style="list-style-type: none"> <li>1. Correct methanator operation to remove all CO. Check bypass.</li> <li>2. Regenerate drier to monitor for CO<sub>2</sub> breakthrough.</li> <li>3. Methanator required to remove CO; additional mol sieves to remove CO<sub>2</sub> or PSA needed.</li> <li>4a. Check water oxygenate content of CCR Platforming feed. 4b. Check water content of CCR regeneration air. Possible spent drier.</li> <li>5. Adjust PSA to reject carbon oxides.</li> <li>6. Blind contaminated sources from Penex makeup gas.</li> </ol>

**TABLE X-2****PENEX STREAMS CONTAMINATION LIMITS  
AND PERFORMANCE IDENTIFIERS**

<b>Penex Stream</b>	<b>Test Performance Identifiers</b>	<b>Contamination Units/ Performance Identifiers</b>
Liquid Feed	Total Sulfur	Target <0.1 ppm (0.5 wppm MAX.)
	Total Nitrogen	Target <0.1 ppm (0.5 wppm MAX.)
	Water	0.0 ppm (0.1 ppm MAX.)
	Oxygen and Oxygen Compounds, Methanol, Carbonyl	Nil. (Less than the lowest detectable limits)
	Arsenic	1 ppb (Less than the lowest detectable limits)
	Lead	10 ppb (Less than the lowest detectable limits)
	Copper	<20 ppb (Less than the lowest detectable limits)
	Fluoride	<0.5 ppm (Less than the lowest detectable limits)
	Other Metals: Iron, Sodium	Nil. (Less than the lowest detectable limits)

<b>Penex Stream</b>	<b>Test</b>	<b>Contamination Units/ Performance Identifiers</b>
Makeup Hydrogen	Composition (by GC)	Sufficient H <sub>2</sub> so outlet H <sub>2</sub> /HC can be maintained above 0.05 mol/mol. (Usually >70% H <sub>2</sub> )
	Basic Nitrogen	Target <0.1 ppm (0.5 ppm MAX.)
	Water	0.0 ppm (0.1 ppm MAX.)
	Oxygen and Oxygen Compounds	CO + CO <sub>2</sub> <10 ppm (Less than lowest detectable limits) CO <1 ppm
	H <sub>2</sub> S (by Draeger)	Target <0.1 ppm (1.0 ppm MAX.)
Lead Reactor Effluent	Composition (by GC)	$\frac{iC_5}{iC_5 + nC_5} = >70\%$
	Composition (by GC)	no benzene
Stabilizer Off-Gas	Composition (by GC)	low C <sub>5</sub> + minimize C <sub>4</sub> 's
	H <sub>2</sub> S (by Draeger)	0.0 ppm (Less than lowest detectable limits)
Caustic Scrubber Off-Gas	HCl	0.0 ppm (Less than lowest detectable limits)

<b>Penex Stream</b>	<b>Test</b>	<b>Contamination Units/ Performance Identifiers</b>
Stabilizer Bottoms	Composition (by GC)	no C <sub>3</sub> -
		$\frac{iC_5}{iC_5 + nC_5}$ = >70% = 76-78%
		$\frac{2 - 2 DMB}{C_6P}$ = 30-35%
		$\frac{2 - 3 DMB}{C_6P}$ = 10%
		$\frac{2 MP}{C_6P}$ = 30%
		$\frac{3 MP}{C_6P}$ = 16%
		$\frac{nC_6}{C_6P}$ = 9-12%
		$\frac{MCP}{MCP + CH}$ = 50%
		C <sub>6</sub> Ring Opening = 40%
	Total Chloride, HCl	<1.0 ppm (Less than the lowest detectable limits)
Scrubber Circulating Caustic	Composition (by titration)	10 wt-% to 2 wt-% NaOH
	Visual Inspection	Not excessively graying

## XI. NORMAL SHUTDOWN

### A. TOTAL UNIT SHUTDOWN

If the entire unit is to be shut down for an extended period, the following procedure can be used.

1. Discontinue all drier regenerations at a point where the drier being regenerated has just completed its regeneration cycle.
2. Increase the makeup gas flow to the maximum possible.
3. Reduce the reactor inlet temperatures to 121°C (250°F) at a rate of 28°C (50°F) per hour. Leave the charge rate constant since a sharp reduction could result in high reactor severity and a temperature excursion.
4. When the reactor temperatures reach 121°C (250°F), decrease the charge rate slowly to 50% of design. Reduce the charge in increments of 5% of scale every 15 minutes. Continue to sweep the reactor with at least a design flow of makeup gas. Maintain the reactor temperatures at 121°C (250°F).
5. After the charge rate has been reduced, depressurize the reactor circuit to 21 kg/cm<sup>2</sup>g (300 psig). Depressurize at a rate which allows stabilizer pressure control.
6. Cool the reactors to 93°C (200°F) and stabilize the temperature. When the reactor temperatures reach approximately 105°C (220°F) stop the chloride injection. Maintain these conditions for 1 hr. after the chloride injection has been stopped, in order to sweep chloride from the feed circuit upstream of the reactors, then proceed to step 7.

7. Bypass the reactor feed to the stabilizer. During the period charge is cut out, try to minimize low flow of liquid over the catalyst, i.e. cut the feed out as quickly as possible.
8. Sweep the reactor circuit with the design flow of hydrogen until the temperatures are 65°C (150°F). Stop the hydrogen flow when the reactors have cooled.
9. Maintain pressure on the reactors and ensure that they are fully isolated. The reactor circuit pressure should be kept positive to avoid ingress of contaminants. As the reactor cools, there is a risk of developing a vacuum on the system which could result in air ingress. Block in steam heaters and water coolers as they are taken out of service and drain the water side.
10. If the shutdown is going to be short in duration, the stabilizer can be left in operation. If not, the stabilizer should be shut down in an orderly manner.
11. If the stabilizer is shut down, be careful to avoid depressurizing the stabilizer below the scrubber pressure. There is a risk, if the check valve in the stabilizer off-gas line does not hold, of backing up caustic from the scrubber to the stabilizer. When the stabilizer has been shut down, block in the off-gas line to the scrubber.
12. Depending upon the extent and the reason for the shutdown, the following will apply:
  - a. If any equipment or vessel upstream and downstream of the reactor circuit is to be opened, it is to be properly purged with nitrogen. If personnel entry to this equipment is then to be made, it must be prepared for entry by purging it with air (after N<sub>2</sub> purge) followed by a check by the refinery safety department.

- b. If any equipment or vessels in the reactor circuit (excluding the reactors) are to be opened, they are to be properly purged with nitrogen. If personnel entry to this equipment is then to be made, it must be prepared for entry by purging it with air (after N<sub>2</sub> purge) followed by a check by the refinery safety department. If the work (whatever it may be) is extensive in this area, it may be necessary to reacidize the entire reactor circuit with anhydrous HCl as outlined in the initial startup procedures.
- c. If the reactors are to be unloaded, refer to Catalyst Unloading section.
- d. If the stabilizer is to be opened for inspection, the tower should be operated for a period of time on feed which is bypassing the reactor. A purge of makeup gas should be sent to the tower to help purge HCl from the overhead. After there is no measurable HCl in the overhead, the tower may be shut down and purged of hydrocarbon per normal refinery procedure.

## B. PARTIAL UNIT SHUTDOWN

In the event it becomes necessary to change the catalyst in one reactor, carry out the steps detailed in Section XI A. through step 5., then follow the steps below.

1. Open the makeup gas purge line to the reactor to be taken off line. Maintain the purge gas flow at the design value.
2. Begin admitting charge heater outlet material into the reactor to be left on-stream, and block in the feed to the reactor to be replaced.
3. After purging the lead reactor for at least 4 hours, temporarily stop the purge. Block in the valve in the return line from hot combined feed exchanger to the reactor to be left on stream and immediately open the single reactor bypass. Immediately re-establish the hydrogen purge.

4. Open the valve on the outlet of the reactor to be left on stream to the hot combined feed exchanger.
5. Close the valve on the outlet from the reactor to be left on stream to the cold combined feed exchanger. Process flow will now be from the combined feed heater through the reactor left on stream, through the hot combined feed exchanger, and on into the cold combined feed exchanger.
6. Open the valve in the outlet from the reactor to be replaced to the cold combined feed exchanger, and close the outlet valve from this reactor to the hot combined feed exchanger.
7. Continue to purge the reactor to be unloaded. This reactor should be purged for a period of time long enough to remove hydrocarbon from the reactor and to cool the catalyst bed below 65°C (150°F). Increase reactor pressure back up to the design normal operating pressure.
8. Block in the gas purge to the reactor to be replaced, block in the outlet valve of the reactor being replaced going to the cold combined feed exchanger, and then depressurize the reactor to the flare. Increase the reactor circuit pressure back to design.
9. Evacuate the reactor three times to about 25" Hg, breaking the vacuum with dry nitrogen to 0.35 kg/cm<sup>2</sup>g (5 psig) each time. Purge the reactor to the flare with nitrogen for an hour after breaking each vacuum.
10. With a small nitrogen purge on the reactor, insert spectacle blinds at the inlet and outlet of the reactors, and proceed to unload the catalyst as outlined in the following section "C."

## C. PENEX CATALYST UNLOADING AND HANDLING

The same precautions used to keep air away from fresh catalyst must be used when unloading spent catalyst from a reactor. Spent catalyst contains a large amount of chloride, and any moisture that contacts the catalyst will make the material very corrosive. At all times during the opening of the reactor and unloading of the catalyst, a dry nitrogen gas blanket of 1.0 to 1.5 inches of water should be maintained on the reactor. With the reactor to be replaced, taken off line and prepared as previously outlined the following procedure can be followed:

1. Remove the blind flange on the catalyst withdrawal nozzle and attach the catalyst unloading spout.
2. The spent catalyst must be loaded into the original catalyst drums and plastic liners to protect against corrosion during shipment. During the catalyst run, the drums should be stored in a dry location and protected from damage. Detailed unloading steps are outlined below:
  - a. Place an empty catalyst drum on a scale, then put the inner plastic catalyst bag with the unloading neck inside the outer heavy plastic bag. N<sub>2</sub> purge the inner bag.
  - b. Slip the plastic unloading neck over the catalyst unloading spout, then remove the catalyst support plate from the withdrawal nozzle.
  - c. Load approximately 115 kgs (250 lbs) of catalyst into each drum. A minor modification to the catalyst unloading spout will allow the catalyst flow to be regulated and stopped easily (see Figure XI-1).
  - d. When a drum is full, wire clamp the plastic unloading neck in two places, then clamp the heavy catalyst bag around the inner bag. Close the drum tightly using the original lids and retaining rings.
  - e. Take samples of the spent top, middle and bottom Penex catalyst and send to UOP for analyses and comments.

3. There is no need to screen the catalyst prior to returning it for platinum recovery, since it will be screened prior to processing. However, the ceramic holddown material will result in increased shipping costs if the catalyst is not screened. The catalyst unloading spout could be modified to insert specially fabricated or purchased screening equipment. The holddown material that is collected should then be manually screened a second time and any catalyst or fines that are collected should be added to one of the drums.
4. During the unloading of the catalyst, the top manway of the reactor can be opened in preparation for the loading of fresh catalyst. As the manway is opened, tightly cover the open flanges with plastic. The manway and distributor should be wrapped in plastic to protect it from moisture. The reactor manway should be tightly covered with plastic or the catalyst loading assembly installed to conserve nitrogen during the unloading.
5. A small amount of spent catalyst will be left in the bottom of the reactor, because the support material is level and is not sloped towards the withdrawal nozzle. This catalyst can be removed by using a very long handled, flat, shovel to “sweep” the catalyst towards the withdrawal spout.
6. Once all spent catalyst has been removed, the catalyst support plate should be installed, along with a coiled layer of 1/2" diameter ceramic fiber rope on top of the plate, in the withdrawal nozzle. The unloading spout should be removed. Replace the gasket on the withdrawal nozzle flange and close the withdrawal nozzle. The withdrawal sleeve can be filled with the appropriate sized support material from the top of the reactor by using a long piece of 1-1/2 inch pipe or plastic tubing and a funnel to channel the material into the sleeve.
7. Fresh catalyst can then be loaded using the procedures outlined in Section XIII.

NOTE: The above procedure is based on the unit being shut down for a catalyst change in one reactor only with the unit being kept in operation with the second reactor set or being kept under a positive hydrogen pressure. If the unit has been completely shut down and equipment in the reactor section exposed to air and moisture, the reactor circuit must be dried (including HCl addition) before the unit is placed back on stream. If the reactor was opened to the air during the unloading, it must be included in the drying circuit before fresh catalyst is loaded.

8. It will be necessary for a man to enter the reactor and prepare it for loading. Suitable safety precautions must be taken, including fresh air masks and safety lines, for a person to enter a nitrogen atmosphere.
9. Catalyst spillage should be minimized using the above procedure and the specified unloading equipment. However, the concrete pad at the base of the reactors should be cleaned prior to the unloading operation so that any spilled catalyst can be swept up and placed in one of the drums.
10. The weight of catalyst unloaded should be recorded as a check on possible loss during shipment. When the catalyst is returned for platinum recovery, it is screened to remove oversized particles and fines (particles smaller than 14 mesh). The platinum content of the catalyst and the fines are determined separately. As a general rule, fines will contain approximately 20% catalyst.
11. The difference between the catalyst loaded and unloaded should be noted for bookkeeping charges for catalyst losses.

#### D. ADS-11 UNLOADING AND HANDLING

Analysis of guard bed effluent will determine the capacity of the ADS-11 for sulfur removal. Once the guard bed is saturated it is taken off-line, unloaded and loaded with fresh adsorbent. The Penex Unit can be operated for a short period of time with the guard bed bypassed as long as the hydrotreated naphtha sulfur level is less than 0.3 wt ppm.

Spent ADS-11 is pyrophoric and must be dumped into nitrogen blanketed drums. This toxic waste poses a disposal problem. A suitable toxic land fill site or metals reclaiming company should be found well in advance. A material safety data sheet for ADS-11 is enclosed.

1. Bypass the guard bed that will be unloaded.
2. Block in the guard bed adsorber that is to be unloaded. Install blinds between the double block valves at the inlet and outlet of the adsorber to completely isolate it from the process.
3. Line up the flow of naphtha from the bottom of the adsorber that is to be unloaded to the flare header. Using the globe valve that is in the line, slowly depressurize the vessel to the flare. Start nitrogen to the top of the adsorber and pressure the liquid in the adsorber to the flare.
4. Keep about 1 kg/cm<sup>2</sup>g (14.2 psi) of nitrogen pressure on the adsorber.
5. Commission the low pressure steam to the top of the adsorber. Be sure to blow down the steam line well to remove any condensate and to heat up the steam line.
6. Line up the flow out of the bottom of the vessel to the flare line. Start steam flow to the top of the vessel. Check a drain valve at the outlet of the vessel to determine if steam or condensate is coming out of the tower. Continue steaming the vessel for 24 hours after steam begins to exit the vessel. This insures that all of the hydrocarbon has been removed and that the ADS-11 adsorbent is dry, free of hydrocarbons and will flow easily when unloaded.
7. Stop the steam and at the same time begin adding nitrogen to break any vacuum that may form. Purge with nitrogen to the flare until the adsorbent is cooled to 65°C (150°F) or below. Keep the vessel under 1 kg/cm<sup>2</sup> (14.2 psig) of nitrogen pressure.

8. When the vessel is ready to be unloaded, depressurize slowly to flare. Maintain a nitrogen purge on the vessel.

NOTE: THE ADS-11 ADSORBENT CONTAINS A NICKEL TYPE COMPOUND. IT IS POSSIBLE THAT IF THE ADS-11 IS EXPOSED TO AIR THAT NICKEL CARBONYL MAY BE FORMED. NICKEL CARBONYL IS A HIGHLY POISONOUS GAS THAT CAN FORM IN THE PRESENCE OF OXYGEN. FOR THIS REASON, THE GUARD BED ADSORBER SHOULD ALWAYS BE KEPT UNDER NITROGEN. THE DRUMS THE ABSORBENT ARE LOADED INTO SHOULD BE PRESSURED WITH NITROGEN. ALL PERSONNEL IN THE AREA OF THE LOADING SHOULD BE PROVIDED WITH FRESH AIR MASKS. ANY PERSONNEL ENTERING THE ADSORBER SHOULD ALSO HAVE A FRESH AIR MASK. THIS IS VERY IMPORTANT.

9. Open the catalyst unloading flange and install a slide valve on the flange. Insure there is either a plastic tube or canvas loading sock to take the adsorbent to the drums for unloading.
10. Begin unloading the adsorbent, always keeping the vessel and the drums under nitrogen.
11. When the adsorbent has stopped flowing, open the side manway of the vessel and level the adsorbent bed by pushing the adsorbent with a long board to the inlet of the unloading nozzle. TAKE CARE NOT TO DISTURB THE ADSORBENT SUPPORT MATERIAL THAT IS JUST UNDER THE ADSORBENT.
12. When the adsorbent is level, install the loading clip back into the unloading nozzle. Remove the slide valve. Install the blind flange back on the unloading nozzle.

13. Load the new adsorbent as per the loading instructions given during the start-up period. NOTE: KEEP THE VESSEL UNDER NITROGEN DURING THE LOADING. ANY PERSONNEL THAT ENTER THE VESSEL TO INSTALL THE SUPPORT BALLS MUST HAVE A FRESH AIR MASK AND BE PROPERLY TRAINED FOR INERT ENTRY.
14. Keep the new adsorbent as dry as possible as any water or moisture introduced into the adsorber will go to the Penex Unit upstream of the liquid feed driers.

NOTE: ATTACHED IS A SECTION CONCERNING NICKEL CARBONYL. THIS IS INCLUDED FOR YOUR UNDERSTANDING OF THIS DANGEROUS MATERIAL.

## E. PRECAUTIONS

### 1. Background on Nickel Carbonyl

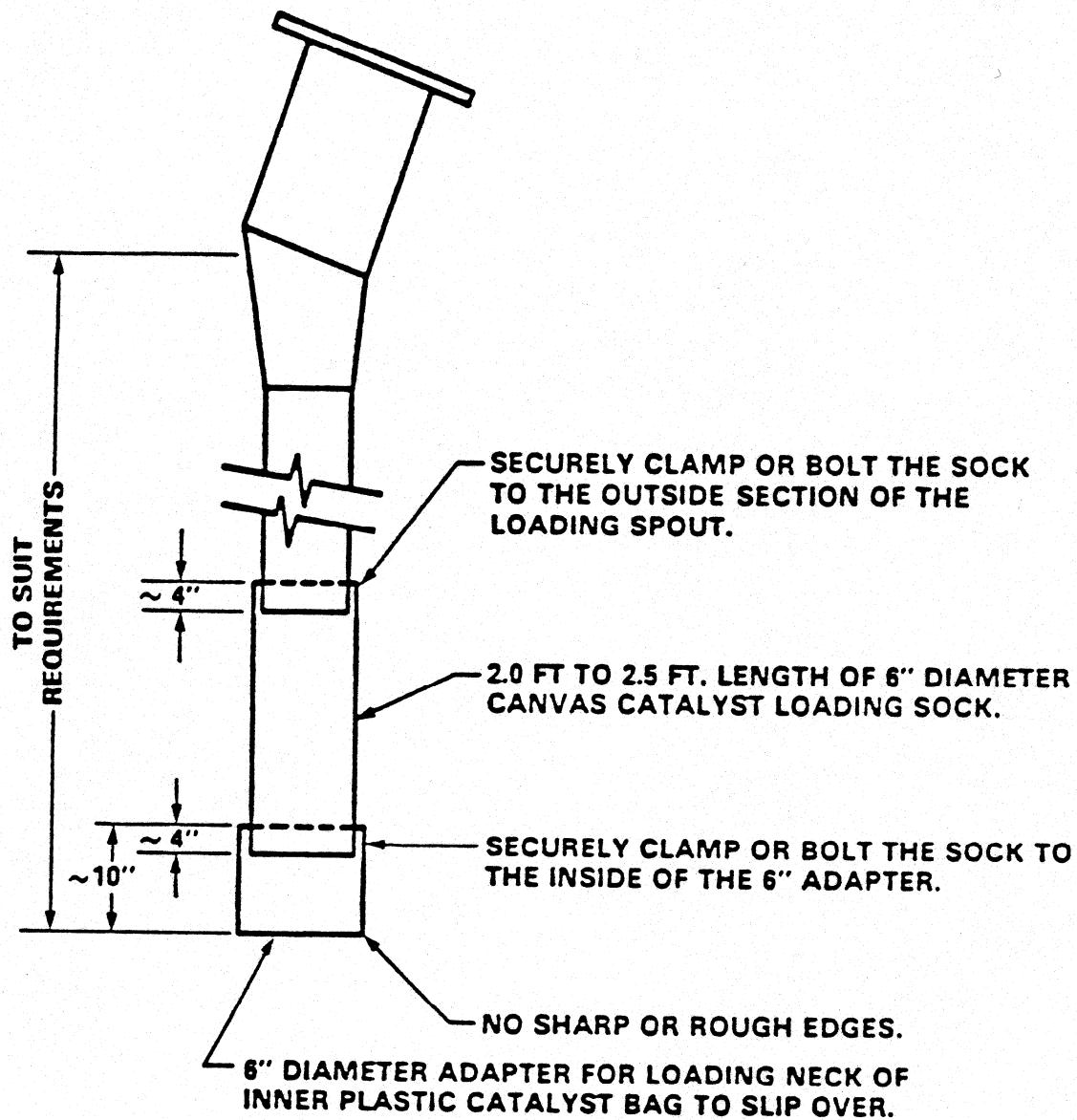
In Process units such as Naphtha Hydrotreating units and sulfur guard bed adsorbers, the potential for forming nickel carbonyl exists only with the catalysts and adsorbents containing nickel (S-6, S-7, S-15, S-16, ADS-11), and only during regeneration or during the handling of unregenerated catalyst. Care must be used to ensure that the procedures used will prevent the formation of nickel carbonyl. Data has been published showing the equilibrium concentration of Ni(CO)<sub>4</sub> versus temperature, pressure and CO concentration in a gas. The nickel carbonyl concentration drops rapidly with increasing temperature and decreasing CO concentration. At 7 kg/cm<sup>2</sup>g (100 psig) with 0.5 mol-% CO in the gas, the nickel carbonyl concentration is at the maximum recommended spot level of 0.04 ppm at 149°C (300°F), and 0.001 ppm at 182°C (360°F).

The following practices should be followed to prevent the formation of nickel carbonyl:

1. Once a reactor containing a nickel catalyst has been exposed to oxidizing conditions (regeneration), a measurable concentration of oxygen must be maintained until the combustion of all carbon ceases and all CO<sub>2</sub> has been purged from the system.
2. Once a reactor containing a nickel catalyst is in a reducing atmosphere and regeneration is not desirable, maintain the system in a reducing or inert atmosphere until all the catalyst has been cooled to at least 65°C (150°F). Unregenerated catalyst should be unloaded with both the vessel and drum N<sub>2</sub> purged before receiving used catalyst. Oxidation (burning) must be avoided.

There are many published techniques for determining the concentration of nickel carbonyl in air (such as a vessel to be entered for maintenance), and several direct reading instruments are available commercially. For further information, see:

American Industrial Hygiene Assoc. Journal  
May-June, 1968  
January-February, 1965

**FIGURE XI-1****CATALYST UNLOADING SPOUT FOR SPENT 1-8 CATALYST**

**NOTE: CONTROL OR STOP CATALYST FLOW BY TWISTING  
THE SECTION OF CANVAS SOCK TO RESTRICT  
OR CLOSE THE FLOW AREA.**

## XII. EMERGENCY PROCEDURES

Emergencies must be recognized and acted upon immediately. The best way to be prepared for an emergency is to ensure that the proper procedures are in place and that all operators are fully trained in these procedures. The operators should have an understanding of the unit and the procedures which enables them to devise a course of action.

Some general outlines are provided for the following emergency situations.

- A. Explosion, Fire, Line Rupture
- B. Leaking Valves or Vessels
- C. Power Failure
- D. Instrument Air Failure
- E. Heating Failure
- F. Cooling Water Failure
- G. Loss of Feed
- H. Loss of Makeup Gas
- I. High Reactor Temperature Differential
- J. Catalyst Protection Procedures

Some special considerations regarding the Penex Unit in an emergency:

- 1. The unit contains light hydrocarbons and hydrogen which are explosive and/or highly flammable.
- 2. The unit contains benzene and perchloroethylene which are known health hazards.
- 3. The unit contains HCl downstream of the reactor 1 inlet. The concentration is particularly high in the stabilizer overhead.

4. Benzene and olefins in the Penex feedstock will saturate in the reactor. Much of the C<sub>7+</sub> will hydrocrack. The saturation and cracking reactions are exothermic. If the levels of these components in the feed increase significantly, the heat produced could raise the lead reactor temperature beyond the normal operating range.
5. A reactor temperature excursion could occur if the flow of liquid through a hot reactor is too low or if the reactor temperatures are too high. Each reactor LHSV should always be kept above 1.0 Hr.<sup>-1</sup>.
6. The caustic scrubber vents to a system which runs under pressure. During an emergency the stabilizer could depressurize below the scrubber pressure. There is a check valve in the stabilizer off-gas line. However, if the check does not hold, water and caustic could back up into the stabilizer causing a potential corrosion problem. There is a double block and bleed on the line which should be closed once gas flow from the stabilizer stops.
7. If a reactor temperature excursion occurs and temperatures climb above 232°C (450°F), the reactors must be depressured to prevent mechanical damage. At the usual operating pressure of 31.6 kg/cm<sup>2</sup>g (450 psig) the reactor design temperature is typically 260°C (500°F). Action should be taken before the temperature climbs to the point that mechanical problems could occur.
8. During a temperature excursion, the reactors should be depressured. If for some reason the reactors cannot be depressured to the stabilizer or if after depressuring to the stabilizer the reactor temperatures are over 232°C (450°F), and climbing, then the reactors should be depressured to the flare. **Whenever the reactors are depressured to the flare the lead reactor inlet, the hydrogen purge quench lines and the reactor back pressure control valve station should be blocked-in.**

Exact procedures cannot be provided for every type of emergency situation. General procedures for the most common types of emergency situations follow. With an understanding of these procedures and the various concerns outlined above, the operators should be able to devise a course of action for the various situations that can arise.

### **A. EXPLOSION, FIRE, LINE RUPTURE**

The major considerations in this case are to minimize personnel injury, prevent the fire or potential for fire from spreading and to put the fire out.

1. Sound alarm and notify proper services.
2. Stop hydrocarbon and gas feed to the unit and stop all heat input.
3. Depressurize the plant to the flare and try to isolate the effected area.
4. Shut down the remainder of the equipment as the situation permits.

### **B. LEAKING VALVES OR VESSELS**

Leaking valves and vessels in the sections of the plant which contain HCl are considered an emergency since the contact of HCl with the atmospheric moisture can cause rapid corrosion. Leaks should be repaired quickly.

### **C. POWER FAILURE**

If electrical equipment fails, all electrically driven equipment, pumps, compressors, fin fans, etc. will stop. Due to the loss of flow through the reactors which results from the power failure, a severe condition will exist in the reactor which could result in a temperature excursion. The immediate concern is to remove hydrocarbon from the reactor and to lower the pressure.

Following is the procedure:

1. Block in the steam to the reactor charge heater and the stabilizer reboiler.
2. Restart cooling water pumps and fin fans, if possible.
3. Block in the lead reactor inlet using the board mounted controller.
4. Depressure the reactors to the stabilizer to remove hydrocarbon from the reactors. Depressure the stabilizer to 3.5 kg/cm<sup>2</sup>g (50 psig) above the caustic scrubber. The reactor circuit should be depressured at a rate which avoids lifting of the stabilizer safety valve.

If instrument air has also failed the reactor back pressure control valve should fail in position. This position may or may not be adequate for depressurization of the reactor circuit at the desired rate. The back pressure control valve is equipped with a bypass so that the rate of depressurization can be changed if necessary. Air failure will require that the stabilizer and scrubber be depressured manually using the control valve assembly bypasses.

If the reactor cannot be depressured to the stabilizer then depressure to the flare system. Whenever the reactors are depressured to the flare the lead reactor inlet, hydrogen purge lines and back pressure control valve station should be closed.

5. If possible establish a hydrogen purge across the reactors to accelerate cooldown. The hydrogen purge line which is routed to the lead reactor inlet should be used.
6. Continue depressuring to the stabilizer until the reactors have been depressured as low as possible. Maintain the purge if available and cool the reactors to 65°C (150°F).

7. If, after depressuring to the stabilizer, the reactor temperatures climb above 232°C (450°F), then depressure to the flare. When depressuring to the flare, do so from the lag reactor outlet. Block in the reactor back pressure control valve and the hydrogen purge line when this is done.
8. After cooling the reactors to 65°C (150°F), restart the unit following the normal startup procedure.

#### D. INSTRUMENT AIR FAILURE

1. When instrument air fails, all control valves, etc. will assume their fail positions. For a control valve the position is designed to be either fully open, fully closed, or locked in position. The fail position depends on the service. The operators should be aware of the valve fail positions.
2. If there is a plant-wide air failure, the chances are that the unit will have to be shut down. This will be the safest way to proceed. If the reason for the failure can be located quickly, a shutdown may be prevented. For example if the shutdown is the result of failure of the air drying section, that section can be bypassed and repaired.
3. If the air fails to one or two valves, operation could perhaps proceed using a bypass. This ability depends on the service. Operating with a manual bypass will require constant operator attention.
4. If there is an instrument air failure and the air pressure cannot be regained, proceed as follows:
  - a) Ensure that all heat inputs are shut-off to prevent overheating and over pressuring. The reactor charge heater and the stabilizer reboiler should be shut down and the steam supply blocked-in.
  - b) Stop chloride injection.

- c) In general spillback and reflux valves will fail open. The reactor effluent pressure control valve will fail in position. Most other valves will fail closed. For the valves which fail closed, make sure the associated block valves are closed. This will prevent loss of control if air pressure is regained.
- d) The reactor circuit should be depressured to the stabilizer to remove hydrocarbon from the reactors and minimize the potential for high reactor severity. Since the reactor back pressure control valve fails in position, the reactor circuit will depressurize to the stabilizer as soon as air fails and feed and makeup gas are lost. Block in the lead reactor inlet using the emergency block valve to prevent feed from entering the reactors from the feed circuit when the reactors are depressuring.

The stabilizer and scrubber pressures will have to be manually controlled using the control valve bypasses since these valves fail closed.

- e) If, during the instrument air failure, the reactor temperatures climb above 232°C (450°F), block in the reactors and depressurize to the flare. Depressurize to 3.5 kg/cm<sup>2</sup>g (50 psig).
- f) When air pressure is regained, and if the reactor temperatures are below 232°C (450°F), establish maximum makeup gas flow to the lead reactor inlet via the hydrogen purge line.

## E. HEATING FAILURE (CHARGE HEATER, REBOILERS, ETC.)

If steam is lost, the Penex Unit must be shut down. Steam is usually used in the reactor charge heater and the stabilizer reboiler. Since the stabilizer reboiler will stop functioning, unstabilized product could be produced if feed is continued to the unit. To stop the production of unstabilized product the feed must be removed from the unit. The procedure follows:

1. Increase the makeup gas flow to maximum. Open the lead reactor inlet makeup gas purge line to accelerate cooldown. Establish design flow on the hydrogen purge line.
2. Stop chloride injection.
3. Remove feed from the reactor circuit and immediately depressurize the reactors to the stabilizer. Drop the pressure to 3.5 kg/cm<sup>2</sup>g (50 psig) above the stabilizer.
4. Cool the reactors down to 65°C (150°F).
5. When steam is regained, restart the unit.
6. If during the Heating Failure procedure the reactor temperatures climb above 232°C (450°F) the reactors must be depressured to as low a pressure as possible. If the reactors have been depressured as far as possible to the stabilizer and the reactor temperatures are over 232°C (450°F) and climbing then the reactors must be depressured to the flare.

## F. COOLING WATER OR FIN FAN FAILURE

Coolers can be located on the liquid feed to the driers, makeup gas to the driers, stabilizer overhead and the product streams. If the coolers stop working, there will be overpressuring in the stabilizer. If the driers operate too hot, the water retention capability is reduced, jeopardizing the Penex catalyst. If products cannot be cooled properly, there is a risk of overheating storage tanks and causing a fire hazard.

If cooling water fails for an extended period of time, the unit will need to be shut down using an accelerated shutdown procedure. The procedure follows. This procedure assumes that the stabilizer condenser has been lost and cannot be restarted.

1. Stop the flow of steam to the charge heater.
2. Maintain makeup gas flow and reactor feed.
3. Stop chloride injection when the lead reactor temperature is 105°C (220°F).
4. Reduce the heat input to the stabilizer to maintain the stabilizer pressure.
5. Follow the normal shutdown procedure as closely as possible.

## G. LOSS OF FEED

Loss of feed to the Penex reactor is an emergency situation. When feed flow stops, the feed which is in the reactor circuit will flow through the reactor at a low LHSV. The feed will be swept through the reactor by the makeup gas. The feed could be heated to a high temperature, by the charge heater, if the charge rate drops suddenly. The reactor pressure will drop as a result of the throughput reduction which will cause the back pressure control valve to close off. The combined effect of these responses to a loss of feed is high reactor severity which could result in overconversion of the feed and a reactor temperature excursion. The procedure below will minimize the possibility of a temperature excursion occurring when feed is lost.

Two loss of feed procedures are detailed below. Procedure 1 is for complete loss of feed, such as if the charge pumps cannot work. Procedure 2 is for low feed availability, such as loss of feed from the hydrotreater.

### Procedure 1

When feed flow is lost:

1. Stop the flow of steam to the charge heater. This should happen automatically when the feed flow drops below the charge heater shutdown point.

2. Increase the makeup gas flow to maximum. Route the makeup gas to the lead reactor inlet purge line.
3. Slowly depressurize the reactor circuit to the stabilizer. Depressurize at a rate which allows stable pressure control of the stabilizer.
4. Stop C<sub>2</sub>Cl<sub>4</sub> injection when the lead reactor temperature is 105°C (220°F).
5. Observe the reactor temperatures. If the temperatures are below 232°C (450°F) and stable, continue with the makeup gas purge and cool down the reactor to 65°C (150°F). If depressuring to 3.5 kg/cm<sup>2</sup> (50 psig) above the stabilizer does not stop the temperature excursion, depressurize the reactors to the flare. Cool down the unit and restart according to the normal startup procedure.

## Procedure 2

If feed is lost to the Penex Unit battery limits or if for some reason low feed flow (Lower than required to maintain 0.5 LHSV overall) is expected, then open the stabilizer bottoms recirculation line to the liquid feed driers. This action will prevent an emergency shutdown of the reactor circuit.

## H. LOSS OF MAKEUP GAS

When makeup gas flow is lost, there will be a drop in reactor pressure and an increase in reactor liquid content. This will result in an increase in reactor residence time which could result in more complete isomerization of feed and possibly cause a reactor temperature excursion. The loss of makeup gas also increases the risk of catalyst coking. If makeup gas flow is lost for a short time, the unit can be secured by reintroducing the gas.

If the loss of makeup gas is long term, the unit will have to be shut down since it will eventually not be possible to isomerize the feed without hydrogen present. Also it may not be possible to maintain circulation. Circulation cannot be maintained because there will be no pressuring medium for the stabilizer to move stabilizer bottoms. If there is a long-term loss of makeup gas, proceed as follows:

1. Stop the steam flow to the charge heater.
2. Stop the C<sub>2</sub>Cl<sub>4</sub> injection when the lead reactor temperature reaches 105°C (220°F).
3. Slowly depressurize the reactor circuit to 24.6 kg/cm<sup>2</sup> (350 psig) to keep the back pressure control valve open and feed flowing through the reactors.
4. Maintain feed flow as long as a level can be controlled in the bottom of the stabilizer. If the makeup gas is still available at a low pressure, and if the pressure is high enough to keep pressure on the stabilizer, open the pressuring line to the stabilizer. The stabilizer pressure can be reduced to achieve pressure control on the column and flow of bottoms.
5. Cool the reactor to 93°C (200°F) and remove feed. If circulation cannot be maintained, cool the reactor circuit as much as possible and remove the feed.
6. Restart the unit following the normal startup procedure.
7. If the reactor temperatures climb above 232°C (450°F) during this procedure, stop the feed, block in the reactor, and depressurize the reactor to the flare.

## I. HIGH REACTOR TEMPERATURE DIFFERENTIAL

A high reactor temperature differential could result from the presence of larger than normal amounts of benzene, olefins, or C<sub>7+</sub> material in the feed. Or a high reactor temperature differential could result from high catalyst severity, i.e. low throughput and too high of a temperature for the feedrate being maintained.

In order to avoid a reactor temperature excursion:

1. Avoid low reactor liquid feedrates. The reactors should never be operated below 0.5 LHSV overall (1 LHSV per reactor).
2. Avoid large quantities of benzene, olefins or C<sub>7</sub>+ in the feed. Limits on these materials in the feed depend on the unit design. Typical limits are:

Benzene — 5%  
Olefins — 2%  
C<sub>7</sub>+ — 5%

3. Avoid overheating the reactor charge.

During an emergency such as a power failure or instrument air failure, it will be difficult if not impossible to avoid 1. and 3. above. The emergency procedures are written with the possibility of a reactor temperature excursion in mind.

Following are the procedures for high reactor temperature differential. There are two different procedures depending on the cause of the temperature excursion. If the temperature excursion was caused by an increase in feedstock benzene, olefins or C<sub>7</sub>+, Procedure 1 is used. If the excursion is the result of cracking (Usually due to low throughput) then Procedure 2 is used.

### **Procedure 1**

If the lead reactor temperatures increase and the increase did not coincide with low reactor throughput, loss of makeup gas or an excessively high reactor inlet temperature, then the high temperatures are probably the result of an increase in the reactor feed benzene, olefins or C<sub>7</sub>+ content. Following is the procedure.

- a) Stop flow of steam to the charge heater. Reduce the reactor inlet temperatures to 105°C (220°F).

- b) Open the lead reactor purge valve and establish design flow to the lead reactor inlet and increase the makeup gas flow to maximum. This will accelerate the rate of reactor cooldown.
- c) Stop chloride injection when the lead reactor temperature drops to 105°C (220°F).
- d) Modify upstream fractionation conditions to remove the benzene and other heavy materials from the Penex feed. Consider use of the emergency recirculation line (stabilizer bottoms to liquid feed driers).
- e) Stabilize the unit and increase the reactor inlet temperatures as the temperature differential in the lead reactor comes down.
- f) If any of the reactor temperatures increase above 232°C (450°F), proceed to Procedure 2, step e.

## Procedure 2

If the reactor temperature differential increases and the increase coincides with a reduction in charge rate or an increase in reactor inlet temperature, the reactor severity is too high causing the temperature excursion. When any of the reactor bed temperatures get over 204°C (400°F), immediate action must be taken. Following is the procedure:

- a) Stop flow of steam to the charge heater to remove heat input.
- b) Open the reactor purge valve to the lead reactor inlet and increase the makeup gas flow to maximum. This will accelerate the rate of reactor cooldown and reduce the reactor residence time.

- c) Ensure that the feedrate to the reactor is equivalent to at least 0.5 LHSV across the unit or 1 LHSV per reactor. Use the emergency RECIRCULATION line (stabilizer bottoms to the driers) to increase charge if fresh feed is not available.
- d) Stop the chloride injection.
- e) Slowly depressurize the reactor circuit to the stabilizer. Depressurize the stabilizer to 3.5 kg/cm<sup>2</sup> (50 psig) above the caustic scrubber to allow the reactor circuit to be depressured to the lowest possible pressure without venting to the flare.
- f) When the reactors have been depressured, monitor the reactor temperatures. If the reactor temperatures are increasing and are above 232°C (450°F), do the following:
  - 1) Remove the liquid feed.
  - 2) Block in the lead reactor inlet and the makeup gas purge line.
  - 3) Block in the stabilizer feed line at the reactor pressure control valve.
  - 4) Depressurize the reactors to the flare from the outlet of the lag reactor. Depressure to a pressure of 3.5 kg/cm<sup>2</sup>g (50 psig).
  - 5) The reactors can be cooled by purging with dry oxygen-free nitrogen. The nitrogen can be routed through the gas driers, if required, to ensure dryness.
  - 6) Restart the unit following the normal startup procedure once the reactors have been cooled below 65°C (150°F).

- g) If, after step e), the reactor temperatures are decreasing below 232°C (450°F) then:
- 1) Restart the chloride injection.
  - 2) Cool down the reactors to the normal operating temperature.
  - 3) Raise the reactor pressure to a normal level.
  - 4) Decrease the makeup gas flow to a normal level.
  - 5) Establish normal operations

## J. CATALYST PROTECTION PROCEDURES

Following are some guidelines regarding protection of the Penex catalyst. These guidelines are being provided in addition to the information covered in the normal operating and emergency procedures sections of this manual.

### a. Liquid Feed Drier Water Breakthrough

If water breaks through a drier, as indicated by the moisture analyzer located at the lead drier outlet, immediate action must be taken. Generally the driers are taken off line and regenerated on a timed schedule rather than on water breakthrough. Water breakthrough is considered an unusual occurrence.

Water entry to the reactor circuit will cause irreversible catalyst damage. The moisture analyzer is the only warning available of water entry to the unit and it must be assumed to be reading correct if breakthrough occurs. Any debate regarding its accuracy should be made only after the feed or makeup gas has been removed from the reactor circuit.

If the feed or gas are cut out the appropriate loss of feed or loss of makeup gas emergency procedure must be followed.

After the unit has been secured the drier which experienced the breakthrough should be regenerated. The moisture analyzer should be checked and the regenerated drier effluent analyzed to verify the water removal capability. If the drier is not capable of removing water after a proper regeneration procedure the drier temperature and water content should be checked. The driers will not function properly if the feed contains a large quantity of free water. If no other problems can be found the drier must be opened and inspected for problems such as channeling. If no disturbance of the bed is noticed it is possible that the drier sieve was contaminated. If the drier sieve does not function properly it must be reloaded with fresh sieve.

#### **b. Loss of Perchloroethylene Injection**

If C<sub>2</sub>Cl<sub>4</sub> injection is lost, chloride will be stripped from the catalyst resulting in a loss of catalyst isomerization activity. The stripping action will increase at higher temperature and throughput. If chloride is lost for only a few hours (less than 6) the catalyst activity can be regained by resuming chloride injection. If the chloride stripping is continued for a long period of time (more than 6 hours) the ability for the catalyst to regain activity is reduced and irreversible catalyst damage results.

If, after losing chloride, it appears that chloride will not be available for more than six hours the unit should be shutdown. After four hours of operation preparations for shutdown should be made. If chloride is lost the reactor temperatures then feedrate should be reduced to minimize stripping. Operation at 50% of design feedrate is recommended.

When chloride is made available the chloride injection rate should be maintained at 300 wt ppm until the stabilizer off gas chloride content increases back to its normal level.

### c. Sulfur Poisoning

Sulfur poisoning of the Penex catalyst is indicated by loss of isomerization activity and in a severe case by loss of benzene saturation. If benzene saturation is lost the lead reactor temperature differential will shift further down the reactor or be reduced across the entire reactor. If sulfur poisoning occurs it is possible to detect H<sub>2</sub>S in the stabilizer off gas, although high HCl tends to interfere with H<sub>2</sub>S detector tubes. Caustic Na<sub>2</sub>S concentration increases could help confirm sulfur levels.

If sulfur poisoning occurs it is possible to regain activity by stripping the sulfur of the catalyst. Good recovery has been achieved commercially after the sulfur strip operation. However complete recovery should not be expected. Following is the sulfur stripping procedure:

1. Discontinue all drier regenerations at a point where the drier being regenerated has just completed its regeneration cycle.
2. Increase makeup gas flow to the maximum possible.
3. Reduce the reactor inlet temperatures to 121°C (250°F) at a rate of 28°C (50°F) per hour. Leave the charge rate constant since a sharp reduction could result in high reactor severity and a temperature excursion.
4. When the reactor temperatures reach 121°C (250°F), decrease the charge rate slowly to 50 percent of design flow in increments of 5% of scale every 15 minutes. Maintain the reactor temperatures at 121°C (250°F) and maintain at least the design flow of makeup gas through the reactors.
5. After the charge rate has been reduced, depressurize the reactor circuit to 21 kg/cm<sup>2</sup>g (300 psig). Depressurize at a rate which allows stabilizer pressure to remain in control.

6. After depressuring to 21 kg/cm<sup>2</sup>g (300 psig), discontinue feed to the unit. Feed should be cut out as quickly as possible to minimize low flow of liquid across the catalyst.
7. Maintain at least the design flow of makeup gas to the reactors. Hold the reactor temperatures at 121°C (250°F) and the pressure at 21 kg/cm<sup>2</sup>g (300 psig). Sweep the reactors for at least **four hours** at these conditions to remove hydrocarbon from the catalyst.

Note: Lower pressures may be used for sulfur stripping but it is generally not recommended to reduce the reactor pressure below the charge heater heating medium (steam or hot oil usually) pressure to avoid potential leakage from the charge heater into the reactors. If the regenerant superheater is used for sulfur stripping, the charge heater heat source should be blocked in and depressured. If the charge heater is required for sulfur stripping, it is recommended to leak test the charge heater tube bundle prior to performing the sulfur strip.

8. Raise the reactor inlet temperature to 260-315°C (500-600°F). Do not exceed the design limitation on the heater or any other equipment during this operation. **CHECK ALL VENDOR SPECIFICATION SHEETS.** The regeneration electric superheater is typically used for this service.
9. Maintain maximum hydrogen gas flow allowed by the superheater design duty. Minimize the amount of heavier hydrocarbon in the makeup gas if possible to reduce the chance of a temperature excursion during stripping.
10. Continue to inject chloride into the hydrogen purge gas to the reactor, at a rate equivalent to injecting 100 wt ppm chloride on a design reactor liquid charge basis.
11. Consistent with maintaining normal operating pressure, increase the makeup gas hydrogen to maximum, venting off the stabilizer through the scrubber.

12. Monitor the H<sub>2</sub>S content of the stabilizer offgas with time. The H<sub>2</sub>S will slowly increase to a maximum (perhaps 200-1000 mol ppm, depending on the amount of sulfur present on the catalyst and the severity of the stripping operation). Over a period of 12-24 hours, the H<sub>2</sub>S content will decrease to some fairly stable level.
13. At this point the stripping operation can be considered complete, for practical purposes.
14. Cool the catalyst bed to 65°C (150°F) and begin charging feed to the unit again according to the normal startup procedures.
15. After charging feed to the reactor, adjust the chloride injection rate for 200 wt ppm on feed.
16. Maintain 200 wt ppm chloride injection for 12 hours (minimum); then reestablish the normal rate of 150 wt ppm based on the reactor charge rate.

#### **d. Hydrotreater Operation**

If the hydrotreater reactor shuts down or if there is an upset in the hydrotreater which causes the reactor temperatures to drop below the level required to properly treat the feed there is a risk that catalyst poisons will not be removed and the feed must be removed from the Penex Unit.

The sulfur guard bed is not designed as a substitute for the hydrotreater. The guard bed is designed to operate with ppm sulfur in the feed. The adsorbent is non regenerable and the total loading of sulfur on the adsorbent before breakthrough is approximately 10% of the adsorbent weight. If the hydrotreater reactor is bypassed or not removing sulfur the guard bed will be quickly saturated. For example 300 ppm sulfur in the guard bed feed will kill the guard bed in about 24 hours.

The Penex Unit should be shutdown in as orderly a manner as possible, however the longer the contaminated feed passes over the catalyst the more likely permanent catalyst damage will occur. If the only contaminant is sulfur there is the possibility of recovery. Oxygenates, metals and nitrogen will permanently deactivate the catalyst.

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## A. Vessel Loading And Unloading

Procedures for the loading the sulfur guard bed, makeup gas driers, liquid feed driers, offgas scrubber and the Penex reactors are provided. Note that the initial loading of the reactors will take place in two stages. First, only the reactor support material is loaded. After unit dryout and acidizing are completed, the actual catalyst is loaded. Section VI: Commissioning of this manual should be followed to ensure the unit is ready for the initial loading of these vessels before continuing with any of these procedures.

### 1. Sulfur Guard Bed

When the guard bed vessel has been pressure tested, dried and cleaned it may be loaded.

Prior to and during the loading of the adsorbent, certain precautions should be taken to ensure that the adsorbent will perform optimally. The adsorbent is shipped in drums which should not be opened until just prior to loading. Exposure to excessive moisture can alter the chemical properties of the adsorbent and thus reduce its effectiveness. Therefore, the guard bed adsorbers must be kept free of water.

ADS-11 is normally sock-loaded into the adsorber. Dust masks and gloves must be worn to avoid irritation when handling the adsorbent. The adsorber vessels should be dry before ADS-11 is loaded.

- a. The support plate should be installed in the unloading nozzle and a coil of 6 mm ceramic rope should then be laid over it.
- b. Install the sleeve in the unloading nozzle and fill with 6 mm balls to within 100 mm of the top. Add a 100 mm layer of 3 mm diameter balls.

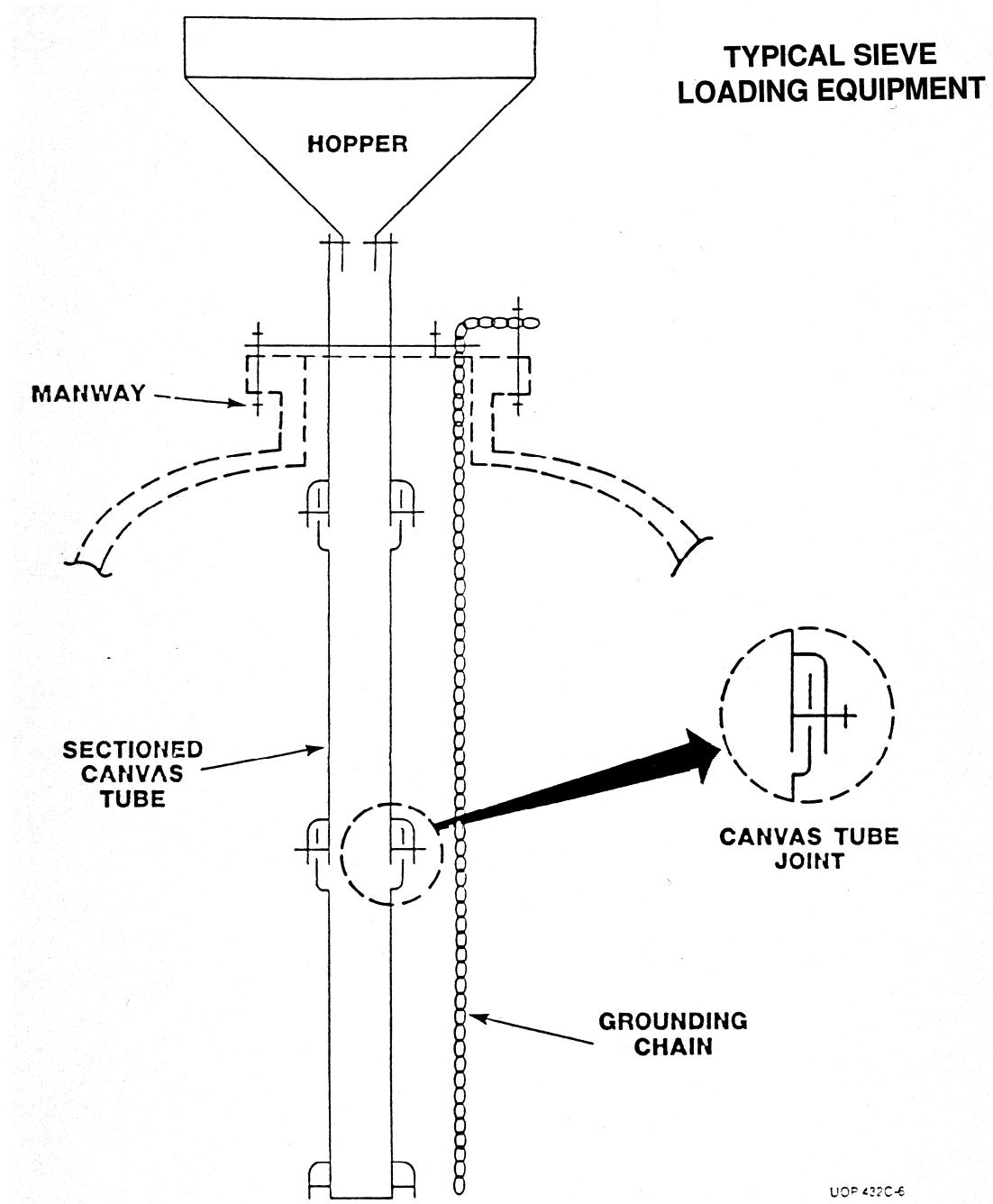
- c. Install the outlet basket over the outlet nozzle. Check to assure there is a good fit in order to avoid passage of adsorbent support material between the bottom of the basket and the outlet nozzle.
- d. For loading of the ceramic support and the adsorbent the upper manway should be used.
- e. With the bottom internals in place, load 19 mm (3/4") diameter ceramic balls up to a height 150 mm (6") above the top of the outlet basket. The top of this layer should be level.
- f. A 100 mm (4") layer of 6 mm (1/4") diameter ceramic balls is loaded on top of the 19 mm (3/4") balls; again taking care to avoid disturbing the layer below and making sure each layer is level.
- g. A 100 mm (4") layer of 3 mm (1/8") diameter ceramic balls is loaded on top of the 6 mm (1/4") balls; again taking care to avoid disturbing the layer below and making sure each layer is level.
- h. Connect a nitrogen hose to the bottom of the guard bed and start a small purge of nitrogen through the vessel. The nitrogen purge should be maintained throughout the loading to minimize adsorbent contact with air.
- i. For loading of the adsorbent, use a hopper with a sock attached. Pour the adsorbent in slowly to avoid washing away or disturbing the adsorbent and ceramic support already loaded. The sock should be kept moving in a figure eight to prevent the adsorbent forming a hill. The adsorbent bed should be kept as level as possible during loading so the density is uniform throughout the bed.
- j. Continue to load the adsorber with the adsorbent to a level that is prescribed on the loading diagram below the top tangent line of the vessel. The top of the bed should be leveled.

- k. Load a 100 mm (4") layer of 6 mm (1/4") ceramic balls on top of the adsorbent. Load a 100 mm (4") layer of 19 mm (3/4") balls on top of the 6 mm (1/4") balls.
- l. The vessel may be headed up after checking that the inlet distributor is properly installed. All rings and flanges should be thoroughly cleaned before assembly.

## **2. Drier Loading**

When the driers are hydrotested, dry and clean, they may be loaded. Install the slotted support cap over the bottom nozzle. One-quarter inch ceramic rope may be required as packing around the base of the support cap to prevent it from moving.

A specific type of support balls are lowered next into the driers. (UOP Project Specification 312 details the quality and quantity of support balls loaded in each reactor and drier.) The bottom of each drier is loaded per Specification 301. Ceramic support balls of 19 mm (3/4") diameter are loaded to the prescribed depth and leveled. Next, 6 mm (1/4") balls are loaded and leveled, and finally 3 mm (1/8") material is loaded and leveled. A rope and equipment will be similar to that used for loading typical catalyst, i.e., hopper and loading sock (Figure XIII-1).

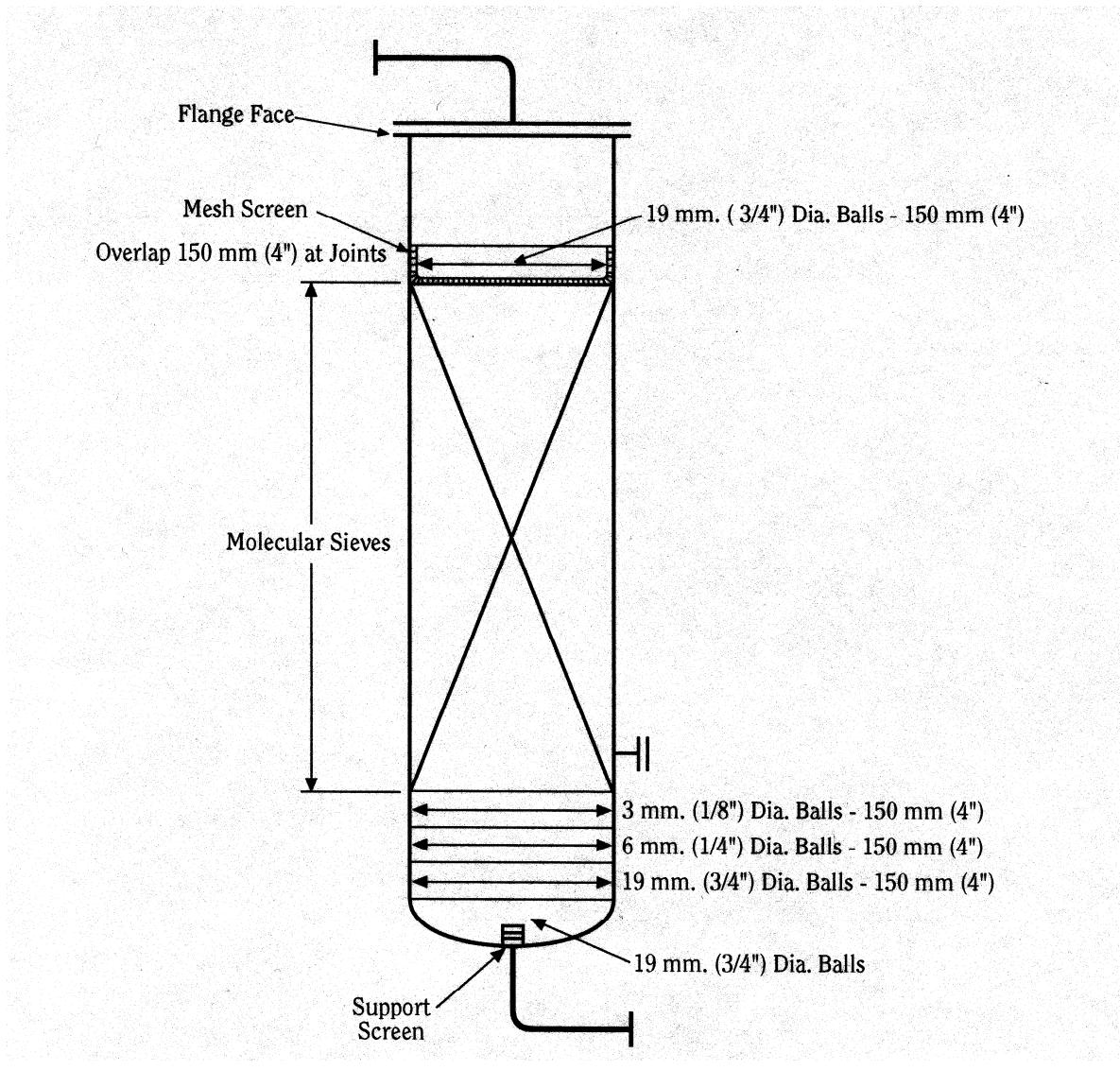
**Figure XIII- 1: Sieve Loading Equipment**

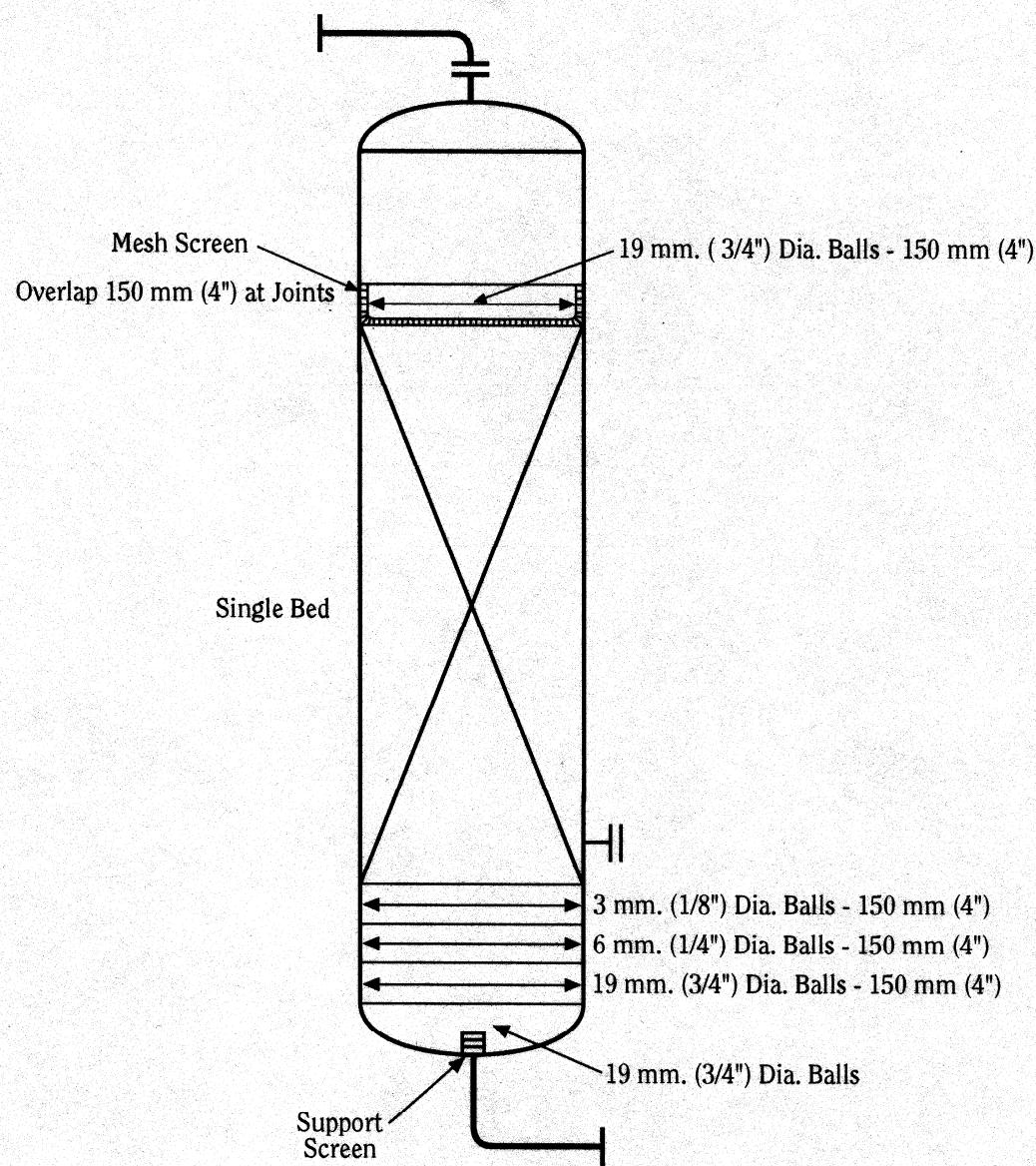
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**Static electricity may build up during the sieve loading. It will be necessary to lower a metal weight fastened to a wire or chain that has been grounded. This will discharge the buildup of static electricity. Shorten the chain and sock together as the sieve bed level rises. Level the sieve bed.**

When the sieves have been loaded, place the specified holddown material on top of the sieves.

Loading diagrams for both the makeup gas and liquid feed driers are provided in Figures XIII-2 and XIII-3 respectively.

**Figure XIII- 2: Makeup Gas Drier**

**Figure XIII- 3: Feed Drier**

### 3. Drier Unloading

Adsorbents or molecular sieves exposed to a gas or liquid stream can pick up various materials. Trace materials can be concentrated. Some may be toxic, flammable, or explosive, or, when exposed to air, may heat up or become poisonous. Grounding of equipment is recommended, however, static sparks might still occur, for example, when dumping molecular sieves from non-conducting containers or when a person removes outer garments in low-humidity conditions. It is very important that you install appropriate blind flanges and properly remove any potentially hazardous materials from the molecular sieves, vessel interiors, and connected piping. Do so before you open the vessel, piping or valve bodies to the atmosphere done by gas purging as discussed below.

The driers are typically unloaded through the manway on the side near the bottom of the vessels. A steel unloading chute is usually attached to the manway to direct the molecular sieve into unloading hoppers or drums. The molecular sieve may also be unloaded by vacuuming via the top manway. The holddown grating or screen should be removed from the top manway prior to unloading. The support balls located at the bottom of the drier usually do not require replacement or reloading unless there has been a problem with sieve containment or pressure drop.

The following guidelines are provided for drier unloading. Additional unloading details should be obtained from the supplier of the adsorbents in the driers.

- a. Prior to unloading the liquid feed driers it is recommended that a partial regeneration is conducted. This step removes benzene from the molecular sieve and helps hydrocarbon free the sieve by heating it prior to purging with nitrogen. The partial regeneration should include the normal regeneration steps, up to the hold step at 288°C (550°F), to displace and remove benzene. Once the sieve bed has been heated, the drier should be isolated and depressured. A nitrogen purge to flare should follow for removing the hydrocarbons from the sieve. Occasionally, pressurize and depressurize the vessel to ensure more complete purging. The makeup gas driers may be evacuated and purged to aid in hydrocarbon freeing the vessels.
- b. Continue to purge until the outlet nitrogen mixture is 50% below the lower explosive limit and free of toxic materials. Then, shut off the nitrogen purge and the flare line.
- c. Maintain a nitrogen blanket on the top of the vessel during unloading.

Always assume that some hazardous materials remain on the molecular sieve. Therefore, do not enter the vessel while the molecular sieve remains inside. Toxic fumes may be released during dumping. Always keep self-contained breathing apparatus and fire hoses available.

If at any time during unloading, materials on the molecular sieve start to burn or to react (give off large amounts of heat) cease dumping. Personnel should be cleared from the area. Properly trained personnel with self-contained breathing apparatus can then return to stop the reaction or put out the fire. To stop the reaction, or put out the fire, use water from fire hoses to flood the molecular sieve outside the vessel.

As with fresh molecular sieve, used molecular sieve should not be put into the mouth or allowed to touch the eyes or skin. Workers unloading the molecular sieve should wear gloves, eye protection, dust masks, safety shoes, and clothing that covers the body.

- d. Normally, there is a stainless steel screen on top of the molecular sieve bed. Inert balls lie on top of the screen. To make dumping easier, secure the screen to the top of the vessel. You can do this without entering the vessel and secure the screen using a harpoon-type tool.
- e. For unloading, open the dump port and allow the molecular sieve to flow out. Once the molecular sieve no longer flows out freely, remove the remaining portion using a rake, hoe, shovel or a vacuum truck. Never enter the vessel to remove the remaining molecular sieve.

When you discard the used molecular sieve, make sure that you discard it in an environmentally acceptable manner. Comply fully with Federal, state, and local regulations.

- f. Once all the molecular sieve have been removed, the atmosphere in the vessel should be prepared for safe entry. Remove the nitrogen purge line if used and attach an air mover so that air is expelled out of the bottom of the vessel below the bed support. The air will carry any remaining vapors out of the vessel and away from the workers. Such vapors may be released by molecular sieve trapped under the bed support. Leave the air mover on at all times. Never use a plant air supply to purge the vessel with air – a plant supply could become contaminated or be hooked up to another source by mistake.
- g. After safety personnel have determined that the atmosphere inside the vessel is safe to breathe, and is not over 10% of the lower explosive limit (LEL), a properly equipped and trained worker may enter the vessel to inspect the bed support. Before entry, the worker must be attached to a safety rope. Two properly trained and equipped co-workers standing outside the entry port should constantly observe the worker in the vessel. The co-workers should use the safety rope to prevent falls from the ladder used to enter or leave the vessel. Also, if disabled, the worker can be removed using the rope.

#### **4. Net Gas Scrubber**

This vessel is to be carefully loaded with carbon Raschig rings. Care is to be taken during loading since these rings are easily broken. Therefore, the tower is to be filled with water to break the fall of the rings, and once the rings are loaded, the hold-down grating is to be installed. Then the water is to be drained, and the loading manway closed. Do not use berl or ceramic rings as they are attacked in a caustic environment.

#### **5. Loading Reactor Support Material**

The loading of the reactors will take place in two distinct stages. The first is the installation of the catalyst support material before the unit is dried and the second is the actual catalyst loading after the unit has finally been dried. Only the first phase will be presented at this time.

##### — For Each Reactor —

- a. With the completion of the sand-blasting and oil coating, the reactors are ready for the installation of the catalyst support materials.
- b. Install the slotted metal cap over the bottom outlet.
- c. Install the thermocouple bundles. Verify that the thermocouple lengths were constructed as specified in the UOP Project Specification 640. (**Note:** Some units may have thermocouples installed on the reactor shell.)
- d. The loading of the support material will be per Project Specification 304.
- e. Verify that the catalyst support material is of the proper type. A rope and buckets may be used to lower the support material into the reactors.

- f. Load the 19 mm (3/4") support material in the reactors bottom head and level the bed.
- g. Load the 6 mm (1/4") support material above the 19 mm (3/4") support material and level the bed.
- h. Load the 3 mm (1/8") support material above the 6 mm (1/4") support material and level the bed.
- i. Install the inlet distributor and head up the vessels.

## 6. Catalyst Loading

The following outlines the general procedures to be used for loading the reactors. Detailed loading diagrams for each reactor appear in the Project Specifications. A mixed phase Penex reactor loading diagram is outlined in Figure XIII-4. The Penex catalyst in two phase flow is typically dense loaded. **UOP recommends the reactors be dense loaded using the UOP Inert Dense Loading Technique if there is a liquid and vapor phase present in the reactors.** This recommendation is made to ensure good flow distribution throughout the catalyst bed. If the unit was designed with a vapor and liquid distributor tray inside the reactor (in addition to the inlet distributor) the catalyst should be dense loaded. For details of the UOP Inert Dense Loading Device, the UOP Dense Loading Coordinator should be contacted at the following address:

UOP Dense Loading Coordinator  
UOP  
25 East Algonquin Road  
Des Plaines, IL 60017-5017  
USA

The catalyst loading procedure follows:

**a. General**

There are problems which are inherent to accomplishing reactor catalyst loadings and it is therefore beneficial that the following procedures and details be thoroughly understood by everyone who will be associated with the job prior to actual loading.

- 1) As the reactor circuit has been acidized to remove mill scale and has been dried especially well, care must be taken to ensure that no air or moisture enters the reactor circuit during the catalyst loading period.
- 2) The Penex Catalyst is shipped in sealed 55-US gallon drums that have a special protective lining (refer to Figure XIII-7). The catalyst is contained in a heavy plastic bag with a long neck. The neck is crimped in two places with wire and heat-sealed at the end. This bag is inside another heat-sealed plastic bag.
- 3) Before, during and after catalyst loading, the catalyst must be protected from moisture at all times. Any contact with water or air will result in permanent deactivation of the catalyst.
- 4) Rough handling of the catalyst drums should be avoided since the heat seals on the plastic catalyst bags could be broken. Care should be taken not to damage the empty drums because they will be used to return spent catalyst for platinum recovery.
- 5) The catalyst must be loaded into the reactors directly from the 55 gallon drums. No other temporary loading hoppers may be used due to the water sensitivity of the catalyst.

**b. Equipment and Materials Required**

Prior to the loading of the reactors with catalyst, the following will be required:

- 1) Fresh UOP Penex catalyst.
- 2) Catalyst loading assembly and UOP Dense Loading Device.
- 3) Loading sock.
- 4) Special unloading lids (two required).
- 5) Bailing wire.
- 6) Plastic sheeting.
- 7) Wide rubber bands – to fit a 6-inch diameter tube or surgical tubing.
- 8) Quick release drum lid retainer rings (two required).
- 9) Ample dry nitrogen (less than 5 ppm H<sub>2</sub>O).
- 10) Knife.
- 11) Tools to open catalyst drums.
- 12) Grounding wire.
- 13) Masking tape (2 to 3 inches in width).
- 14) Low range pressure gauge (0-10 inches H<sub>2</sub>O).
- 15) Dry hoses for nitrogen purging.
- 16) Dried ceramic balls for catalyst hold-down material.
- 17) Measuring tape to determine outages on reactor.
- 18) Two sets of air masks, harnesses, rope and other safety equipment for person entering the reactor.
- 19) Metal sling for hoisting catalyst drums.
- 20) New gaskets for flanges and manways which were opened.

- 21) Shovel or scoop for leveling the catalyst bed (handle should be at least 2.5 meters (8 ft)).
- 22) Scissors to cut the heat seal on the loading neck of the plastic catalyst bag.
- 23) A light, suitable for a hazardous atmosphere that will fit through pressure relief door opening.
- 24) GOOD WEATHER.

**c. Catalyst Loading Equipment Details**

**1) Catalyst Loading Assembly**

The attached figures represent the special loading assembly that is required to load the Isomerization catalyst. As the catalyst is sensitive to both air and moisture, there should be no deviation from what is specified in the drawings.

- i. To conserve nitrogen, a soft rubber gasket should be glued to the bottom side of the catalyst loading assembly. The pressure relief door should also fit tightly against the assembly.
- ii. The top edge of the six-inch loading adapter should have no sharp edges or corners to reduce the chance of tearing the loading neck of the plastic catalyst bag.
- iii. The location of the UOP Dense Loading Device is indicated in Figure XIII-6. The dimensions of the sock attachment from the loading assembly to the UOP Dense Loading Device vary from unit to unit as do details of the device itself. These details will be furnished by the UOP Dense Loading Coordinator.

## 2) Loading Sock

The catalyst will be transferred from the loading assembly to the dense loader using a canvas sock. The sock should be secured to the bottom of the loading assembly and extend of a length of 12 inches below the top of the dense loading hopper. The dense loading device will be mounted on the top manway of the liquid/vapor mixing tray. The loading sock will simply hang inside the dense loading hopper.

## 3) Drum Unloading Lid

The special drum lid which will be required for the loading of the Penex catalyst is shown in Figure XIII-7. For the ease of loading and to load in an efficient manner, there should be two of these lids available.

### d. Catalyst Loading Procedures

#### 1) Reactor Opening

- i. For the initial catalyst loading, shutdown the unit following the normal shutdown procedure.
- ii. Block in the reactor to be loaded, using the double block and bleed valves.
- iii. Depressurize the reactor to flare.
- iv. Connect the reactor ejector and evacuate the reactor to 25 inches of mercury. Break the vacuum with nitrogen to 0.35 kg/cm<sup>2</sup>g (5 psig), then repeat the evacuation and pressuring. Minimize the time at which the reactor is under a vacuum.

**NOTE:** The nitrogen used for breaking the vacuums and gas blanketing the reactor should contain less than 5 ppm water. If there is any doubt about the

water content of the nitrogen, it can be dried by passing it through one of the makeup hydrogen driers using temporary piping.

- v. The nitrogen for breaking the vacuums should be connected to the reactor inlet.
- vi. Start a small purge of nitrogen into the reactor and out the inlet PI. Unbolt and remove the reactor inlet elbow and top head. As the reactor is opened, tightly cover the open flanges with plastic. When the reactor inlet elbow is removed, wrap it and the inlet distributor in plastic and immediately install the catalyst loading assembly. The loading assembly should be installed on the top manway and the loading sock extended to just below the liquid/vapor distribution tray.
- vii. Connect the nitrogen hose to the loading assembly. Throughout the loading a separate nitrogen purge to the reactor should be maintained through the hard piped nitrogen connection. Ensure that a positive pressure of nitrogen is maintained on the reactor during the loading. 1-2 inches of water on the low range pressure gauge will suffice.
- viii. The dense loader is mounted on the V/L tray (refer to Figure XIII-6), the loading assembly should be attached to the top manway. The loading sock should fit inside the dense loader hopper. The nitrogen connection for the dense loader motor and the tachometer connection should be made before the loading assembly is installed on the top manway.
- ix. Ground the loading assembly and adaptor to the reactor and connect the loading sock grounding wire to the reactor.

**NOTE: AT NO TIME SHOULD A PERSON ENTER A REACTOR HAVING A NITROGEN PURGE ON IT WITHOUT FULL INSTRUCTION AND EXPERIENCE WITH A FRESH AIR MASK, SAFETY HARNESS AND LIFE LINE.**

## 2) Catalyst Loading

### i. At ground level:

Remove the drum lid and open the outer (heavy) plastic bag.

Install the special loading lid with the 150 mm (6") hole using a "quick release" lid retaining ring.

Pull the loading neck of the inner plastic catalyst bag through the hole. DO NOT remove the wire clips or break the heat seals on the loading neck.

Position the drum for hoisting to the top of the reactor with the drum horizontal and the six-inch hole in the lid orientated downward.

**NOTE: NO MORE THAN TWO DRUMS ARE TO BE OPEN AT ANY TIME AT GROUND LEVEL, one drum ready to be hoisted and one drum being prepared.**

### ii. At the reactor:

Hoist the drum to the reactor and position the drum for loading.

Cut the heat seal on the loading neck close to the seal and slip the neck over the adaptor. Hold or secure the neck with a web band or surgical tubing.

Remove the wire clamps on the loading neck and start to load the catalyst. Securely hold the neck so that the heat seals on the sides of the neck do not break during the loading.

When most of the catalyst has been loaded, start to gently pull the plastic bag and remaining catalyst through the hole in the lid until the bag is removed from the drum and all of the catalyst has been loaded.

It is not necessary to remove the lid as the inner bag can be pulled through the hole as the bag is emptied.

Adjust the nitrogen flow to the dense loader motor to achieve the correct RPM's. When most of the catalyst has been loaded, start to gently pull the plastic bag and remaining catalyst through the hole in the lid until the bag is removed from the drum and all of the catalyst has been loaded. It is not necessary to remove the lid as the inner bag can be pulled through the hole as the bag is emptied.

It will be necessary to stop the loading 3 or 4 times to check the surface of the catalyst bed to ensure that the catalyst is being loaded properly. To do this, the loading assembly must be removed from the reactor manway to allow an inert entry specialist to enter the reactor to make an observation. Based on the condition of the surface of the bed, the dense loading RPM's will be adjusted.

Return the drum, plastic bags and loading lid to the ground level. Keep the adaptor on the loading assembly covered when loading is not in progress to conserve on nitrogen.

iii. Finish of loading:

After the last drum of catalyst has been loaded, per the reactor loading diagram, hoist the drum of hold-down balls to the reactor. An inert entry specialist must remove the dense loader and level the catalyst bed with a scoop or shovel. After leveling the bed, check the outage to the catalyst.

Using buckets, load the hold-down balls into the reactor. Level each layer with a scoop or shovel.

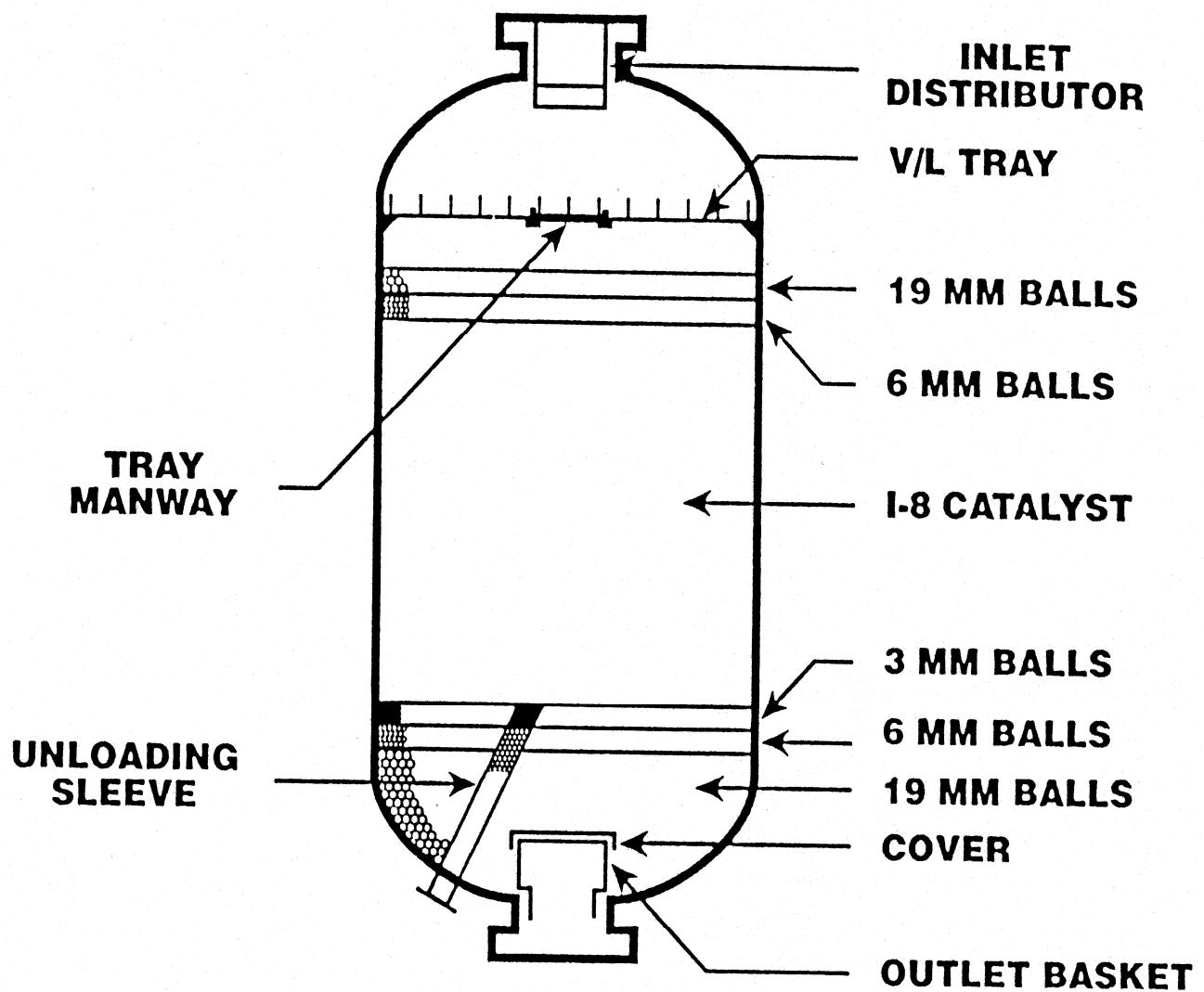
A nitrogen purge into the reactor upper head is maintained throughout these final loading steps.

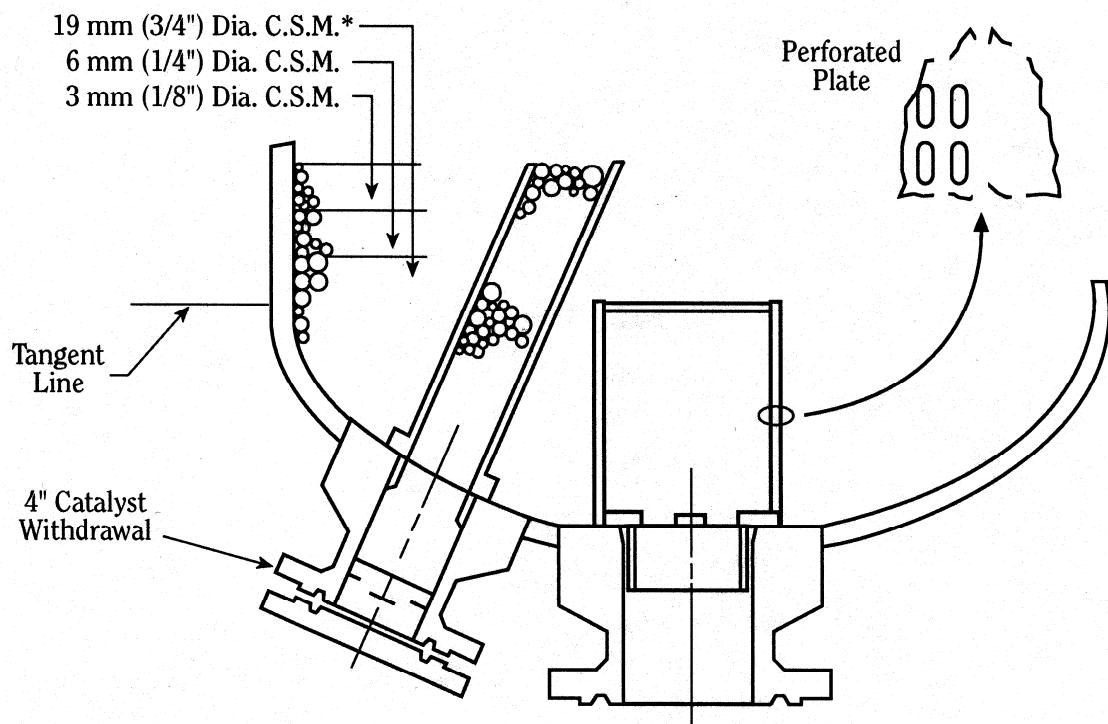
After the last layer of ceramics is leveled and the vapor/liquid tray manway is reinstalled, then cover the manway with plastic once the inert entry specialist leaves the reactor.

### **3) Reactor Closing**

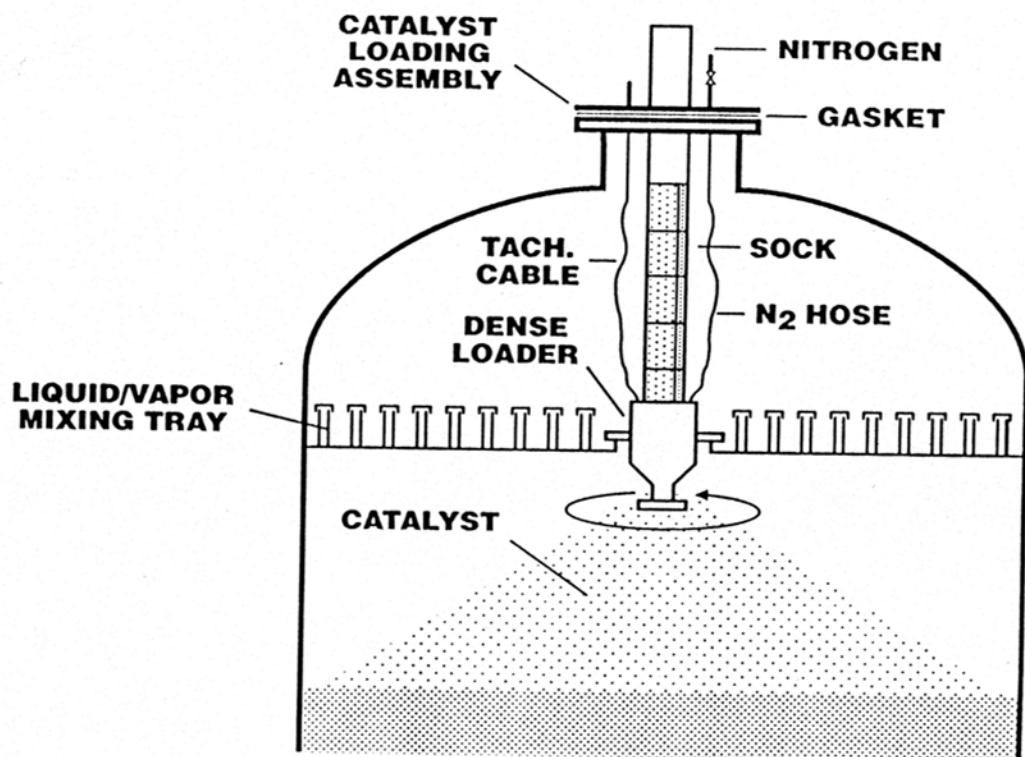
- i. As quickly as possible after the loading is completed, install the inlet distributor, ceramic fiber rope, reactor head and inlet elbow.
- ii. Continue the nitrogen purge to the top of the reactor and purge out the bottom to flare. Check that the purge gas at the reactor outlet is below refinery standards for admitted hydrocarbons and is free of oxygen. Pressure the reactor to 0.35 kg/cm<sup>2</sup>g (5 psig). Disconnect; blind plug all nitrogen purge lines.

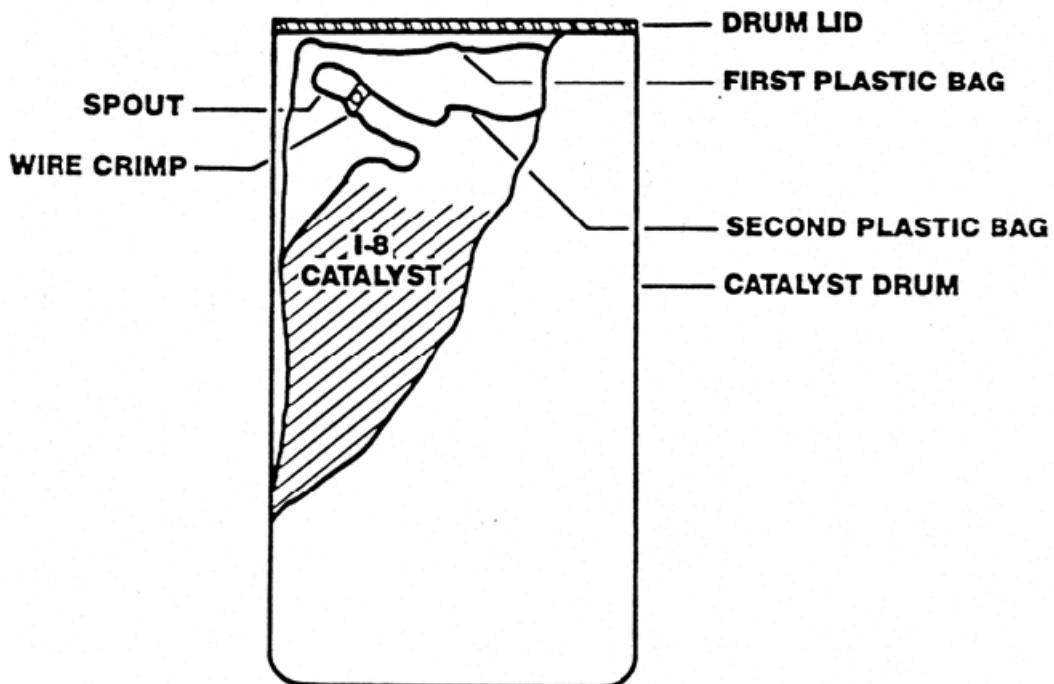
NOTE: The opening, loading and closing of the reactors should be a continuous operation with no breaks. During the opening, loading and closing of the reactors, a dry nitrogen blanket MUST be maintained at all times.

**Figure XIII- 4: Mixed Phase Penex Reactor**

**Figure XIII- 5: Reactor Bottom Head Details**

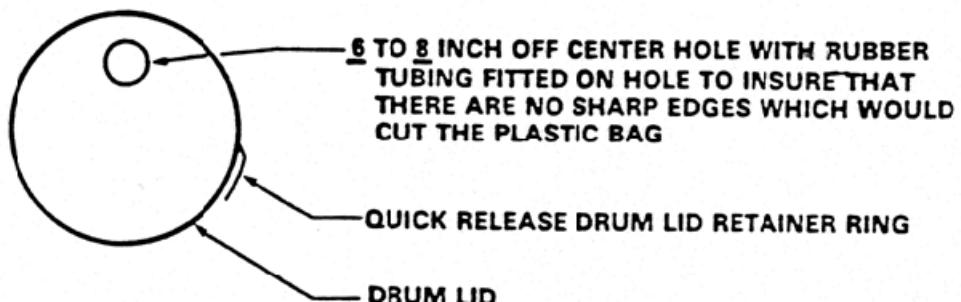
\* C.S.M. = Catalyst Support Material

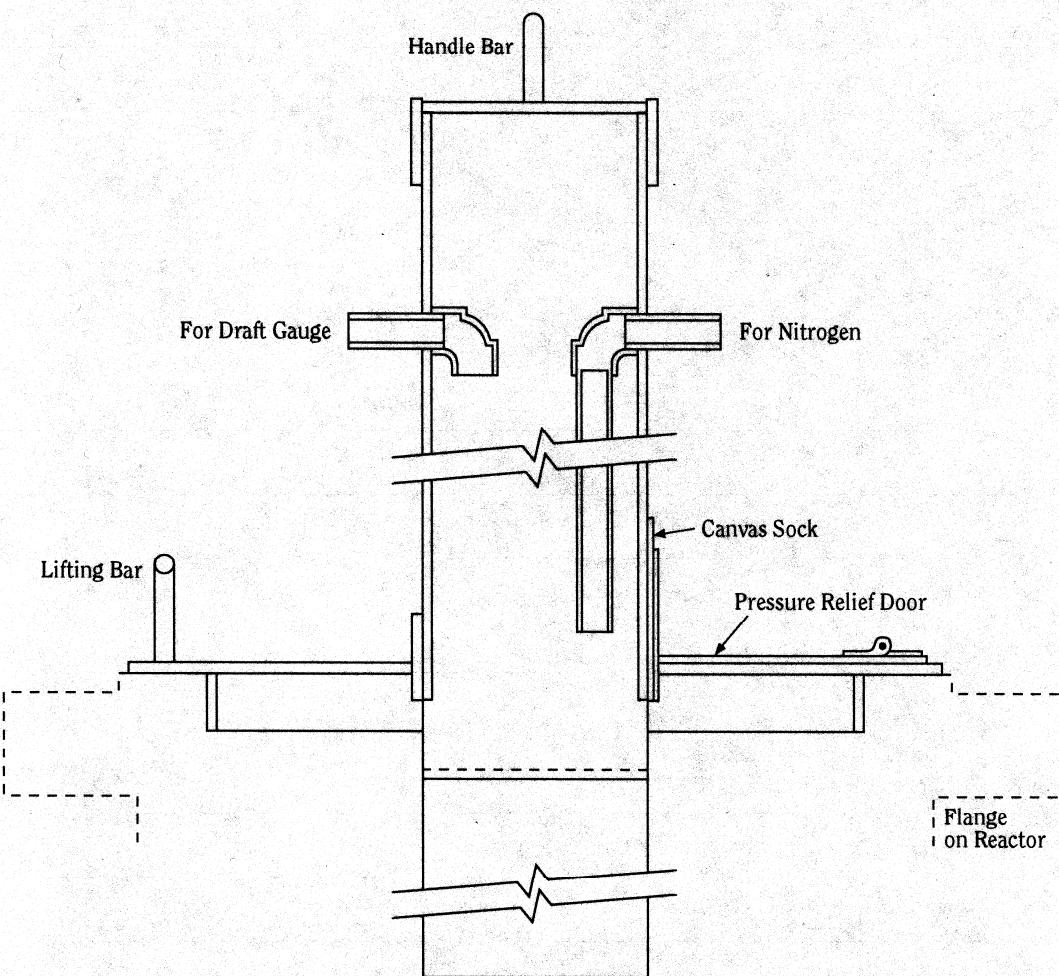
**Figure XIII- 6: Inert Catalyst Loading**

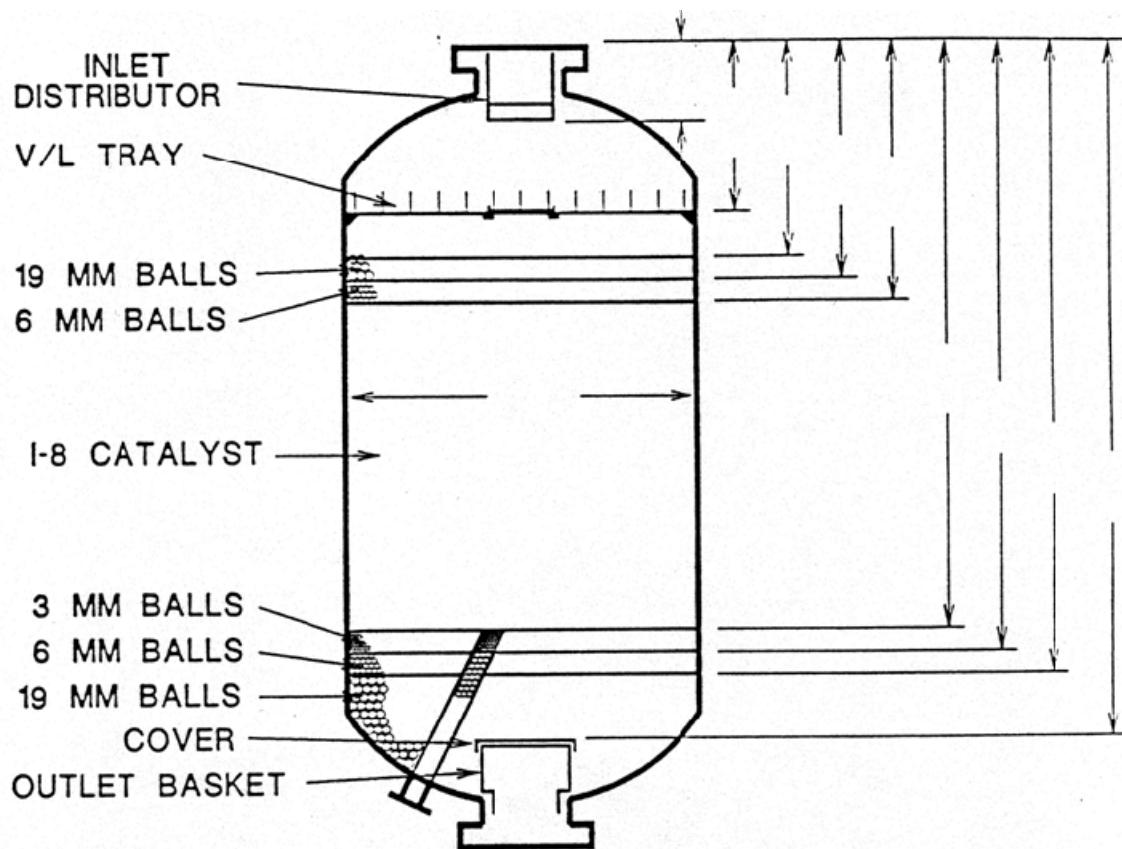
**Figure XIII- 7: Catalyst Drum Detail**

## **CATALYST LOADING EQUIPMENT**

### **SPECIAL UNLOADING LID**



**Figure XIII- 8: Catalyst Handling Equipment**

**Figure XIII- 9: Penex Reactor Loading Diagram**

CATALYST WEIGHT: \_\_\_\_\_

CATALYST VOLUME: \_\_\_\_\_

LOADED BED DENSITY: \_\_\_\_\_

## B. Catalyst Unloading and Handling

### Preparation for Unloading

When it is determined that the catalyst in the lead reactor has been completely deactivated, the catalyst may be changed out while maintaining the lag reactor in service. Single reactor operation is established by starting flow to the inlet of the "lag" reactor and blocking in flow at the "lead" reactor inlet. The hydrocarbons are purged from the deactivated reactor by establishing H<sub>2</sub> purge gas flow through the reactor purging out to the reactor effluent section. The reactor is then evacuated and purged with nitrogen. The "Partial Unit Shutdown Procedure" in this manual should be followed to shutdown the lead reactor for catalyst changeout.

### Catalyst Unloading and Handling

The same precautions used to keep air away from fresh catalyst must be used when unloading spent catalyst from a reactor. Spent catalyst contains a large amount of chloride, and any moisture that contacts the catalyst will make the material very corrosive. At all times during the opening of the reactor and unloading of the catalyst, a dry nitrogen gas blanket of 1.0 to 1.5 inches of water should be maintained on the reactor. With the reactor to be replaced, taken off line and prepared as previously outlined the following procedure can be followed:

1. Remove the blind flange on the catalyst withdrawal nozzle and attach the catalyst unloading spout.
2. The spent catalyst must be loaded into the original catalyst drums and plastic liners to protect against corrosion during shipment. During the catalyst run, the drums should be stored in a dry location and protected from damage. Detailed unloading steps are outlined below:
  - a. Place an empty catalyst drum on a scale, then put the inner plastic catalyst bag with the unloading neck inside the outer heavy plastic bag. N<sub>2</sub> purge the inner bag.

- b. Slip the plastic unloading neck over the catalyst unloading spout, and then remove the catalyst support plate from the withdrawal nozzle.
  - c. Load approximately 113 kg (250 lbs) of catalyst into each drum. A minor modification to the catalyst unloading spout will allow the catalyst flow to be regulated and stopped easily (refer to Figure XIII-10).
  - d. When a drum is full, wire clamp the plastic unloading neck in two places, and then clamp the heavy catalyst bag around the inner bag. Close the drum tightly using the original lids and retaining rings.
3. There is no need to screen the catalyst prior to returning it for platinum recovery, since it will be screened prior to processing. However, the ceramic hold-down material will result in increased shipping costs if the catalyst is not screened. The catalyst unloading spout could be modified to insert specially fabricated or purchased screening equipment. The hold-down material that is collected should then be manually screened a second time and any catalyst or fines that are collected should be added to one of the drums.
4. During the unloading of the catalyst, the top manway of the reactor can be opened in preparation for the loading of fresh catalyst. As the manway is opened, tightly cover the open flanges with plastic. The manway and distributor should be wrapped in plastic to protect it from moisture. The reactor manway should be tightly covered with plastic or the catalyst loading assembly installed to conserve nitrogen during the unloading.
5. A small amount of spent catalyst will be left in the bottom of the reactor, because the support material is level and is not sloped towards the withdrawal nozzle. This catalyst can be removed by using a very long handled, flat, shovel to “sweep” the catalyst towards the withdrawal spout.
6. Once all spent catalyst has been removed, the catalyst support plate should be installed, along with a coiled layer of 12 mm (1/2") diameter ceramic fiber rope on top of the plate, in the withdrawal nozzle. The unloading spout should be removed. Replace the gasket on the withdrawal nozzle flange and

close the withdrawal nozzle. The withdrawal sleeve can be filled with the appropriate sized catalyst support material from the top of the reactor by using a long piece of 1-1/2 inch pipe or plastic tubing and a funnel to channel the material into the sleeve.

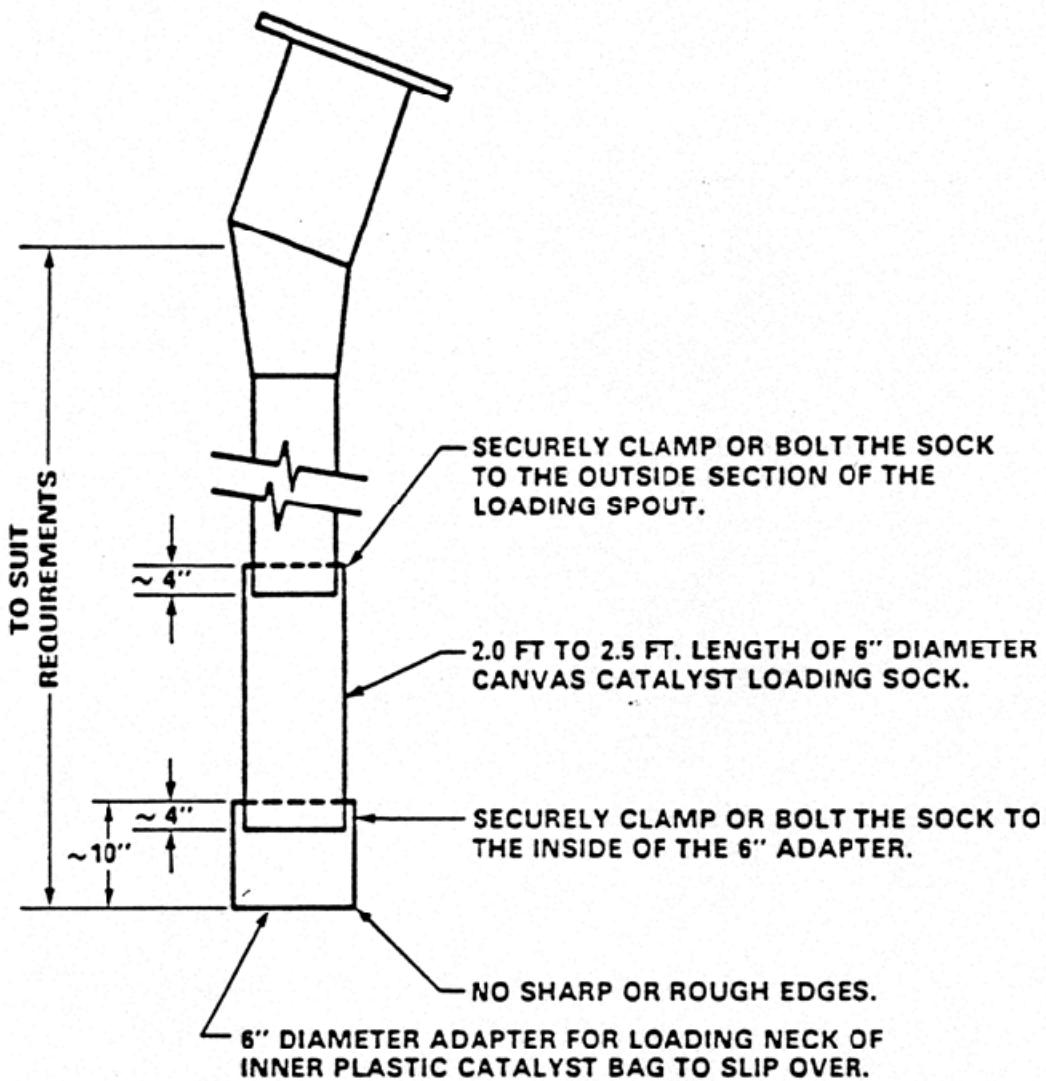
7. Fresh catalyst can then be loaded using the procedures previously outlined in this manual.

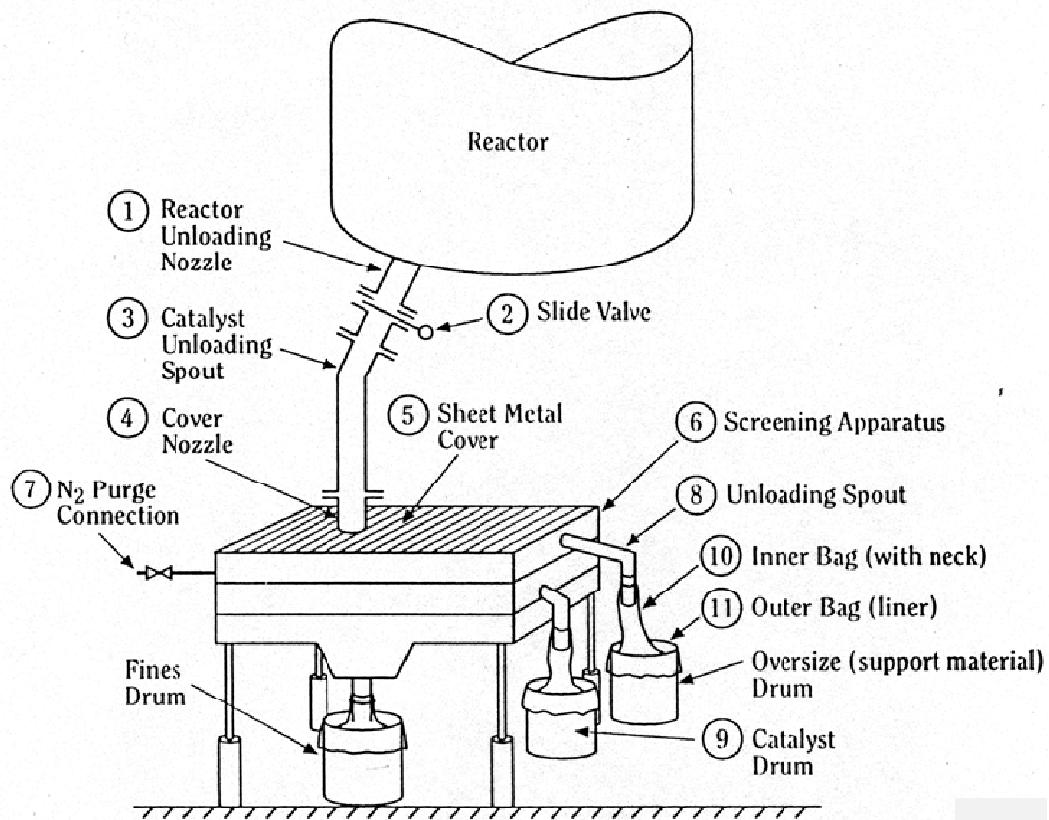
NOTE: The above procedure is based on the unit being shut down for a catalyst change in one reactor only with the unit being kept in operation with the second reactor set or being kept under a positive hydrogen pressure. If the unit has been completely shut down and equipment in the reactor section exposed to air and moisture, the reactor circuit must be dried (including HCl addition) before the unit is placed back on stream. If the reactor was opened to the air during the unloading, it must be included in the drying circuit before fresh catalyst is loaded.

8. Using the above procedure, it is not necessary for a man to enter the reactor to finish the unloading. If for any reason it becomes necessary for a person to enter the reactor, only persons trained for inert entry taking suitable safety precautions may enter. Safety precautions include use of a fresh air mask, safety harness, and life line for a person to enter a nitrogen atmosphere.
9. Catalyst spillage should be minimized using the above procedure and the specified unloading equipment. However, the concrete pad at the base of the reactors should be cleaned prior to the unloading operation so that any spilled catalyst can be swept up and placed in one of the drums.
10. The weight of catalyst unloaded should be recorded as a check on possible loss during shipment. When the catalyst is returned for platinum recovery, it is screened to remove oversized particles and fines (particles smaller than 14 mesh). The platinum content of the catalyst and the fines are determined separately. As a general rule, fines will contain approximately 20% catalyst.

11. The difference between the catalyst loaded and unloaded should be noted for bookkeeping charges for catalyst losses.

**Figure XIII- 10: Catalyst Unloading Spout for Spent Catalyst**



**Figure XIII- 11: Reactor Inert Unloading**

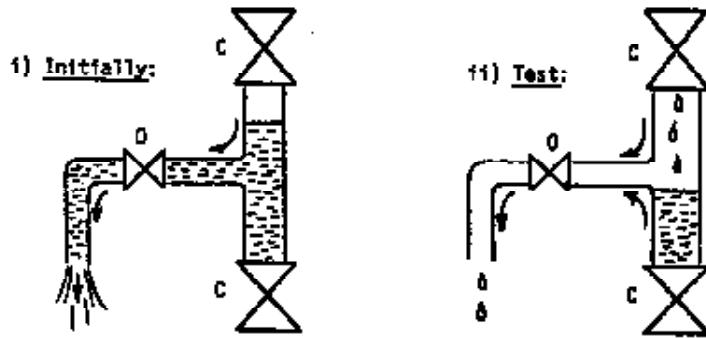
## C. Drier Manifold Valve Leak Testing Procedure

Testing of valves on both liquid feed and makeup gas driers should be carried out at least once per month, with the driers lined up in A → B series and B → A series.

The following steps should be carried out:

### 1. Liquid Feed Drier

1. Wait until the driers are in either A → B or B → A line up.
2. Provide a water hose to wash away liquid hydrocarbons to sewer.
3. Ensure that lines on which valves are to be checked are not in use, and that both valves of the double block are in the fully closed position.
4. Slowly open the bleeder valve and allow any liquid to drain to the sewer. Initially there will be a good flow, as the liquid which has accumulated in the space, flows out. (Refer to figures below.) After a short time, the flow should decrease or stop completely. It is the leak after this time that should be measured.



5. Try to estimate the leak rate in cc/minute using a graduate or small bottle of known volume. Note the rate, along with any other observations, on the Leak Survey Report Sheets.

6. Once the leak has been estimated, close of the bleeder valve (except the cross-over bleeder valves, X<sub>1</sub> and X<sub>2</sub>, which must be left open when the cross-over is not in use).
7. Repeat Steps 3 through 6 on as many of the lines as possible with the existing drier line up.
8. Wait until the next time that the drier line up order is reversed and repeat Steps 1 through 6.

## **2. Makeup Gas Drier**

1. Wait until the driers are in either A → B or B → A line up.
2. Provide a water hose to wash away liquid hydrocarbons to sewer.
3. Ensure that lines on which valves are to be checked are not in use, and that both balls valves of the double block are in the fully closed position.
4. Slowly crack open the bleeder valve and allow the section between the valves to depressurize, and any liquid hydrocarbons to drain.
5. If this section cannot be depressured safely, do not attempt to open the bleeder valve fully. Note this on the Leak Survey Report Sheet.
6. Open bleeder valve and try to estimate the size of any leak (e.g., "none", "very small", "small", "moderate" and "large") according to the sound made by the escaping gas. Note this, and any other observations, on the Leak Survey Report Sheets.

7. Once the leak has been estimated, close off the bleeder valve (except the cross-over bleeder valves, which must be left open when the cross-over is not in use).
8. Repeat Steps 3 through 7 on as many of the lines as possible with the existing drier line-up.
9. Wait until the next time that the line-up is reversed and repeat Steps 1 through 8.

#### D. Sulfur Stripping

Sulfur poisoning of the Penex catalyst will cause a decrease in the activity of the catalyst, both in isomerization activity and benzene saturation. Often the first symptom of sulfur poisoning is that the Lead Reactor benzene saturation temperature differential will shift further down the bed. In severe cases, there can be benzene breakthrough from the Lead Reactor. If sulfur poisoning occurs, it is possible to detect H<sub>2</sub>S in the stabilizer off gas, **although high levels of HCl can interfere with the detection of H<sub>2</sub>S with the use of detector tubes**. The presence of Na<sub>2</sub>S and NaSH in the circulating caustic at the Net Gas Scrubber can assist in confirming sulfur levels (UOP Method 209).

If sulfur poisoning occurs, it is possible to regain activity by stripping the sulfur off of the catalyst. Once the source of the sulfur has been found and eliminated, increasing reactor temperatures during normal operation is often enough to drive the sulfur off the catalyst. In more severe cases of sulfur poisoning, an offline hot hydrogen sulfur strip is necessary to remove the sulfur. Good recovery of catalyst activity has been achieved commercially after the sulfur strip operation. However complete recovery should not be expected.

**Note: It is recommended to contact UOP for advice before performing a sulfur strip procedure**

## 1. Online Sulfur Stripping Procedure

### **Following is the ONLINE sulfur stripping procedure:**

During mild sulfur upsets, the following online procedure might be conducted before deciding to conduct the offline hot hydrogen sulfur stripping procedure. This will help maintain the unit online. The product may initially be off spec for octane and possibly benzene but should improve over time.

**NOTE: The caustic in the Net Gas Scrubber may be consumed more rapidly than normal as both H<sub>2</sub>S and HCl are being neutralized. Pay close attention to the caustic strength. In addition to the normal caustic strength monitoring for % NaOH, the caustic strength should be checked frequently to avoid H<sub>2</sub>S or HCl breakthrough. The caustic “percent” spent as well as “percent” NaOH (UOP Method 209) should be reported due to the presence of weak acids and bases while scrubbing H<sub>2</sub>S and HCl.**

1. Identify the cause of sulfur ingress and correct the problem. Ensure hydrocarbon liquid feed to the Reactors contains < 0.1 wt-ppm sulfur and the makeup gas contains less than 1 mole-ppm of H<sub>2</sub>S.
2. Maintain the makeup gas flow at the design flowrate.
3. Increase the Lead and Lag Reactor inlet temperatures increments of 10°C (18°F). Allow catalyst bed temperatures to stabilize before increasing reactor inlet temperatures. Do not exceed 204°C (400°F) in any of the catalyst bed temperatures.
4. Monitor H<sub>2</sub>S content in the Stabilizer offgas every 2 hours.
5. Continue to operate at these conditions until the exotherms are close to what they were before the sulfur upset. This may from a few days to a few weeks depending on the severity of the sulfur upset.
6. **Continuously monitor the catalyst bed temperatures for any signs of temperature excursion and adjust the reactor inlet temperatures as**

**needed. Operators should review Emergency Procedures in the event of a Reactor Temperature Excursion during the online sulfur strip.**

7. Once the online sulfur strip operation is considered complete as evidenced by stable levels of H<sub>2</sub>S in the Stabilizer offgas, the reactor inlet temperatures can be returned to previous values.

## **2. Offline Sulfur Stripping Procedure**

For more severe cases of sulfur upset, the **OFFLINE Hot Hydrogen Sulfur Stripping** procedure may be performed according to the guidelines below. This procedure generally takes 1-2 days to complete.

Typically, only one reactor will be stripped at a time. Depending on the severity of the sulfur upset, a decision may be made to strip only the Lead reactor with the Lag Reactor bypassed or it may be decided to strip the Lag Reactor in sequence after the Lead Reactor strip is complete. The concern is that any sulfur removed off the hotter Lead Reactor may then lay down on the colder Lag Reactor.

It is recommended to contact UOP for advice before performing a sulfur strip procedure.

**NOTE: The caustic in the Net Gas Scrubber may be consumed more rapidly than normal as both H<sub>2</sub>S and HCl are being neutralized. Pay close attention to the caustic strength. In addition to the normal caustic strength monitoring for % NaOH, the caustic strength should be checked frequently to avoid H<sub>2</sub>S or HCl breakthrough. The caustic “percent” spent as well as “percent” NaOH (UOP Method 209) should be reported due to the presence of weak acids and bases while scrubbing H<sub>2</sub>S and HCl.**

**NOTE:** Drier regenerations will not be possible during the offline sulfur stripping process. Therefore, care should be taken while planning for sulfur stripping.

1. Discontinue all drier regenerations at a point where the drier being regenerated has just completed its regeneration cycle.

2. Increase the makeup gas flow to maximum design flowrate.
3. Reduce Reactor inlet temperatures to 121°C (250°F) at a rate of no more than 25°C (45°F) per hour. While reducing temperatures, maintain a constant reactor feedrate; a sharp reduction in feedrate could result in high reactor severity leading to a temperature excursion.
4. When the Reactor outlet temperatures reach 121°C (250°F), decrease the feedrate slowly to the minimum throughput, nominally 50% of design rate. The charge rate should be reduced in increments of no more than 5% of scale every 15 minutes. Monitor the catalyst bed temperatures, particularly the bottom and outlet temperatures. With any sign of increase in the bottom or outlet reactor temperatures, the reactor feed flowrate should not be decreased any further until temperatures are steady.

**NOTE: Sharp reduction in feed flow rate can result in high reactor severity and temperature excursion.**

5. After the charge rate has been reduced, slowly reduce Penex Reactor pressure to 28.0 kg/cm<sup>2</sup> (400 psig) or 3.5 kg/cm<sup>2</sup> (50 psig) below normal operating design pressure on the Reactor Back Pressure Controller. The reduction in pressure should be performed at a rate that will not upset the Stabilizer and Net Gas Scrubber operations. During the reduction in pressure, the Charge Heater steam condensate flow should be adjusted, as necessary, to maintain reactor inlet temperatures near 121°C (250°F).
6. Maintain at least the design makeup gas flow to the Penex Reactors to remove hydrocarbon from the catalyst beds. Maintain the Reactor temperatures at 121°C (250°F) and the pressure at 28.0 kg/cm<sup>2</sup> (400 psig) on the Reactor Back Pressure Controller.
7. When all the Reactor temperatures are stable at 121°C (250°F), remove the feed from the Reactors all at once and route it to the Stabilizer via the startup bypass line.

8. If desired, place the unit under isomerate product recycle operation mode with no feed intake or product make. The isomerate product can be routed back to the Feed Driers via the emergency circulation line during this time.
9. Increase makeup gas flow to the design rate while still maintaining adequate pressure control on the Stabilizer and Net Gas Scrubber. Sweep the reactors for **at least four hours** at these conditions to remove hydrocarbon from the catalyst beds. For more effective sweeping, the Penex Reactor pressure could be reduced further to ~21 kg/cm<sup>2</sup> (300 psig). **Complete purging is critical to minimize the chances a reactor temperature excursion from occurring while conducting Hot H<sub>2</sub> Sulfur Strip.** Every effort should be made to ensure that reactors are adequately purged free of hydrocarbon.

**NOTE: Lower pressures may be used for sulfur stripping but it is not recommended to reduce the reactor pressure below the Charge Heater steam pressure. This is done to avoid potential leakage from the Charge Heater into the process.**

10. Verify that the block valves of the sulfur stripping lines are closed at the Reactor inlet and at the inlet and outlet of the Regenerator Superheater.
11. Block in the valve from the Regenerator Vaporizer to the Regenerator Superheater. Block in the valve from the Regenerator Superheater to the Makeup Gas and Feed Driers.
12. Purge the Regenerator Superheater piping to flare with nitrogen connected to the 1" Dry Nitrogen Purge connection near the inlet to the Superheater. This purge removes regenerator in the piping prior to routing hot H<sub>2</sub> to the Penex Reactor that is to be stripped.

**NOTE: Adequate purging is essential to ensure that liquid hydrocarbon isn't carried to the Reactors that could condense in the Reactors and later lead to a possible temperature excursion.**

13. Swing the spectacle blinds at the Regenerator Superheater inlet and outlet lines, marked "BLANKOFF DURING SULFUR STRIPPING" on the UOP

P&ID, to the closed position. Maintain slight dry N<sub>2</sub> purge during the blind swinging.

14. Turn the two spectacle blinds on the sulfur stripping lines, "MARKED BLANKOFF DURING NORMAL OPERATION" on the UOP P&ID, to the open position in presence of slight dry N<sub>2</sub> purge. These lines should be under dry N<sub>2</sub> or H<sub>2</sub> atmosphere after the completion of purging during acidization. Nevertheless, when changing blinds, check that there is no water in the pipes before the block valves. Also drain all low points in sulfur stripping lines before proceeding to the next step.
15. Gradually open the valves on the sulfur stripping lines at the Reactor inlet and at the Regenerator Superheater. Pressure up the lines to the same pressure as the reactor pressure. Check for leaks. **Proceed further only after the leak test has passed.**
16. Turn the Regenerator Superheater Shutdown and Reactor Inlet Shutdown to BYPASS positions. These bypass switches allow the Regenerator Superheater to be operated and prevents closure of the makeup gas shutdown valve and steam to the Charge Heater shutdown valve during Sulfur Stripping, respectively.
17. Close the Reactor inlet isolation valve via the Reactor Inlet Emergency Shutdown Switch to force hydrogen flow through the sulfur stripping lines to the Regenerator Superheater and back to the Penex Reactors.
18. Open the Single Reactor operation valve. Close the block valve closest to the inlet and outlet of the Lag Reactor, isolating it from the process. This action lines up the Lead Reactor outlet to the Stabilizer. At this stage, makeup gas is flowing in the following direction: CCFE → HCFE → Charge Heater → Regenerator Superheater → Lead Reactor → HCFE → CCFE → Stabilizer → Net Gas Scrubber
19. Continue to inject chloride into the makeup gas to the Reactor, at a rate equivalent to injecting 100 wt-ppm chloride on a design reactor liquid charge basis.

**NOTE:** Before proceeding further, the following activities should be completed:

- Ensure that the makeup gas is as per the design composition. The presence of high molecular weight components in the makeup gas (excessive C5+) can lead to a temperature excursion during the hot hydrogen strip.
  - Confirm that the existing makeup gas flow orifice plates are adequate to handle the sulfur stripping makeup gas rate. It may be necessary to replace the makeup gas flow orifice plate and re-range the flowmeter to handle the higher gas flowrate.
  - Confirm the Makeup Gas Driers can handle the Sulfur Stripping gas rate. It may be necessary to place the Makeup Gas Driers in parallel flow mode to prevent lifting and fluidizing the drier beds.
  - Regenerator Low Flow Shutdown switch should be in BYPASS position.
  - Reactor Inlet Isolation Valve Shutdown switch should be in BYPASS position.
20. After replacing the makeup gas flow orifice and re-ranging the flowmeter, the Methanator Reactor, if present, can be bypassed and shutdown at this time. The Methanator Reactor is generally not sized to handle the Sulfur Stripping gas rate.
21. Slowly establish maximum possible flow rate of makeup gas flow. Ensure stable operations on the Stabilizer and Net Gas Scrubber.
22. Start heating the makeup gas using the Charge Heater at a rate of no more than 25°C (45°F) per hour. Once the Reactor inlet temperature reaches 130-140°C (265-285°F), the Regenerator Superheater can be started.
23. Begin increasing the Regenerator Superheater outlet temperature to 260°C (500°F). If H<sub>2</sub>S is being detected at the Stabilizer offgas at a steady rate at a

certain reactor inlet temperature, do not increase the reactor inlet temperature any further than necessary to minimize the possibility of a reactor temperature excursion.

**NOTE: Do not exceed the design limitations with respect to temperature on the Regenerator Superheater or any other equipment or instruments. Verify with the vendor the temperature withstanding capability of all the equipment and instruments in this circuit.**

**Directionally, higher reactor inlet temperature during sulfur stripping will result in faster and more efficient sulfur removal off the catalyst. However, care must be exercised that temperatures are not increased more than necessary. Higher temperatures may also directionally lead to increased chances of a possible temperature excursion due to improper purging of Reactors or presence of heavies in the makeup gas. An adequate sulfur strip can be achieved at 260°C (500°F).**

24. Maintain the maximum makeup gas flow possible, depending on the Regenerator Superheater design duty. Be careful that heavier hydrocarbon content in the makeup gas should be the minimum possible. If an alternate clean source of makeup gas with less C5+ content is available, this can be used as the source of makeup gas during the Sulfur Stripping operations. Ensure this alternate gas source meets the typical contaminant maximum limits.
25. Monitor the H<sub>2</sub>S content of the Stabilizer off-gas regularly. The H<sub>2</sub>S content will slowly increase to a maximum (perhaps 200-1000 mol ppm, depending on the amount of sulfur present on the catalyst). Over a period of 12-24 hours, the H<sub>2</sub>S content will decrease to a fairly stable low level.
26. At this point, the stripping operation of the Reactor can be considered complete.
27. Start decreasing the reactor inlet temperature slowly by reducing the output of the Superheater outlet temperature controller in manual. Once the Superheater outlet temperature has been reduced to 140-150°C (285-

300°F), the Regenerator Superheater can be stopped. Continue decreasing the Penex Reactor inlet temperature by reducing steam flow through the Charge Heater.

28. If only the Lead Reactor is planned to be sulfur stripped, continue with Step 37. If the Lag Reactor is also planned to be sulfur stripped, switch the gas flow when the Lead Reactor temperatures reaches 121°C (250°F). Ensure pressure on the Lag Reactor is equal to that of the process pressure. If necessary, equalize pressure so as to not upset the process or the Reactors. Open the inlet and outlet valves at the Lag Reactor. Close the inlet valve closest to the Lead Reactor; the outlet valve is left open.
29. Open the block valves on the 1-1/2" purge line to establish a flow of cold hydrogen into the Lead Reactor in order to continue cooling the catalyst.
30. Cool the Lead Reactor catalyst bed to 65°C (150°F).
31. Meanwhile start heating the makeup gas to the Lag Reactor using Charge Heater at a rate of no more than 25°C (45°F) per hour. Once the Reactor inlet temperature reaches 130-140°C (265-285°F), the Regenerator Superheater can be started.
32. Increase the Regenerator Superheater outlet temperature to 260°C (500°F).
33. Monitor the H<sub>2</sub>S content of the Stabilizer off-gas regularly. The H<sub>2</sub>S content will slowly increase to a maximum (perhaps 200-1000 mol ppm, depending on the amount of sulfur present on the catalyst). Over a period of 12-24 hours, the H<sub>2</sub>S content will decrease to a fairly stable low level.
34. At this point the stripping operation of the Lag Reactor can be considered complete.
35. Start decreasing the Lag Reactor inlet temperature slowly by reducing the output of the Superheater outlet temperature controller in manual. Once the Superheater outlet temperature reaches 140-150°C (285-300°F), the

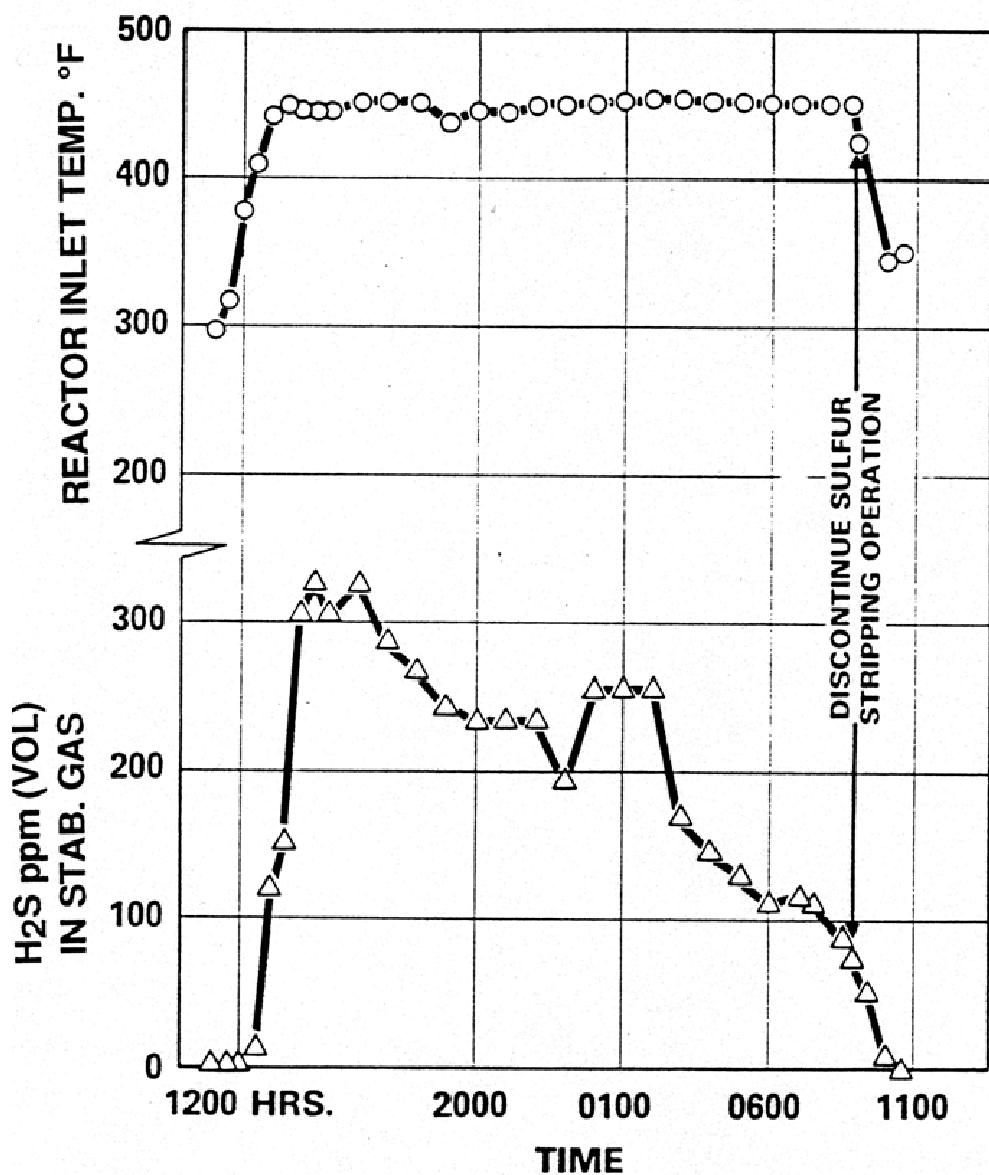
Superheater can be shutdown. Continue decreasing the Reactor inlet temperature by reducing steam flow through the Charge Heater.

36. Cool the Lag Reactor catalyst bed to 65°C (150°F).
37. If used, replace the makeup gas flow orifice plate used for sulfur stripping with the one used for normal operation, and return the makeup gas flowmeter back to its normal range.
38. The unit can be restarted per normal startup procedures. If driers were in parallel flow, place them back in the normal Lead to Lag series configuration. Place the Methanator Reactor back online per normal startup procedure.
39. Ensure the following activities have been performed upon completion of the Sulfur Stripping operations.
  - Ensure proper valve alignment for reactor flow configuration.
  - Purge the Regenerator Superheater and piping to the flare through the flare line with nitrogen connected to the 1" Dry Nitrogen Purge connection near the inlet to the Superheater.
  - Close the block valves on the 1-1/2" hydrogen purge lines if they were opened for cooling the Reactors.
  - Close the block valves on the sulfur stripping lines at the Regenerator Superheater inlet and outlet, then swing the spectacle blinds to the closed position.
  - Swing the blind open on the line from the Regenerator Vaporizer to the Regenerator Superheater. Swing the blind open on the line from the Superheater outlet to the Feed and Makeup Gas Driers. Ensure the proper valves and piping are aligned for normal regenerations.

40. Restart the unit according to the normal start up procedure. Ensure bed temperatures are less than 65°C (150°F) before feed introduction to the Reactors.
41. Resume regenerations of the Feed and Makeup Gas Driers according to the normal schedule.
42. After charging feed to the Reactors, adjust the chloride injection rate to 200 wt-ppm based on reactor feed.
43. Maintain 200 wt-ppm chloride injection for 12 hours (minimum) or HCl breakthrough in the Stabilizer offgas; then re-establish the normal rate of 150 wt ppm based on the Reactor charge rate.

Figure XIII-12 provides an indication of the relationship between reactor inlet temperature and H<sub>2</sub>S concentration in the stabilizer off gas over time.

Any time signs of catalyst deactivation are noticed, an attempt must be made to find the source of the contamination and fix it. The longer the contaminated feed passes over the catalyst, the more likely permanent catalyst damage will occur. If the only contaminant is sulfur, it is possible to recover the activity of the Penex catalyst close to the initial level. However, oxygenates, metals and basic nitrogen will permanently deactivate the catalyst.

**Figure XIII - 12: Catalyst Sulfur Stripping**

## E. Online Acidizing of (Empty) Lag Reactor with HCl from Decomposed Perc from Lead Reactor

The following section will outline the general steps for performing an online acidizing of the Lag Reactor using HCl from perchloroethylene decomposed in the Lead Reactor.

In general, the preferred method is to perform the acidizing procedure as outlined in Section XI. Commissioning using anhydrous HCl with the intended Reactor vessel empty of catalyst, with the exception of inert ceramic support material loaded in the bottom of the Reactor. It is recognized that due to time constraints, the decision may be made to forgo acidizing.

For ultimate catalyst protection, acidizing of equipment and piping in the reactor section for new Penex units is a requirement.

For units that are undergoing turnarounds or have been shut down for a significant amount of time, it is UOP's recommendation that if any equipment upstream of the isomerization reactors and including the Penex Reactors were to be exposed to air, the reactor circuit should be acidized to remove any rust that could have formed from exposure to air. However, the decision to acidize can also be made based on a risk analysis that the refiner must undertake. At risk is the amount of catalyst that can be permanently deactivated due to the presence of rust in the unit that was not removed due to the decision to not acidize. Approximately 1.6 kilogram (or pound) of an oxygenate, in any form, will permanently deactivate 100 kilograms (or pounds) of Penex catalyst. Even the oxygen "O" in rust will deactivate the Penex catalyst when rust converts to water. Due to the many variations that rust can exist as iron-oxide, it is estimated that approximately 21 kilograms (or pounds) of rust will permanently deactivate 100 kilograms (or pounds) of Penex catalyst.

Exposure to air should be minimized or altogether avoided to prevent oxidation of the carbon steel piping, heat exchangers and vessels in the reactor circuit. Strategies may include not introducing air into the vessels that are undergoing inspection and limiting the equipment that is to be exposed to air. If at all possible,

inspections should be performed with a camera or other methods to prevent having to expose the vessels to air, especially wet air.

During the online acidizing period, the startup moisture analyzer on the inter-reactor sample station should not be used as the highly acidic environment can damage the analyzer probe. To track rust and moisture removal, water detector tubes will be used to measure moisture in the Stabilizer offgas.

Step wise procedure is as outlined below:

## 1. Unit Preparation

At this point, the unit is in single reactor mode of operation. One reactor is offline, isolated from the process and empty with no catalyst loaded. Inert Ceramic Balls (ICB) or Ceramic Support Material (CSM) are loaded at the bottom of the Reactor. The reactor is under a dry nitrogen blanket at ambient pressure.

All blinds as per blind list are removed.

The Net Gas Scrubber should be confirmed that it is operating stably per normal operations.

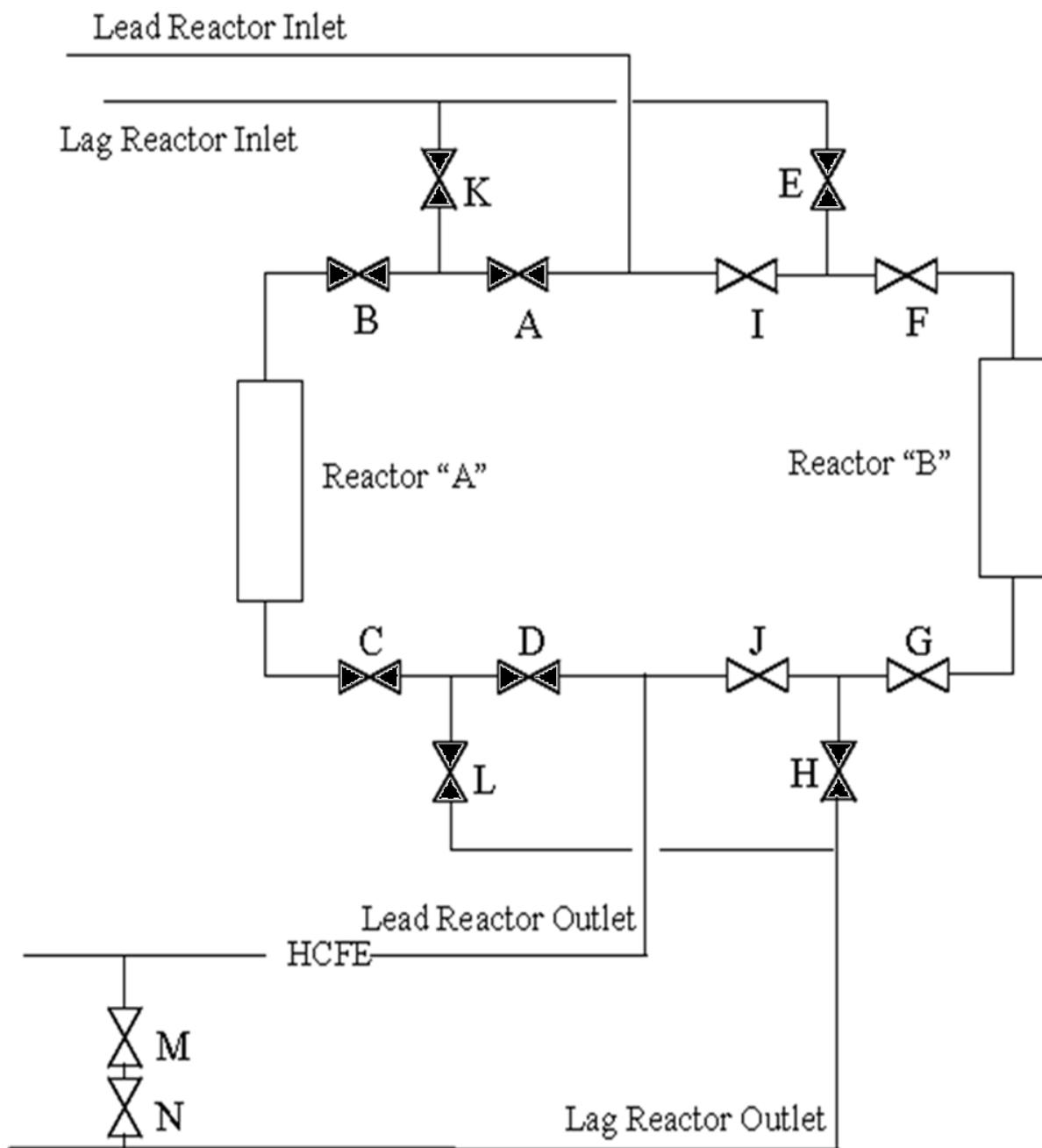
Ensure one Feed Drier has completed a regeneration.

Ensure one Makeup Gas Drier has completed a regeneration.

For Reactor B Single Operation flow, the valves are in the following position:

Valves open: I, F, G, J, M and N

Valves closed: A, B, C, D, E, H, K and L

**Figure XIII- 13: Valve Position Reactor B Single Operation**

## **2. Pressure Test Reactor with Nitrogen (N<sub>2</sub>)**

Increase pressure on Reactor to be loaded with N<sub>2</sub> to about 7 kg/cm<sup>2</sup>-g (100 psig). For a successful pressure test, the pressure loss should be less than 0.2 kg/cm<sup>2</sup> (3 psi) over the two hour hold.

Drain low point drains, as necessary.

Ensure dead legs have been properly purged out.

Upon a successful pressure test, the Reactor can be depressured to flare.

## **3. O<sub>2</sub>-Free Reactor with Nitrogen (N<sub>2</sub>)**

The Reactor can be pressurized and depressured several times to remove O<sub>2</sub> content to an acceptable level.

## **4. Hydrogen Pressure Test**

The 1-½" pressure-up line from the Makeup Gas Driers is used to increase pressure on the Reactor.

Increase pressure slowly to about 10 kg/cm<sup>2</sup>-g (150 psig). Continue to check for leaks. Hold pressure for two hours. For a successful pressure test, the pressure loss should be less than 0.2 kg/cm<sup>2</sup> (3 psi) over the two hour hold.

The pressure test can be repeated by increasing the pressure to incremental amounts until reaching the design operating pressure of the Reactor.

## 5. Place Reactor in Lag Position

With the unit operating in single reactor mode of operation, the Reactor to be loaded will be placed in the Lag position.

The Lag Reactor inlet valve should be open. As per the diagram below, Valve K should be open.

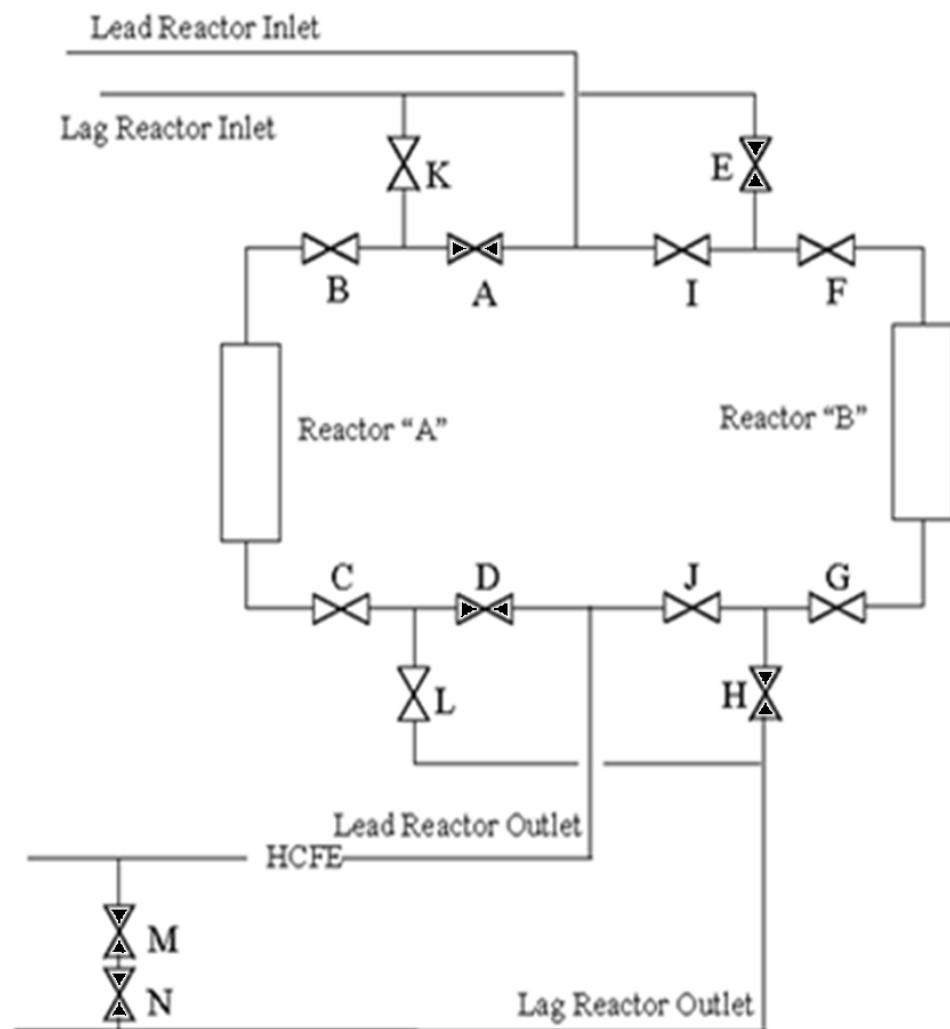
The Lag Reactor outlet valve should be open. As per the diagram below, Valve L should be open.

The single reactor bypass valve(s) should be closed. As per the diagram below, Valves M and N should be closed.

For Reactor B to Reactor A series flow, the valves are in the following position:

Valves open: I, F, G, J, K, B, C and L

Valves closed: A, D, E, H, M and N

**Figure XIII- 14: Valve Position Reactor B to A Series Operation**

Operations of the unit should be monitored to ensure stable operations during the commissioning of the Reactor.

The perchloroethylene injection rate is maintained at 150 wt-ppm of reactor charge.

The Lead Reactor inlet temperature should be maintained at least 105°C.

The reactor feedrate should be maintained at least 50% of design rate.

The makeup gas rate should be maintained at least 100% of design rate.

## 6. Acidization

A detector tube is used to check the water vapor concentration in the Stabilizer offgas. A moisture level of <10 ppm in the Stabilizer overhead is an indication that the acidization is complete.

The duration of the online acidization will depend on the extent of rust formation and presence of moisture. It is expected that the online acidization may take anywhere from 2 days to 10 days. The length of online acidization can be reduced by minimizing exposure to air and humidity.

Track and monitor the amount of water that is being drained from the Stabilizer Overhead Receiver.

Ensure the drain line underneath the raised vortex breaker in the Stabilizer Overhead Receiver is opened occasionally to drain free water that can collect at the bottom of the Receiver. Additionally, ensure all stagnant and low point areas are drained adequately to remove free water. Free water in the presence of HCl will result in excessive corrosion in the Penex unit.

## 7. Cool Down and Hydrocarbon Sweeping

Upon completion of the online acidization, the Lag Reactor can be shutdown per the Partial Unit Shutdown procedures as outlined in Section XI. Normal Shutdown.

## 8. Catalyst Loading

The catalyst can be loaded as per the Catalyst loading procedure as outlined in Section XIII. Special Procedures.

## F. Drier Regeneration

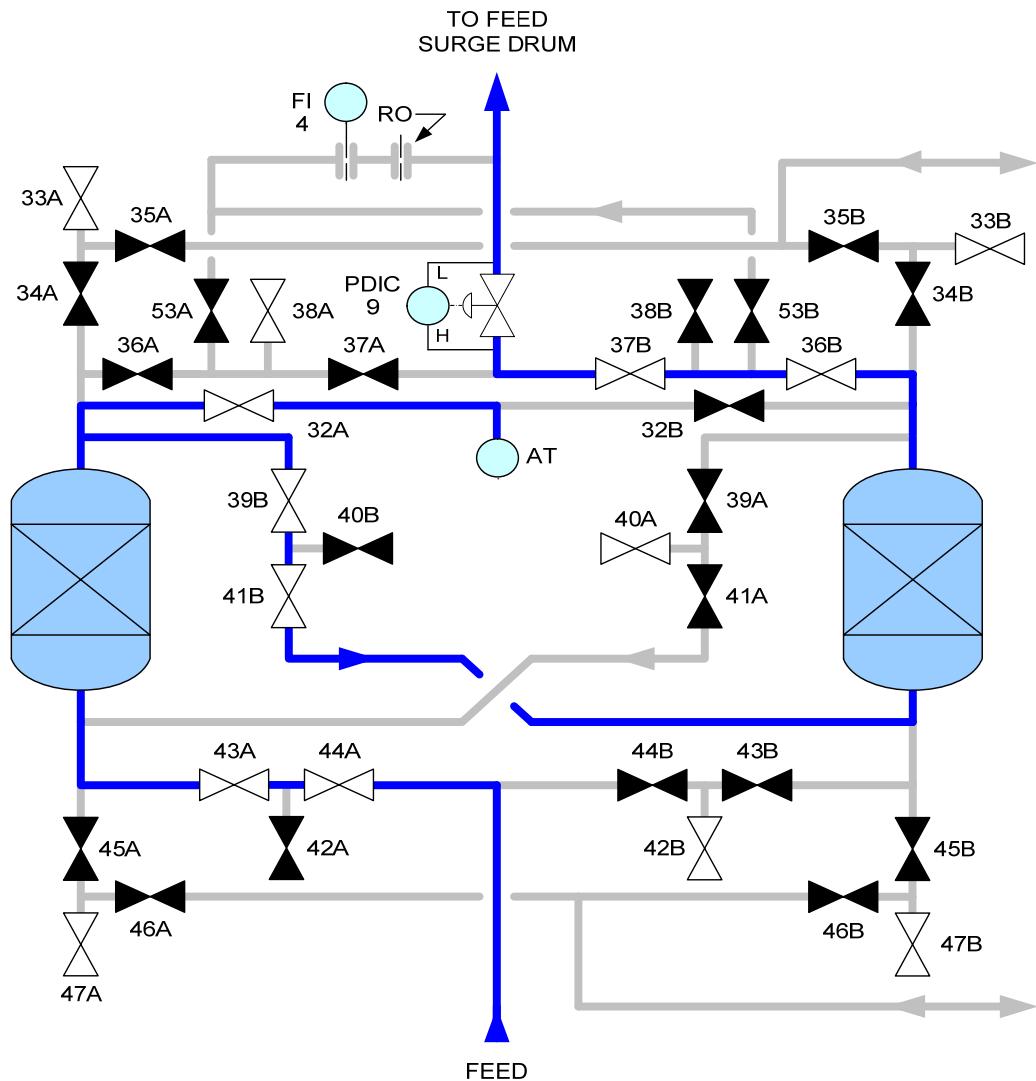
### 1. Liquid Feed Drier Regeneration

Liquid Feed Driers are sized by UOP to operate 24 hours each before requiring regeneration. Driers are operated such that one drier is in the “lead” position and the other is in the “lag” position, or is being regenerated. Lead Drier must be regenerated once its effluent indicates more than 1 wt-ppm water. As operating experience is gained, and providing a water breakthrough is not observed, the drying periods may be extended. Typically the driers are regenerated on a frequent enough basis to avoid moisture breakthrough of one drier. The following guidelines can be followed to take a drier off line, regenerate it, and bring it back on line.

Assume feed is flowing through both driers, i.e. the driers are in series with Drier “A” first (“lead” position) and Drier “B” second (“lag” position). The moisture analyzer sample is from the outlet of Drier “A”. At this stage: process valves 44A, 43A, 39B, 41B, 36B and 37B are open and the other process valves are closed.

For inline process valves that are closed, the bleeder valve in between the process valves should be open. For example, with Drier B-to-A crossover process valves 39A and 41A closed, the bleed valve in between (40A) is open.

Likewise, for inline process valves that are opened, bleed valve in between the process valves should be closed. For example, with Drier A-to-B crossover process valves 39B and 41B opened, the bleed valve in between (40B) is close. Figure XIII-15 shows position of valves at this stage.

**Figure XIII- 15: Fresh Feed Drier “A” to “B” Flow Line-up**

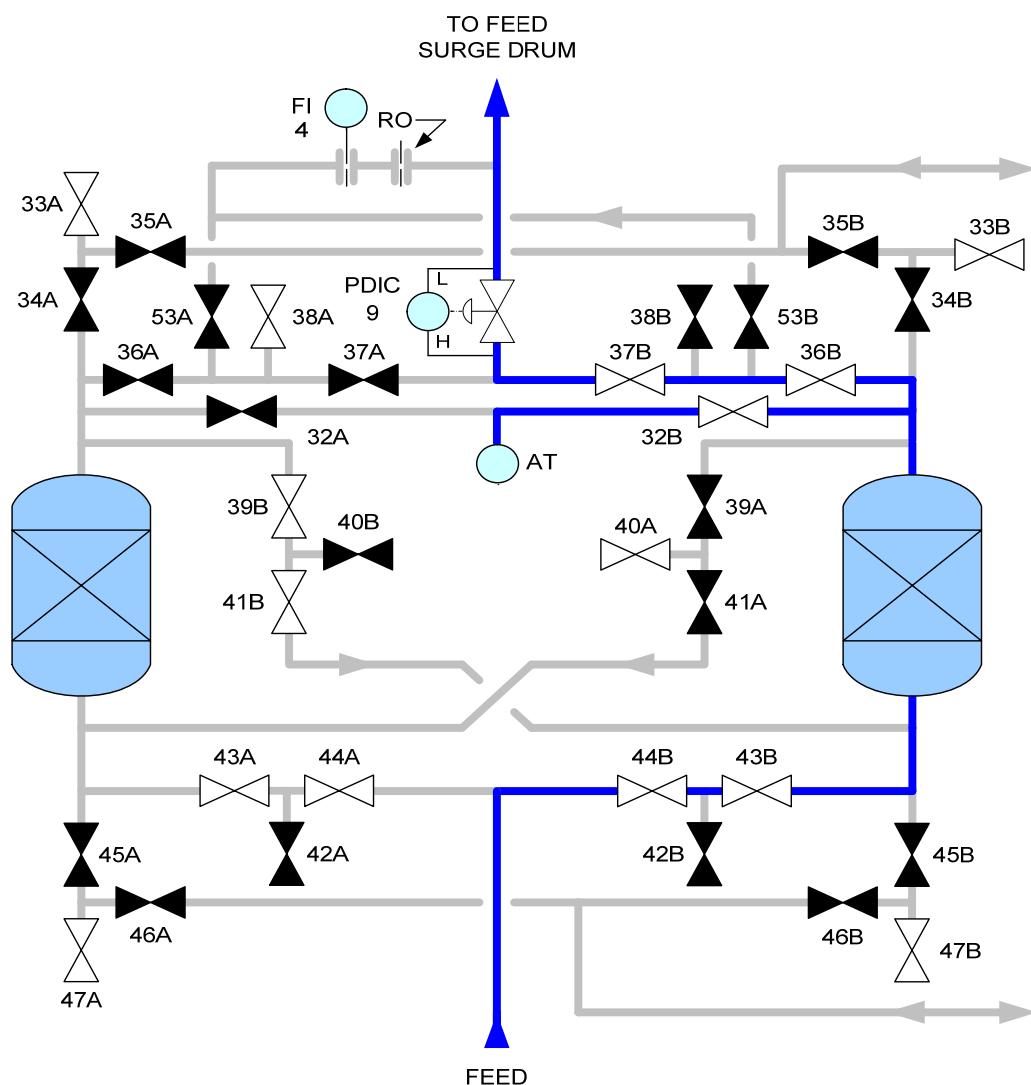
When the moisture analyzer indicates a need to regenerate or when the scheduled regeneration time arrives, drier "A" will be isolated, regenerated, cooled and put back into service in the "Lag" position. The liquid feed drier regeneration sequence will be as follows:

## I. Start Flow to Drier “B” Inlet

Open Drier “B” inlet valves (44B and 43B). Open moisture analyzer inlet valve from Drier “B” effluent (32B). Close the moisture analyzer sample from Drier “A” (32A).

Flow is now essentially going through Drier “B” only, since it is the path of least resistance. Figure XIII-16 shows the position of valves at this stage.

**Figure XIII- 16: Feed Flow through Drier B**



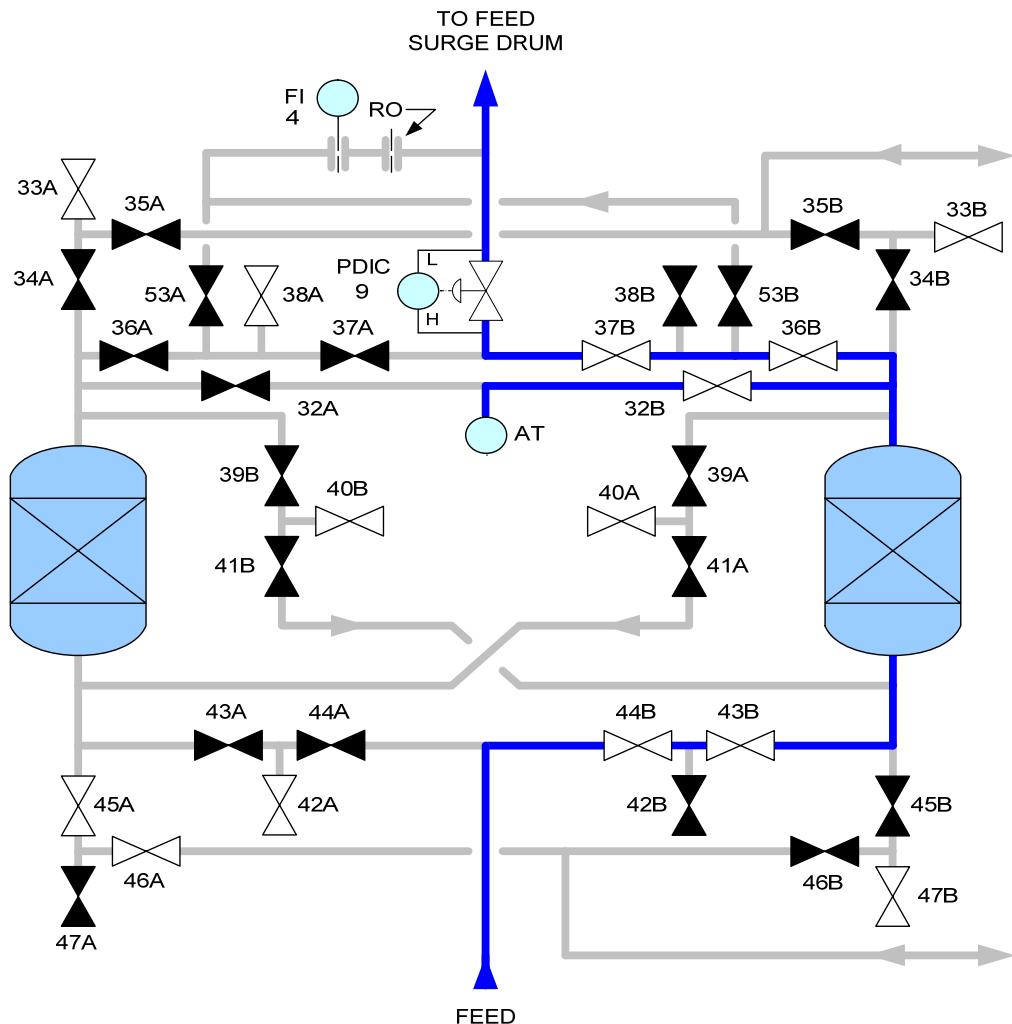
## **II. Isolate Drier "A"**

Close the inlet process valves to Drier "A" (43A and 44A). Close the process valves on Drier A-to-B crossover line (39B and 41B). Open the corresponding bleed valves, 42A and 40B to verify that the process valves are not leaking.

### **III. Depressurization Feed Drier "A"**

Depressurize feed Drier "A" by opening the regenerant outlet valve. Close the bleed valve 47A. Open the regenerant outlet valve 45A and 46A.

**Figure XIII- 17: Isolated Feed Drier A**



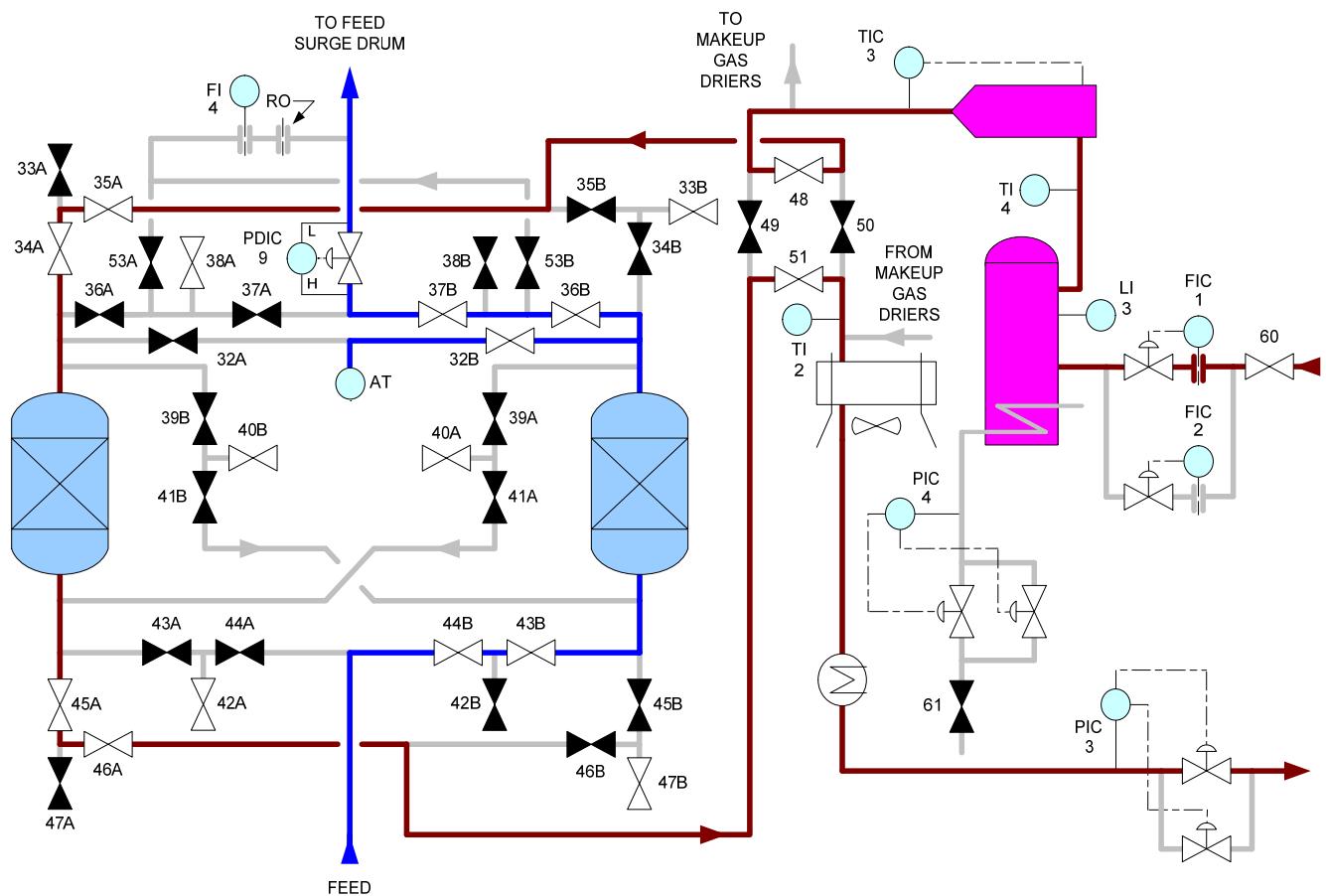
#### IV. Line up Regenerator Flow to Drier “A”

Close Drier “A” regenerator inlet bleed valve 33A. Open Drier “A” regenerator inlet valves 35A and 34A.

#### V. Start Regenerator Flow to Drier “A”

Open the regenerator inlet valve (48) and regenerator return valve (51). Line up flow of regenerator to Regenerator Vaporizer. Liquid fill the Vaporizer and send flow forward through the Superheater then establish the design regenerator flowrate. The Regenerator Condenser and pressure controller should also be commissioned. Route the Regenerator Condenser outlet to storage.

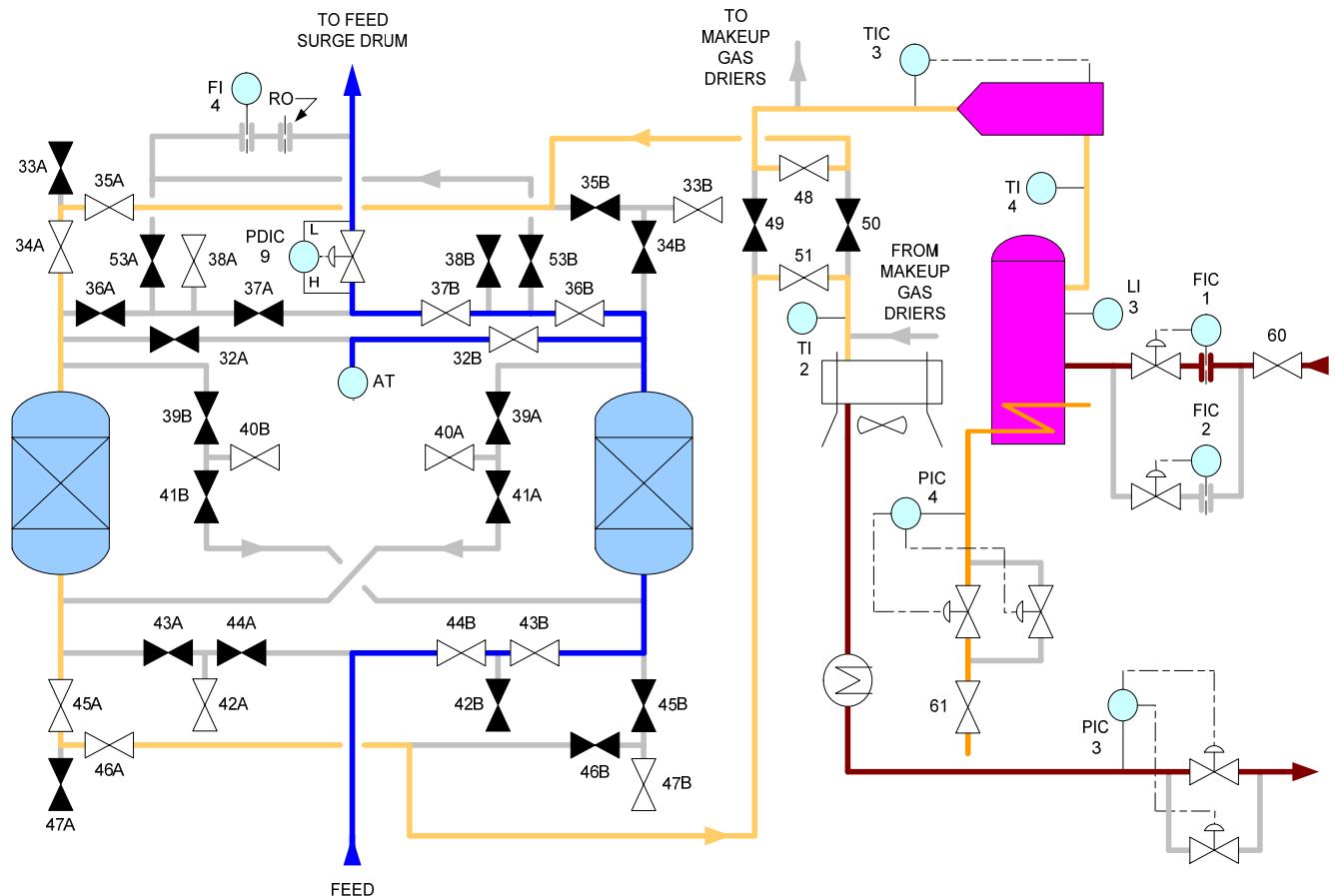
**Figure XIII- 18: Regenerator Flow to Drier A**



## **VI. Increase Regenerant temperature**

Open steam inlet valve (61) and start flow of Steam to the Regenerator Vaporizer. After a low and stable level has been maintained in the vaporizer, the Electric Superheater may be commissioned. Increase the Superheater outlet temperature at a rate of 70°C/hr (125°F/hr) to 315°C (600°F). Following figure shows the valve positions at this stage.

**Figure XIII- 19: Regenerator Heat Up**



## VII. Hot Soak Drier temperature

Monitor the outlet temperature (TI-2) of the Drier. As the water is driven off of the sieves, the temperature will gradually increase. Hold the outlet at a minimum of 288°C (550°F) for four hours.

## VIII. Reduce Regenerator Temperature

After the 4 hour hot hold, reduce the Superheater outlet temperature to 177°C (350°F) and then shut down the Superheater. Continue to circulate vaporized regenerator from the vaporizer and cool the sieve bed to about 93°C (200°F).

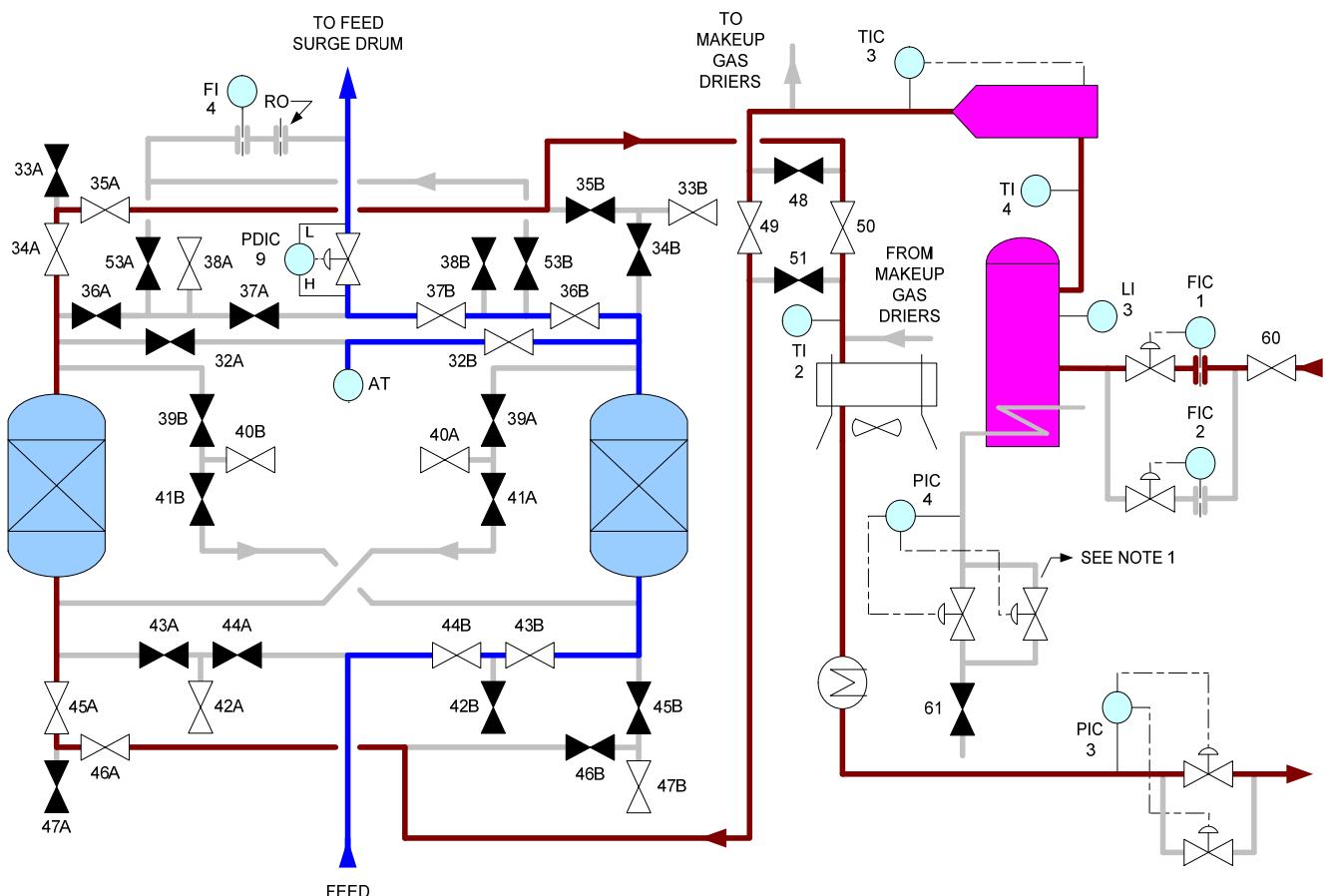
## IX. Cooldown Drier “A”

After the drier has reached the approximate temperature of the Vaporizer outlet, the sieves are further cooled with liquid regenerator. The vapor phase cooling prevents rapid generation of vapors during the liquid phase cooldown.

If connections are provided, switch the draw point of regenerator from upstream of the product cooler (hot regenerator) to the product cooler effluent (cold regenerator) and shut-off steam to the Vaporizer. This provides the coldest stream temperature and, hence, the most rapid cooling rate.

Open the liquid coolant inlet valve (49) and the liquid coolant return valve (50). Close the regenerator inlet valve (48) and close the regenerator return valve (51). Cool the drier sieves upflow until the outlet regenerator return temperature is less than 65°C (150°F).

### **Figure XIII- 20: Drier A Cooldown**



## X. End the Cooldown period

Close the liquid coolant inlet valve (49) and close the liquid coolant return valve (50). Close Drier "A" regenerant inlet valves (34A and 35A) and close Drier A regenerant outlet valves (45A and 46A). Open the associated bleed valves 33A and 47A. Manually close and isolate the regenerant FIC control valve FIC-1.

## XI. End Regeneration

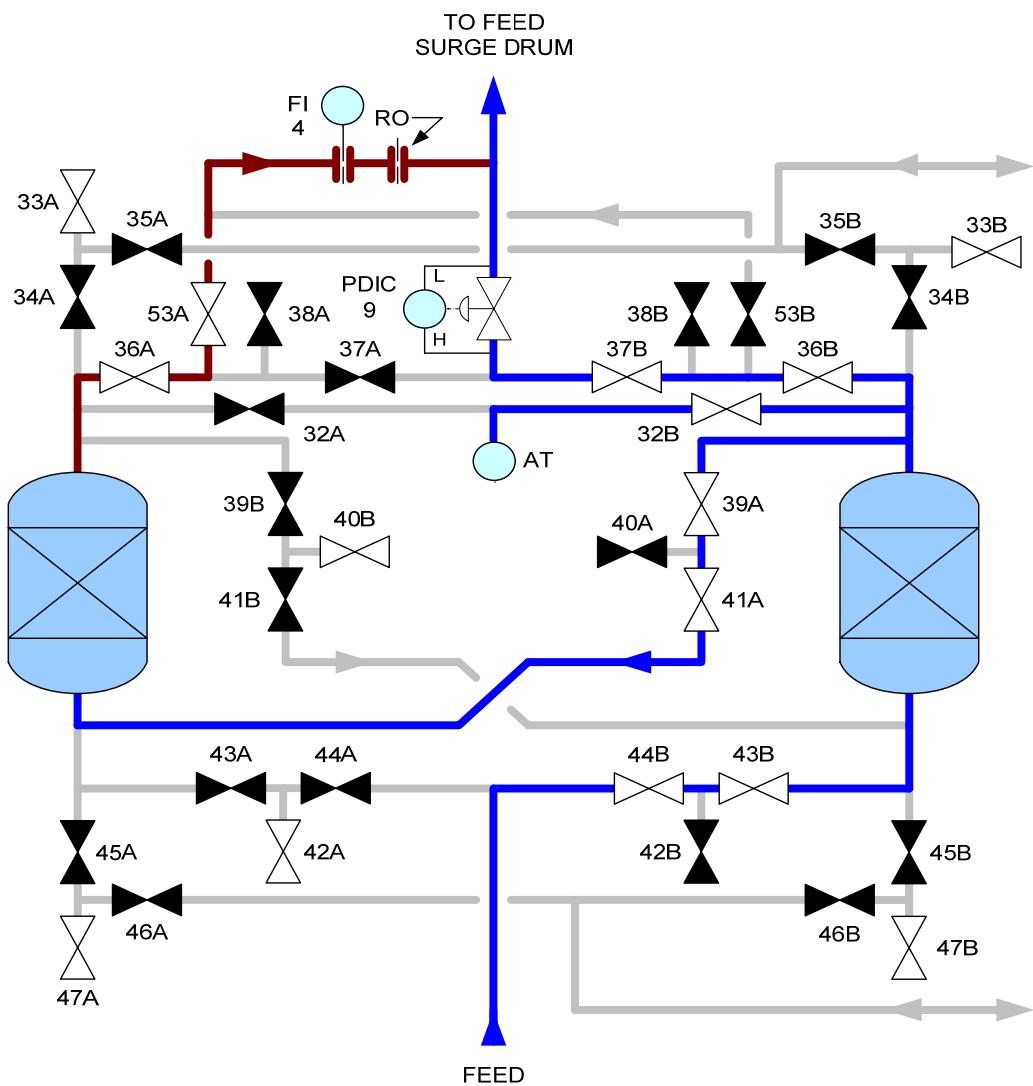
Close Drier "A" process outlet bleed valve 38A. Open Drier "A" outlet valve 36A  
Close the Drier B-to-A crossover bleed valve 40A.

After this step there are two options to proceed in the regeneration process, they are as follows:

1. If desired, regenerant can be displaced from the freshly regenerated drier to minimize process upsets to the unit, when the drier is placed back online. Proceed to step XII to displace the regenerant.
2. Alternatively, Drier can be placed in lag position. Proceed to step XIII to place the freshly regenerated drier in the lag position.

## **XII. Displace Regenerant from Drier “A”**

Open Feed Drier “A” Regenerator displacement valve 53A. Flow of dried feed from Drier “B” is routed to Drier “A”. A restriction orifice on this line provides controlled flow from Drier “A” to the outlet stream of Drier “B”. Feed Drier process outlet differential pressure controller on the Drier outlet line (PDIC-9) is used to control the flow forward during the step. Valve positions at the end of this step are shown in Figure XIII-21.

**Figure XIII- 21: Drier A Regenerator Displacement**

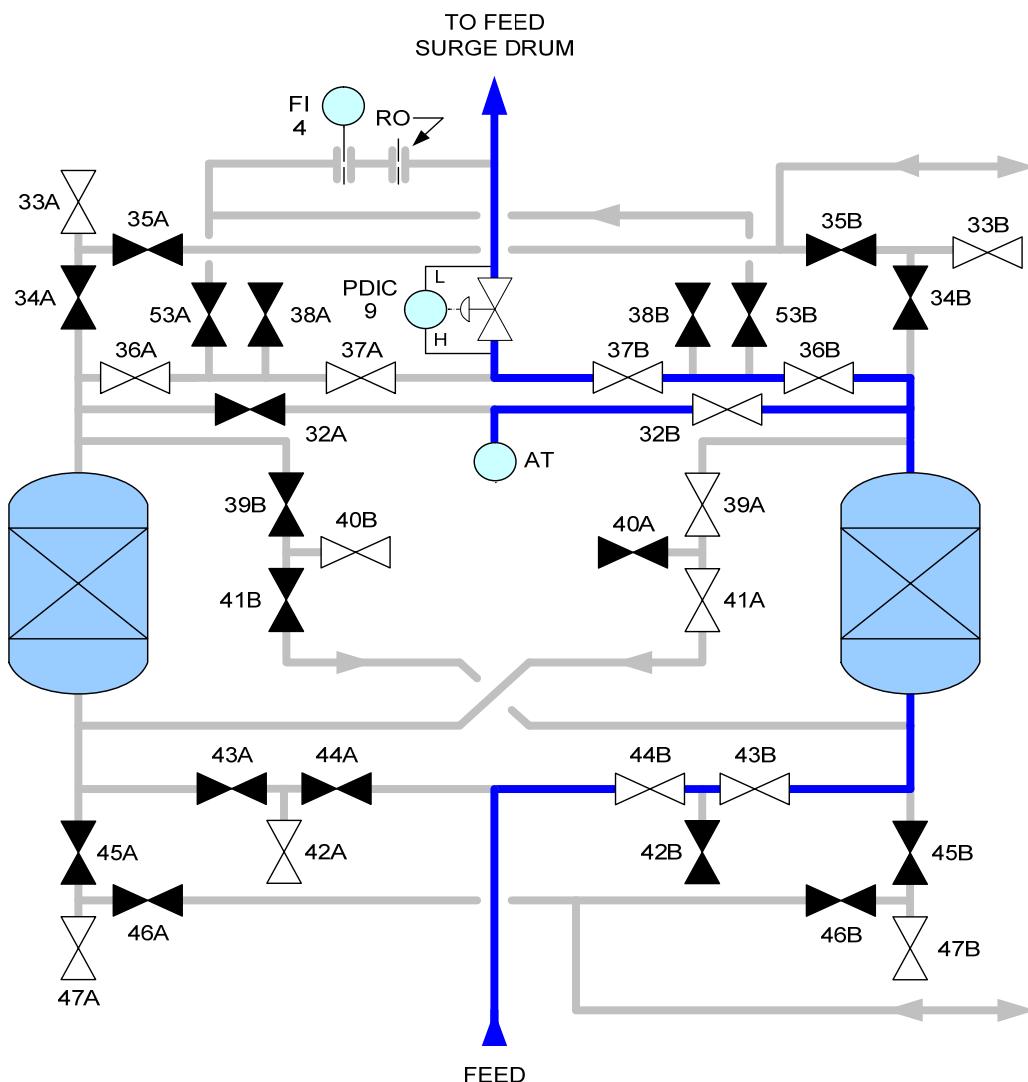
Once regenerant from Drier "A" is displaced, Drier "A" regenerant displacement valve (53A) can be closed; to avoid sudden decrease in forward flow when the valve (53A) is closed. PDIC-9 is opened to 100% and Drier "A" regenerant displacement valve (53A) is closed.

### XIII. Pressurize Drier "A"

In preparation of placing the freshly regenerated Drier "A" in lag position, Pressurize Drier "A"

Open the Drier "A" process outlet valve 37A. The flow is essentially going through the Drier "B" at this stage because of the path of least resistance. Figure XIII-22 shows the position of valves at this stage.

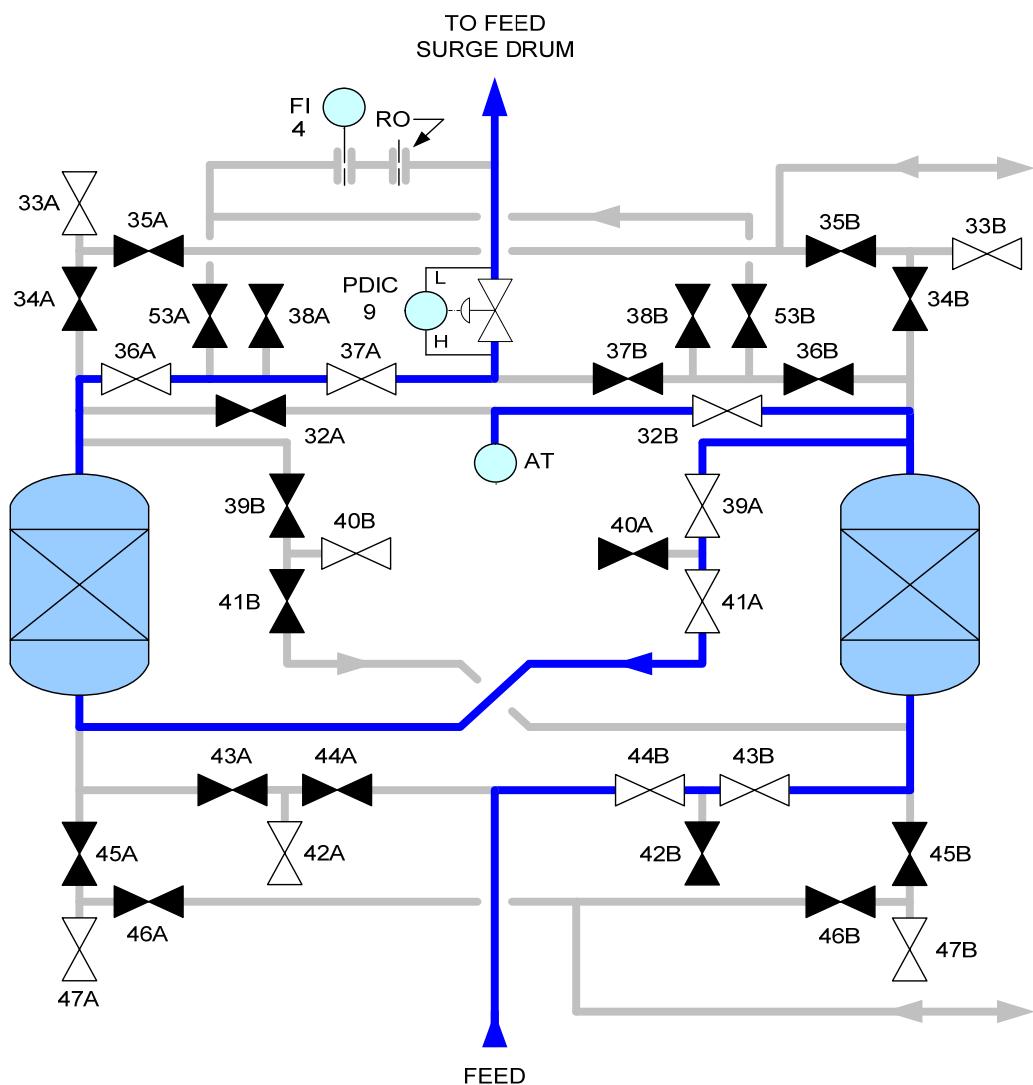
**Figure XIII- 22: Drier A Pressurization**



## XIV. Line up Drier “A” in Lag Position

To direct the flow through Drier “A”, close Drier “B” process outlet valves 36B and 37B. At the completion of this step freshly regenerated Drier “A” is placed in lag position. Figure XIII-23 shows position of valves at the end of this step.

**Figure XIII- 23: Lag Lineup Drier A**



The above procedure may be used to regenerate Drier “B” by using appropriate valve identification nomenclature.

## 2. Makeup Gas Drier Regeneration

Makeup Gas Driers are generally sized to operate for 24 hours each before requiring regeneration. Driers are operated in series flow such that one drier is in the lead position and the other is in the lag position, or is being regenerated. As operating experience is gained, and providing a water break-through is not observed, the drying cycle periods may be extended.

Lead drier is to be regenerated once the effluent indicates more than 1 ppm water. The following guidelines can be followed to take a drier off line, regenerate it, and bring it back on line.

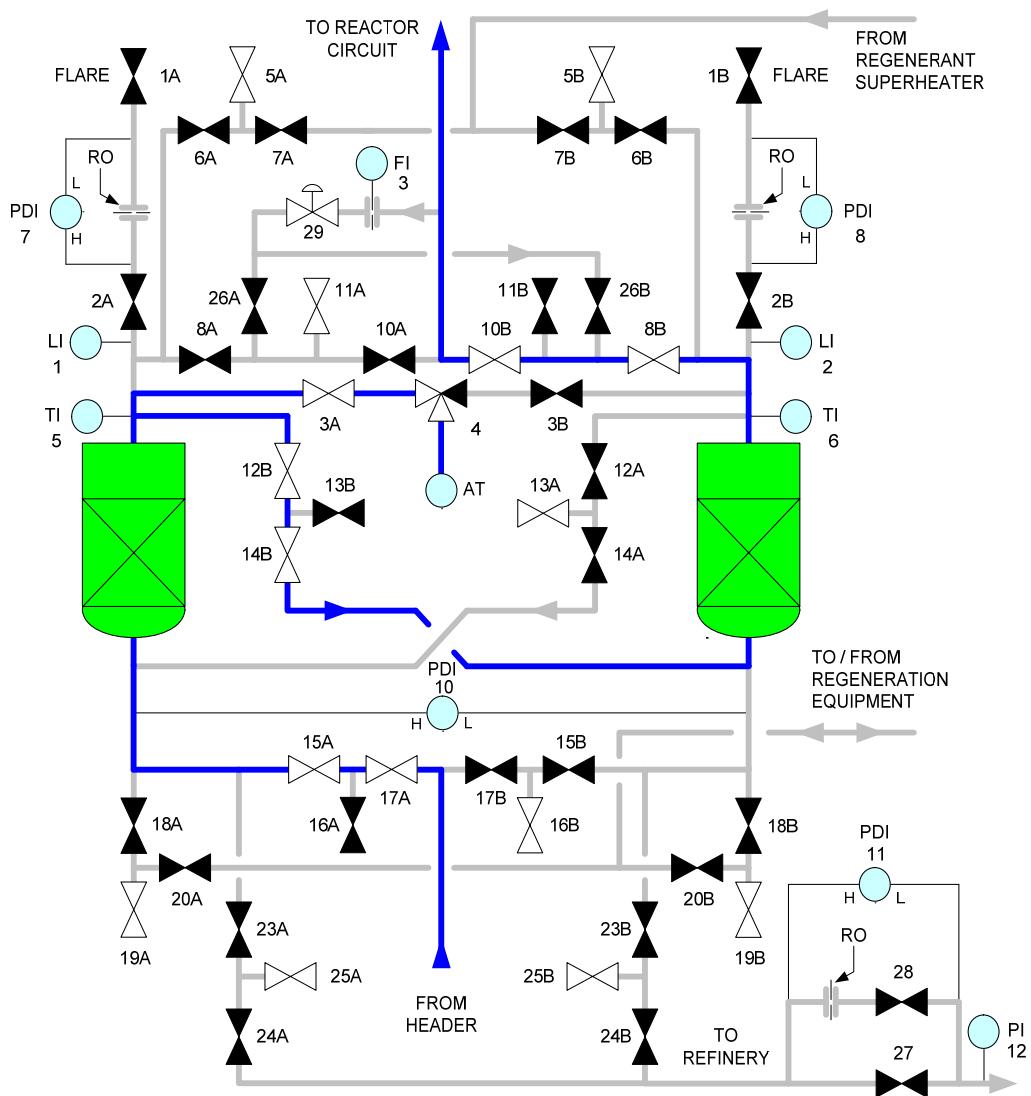
When the moisture analyzer indicates a need to regenerate (1 ppm H<sub>2</sub>O) or when the scheduled regeneration time arrives, Drier "A" will be isolated, depressured, regenerated, regenerant-freed, pressurized up and put back into service in the "Lag" position. The make-up gas drier regeneration procedure will be as follows:

Assume makeup gas is flowing through both driers, i.e., the driers are in series flow with Drier "A" first ("Lead" position) and Drier "B" second ("Lag" position). The moisture analyzer sample is at the outlet of Drier "A". At this stage, process valves 17A, 15A, 12B, 14B, 8B, 10B, and 3A are open and all other process valves are closed

For inline process valves that are closed, the bleed valve in between the process valves should be open. For example, with Drier B-to-A crossover process valves 12A and 14A closed, the bleed valve in between (13A) is open.

Likewise, for inline process valves that are opened, the bleed valve in between the process valves should be closed. For example, with Drier A-to-B crossover process valves 12B and 14B open, , the bleed valve in between (13B) is closed.

It should be noted that not all valve positions may be properly denoted as being in the correct positions in the following figures.

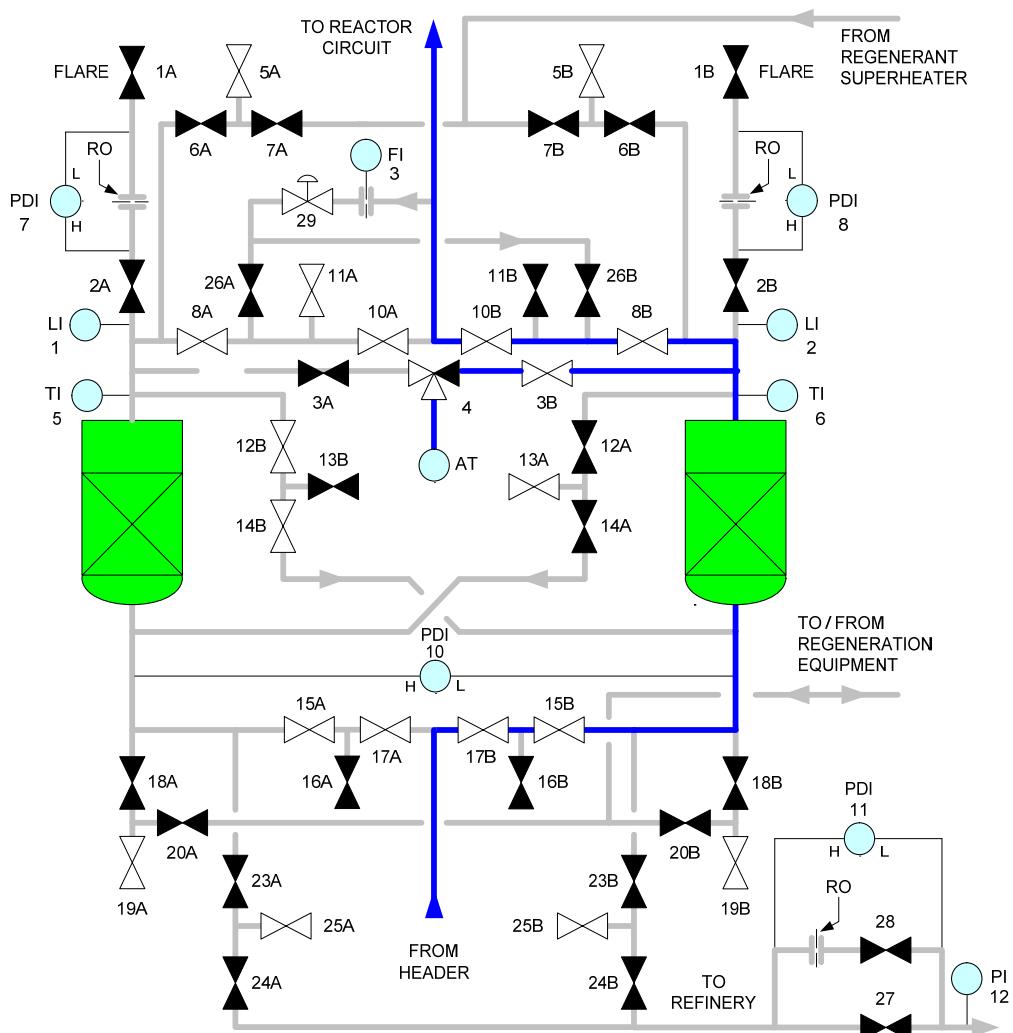
**Figure XIII- 24: Makeup Gas Drier "A" To "B" Flow Line-up**

## I. Start Flow to Drier “B” Inlet

Open Drier “B” inlet valves (17B and 15B). Close the bleed valve in between (16B). Although the process inlet valves to Makeup Gas Drier “A” are still open, most – if not all – of the flow is now essentially going through Drier “B” since it is the path of least resistance.

Open the moisture analyzer sample valve from Drier “B” effluent (3B) and Close the moisture analyzer sample from Drier “A” to switch the sample takeoff point to the moisture analyzer. Moisture is now being analyzed at the outlet of Makeup Gas Drier “B”.

Refer to the figure XIII-25 for the Makeup Gas Driers valve alignment at this stage of the makeup bas drier regeneration of Drier “A”.

**Figure XIII- 25: Makeup Gas Flow to Drier “B”**

## II. Isolate Makeup Gas Drier “A”

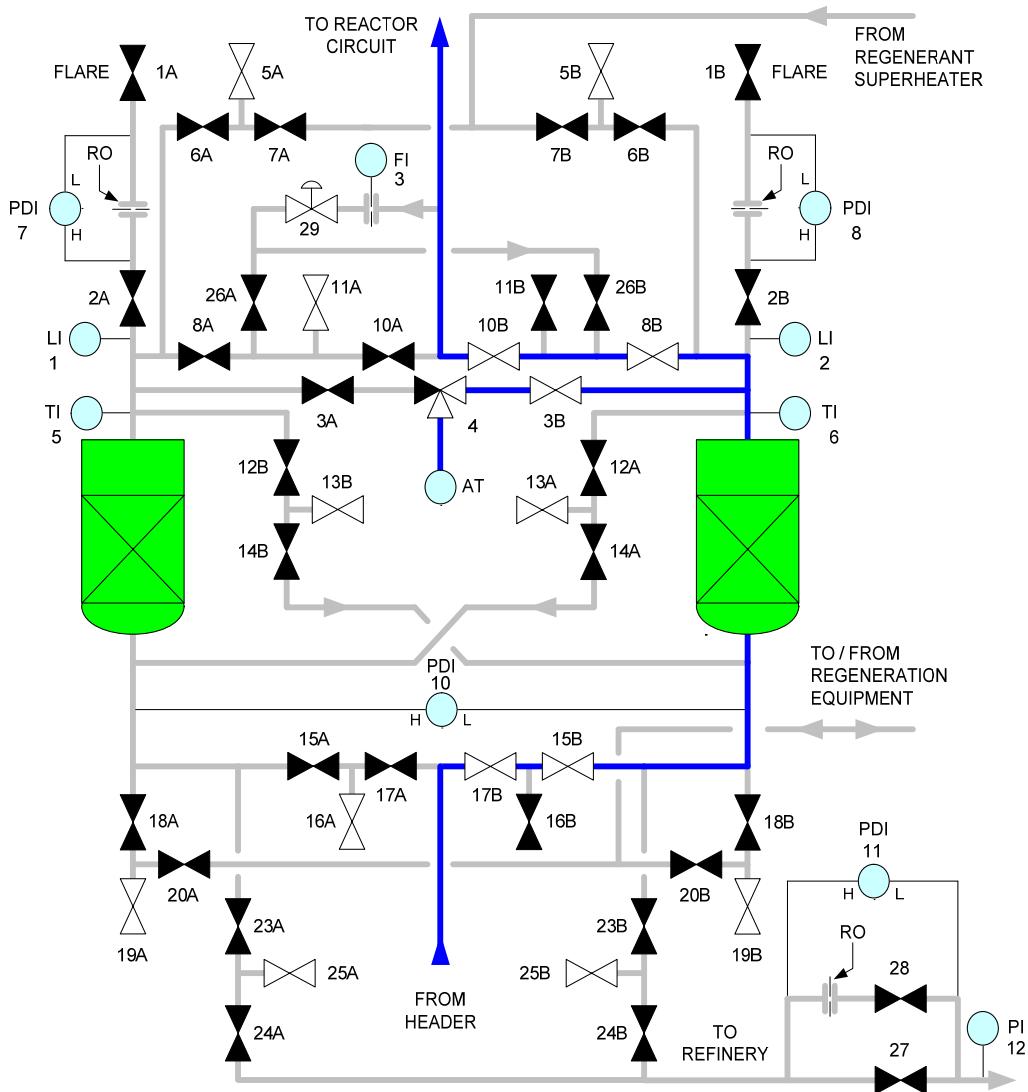
Close the process inlet valves of Drier “A” (17A and 15A). The bleed valve in between (16A) should be opened to ensure valves 17A and 15A are not leaking.

Close the outlet valves of Drier “A” (8A and 10A). The bleed valve in between (11A) should be opened.

Close the valves on the crossover line (12B and 14B). The bleed valve in between (13B) should be opened to ensure valves 12B and 14B are not leaking.

Makeup Gas Drier "A" is now completely isolated from Makeup Gas Drier "B".

**Figure XIII- 26: Isolate Makeup Gas Drier “A”**



In preparation of regeneration, Drier “A” is depressurized. Drier “A” can be directly depressurized to flare or it can be depressurized to an alternate destination first.

If the drier is to be depressurized to alternate destination (such as a separator at in the Platforming Unit or to the Refinery Fuel Gas System), then the pressure difference between the drier and the alternate destination should be taken into consideration, nominally  $0.5 \text{ kg/cm}^2$  (7 psi), as measured by PDI-11.

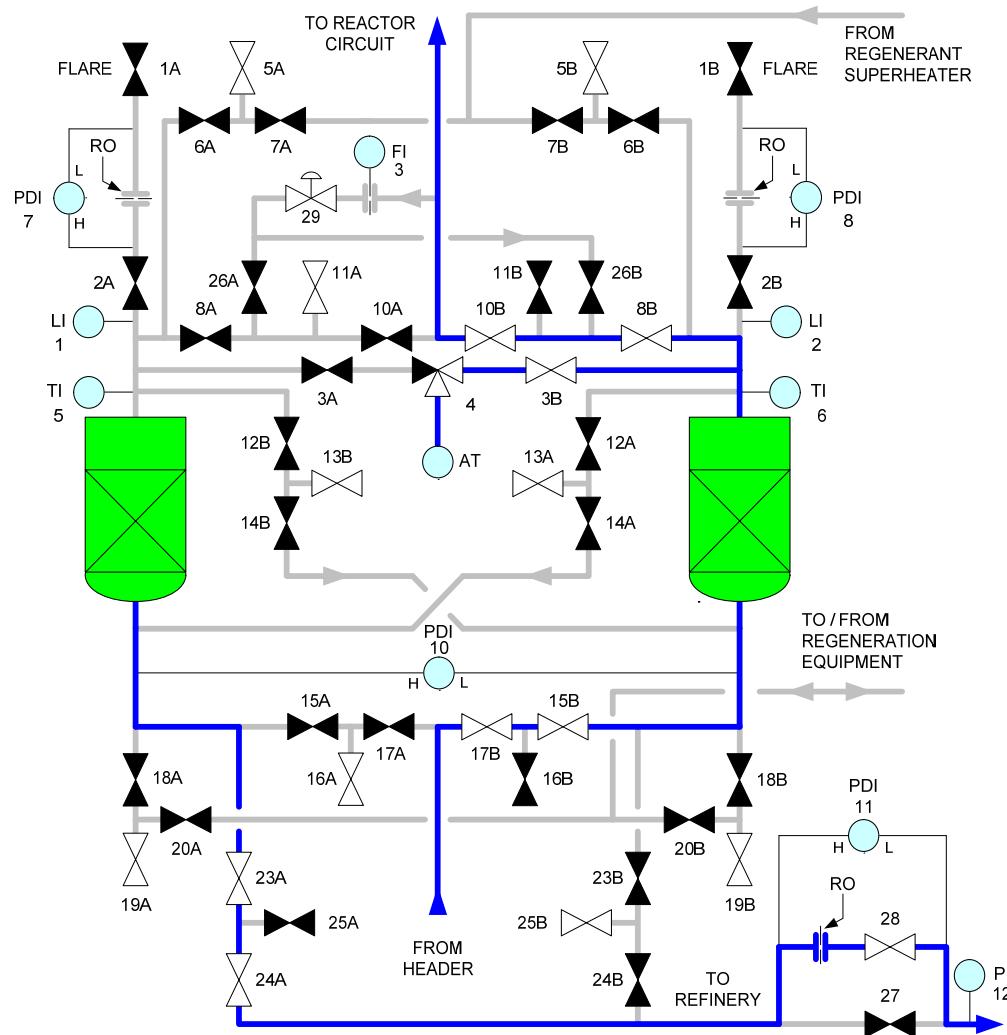
If drier is to be depressurized to an alternate destination first, proceed to Step III and if the drier is to be depressurized directly to flare then proceed to Step IV.

### **III. Depressure Makeup Gas Drier “A” to Alternate Destination (optional)**

Open the lower depressuring valves (23A and 24A) after closing the bleed valve in between (25A). Open valve 28 for controlled depressurization of Drier A through orifice (RO) to the alternate destination.

Figure XIII-27 shows the valve positions during this step.

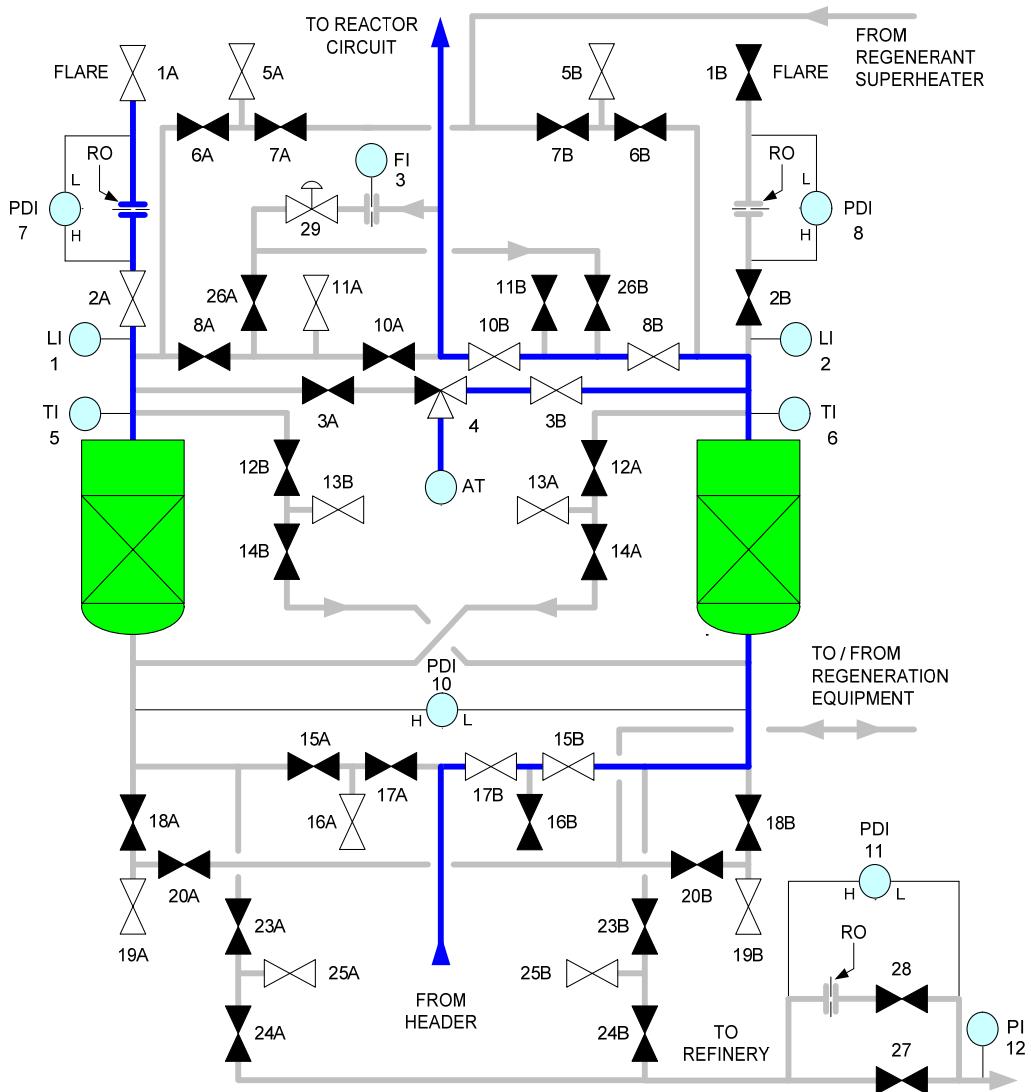
**Figure XIII- 27: Makeup Gas Drier “A” Depressurization to Alternate Destination**



#### IV. Final Depressure Step

Depressure Drier “A” to flare by opening the depressurization valves (2A and 1A) located at the top of the vessel.

There is a restriction orifice (RO) on the line to prevent rapid depressurization and possible disturbance of the bed as the drier is being depressurized from operating pressure to the flare header pressure. PDI-7 is used to reach the target differential pressure. Refer to Figure XIII-28.

**Figure XIII- 28: Makeup Gas Drier A Depressurization to Flare**

## V. Liquid Fill Makeup Gas Drier “A” Upflow

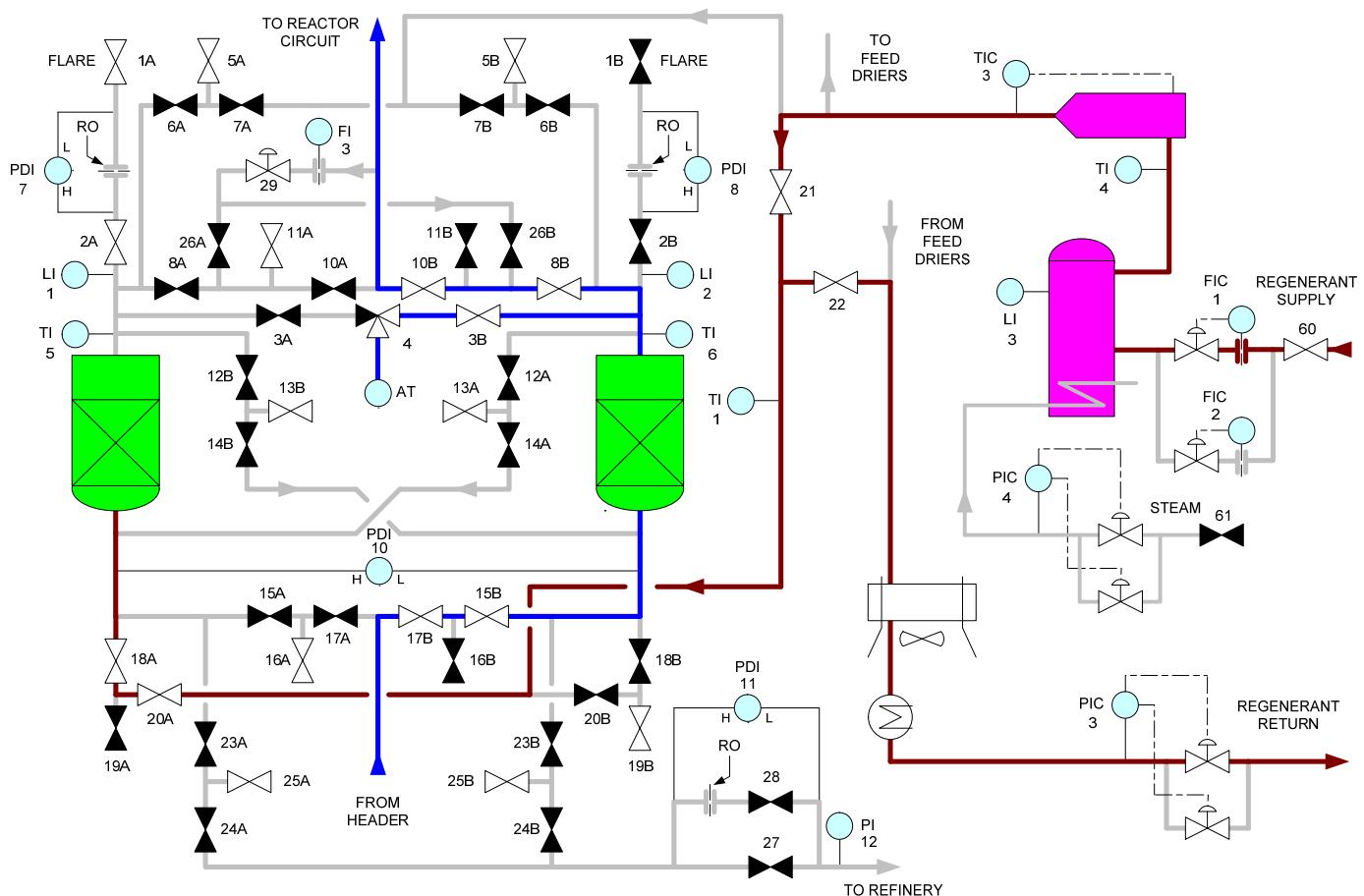
With the Makeup Gas Drier depressured to flare header pressure, it must first be H<sub>2</sub>-freed with cold regenerant liquid before the temperature is increased.

If not already done so, commission the regenerator condenser and regenerator PIC.

Open the regenerant liquid filling valve (valve 21). Open the spent regenerant valve (valve 22). Route the regenerant from the Regenerator Vaporizer to Electric Superheater and to the Regenerator Condenser (through the liquid filling valve, 21; and the Spent Regenerator Valve, 22). Establish stable controls on the regenerant PIC and FIC. At this point, the Vaporizer and Superheater have not been commissioned yet.

Once the flow is established and PIC and FIC are in stable control, Close the bleed valve (19A) in between the regenerant outlet valves, 18A and 20A, at the bottom of the drier. Open the regenerant outlet valves, 18A and 20A. Establish the design regenerant rate and liquid fill Drier "A" with cold regenerant upflow, displacing the hydrogen gas out to the flare header.

Filling is complete when liquid is observed flowing through the sight flow glass at the drier outlet or when the level switch at the top of the drier indicates liquid. Figure XIII-29 shows the position of valves and flows after this step.

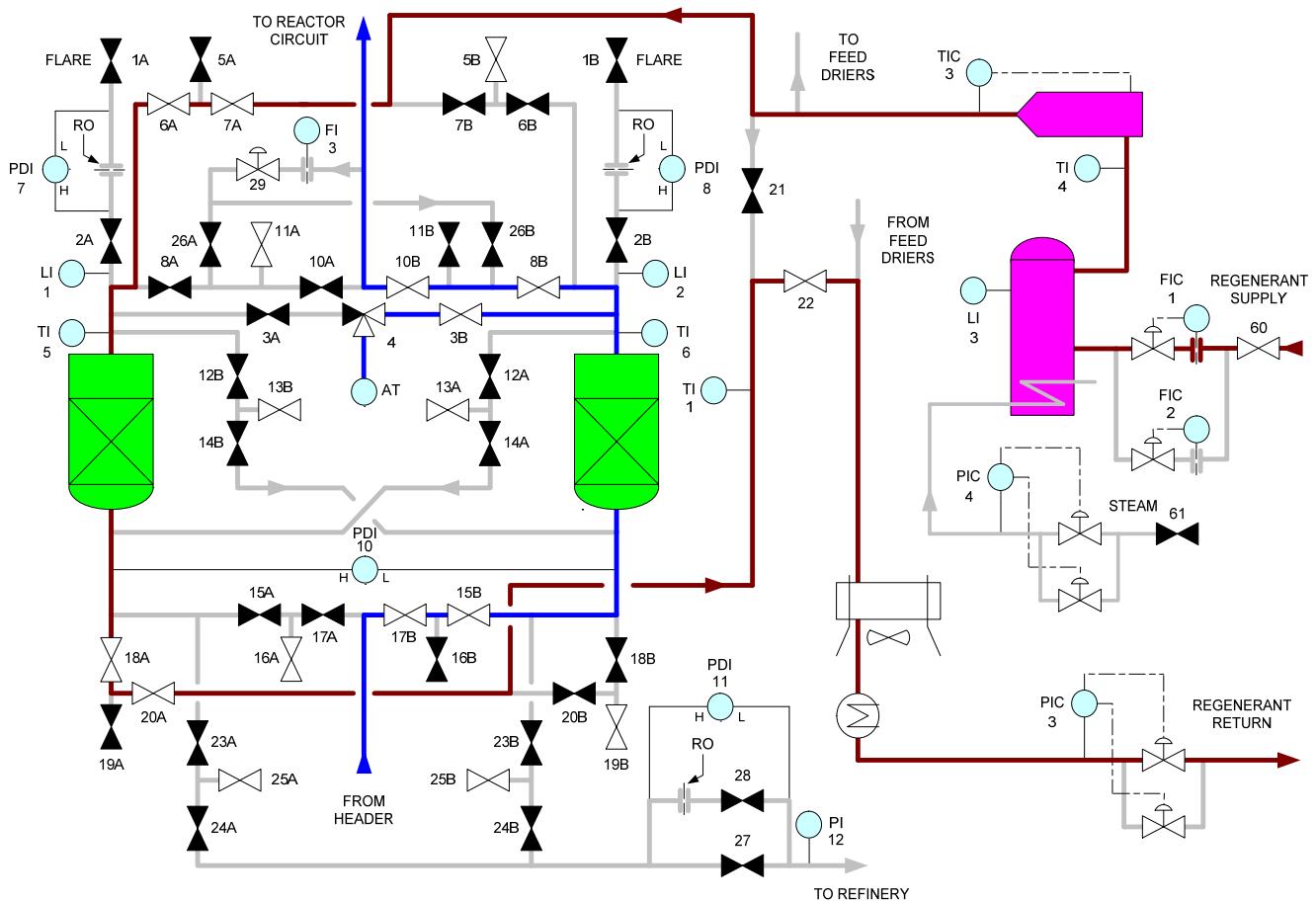
**Figure XIII- 29: Liquid Fill Drier A**

## VI. Line-up Regenerator Flow Downflow

When Drier “A” is confirmed liquid-full, close the depressurization valves to flare (1A and 2A).

Open the regenerator inlet valves to the Drier “A” (6A and 7A after closing the bleed valve in between the regenerator inlet valves (5A)).

Close the regenerator liquid filling valve (21) to direct the flow of regenerator downflow through the drier.

**Figure XIII- 30: Line-up Regenerator Flow Downflow**

## VII. Start Regenerant flow

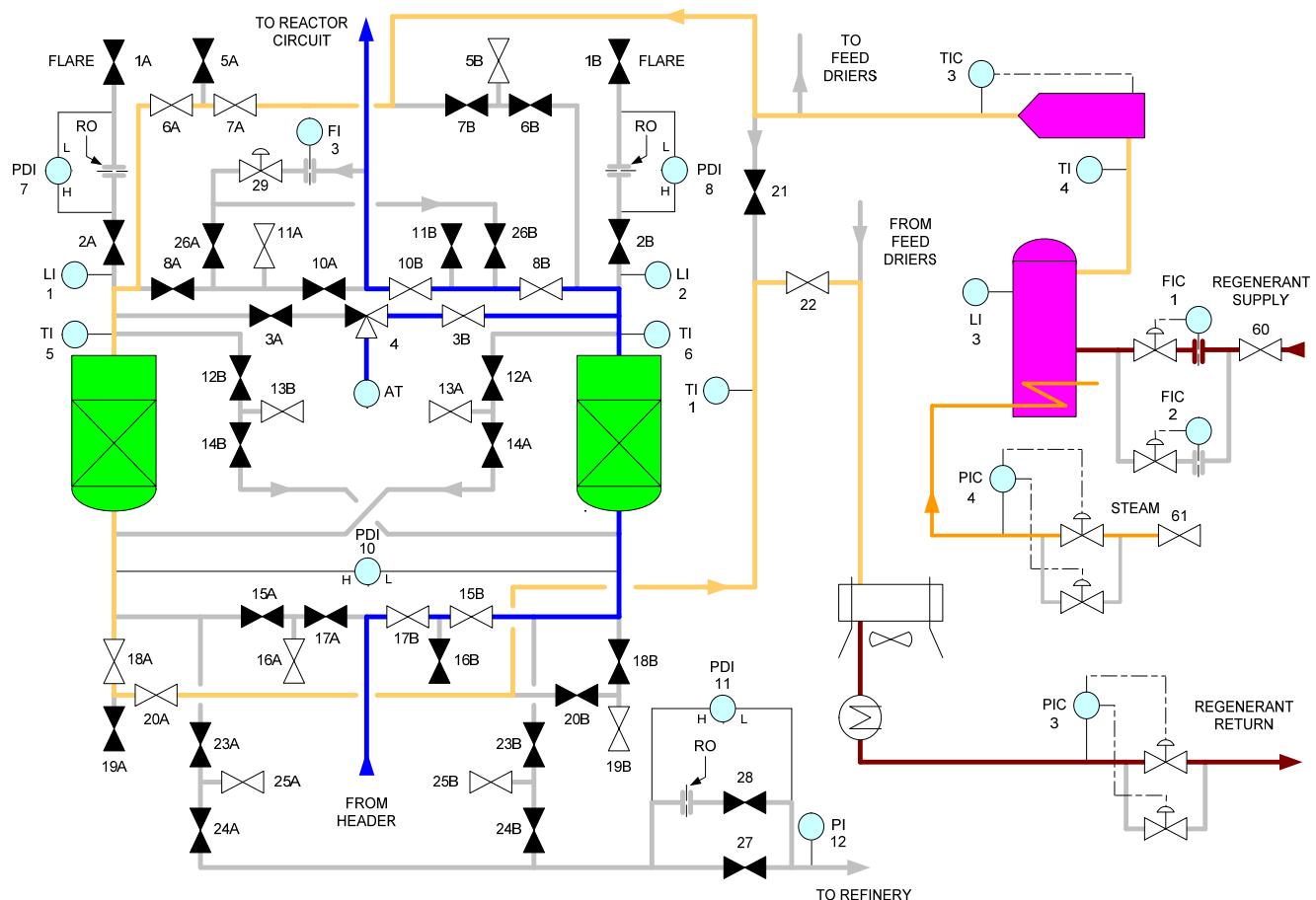
Establish the design regenerant flowrate to drier via the regenerant flow controller (FIC-1). Regenerant condenser and pressure controller (PIC-3) should also be commissioned at this time.

## VIII. Increase the Regenerant Temperature

Commission steam to the regenerant Vaporizer and establish a level in the Vaporizer. At this point, there will be saturated vapors flowing to Drier "A", displacing the liquid through the regenerant condenser and out to storage.

After a stable low level has been maintained in the Vaporizer, the Regenerant Superheater can be commissioned. Superheater outlet temperature can be increased to 315°C (600°F) at a rate of 70°C (125°F) per hour.

Figure XIII-31 shows the valve positions at the end of this step.

**Figure XIII- 31: Regenerator Heatup Stage**

## IX. Hot Soak the Drier Sieve

Monitor the outlet temperature of the Makeup Gas Drier "A". As the water is driven off the molecular sieve, the drier outlet temperature will gradually increase. When the temperature at the drier outlet reaches 288°C (550°F), hold for a minimum of two hours.

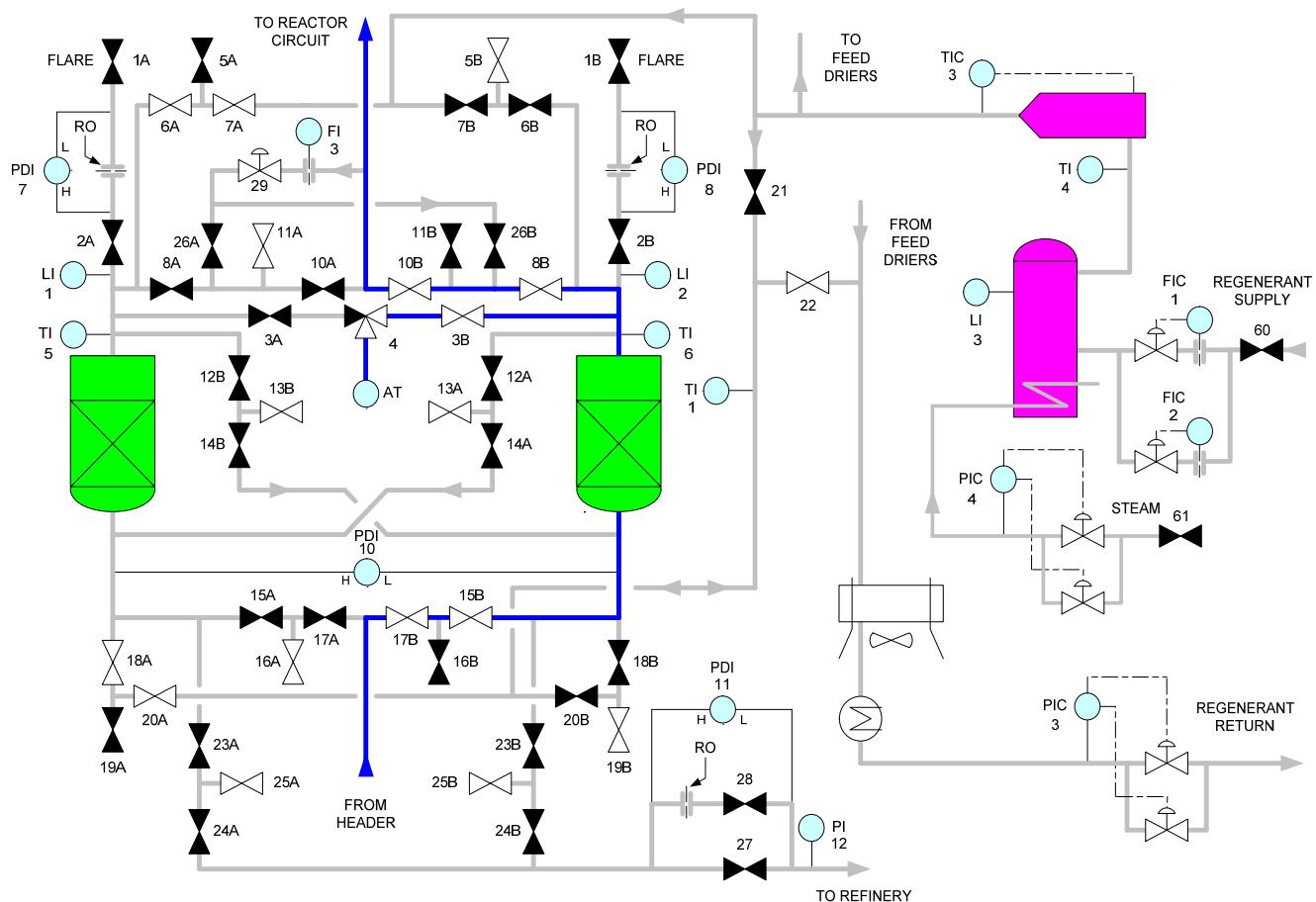
## X. Reduce the Drier temperature

At the end of the two-hour hold period, reduce the Regenerator Superheater outlet temperature to 150°C (350°F) at the rate of 70°C (125°F) per hour and shut down the Superheater. Continue cooling with vapors until the drier outlet temperature reaches 175°C (350°F).

## XI. Stop Regenerator Flow to Drier

Discontinue steam flow to the Vaporizer and stop regenerator flow to Drier "A" by closing valve 60 and 61. Block in the regenerator FIC (refer to Figure XIII-32)

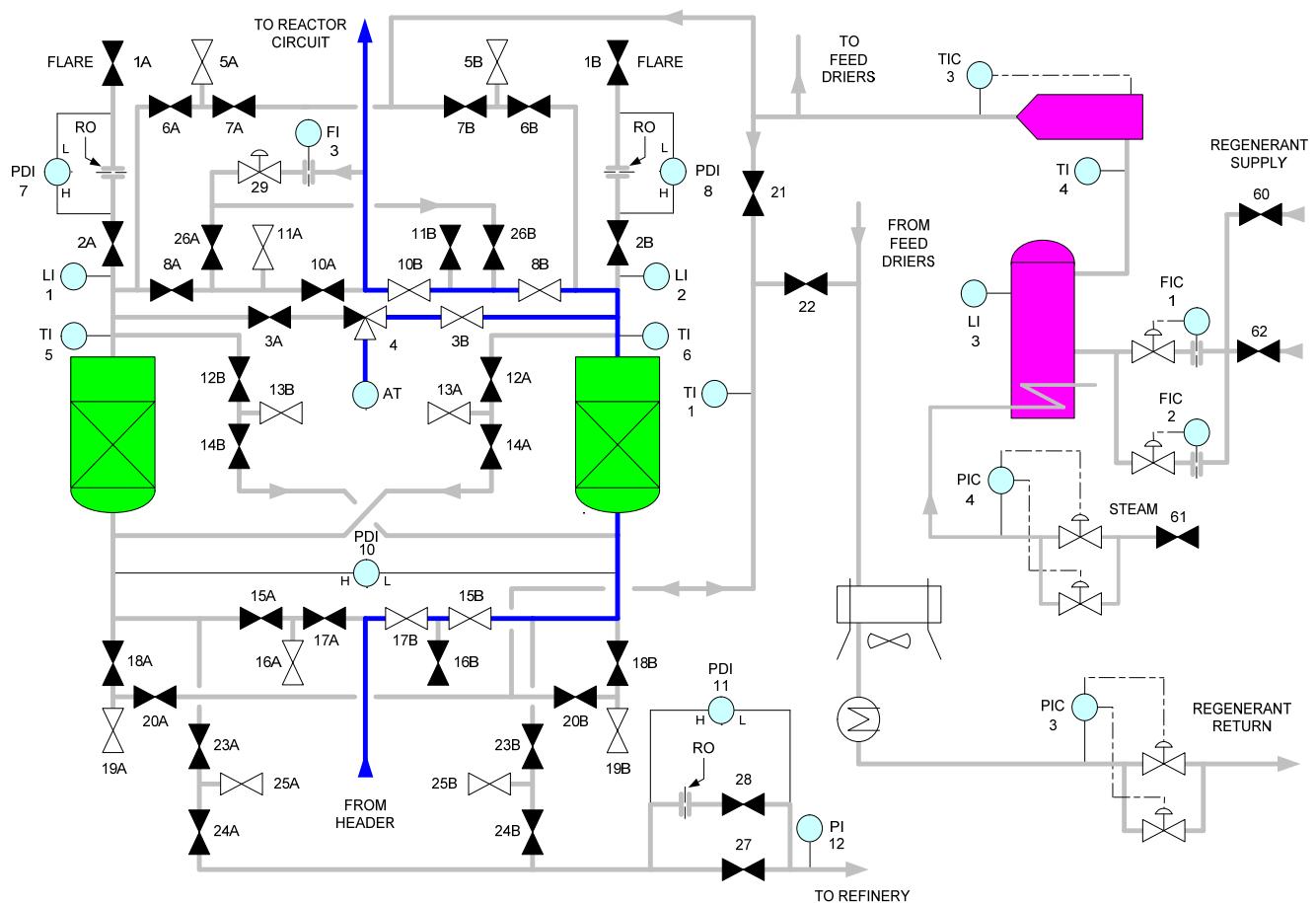
**Figure XIII- 32: Stop Regenerant Flow**



## XII. Isolate Makeup Gas Drier "A"

Isolate Drier "A" from the regeneration section. Close the regenerant inlet valves to Drier "A", 6A and 7A. Open the bleed valve (5A) in between the regenerator inlet valves to Drier "A". Close Drier "A" regenerator outlet valves, 18A and 20A; Open the bleed valve (19A) in between. Close the valve on regenerator return line, valve 22. Regenerator condenser can be taken out of service at this time.

**Figure XIII- 33: Isolate Makeup Gas Drier "A"**



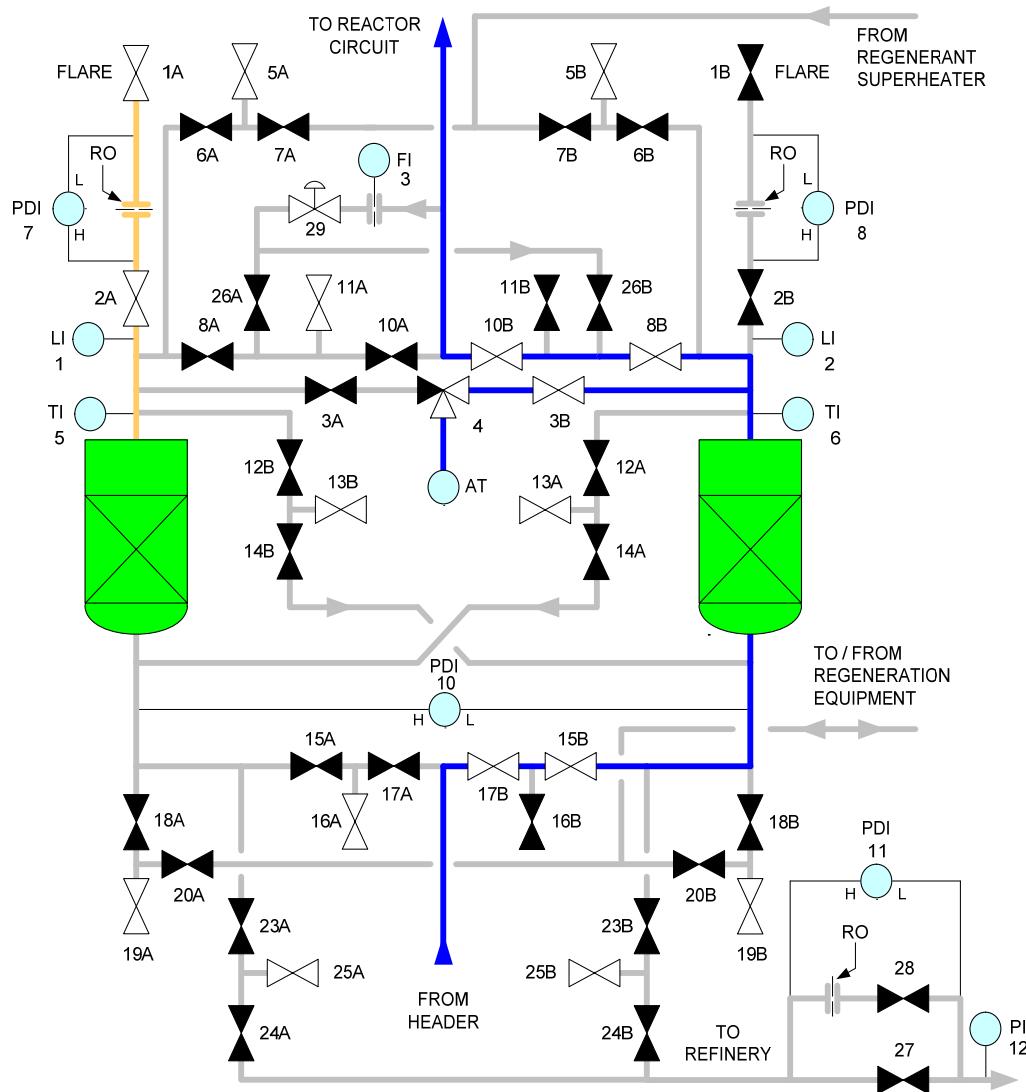
If desired, regenerant can be displaced from the freshly regenerated drier to minimize process upsets to the unit. After this step, there are three options to proceed in the regeneration process, they are as follows:

1. Regenerator is removed from the drier by depressurizing to flare. For this option proceed to step XIII.
2. Regenerator is displaced from the Drier downflow to alternate location. For this option proceed to step XV.
3. Drier is placed online after the regeneration without removing regenerant. For this option proceed to Step XIV.

### **XIII. Depressure Regenerator from Drier “A” to Flare (option 1)**

If desired, the regenerant, still in vapor phase, can be vented from the regenerated Drier “A” to flare via the depressurizing valves located at the top of the drier. Open the drier depressurizing valves to flare, 2A and 1A. Valve positions at this stage are indicated in the figure below.

**Figure XIII- 34: Depressure Regenerator from Drier A to Flare**

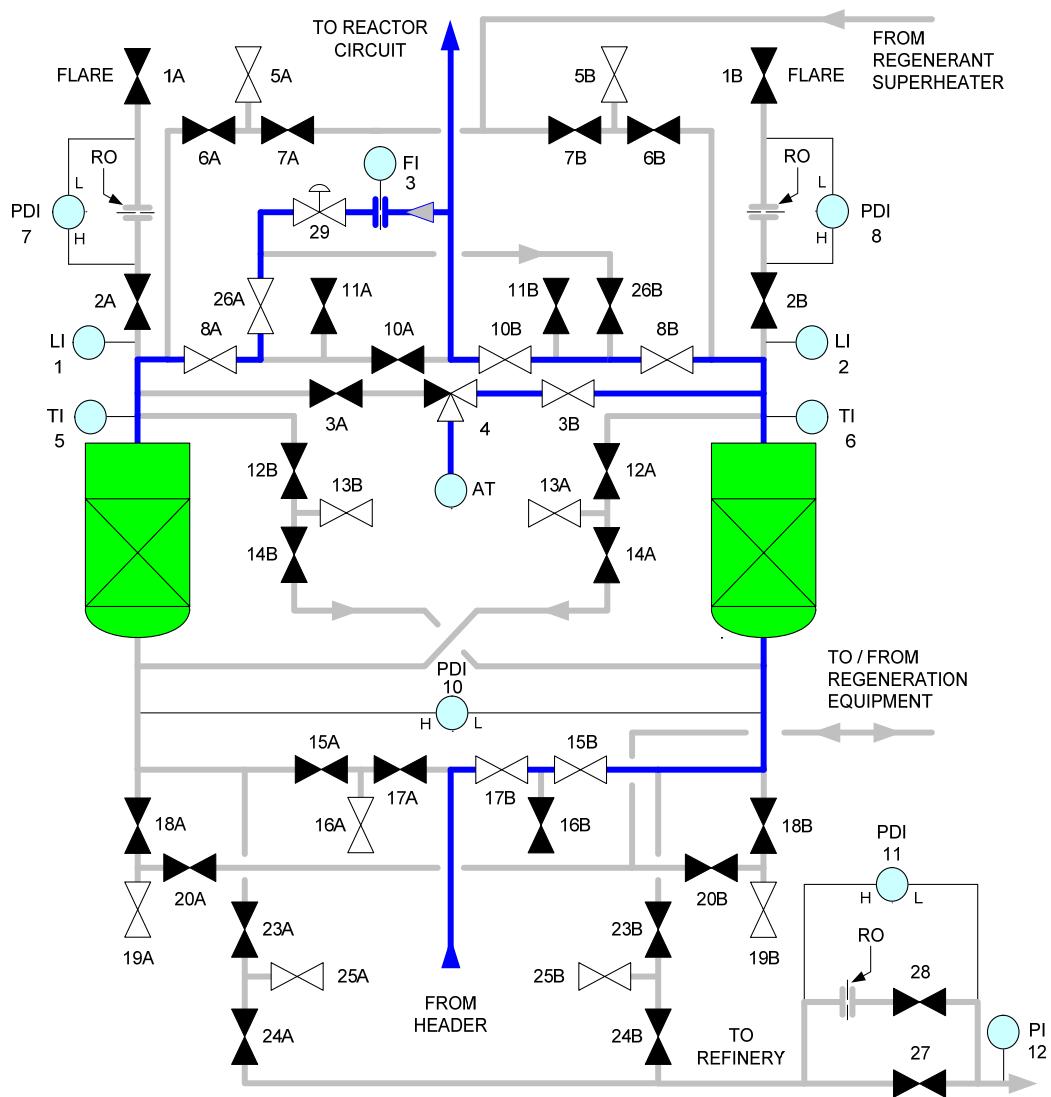


When the PDI at the top of the drier (PDI-7) indicates that the drier has been depressurized to an acceptable value, close the valves 2A and 1A and thus isolate the Drier from flare. This step can be repeated, if necessary. Otherwise proceed to (final pressure up 1) step XIV.

#### XIV. Final pressure up 1 (option 3)

Close Drier "A" Process outlet bleed valve 11A. Open Drier "A" process outlet valve 8A and pressure up/regenerator displacement valve 26A. Flow control valve 29 can be used to pressurize the off line Drier "A" (refer to Figure XIII-35).

**Figure XIII- 35: Final Pressure-up 1**



Once this step is complete proceed to Step XIX for final pressure up 2.

## XV. Regenerator Depressure 1 (option 2)

Close Makeup gas Drier "A" regenerator displacement/ lower depressuring bleed valve 25A. Open the equalization valves 23A and 24A on the regenerator displacement/lower depressuring line.

If the pressure difference as indicated by PDI-11 is at an acceptable value, then proceed to step XVI (intermediate pressure up stage).

If the differential pressure indication is at an acceptable value, then proceed to step XVII for Regenerator depressure 2.

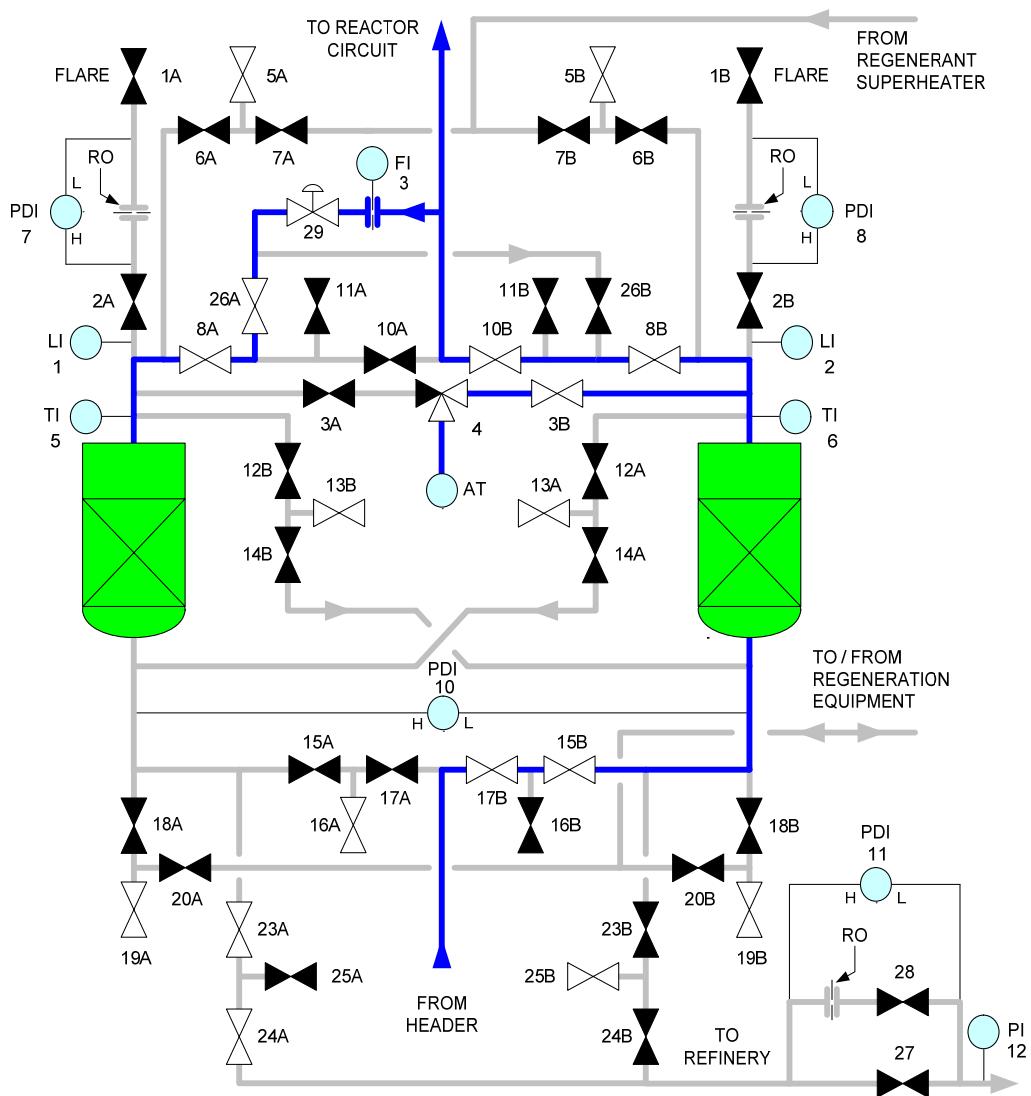
## XVI. Intermediate pressure up

In preparation of intermediate pressure up of Drier A, Close the Makeup gas Drier "A" process outlet bleeder valve 11A.

Open the Makeup Gas Drier "A" process outlet valve (8A) and pressure up/regenerator displacement valve (26A).

Flow control valve 29 is used for controlled pressurization of the offline Drier "A".

Figure XIII-36 shows the position of valves at this stage.

**Figure XIII- 36: Intermediate Pressure-up 1**

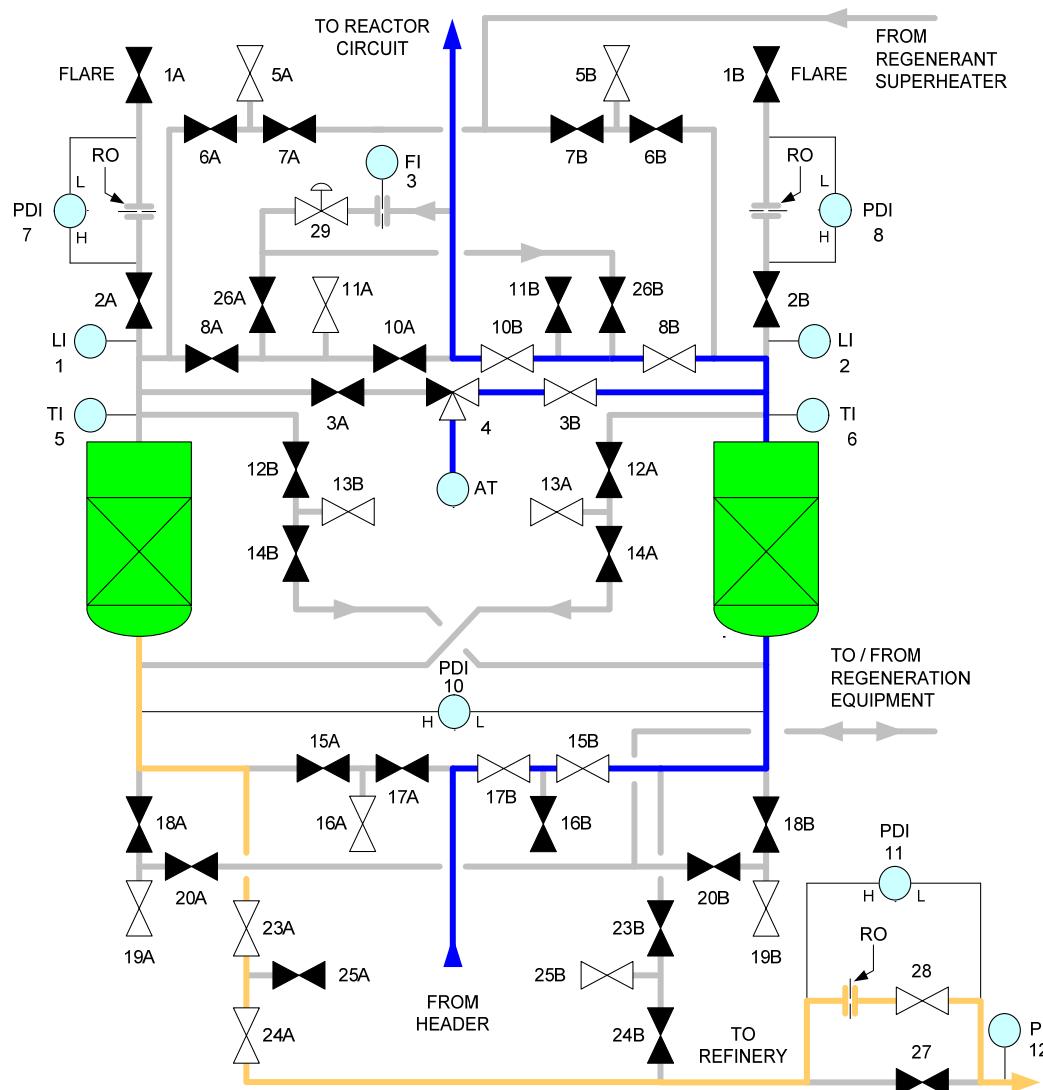
In preparation of regenerant depressurize 2, close Drier "A" process outlet valve 8A and pressurization/regenerator displacement valve 26A. Open Drier "A" process outlet bleed valve 11A.

## XVII. Regenerator Depressure 2

After confirming that the pressure difference as indicated by PDI-11 is at an acceptable value and Drier "A" is isolated from the process, Drier "A" can be depressurized. Open the lower depressurization valve (28) to depressurize Drier "A" (in a controlled manner).

Refer to the figure XII-37 for valve positions at this stage.

**Figure XIII- 37: Regenerator Depressure 2**

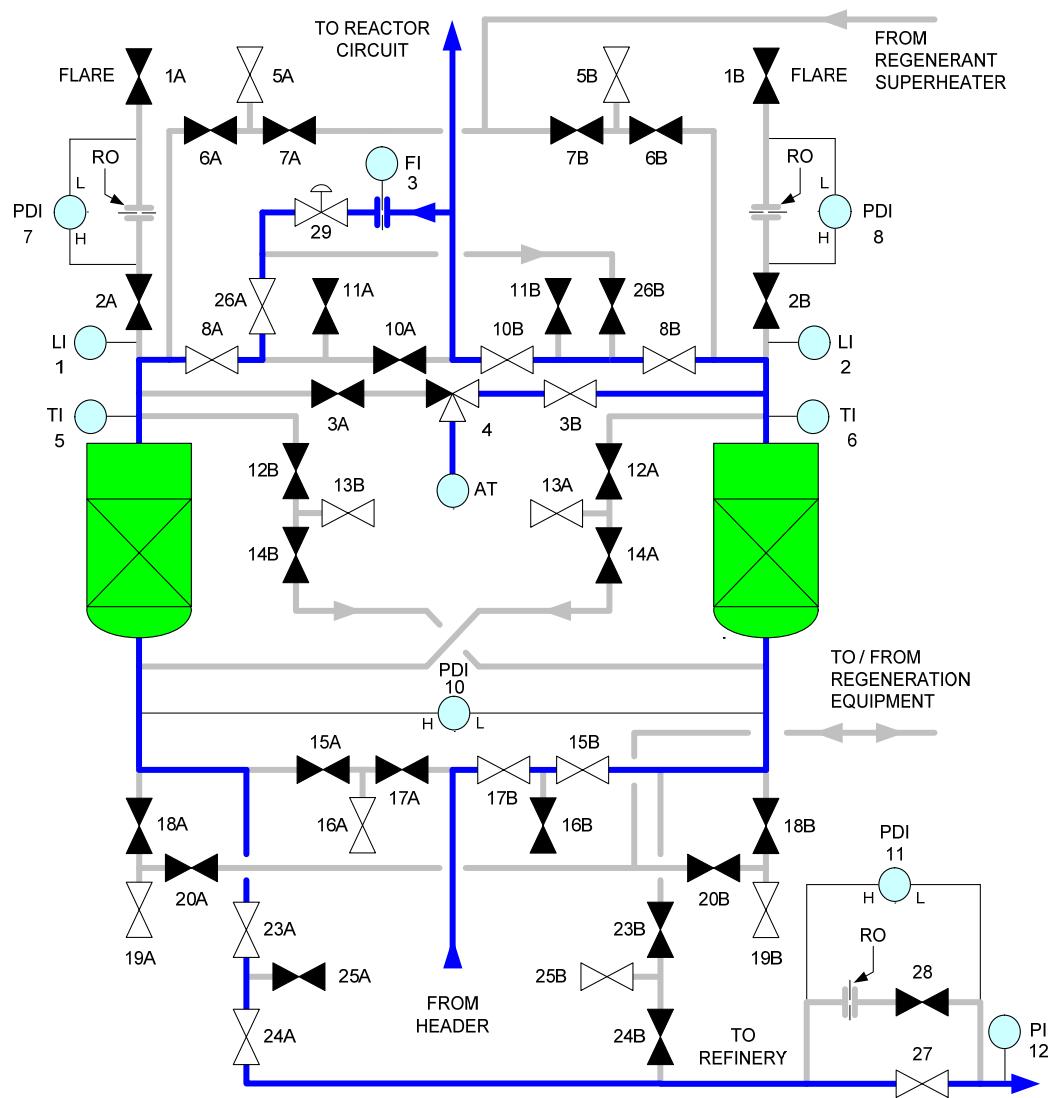


## XVIII. Regenerator Displacement stage

In order to displace the regenerator from Drier “A”, Open regenerator displacement valve (27) and close the lower depressurization valve (28).

Close Drier “A” process outlet bleed valve 11A.

Open Drier “A” process outlet valve 8A and Drier “A” pressurization valve/regenerator displacement valve 26A. FI-3 can be used to calculate the actual volumetric flow of displacement gas through Drier “A”. The regenerator can be displaced until the total regenerator flow is greater than the regenerator displacement target volume of Drier “A”. Valve positions at this stage are shown in the Figure XII-38.

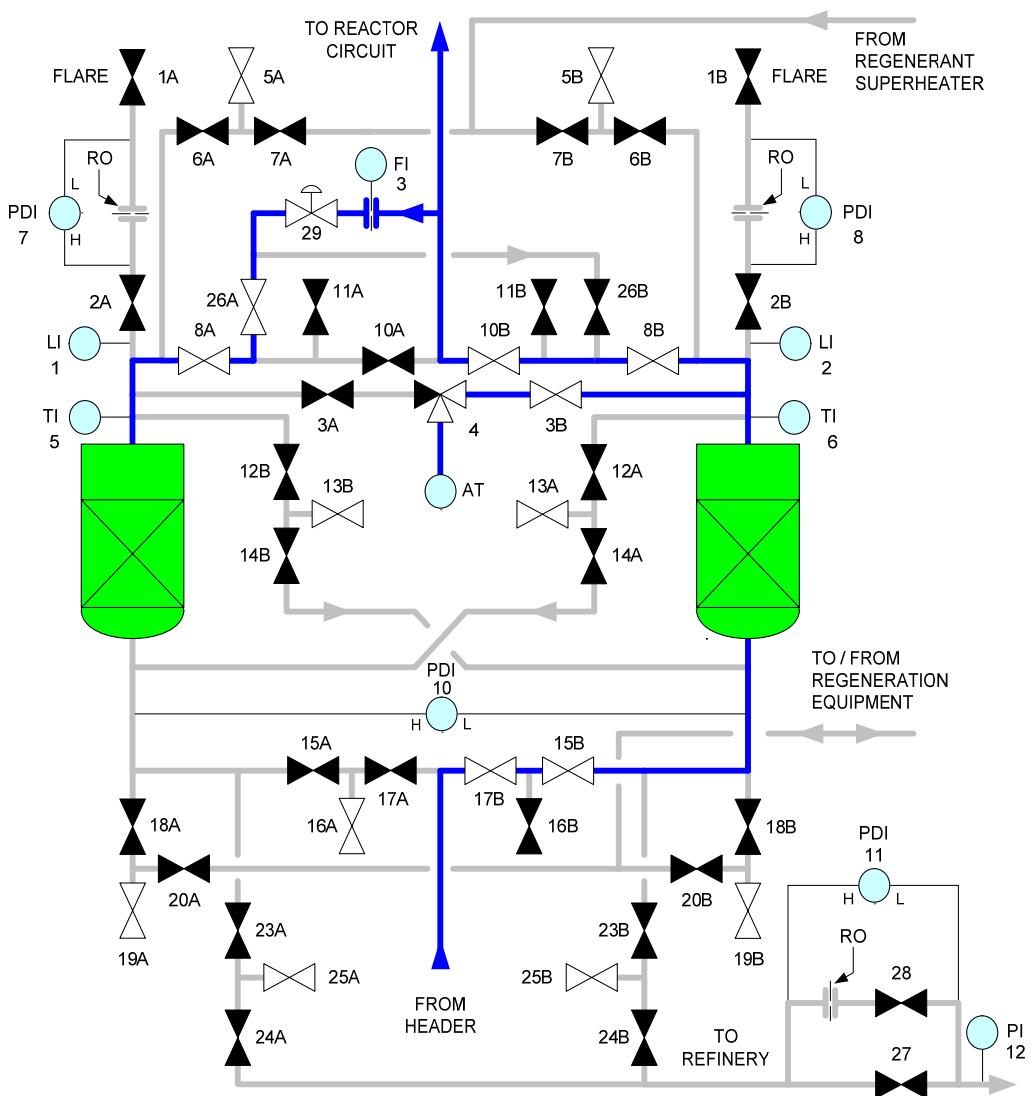
**Figure XIII- 38: Drier A Regenerator Displacement**

Once the regenerator displacement stage is complete, close the regenerator displacement valve (27) and the lower depressurization/regenerator displacement valve (23A and 24A). Open the associated bleed valve, 25A.

## XIX. Final Pressure Up 2

Close the bleed valve of crossover line from Drier B to Drier A (13A). Adjust opening of flow control valve 29 and pressurize Drier "A".

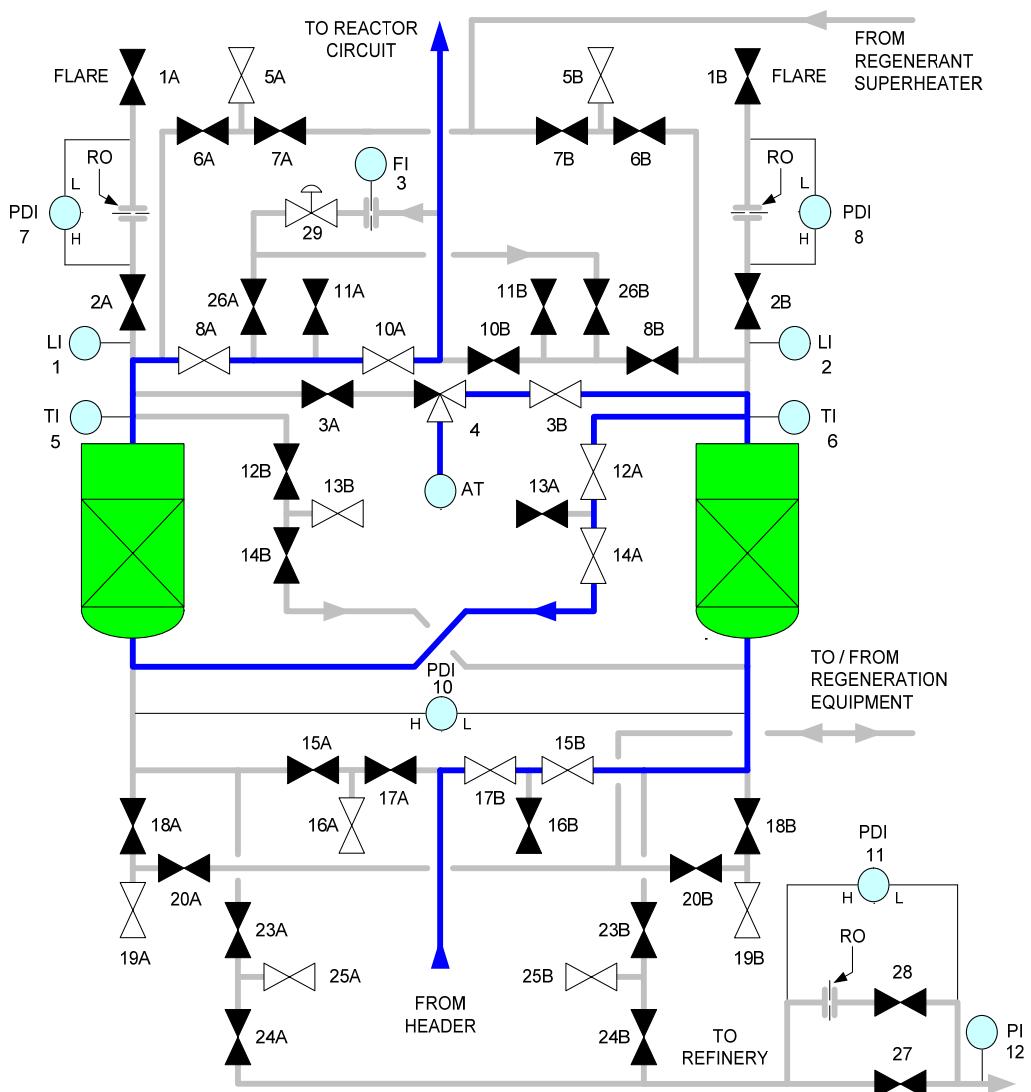
**Figure XIII- 39: Final Pressure up 2**



## XX. Lag Line up

Open Makeup gas Drier B-to-A crossover valves (12A and 14A) and Makeup Gas Drier outlet valve 8A and 10A. Verify that flow control valve at the pressurization/regenerator displacement valve 29 is close with zero percent output. Close the pressurization/regenerator displacement valve, 26A.

Close the Makeup Gas Drier process outlet valve 8B and 10B to direct the Makeup gas flow from Drier B-to-A, thus placing the freshly regenerated Drier (Drier "A") in lag position. Valve positions at this stage are indicated in Figure XIII-40.

**Figure XIII- 40: Drier A Lag Line up**

## XIV. SAFETY

This section on safety includes the following sections:

- I. OSHA Hazard Communication Standard
- II. Potential Hydrocarbon and Chemical Health Hazards

The information and recommendations contained in this manual have been compiled from sources believed to be reliable and to represent the best opinion on the subject as of 1989. However, no warranty, guarantee or representation, expressed or implied, is made by UOP as to the correctness or sufficiency of this information or to the results to be obtained from the use thereof. Each refiner should determine the suitability of the following material for his purposes before adopting them.

Since the use of UOP products by others is beyond UOP control, no guarantee, expressed or implied, is made and no responsibility assumed for the use of this material or the results obtained therefrom. Moreover, the recommendations contained in this manual are not to be construed as a license to operate under, or a requirement to infringe, any existing patents, nor should they be confused with state, municipal or insurance requirements, or with national safety codes.

### I. OSHA Hazard Communication Standard

All references to environmental, occupational safety and material transport laws are based on U.S.A. federal, state and local laws which are applicable only within the U.S.A. and its territories. It cannot be assumed that all necessary warnings and precautionary measures are contained in this manual, or that any additional warning and or measures may not be required or desirable because of particular exceptional conditions or circumstances, or because of applicable federal, state or local law.

As of May 25, 1986, all U.S. employers covered under the Specific Industrial Classification (SIC) Codes 20-39 must be in compliance with the Occupational Safety and Health Standard, Subpart Z - Toxic and Hazardous Substances Hazard Communications, Section 1910.1200 of the Federal Regulations. This standard is commonly referred to as the "Right-to-Know Law."

The OSHA standard is a U.S. Federal regulation requiring chemical manufacturers, importers and distributors to evaluate the hazards of their chemical products and convey hazard information through labels and material safety data sheets to its employees and customers which fall within SIC Codes 20-39. The customers in turn must pass the hazard information on to its employees and contractors which come on the premises. In this context, UOP employees who are working in or visiting a refinery are considered contractors to the refiner. It is the responsibility of the U.S. refiners to inform all contractors of the hazardous chemicals the contractor's employees may be exposed to while performing their work, and any suggestions for appropriate protection measures. It is then the responsibility of UOP to provide the information to its employees about the hazardous chemicals to which they could be exposed by means of 1) a written hazard communications program, 2) training and information, 3) labels and other forms of warning, and 4) material safety data sheets.

## A. WRITTEN HAZARD COMMUNICATIONS PROGRAM

The OSHA standard requires that U.S. employers make available to its employees the company's written Hazard Communication Program. This document is intended to describe how the company will implement the OSHA standard. The program explains the company's labeling system, material safety data sheets (MSDS), and employee information and training. The latter includes a listing of hazardous chemicals known to be present in the work place, and methods the company will use to inform its employees and contractors of the hazardous chemicals.

## B. TRAINING AND INFORMATION

All employees should receive classroom training in compliance with the OSHA standard. This includes an overview of the standard, an explanation on how to interpret and use the information on a MSDS, the location and availability of file of MSDS's, labeling requirements and their meaning, and an introduction to toxicology.

The OSHA standard states that contractors performing work in these refineries are required to train their people before they enter the refinery. However, it is the responsibility of U.S. refiners to inform contractors of the specific hazardous chemicals to which contractors' employees may be exposed. The contractor should comply with the OSHA standard by making available to its employees this list of hazardous chemicals and by appraising them of the hazards they will be exposed, relevant symptoms and appropriate emergency treatment and proper conditions and precautions of safe use or exposure.

## C. LABELS AND OTHER FORMS OF WARNING

The OSHA standard states that all portable containers of hazardous chemicals must have a large, readable label or tag which has on it:

1. The name and address of the manufacturer
2. The name of the chemical
3. A numerical hazard warning or other appropriate warnings supplied by the manufacturer.

For the latter, the National Fire Protection Association (NFPA) Diamond is commonly used. An explanation of the NFPA Diamond may be found in Figure XIV-1 and Table XIV-1.

Labels can also be color coded according to the following:

Orange	Carcinogen Hazard (i.e.: Benzene)
Red	Chemical Burn Hazard (i.e.: Acids, Bases)
Yellow	Toxic Vapor Hazard (i.e.: H <sub>2</sub> S)
White	All Others

An example of the information which can be found on a warning label may be found in Figure XIV-2.

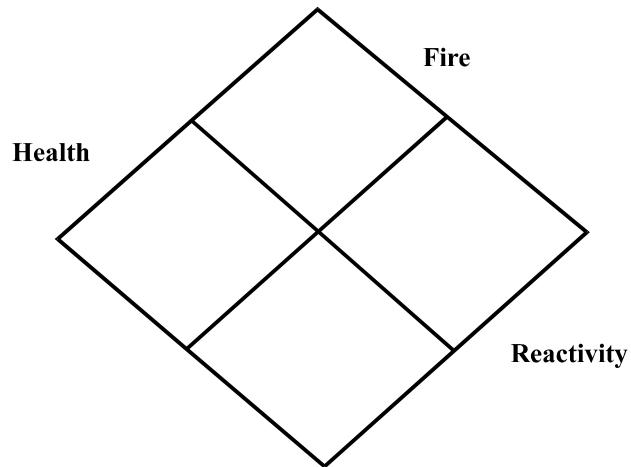
Contractor employees must label all containers of hazardous materials which they bring into the refinery. This applies to UOP employees who are visiting or working in refineries.

#### D. MATERIAL SAFETY DATA SHEET (MSDS)

The MSDS requirement falls primarily on chemical manufacturer, importers and distributors. The OSHA standard requires them to develop and provide a MSDS for each hazardous chemical they produce or handle. These manufacturers, importers and distributors are required to provide the MSDS to the purchasers of the hazardous chemical.

**Figure XIV-1**

**NFPA 704 Diamond**



**CAUTION: CONTAINS HAZARDOUS CHEMICAL**  
Transportation Emergencies . . . Call  
Health Emergencies . . . . .

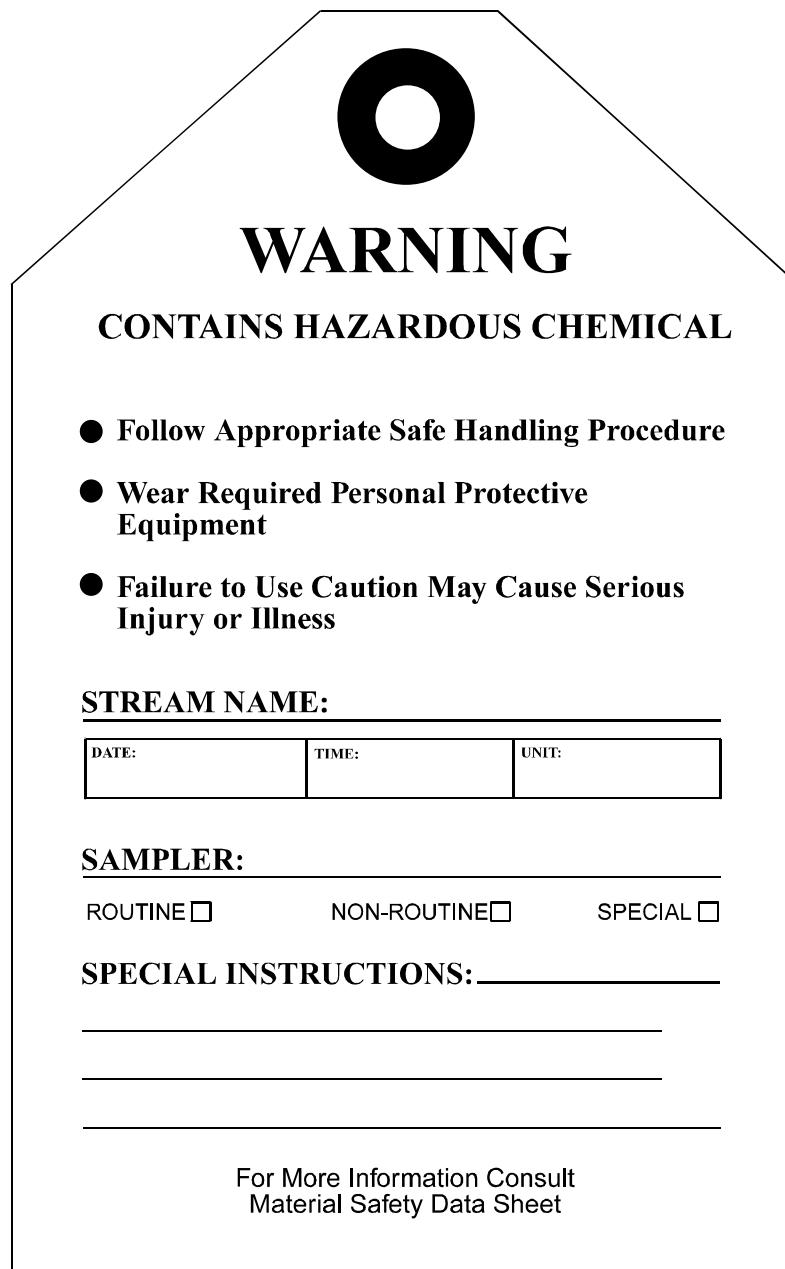
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**HAZARD RANKING**

- 0 = Least**
- 1 = Slight**
- 2 = Moderate**
- 3 = High**
- 4 = Extreme**

PLT-R00-99

**Figure XIV-2**



**WARNING**

**CONTAINS HAZARDOUS CHEMICAL**

- Follow Appropriate Safe Handling Procedure
- Wear Required Personal Protective Equipment
- Failure to Use Caution May Cause Serious Injury or Illness

**STREAM NAME:** \_\_\_\_\_

DATE:	TIME:	UNIT:
-------	-------	-------

**SAMPLER:** \_\_\_\_\_

ROUTINE  NON-ROUTINE  SPECIAL

**SPECIAL INSTRUCTIONS:** \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

For More Information Consult  
Material Safety Data Sheet

**TABLE XIV-1****National Fire Protection Association  
Identification of Color Coding**

<b>Color Blue:</b>	<b>Type of Possible Injury</b>
Signal 4:	Materials which on very short exposure could cause death or major residual injury even though prompt medical treatment was given.
Signal 3:	Materials which on short exposure could cause serious temporary or residual injury even though prompt medical treatment was given.
Signal 2:	Materials which on intense or continued exposure could cause temporary incapacitation or possible residual injury unless prompt medical treatment is given.
Signal 1:	Materials which on exposure would cause irritation but only minor residual injury even if no treatment is given.
Signal 0:	Materials which on exposure under fire conditions would offer no hazard beyond those of ordinary combustible materials.
<b>Color Red:</b>	<b>Susceptibility of Materials Burning</b>
Signal 4:	Materials which will rapidly or completely vaporize at atmospheric pressure and normal ambient temperature, or which are readily dispersed in air and which will burn readily.
Signal 3:	Liquid and solids that can be ignited under almost all ambient temperature conditions.
Signal 2:	Materials that must be moderately heated or exposed to relatively high ambient temperatures before ignition can occur.
Signal 1:	Materials that must be preheated before ignition can occur.
Signal 0:	Materials that will not burn.

**TABLE XIV-1  
(continued)****National Fire Protection Association  
Identification of Color Coding****Color Yellow: Susceptibility of Release of Energy**

- Signal 4: Materials which in themselves are readily capable of detonation or of explosive decomposition or reaction at normal temperature and pressure.
- Signal 3: Materials which in themselves are capable of detonation or explosive reaction but require a strong initiating source or which must be heated under confinement before initiation or which react explosively with water.
- Signal 2: Materials which in themselves are normally unstable and readily undergo violent chemical change but do not detonate. Also materials which may react violently with water or which may form potentially explosive mixtures with water.
- Signal 1: Materials which in themselves are normally stable, but which can become unstable at elevated temperatures and pressures or which may react with water with some release of energy but not violently.
- Signal 0: Materials which in themselves are normally stable, even under fire exposure conditions and which are not reactive with water.

Although the format of the MSDS can vary, they should all include the following information:

- Chemical and common name
- Ingredient information
- Physical and chemical characteristics
- Physical hazards - Potential for reactivity, fire and/or explosion
- Health hazards
- Symptoms of exposure
- Primary route of likely entry into the body upon exposure
- OSHA permissible exposure levels
- Precaution for use
- Waste disposal
- Protective measures and equipment, including during spills and maintenance
- Emergency and first-aid procedures
- Date of MSDS preparation and last revision
- Emergency contact of manufacturer or distributor

The OSHA standard requires that the manufacturer or distributor provide quick and easy access to all MSDS's applicable to their work place.

At the end of this Section XIV on Safety are typical MSDS for some chemicals normally used in the Penex process. These are not meant to replace those which must be supplied by the U.S. refiners nor is this meant to suggest that this is a complete list of the hazardous chemicals which can be found in and around the unit. Some of the information on these typical MSDS may be out of date.

## II. Potential Hydrocarbon and Chemical Health Hazards

There are no hazards associated with the hydrocarbons and chemicals used in the Penex Unit when the unit is maintained and operated in the proper manner. It is during periods of opening equipment, transferring chemicals and sampling that particular care must be exercised.

The following hydrocarbons and chemicals are used in the Penex Unit:

- A. **BENZENE** - Benzene is present in the Penex Unit feedstock. Benzene is a toxic hydrocarbon with a 10 ppm, TLV-TWA (Threshold Limit Value - Time Weighted Average). Exposure to benzene should be minimized by following the guidelines given in Section J of this section of the manual.
- B. **CAUSTIC** - Caustic soda (NaOH) solution is used in the stabilizer off gas scrubber. Persons handling caustic should have rubber gloves and goggles. When liquid caustic is handled in open containers or drains, additional protective rubber or vinyl clothing should be worn. If caustic comes in contact with the skin, it should be washed off with H<sub>2</sub>O immediately. Initially the skin feels soapy at all concentrations. Contact with caustic soda solutions produces severe burns and destruction of skin tissue. The eyes are particularly vulnerable. Caustic soda is poisonous.
- C. **CARBON TETRACHLORIDE** - This chemical (CCl<sub>4</sub>) may be used as a catalyst promoter. Carbon tetrachloride is a highly toxic chemical with a 10 ppm, 8 hr TLV-TWA (Threshold Limit Value-Time Weighted Average). For further documentation on the hazards of CCl<sub>4</sub>, reference should be made to the following subdivision of this sections which references other sources of information.
- D. **PERCHLOROETHYLENE** - This chemical (C<sub>2</sub>Cl<sub>4</sub>) may be used as a catalyst promoter. It is harmful by inhalation and ingestion. Perchloroethane has a 50 ppm, 8 hour TLV-TWA limit for exposure. Consult current Material Safety Data Sheets from suppliers before working with this chemical.

- E. **NITROGEN** - Nitrogen is non-toxic - 79% of the normal air we breathe is nitrogen. However, in vessels or areas where there is a high concentration of nitrogen, there is a deficiency of oxygen for breathing. Breathing an atmosphere deficient in oxygen will rapidly result in dizziness, unconsciousness or death, depending on the time of exposure. Do not enter or even stick your head into a vessel containing a high concentration of nitrogen and, therefore, deficient in oxygen. Do not stand close to bleeders where nitrogen is being bled out of equipment at a high rate which might temporarily cause a deficiency in oxygen close to the bleeder.
- F. **HYDROGEN** - Hydrogen is a colorless, odorless gas. It is highly flammable and forms explosive mixtures in virtually all proportions with air. Leaks from pressure equipment may be self igniting.
- G. **HYDROGEN SULFIDE** - Hydrogen Sulfide can be present in the Penex Unit feed in small quantities. H<sub>2</sub>S can also be found in the fuel gas system. H<sub>2</sub>S is an irritant and a poisonous gas which is dangerous at very low concentrations. The 8 hour TLV value is 10 ppm. H<sub>2</sub>S is discussed in more detail in Section K of this section of the manual.
- H. **HYDROCARBONS** - The hydrocarbons that are processed and evolve from this process are only mildly toxic. Avoid breathing the hydrocarbon vapors and if the clothing becomes wet with the hydrocarbons, immediately remove the clothing, wash the affected area and put on fresh clothing.
- I. **CATALYST** - A separate attachment discussing the Penex catalyst follows at the end of this section.
- J. **HYDROCHLORIC ACID** - HCl is used during the early phase of the unit's start up and is also a product of the decomposition of CCl<sub>4</sub> in the reactor system.

Hydrogen chloride, both as a gas and in solution as hydrochloric acid, is a corrosive substance and can cause severe and painful burns on contact with any part of the body or if taken internally. The mucous membranes of the eyes and the upper respiratory tract are especially susceptible to the irritating effects of high atmospheric concentrations of hydrogen chloride.

## K. BENZENE SAFETY

Benzene is present in the Penex process feedstock. Benzene is extremely toxic. A summary of health effects which can occur from exposure to benzene appear in "Documentation of the Threshold Limit Values (Benzene), 4th edition, 1980, ACGIH."

**Special Instruction:** If clothing (including gloves, shoes) becomes contaminated with benzene, the clothing should be removed immediately. Wash any skin areas exposed to benzene with soap and water. Take a complete bath if the body area is wetted with benzene. Do not wear clothing that has been wet with benzene until the garment has been decontaminated by washing or dry cleaning. Wearing clothing that has been wet with benzene almost assures that the person will inhale benzene vapors over a long period of time, resulting in potential health hazards.

Avoid draining benzene to the concrete or into the sewers where it can vaporize and create a health hazard. If benzene is accidentally spilled, flush it from the concrete and sewer catch basin with large quantities of cold water. Do not use hot water or steam which aggravates the vaporization of benzene. If you must enter an area of high benzene vapor concentration resulting from a spill, wear appropriate respiratory protection, such as self-contained breathing apparatus or an air mask with external supply.

A large benzene spill may result in a health hazard from benzene vapor at the separator. The separator must be skimmed as completely as possible and all slop pumped out of the sump to the refinery recycle system.

Though not specifically a health hazard, an environmental problem can result from benzene entering the sewer, since benzene is much more soluble in water than any other hydrocarbon. This places an extra load on the effluent treating system.

### **Minimizing Exposure to Benzene**

Operating and laboratory personnel involved in obtaining samples should wear chemical-type safety goggles or shield, protective apron or laboratory coat, solvent-resistant gloves, and approved respiratory protective equipment where ambient concentrations exceed allowable limits. This protective equipment is not, however, a substitute for safe working conditions, proper ventilation, good personal practices, and proper maintenance of both operating and safety equipment. In all cases, skin contact (especially eyes) and inhalation must be minimized.

Sampling liquid hydrocarbons always requires some care to limit personal exposure and release to the atmosphere. Even greater care is needed when the liquid to be sampled contains aromatic hydrocarbons, especially benzene. UOP's current design calls for flow-through sampling points which utilize closed sample containers whenever aromatics are present.

In order to minimize vaporization, hot hydrocarbon streams must be routed through a cooler before drawing a sample. In all sampling situations, the personnel involved should be instructed to remain at arm's length from the sample container and to situate themselves upwind of the container if at all possible. These simple precautions will greatly minimize exposure to the hydrocarbon vapors.

### **Medical Attention**

The U.S. NIOSH/OSHA Guidelines attached for benzene set forth recommendations for medical monitoring of personnel working in environments where exposure to these materials can occur. UOP recommends that the NIOSH/OSHA guidelines for medical monitoring be considered in development and implementation of an occupational health monitoring program for employees who may be exposed to benzene.

OSHA has recommended the following medical monitoring for employees who may be exposed to benzene:

Preplacement and quarterly examinations, including a history which includes past work exposures to benzene or any other hematologic toxins, a family history of hematological neoplasms, a history of blood dyscrasias, bleeding abnormalities, abnormal function of formed blood elements, a history of renal or liver dysfunction, a history of drugs routinely taken, alcoholic intake and systemic infections; complete blood count including a differential white blood cell count; and additional tests, where, in the opinion of the examining physician, alterations in the components of the blood are related to benzene exposure. (42 Federal Register 22516, 1977.)

UOP recommends that these guidelines be considered in development and implementation of an occupational health monitoring program for employees who may be exposed to benzene. All new or current employees should be alerted to the early signs and symptoms resulting from exposure to Benzene, and any workers experiencing such symptoms should seek professional medical attention. In addition to the above, all employees should be advised of the hazards involved and precautions to be taken when working with Benzene.

OSHA has established stringent maximum exposure levels for various chemicals, some of which may be found in UOP catalysts. These exposure limits can be found in the **Code of Federal Regulations**, Title 29, Chapter 17, Subpart Z, Section 1910.1000. This information is also contained in **NIOSH/OSHA Pocket Guide to Chemical Hazards**, DHEW (NIOSH) Publication No. 78-210.

## L. HYDROGEN SULFIDE

The operation of any unit processing gases containing H<sub>2</sub>S remains safe, provided ordinary precautions are taken and the poisonous nature of H<sub>2</sub>S is recognized and understood. No work should be undertaken on the unit where there is danger of breathing H<sub>2</sub>S, and one should never enter or remain in an area containing it without wearing a suitable fresh air mask.

There are two general forms of H<sub>2</sub>S poisoning - acute and subacute. A list of symptoms as they relate to the H<sub>2</sub>S concentration level and exposure time may be found in Figure XIV-3.

## **1. Acute Hydrogen Sulfide Poisoning**

Breathing air or gas containing more than 500 mol-ppm H<sub>2</sub>S can cause acute poisoning and possibly be fatal.

## **2. Symptoms of Acute Hydrogen Sulfide Poisoning**

The symptoms of acute H<sub>2</sub>S poisoning are muscular spasms, irregular breathing, lowered pulse, odor to the breath and nausea. Loss of consciousness and suspension of respiration quickly follow.

Even after the victim recovers, there is still the risk of edema (excess accumulation of fluid) of the lungs which may cause severe illness or death in 8 to 48 hours.

***Figure XIV-3***  
***H<sub>2</sub>S Poisoning***  
***Toxicity of Hydrogen Sulfide to Humans***

H <sub>2</sub> S PPM	0-2 Minutes	2-15 Minutes	15-30 Minutes	30 Min- 1 Hour	1-4 Hours	4-8 Hours	8-48 Hours
50 100				Mild conjunctivitis, respiratory tract irritation.			
100 150		Coughing, irritation of eyes, loss of sense of smell.	Disturbed respiration, pain in eyes, sleepiness.	Throat Irritation.	Salivation and mucous discharge, sharp pain in eyes, coughing.	Increased Symptoms.*	Hemorrhage and death.*
150 200		Loss of sense of smell.	Throat and eye irritation.	Throat and eye irritation.	Difficult breathing, blurred vision, light shy.	Serious irritating effects.	Hemorrhage and death.*
H <sub>2</sub> S PPM	0-2 Minutes	2-15 Minutes	15-30 Minutes	30 Min- 1 Hour	1-4 Hours	4-8 Hours	8-48 Hours
250 350		Irritation of eyes, loss of sense of smell.	Irritation of eyes.	Painful secretion of tears, weariness.	Light shy, nasal catarrh, pain in eyes, difficult breathing; conjunctivitis.	Hemorrhage and death.*	
350 450		Irritation of eyes, loss of sense of smell.	Difficult respiration, coughing, irritation of eyes.	Increased irritation of eyes and nasal tract, dull pain in head, light shy.	Dizziness, weakness, increased irritation, death.	Death.*	
500 600	Coughing, collapse and unconsciousness.*	Respiratory disturbances, irritation of eyes, collapse.*	Serious eye irritation, light shy, palpitation of heart, a few cases of death.*	Severe pain in eyes and head, dizziness, trembling of extremities, great weakness and death.*			
600 700 800	Collapse,* unconsciousness,* Death.	Collapse,* unconsciousness,* Death.					

### Effects of Hydrogen Sulfide Gas

Hydrogen Sulfide (H <sub>2</sub> S)			
	Concentration (PPM)	Time	Effect
Subacute	0.13	Sniff	Odor detectable
	10.0	8 Hours	Threshold limit
	50-100	1 Hour	Mucous membrane irritation
	200-300	1 Hour	Mucous membrane irritation (Severe)
Acute	500-700	1/2 Hour	Coma
	900	Minutes	May be fatal
	1000	Minutes	Fatal

### 3. First Aid Treatment of Acute Hydrogen Sulfide Poisoning

Move the victim at once to fresh air. If breathing has not stopped, keep the victim in fresh air and keep him quiet. If possible, put him to bed. Secure a physician and keep the patient quiet and under close observation for about 48 hours for possible edema of the lungs.

In cases where the victim has become unconscious and breathing has stopped, artificial respiration must be started at once. If a Pulmotor or other mechanical equipment is available, it may be used by a trained person; if not, artificial respiration by mouth-to-mouth resuscitation must be started as soon as possible. Speed in beginning the artificial respiration is essential. Do not give up. Men have been revived after more than four hours of artificial respiration.

If other persons are present, send one of them for a physician. Others should rub the patient's arm and legs and apply hot water bottles, blankets or other sources of warmth to keep him warm.

After the patient is revived, he should be kept quiet and warm, and remain under observation for 48 hours for the appearance of edema of the lungs.

#### **4. Subacute Hydrogen Sulfide Poisoning**

Breathing air or gas containing H<sub>2</sub>S anywhere between 10 to 500 mol-ppm for an hour or more may cause subacute or chronic hydrogen sulfide poisoning.

#### **5. Symptoms of Subacute Poisoning**

The symptoms of subacute H<sub>2</sub>S poisoning are headache, inflammation of the eyes and throat, dizziness, indigestion, excessive saliva, and weariness.

These can be the result of continued exposure to H<sub>2</sub>S in low concentrations. Edema of the lungs may also occur.

## 6. Treatment of Subacute Poisoning

Keep the patient in the dark to reduce eyestrain and have a physician treat the inflamed eyes and throat. Watch for possible edema.

Where subacute poisoning has been suspected, the atmosphere should be checked repeatedly for the presence of H<sub>2</sub>S by such methods as testing by odor, with moist lead acetate paper, and by Tutweiler H<sub>2</sub>S determination to make sure that the condition does not continue.

## 7. Prevention of Hydrogen Sulfide Poisoning

The best method for prevention of H<sub>2</sub>S poisoning is to stay out of areas known or suspected to contain it. The sense of smell is not an infallible guide as to the presence of H<sub>2</sub>S, for although the compound has a distinct and unpleasant odor (rotten egg), it will frequently paralyze the olfactory nerves to the extent that the victim does not realize that he is breathing it. This is particularly true of higher concentrations of the gas.

Fresh air masks or gas masks suitable for use with hydrogen sulfide must be used in all work where exposure is likely to occur. Such masks must be checked frequently to make sure that they are not exhausted. People who must work on or in equipment containing appreciable concentrations of H<sub>2</sub>S, must wear fresh air masks and should work in pairs so that one may effect a rescue or call for help should the other be overcome.

As mentioned above, the atmosphere in which people work should be checked from time to time for appreciable concentrations of H<sub>2</sub>S.

**REMEMBER - JUST BECAUSE YOUR NOSE SAYS IT'S NOT THERE, DOESN'T MEAN THAT IT IS NOT.**

Toxicity and safe handling information on most of the materials used in the Penex Unit can be found in the following list of references. Since these references may be revised periodically by the individual publishers, updated copies should be obtained by the refinery safety department.

1. Industrial Hygiene and Toxicity, by Patty, 1979, Wiley-Interscience.
2. Dangerous Properties of Industrial Materials, 6th ed. by N. Irving Sax, 1984, Van Nostrand Reinhold Co.
3. ASTM D-270, "Standard Method of Sampling Petroleum and Petroleum Products."
4. Data Sheet SD-3. "Properties and Essential Information for Safe Handling and Use of CCl4."
5. Data Sheet SD-9. "Properties and Essential Information for Safe Handling and Use of Caustic Soda."
6. Data Sheet SD-39. "Properties and Essential Information for Safe Handling and Use of Hydrochloric Acid, Aqueous Hydrogen Chloride and Anhydrous."
7. Data Sheet D-308 "Benzene" Published by the National Safety Council.
8. Chemical Hazards Response Information System (CHRIS)  
Hazardous Chemical Data Sheets  
United States Coast Guard, June, 1985

The CHRIS sheets are designed to provide information to U.S. Coast Guard personnel during emergencies involving water transport of hazardous chemicals. The first aid and hazard information presented is also applicable to refineries.

9. Documentation of the Threshold Limit Values American Conference of Governmental Industrial Hygienists 1980
10. NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards September, 1978
11. Department of Transportation Emergency Response Guidebook 1980
12. National Safety Council - Chemical Data Sheets, 1984
13. OSHA, Specific Industrial Classification Codes 29-39; Subpart Z; Toxic and Hazardous Substances Communication Act, Section 1910.1200; 1983

## XV. EQUIPMENT EVALUATION

While the majority of UOP unit performance tests are conducted in order to satisfy contractual agreements between UOP and the customer, the potential significance of a mechanical evaluation is much greater. From the information generated and collected during an evaluation test, the refiner has the means to assess the potential of the unit, to plan for future debottlenecking and to optimize refinery operations.

The following description includes data necessary for contractual tests plus information required for evaluating hydraulic systems, heater, exchangers, pumps, compressors, etc. A large amount of the information would be gathered in any case (flows, temperatures, pressures, samples, etc.), and much of the rest can be obtained on a one-time basis.

However, the test information may not be of much value unless the following criteria are met:

1. The unit **must** weight balance. The weight balance must be consistently between 98 and 102 wt.%, and preferably between 99 and 101 wt.%.
2. All operations must be steady, including quality of charge stock, product specifications, exchanger outlet temperatures, etc.
3. Sufficient sample containers and laboratory analytical time must be available, including containers for sample shipment to UOP (optional).
4. Sufficient technical manpower must be available to gather data and take samples, in addition to those normally available for operating the unit.

5. The instrument technicians will be required before and during the performance test in order to calibrate the instrumentation daily during the test.

The following list indicates the amount and type of information required:

1. Flows: All process flows into and out of the unit, and also intermediate streams such as recycle gas and reflux, utility flows such as steam, BFW, instrument and plant air, cooling water, fuel oil and gas, power consumption.
2. Temperatures: All process temperatures, including those not usually measured, but provided for by thermowells, heater and exchanger temperatures, storage tank temperatures.
3. Pressures: All process pressures, including single gauge hydraulic surveys on reactor systems and columns and pump suction and discharge pressures.
4. Levels: Particularly storage tank levels for feed and products, chemical consumption (chloride, caustic, corrosion inhibitors, antifoulants, etc.), process levels in columns, drums, receivers, etc.
5. Samples: Samples of feed and products, intermediate streams such as reflux, recycle gas, fuel gas and oil, flue gas, sour water, catalyst.

Why is all this data required? There are many reasons, but those used most frequently are to establish a unit base line performance, to predict the unit's maximum capacity, and to identify where the unit bottlenecks are. Another reason is for UOP's Engineering Department to evaluate actual unit and equipment performance compared to design. It is suggested that the data be accumulated at one time (during the performance run for contract demonstration), and that evaluation of the equipment be made later. It is important, however, to have **all** the necessary information available. To this end, the following lists and data sheets are given to use as guides in collecting data.

## GENERAL

Ambient air conditions:      temperature  
                                        relative humidity  
                                        barometric pressure  
                                        wind velocity and direction  
                                        (shown on rough plot plan)

General description of unit – includes process flow diagram.

Unit system used (e.g. USA, Imperial, Metric) and definition of any uncommon units (e.g. kPa) and Standard Conditions (0°C, 760 mm; 60°F, 14.7 psia, etc.)

## Guarantee

Data as required for Guarantee Agreement.

Complete weight balance, including meter correction factors.

## Exchangers

Flow through exchangers on both sides (gas and liquid), composition and mass flow.

Temperature in and out on both sides, also between shells, bundles.

Pressures in and out on both sides, if possible.

If air coolers; air temperature out, air velocity out, motor amps, note any belt slippage, variable pitch positions, louver positions, etc.

In preparing data, submit overall heat transfer coefficient, specifics on exchangers.

## Chemical Consumption

Organic chloride

Caustic

BFW chemicals

Corrosion Inhibitor

Antifoulants

Other

## Hydraulic Survey and Process Separations

Single gauge pressure survey of every point available on reactor circuit

All control valve positions (including fuel, BFW, etc.)

Pump motor amps

Pump suction, discharge pressure, flow rates, composition, temperatures, with manufacturer's curve data for comparison

Single gauge pressure survey of fractionation systems, with sufficient data to calculate internal reflux, number of theoretical trays, etc.

Samples of separator liquid and vapor and recontactor liquids and vapors for phase separation data

Utility consumption/production data:

Steam (all pressures)

Air (Plant and Inst.)

N<sub>2</sub>

Cooling water

BFW

Utility water

Steam condensate

Process condensate

## Samples (typical)

- Fresh Feed
- Reactor Feed
- Recycle Liquid
- Lead Reactor Effluent
- Hydrogen Makeup Gas
- Stabilizer Offgas
- Stabilizer Bottoms
- Circulating Caustic
- Circulating Wash Water
- Caustic Scrubber Gas
- Any Other Product Streams

### Comments:

It is not necessary to obtain all the data at one time. It is acceptable to run various segments of the survey at different times, and one possible period would be during the line-out period prior to the guarantee test period. Data collections for heater and air-fin exchangers, in particular, are lengthy processes, and may be done at any time when the unit is stable, provided all the required process data is available.

If the data are collected, it obviously is necessary to have a good weight balance (100 + 2%) for the information to be meaningful. For most pieces of information, if the unit is lined out, spot data will be sufficient, rather than long-term averaged data. It might be possible, taking into consideration, to obtain the spot data in sections spread out during the guarantee test (one exception is column performance).

In presenting the data, some order should be kept. UOP suggests keeping sections by type of information, i.e., one section on the guarantee test results, one on heaters, one on exchangers, one on hydraulics, etc. Attached are some typical summary sheets for his purpose.

**COLUMN SUMMARY**

page \_\_\_\_\_

date \_\_\_\_\_

Item No.: \_\_\_\_\_ by \_\_\_\_\_

Service: \_\_\_\_\_

Type of Operation: \_\_\_\_\_

No. of Trays: \_\_\_\_\_ Reflux Ratio: \_\_\_\_\_

Type of Trays: \_\_\_\_\_

	Feed	Reflux	Off Gas	Btms.	Net Ovhd.	Liquid	Other
Mass Flow,	_____	_____	_____	_____	_____	_____	_____
Temperature, °	_____	_____	_____	_____	_____	_____	_____
Pressure,	_____	_____	_____	_____	_____	_____	_____
Composition, %	_____	_____	_____	_____	_____	_____	_____
H <sub>2</sub>	_____	_____	_____	_____	_____	_____	_____
N <sub>2</sub>	_____	_____	_____	_____	_____	_____	_____
H <sub>2</sub> S	_____	_____	_____	_____	_____	_____	_____
H <sub>2</sub> O	_____	_____	_____	_____	_____	_____	_____
C <sub>1</sub>	_____	_____	_____	_____	_____	_____	_____
C <sub>2</sub>	_____	_____	_____	_____	_____	_____	_____
C <sub>3</sub>	_____	_____	_____	_____	_____	_____	_____
iC <sub>4</sub>	_____	_____	_____	_____	_____	_____	_____
nC <sub>4</sub>	_____	_____	_____	_____	_____	_____	_____
iC <sub>5</sub>	_____	_____	_____	_____	_____	_____	_____
nC <sub>5</sub>	_____	_____	_____	_____	_____	_____	_____
CP	_____	_____	_____	_____	_____	_____	_____
2,2 DMB	_____	_____	_____	_____	_____	_____	_____
2,3 DMB	_____	_____	_____	_____	_____	_____	_____
2 MP	_____	_____	_____	_____	_____	_____	_____
3 MP	_____	_____	_____	_____	_____	_____	_____
nC <sub>6</sub>	_____	_____	_____	_____	_____	_____	_____
MCP	_____	_____	_____	_____	_____	_____	_____
Bz	_____	_____	_____	_____	_____	_____	_____
CH	_____	_____	_____	_____	_____	_____	_____
C <sub>7</sub> +	_____	_____	_____	_____	_____	_____	_____
Mol wt.	_____	_____	_____	_____	_____	_____	_____

(Sketch system showing flows, P, T, Q on separate page) \_\_\_\_\_

Weight balance \_\_\_\_\_ Heat balance \_\_\_\_\_

Deviations from UOP Specifications: \_\_\_\_\_

**CONTROL VALVE SUMMARY**

page \_\_\_\_\_

date \_\_\_\_\_

Item No.: \_\_\_\_\_

by \_\_\_\_\_

Service: \_\_\_\_\_

Description of Valve: \_\_\_\_\_ Design CV: \_\_\_\_\_

Mfgr. and Catalog No.: \_\_\_\_\_

Positioner? \_\_\_\_\_

	<b>Actual</b>	<b>Design</b>
Percent open (valve position)	_____	_____
Flow rate:	_____	_____
Upstream pressure:	_____	_____
Downstream pressure:	_____	_____
Flowing temperature:	_____	_____

Deviations from UOP Specification: \_\_\_\_\_

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**AIR FIN COOLER SURVEY**

page \_\_\_\_\_  
 date \_\_\_\_\_  
 by \_\_\_\_\_

Item No.: \_\_\_\_\_  
 Service: \_\_\_\_\_  
 Manufacturer: \_\_\_\_\_  
 Type, Model: \_\_\_\_\_  
 No. of Bundles: \_\_\_\_\_ No. of Passes: \_\_\_\_\_  
 No. of Tubes per Pass: \_\_\_\_\_ Fans/bundle: \_\_\_\_\_  
 Tube Size \_\_\_\_\_ ID x \_\_\_\_\_ Gauge x \_\_\_\_\_ Length \_\_\_\_\_  
 Piping Geometry: \_\_\_\_\_ Type\*: \_\_\_\_\_  
 Overall Heat Transfer Coefficient: \_\_\_\_\_

		Pressure	Temperature
Inlet			
Outlet			
Air	In		
	Out		
No. fans on	_____	Pitch control	_____
Louver position	_____		
Mass flow		Air	Process
Q (calc.)	_____	_____	_____
Composition, %	_____	_____	_____
H <sub>2</sub>	_____	_____	_____
N <sub>2</sub>	_____	_____	_____
H <sub>2</sub> S	_____	_____	_____
H <sub>2</sub> O	_____	_____	_____
C <sub>1</sub>	_____	_____	_____
C <sub>2</sub>	_____	_____	_____
C <sub>3</sub>	_____	_____	_____
iC <sub>4</sub>	_____	_____	_____
nC <sub>4</sub>	_____	_____	_____
Neo pentane	_____	_____	_____
iC <sub>5</sub>	_____	_____	_____
nC <sub>5</sub>	_____	_____	_____
CP	_____	_____	_____
2-2 DMB	_____	_____	_____
2-3 DMB	_____	_____	_____
2 MP	_____	_____	_____
3 MP	_____	_____	_____
nC <sub>6</sub>	_____	_____	_____
MCP	_____	_____	_____
Benzene	_____	_____	_____
CH	_____	_____	_____
C <sub>7+</sub>	_____	_____	_____
Avg. Mol. Wt.	_____	_____	_____
Gravity	_____	_____	_____
Relative Humidity	_____	_____	_____
Deviations from UOP Specification:	_____	_____	_____

\*Include sketch of piping geometry if different from UOP standard practice types.

**FLOW METER SUMMARY**

page \_\_\_\_\_

date \_\_\_\_\_

Item No.: \_\_\_\_\_

by \_\_\_\_\_

Service: \_\_\_\_\_

Type of Fluid: \_\_\_\_\_ Normal Units of Flow: \_\_\_\_\_

Type of Meter: \_\_\_\_\_

Meter Reading: \_\_\_\_\_

Pressure \_\_\_\_\_

Temperature \_\_\_\_\_

Sp. Gr. \*\* \_\_\_\_\_

Meter Factor \_\_\_\_\_

Corrected Flow Rate \_\_\_\_\_

Mass Flow Rate \_\_\_\_\_

Avg. mol. wt. \_\_\_\_\_

Molar Flow Rate \_\_\_\_\_

\*\*Sketch piping layout, showing distances in nominal pipe IDs.

**HEAT EXCHANGER SURVEY**

page \_\_\_\_\_  
 date \_\_\_\_\_  
 by \_\_\_\_\_

Item No.: \_\_\_\_\_

Service: \_\_\_\_\_

Manufacturer: \_\_\_\_\_

Type, Model: \_\_\_\_\_

No. of Bundles: \_\_\_\_\_

No. of Passes/Bundle: \_\_\_\_\_ Tubes per Pass: \_\_\_\_\_  
 Tube Size \_\_\_\_\_ ID x \_\_\_\_\_ Gauge x \_\_\_\_\_ Length \_\_\_\_\_

Heat Exchange Surface Area/Bundle: \_\_\_\_\_

Piping Geometry (sketch if necessary): \_\_\_\_\_

Length of Service: \_\_\_\_\_

Design Heat Transfer Coefficient: \_\_\_\_\_

Shell Side	Inlet	Stream A	Pressure	Temperature
	Outlet		_____	_____
Tube Side	Inlet	B	_____	_____
	Outlet		_____	_____
Q (calc.) Shell side		_____		
Q (calc.) Tube side		_____		
Composition, _____ %		A	B	
H <sub>2</sub>		_____	_____	
N <sub>2</sub>		_____	_____	
H <sub>2</sub> S		_____	_____	
H <sub>2</sub> O		_____	_____	
C <sub>1</sub>		_____	_____	
C <sub>2</sub>		_____	_____	
C <sub>3</sub>		_____	_____	
iC <sub>4</sub>		_____	_____	
nC <sub>4</sub>		_____	_____	
Neo pentane		_____	_____	
iC <sub>5</sub>		_____	_____	
nC <sub>5</sub>		_____	_____	
CP		_____	_____	
2-2 DMB		_____	_____	
2-3 DMB		_____	_____	
2 MP		_____	_____	
3 MP		_____	_____	
nC <sub>6</sub>		_____	_____	
MCP		_____	_____	
Benzene		_____	_____	
CH		_____	_____	
C <sub>7+</sub>		_____	_____	
Mass Flow		_____	_____	
Mol. Wt.		_____	_____	

Deviations from UOP Specification: \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

**CENTRIFUGAL PUMP SURVEY**

page \_\_\_\_\_  
 date \_\_\_\_\_  
 by \_\_\_\_\_

Item No.: \_\_\_\_\_

Service: \_\_\_\_\_

Manufacturer: \_\_\_\_\_

Type, Model: \_\_\_\_\_

No., Size and Style (Mfgrs. Designation) \_\_\_\_\_

Suction	Pressure	Temperature
---------	----------	-------------

Discharge	_____	
-----------	-------	--

**Other Information**

Rated Flow (STP) \_\_\_\_\_ Seal Type? Single, Tandem, Double, Bellow

Sp. Gr. \_\_\_\_\_ Spillback? Yes/No

Viscosity \_\_\_\_\_ NPSHR? \_\_\_\_\_

Static Suction Head \_\_\_\_\_ Suction Specific Speed: \_\_\_\_\_

Speed \_\_\_\_\_

Differential Head (flowing condition) \_\_\_\_\_

Driver Type: \_\_\_\_\_

Manufacturer: \_\_\_\_\_

No., Size, Rating and Style (Mfgrs. designation): \_\_\_\_\_

Rating: \_\_\_\_\_ Insulation Class: \_\_\_\_\_

Service Factor: \_\_\_\_\_ Voltage/Phase/Cycle: \_\_\_\_\_

**Motor:**

Power consumption \_\_\_\_\_

Speed \_\_\_\_\_

**Turbine:**

Steam consumption	Pressure	Temperature
-------------------	----------	-------------

Steam supply	_____	_____
--------------	-------	-------

Steam exhaust	_____	_____
---------------	-------	-------

Speed	_____
-------	-------

Supply copy of Mfgrs. pump curve and plot operating point.

Deviations from UOP Specification: \_\_\_\_\_

\_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

**ELECTRIC HEATER SURVEY**

Page \_\_\_\_\_

Date \_\_\_\_\_

Item No.: \_\_\_\_\_ By \_\_\_\_\_

Service: \_\_\_\_\_

Manufacturer: \_\_\_\_\_

Type: \_\_\_\_\_

Number &amp; Passes: \_\_\_\_\_ Tubes per Pass: \_\_\_\_\_

Tube Length: \_\_\_\_\_ Tube Skin Temperature: \_\_\_\_\_

Resistance of Each Phase: 1 \_\_\_\_\_ 2 \_\_\_\_\_ 3 \_\_\_\_\_

Current at Peak Firing: \_\_\_\_\_ Voltage: \_\_\_\_\_

Deviations from UOP Specification: \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

Item No.: \_\_\_\_\_

Service: \_\_\_\_\_

Manufacturer: \_\_\_\_\_

Type: \_\_\_\_\_

Number &amp; Passes: \_\_\_\_\_ Tubes per Pass: \_\_\_\_\_

Tube Length: \_\_\_\_\_ Tube Skin Temperature: \_\_\_\_\_

Resistance of Each Phase: 1 \_\_\_\_\_ 2 \_\_\_\_\_ 3 \_\_\_\_\_

Current at Peak Firing: \_\_\_\_\_ Voltage: \_\_\_\_\_

Deviations from UOP Specification: \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

## XVI. METHANATOR INFORMATION

Isomerization Unit in the text of this section can refer to either a Penex or Butamer Unit. The same procedures apply regardless if the methanator is included in a Penex or Butamer Unit.

### I. METHANATOR OPERATIONS (SAFETY CONSIDERATIONS)

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Unloading reduced catalyst (A)

Unloading reduced catalyst (B)

Unloading oxidized catalyst

## I. METHANATOR OPERATIONS – SAFETY CONSIDERATIONS

Before getting into the actual operating procedure for the methanator, the hazardous properties of both nickel and nickel carbonyl ( $\text{Ni}(\text{CO})_4$ ) should be noted. Since the catalyst employed in the methanator uses nickel as part of its make-up there exists, at times, a potential for plant personnel contacting the nickel catalyst and for the formation of nickel carbonyl.

To elaborate on when such occurrences might happen the following will present some of the possible events in which either catalyst contact or nickel carbonyl formation could occur.

### Catalyst Contact

Contact with nickel or the nickel catalyst can cause skin irritations. Breathing air contaminated with nickel dust can cause respiratory tract irritations. Contact with the catalyst can obviously occur during both the catalyst loading and unloading stages.

Avoiding body contact with the nickel catalyst can be achieved by using appropriate safety clothing that may include long sleeve coveralls, gloves, face shields, and dust masks to full protective clothing that provides a complete barrier between the catalyst and any catalyst dust and the individual involved.

Protective equipment is not a substitute for good, safe working conditions, adequate ventilation or intelligent conduct on the part of the operators. When protective equipment is necessary, it must be used properly. The equipment selected must be suitable for the purpose and the person using the equipment must be familiar with it. All protective equipment for safety of personnel must be kept in good working condition at all times. Frequent inspection and immediate repairs are necessary.

Further, any safety clothing used in this work must be decontaminated prior to reuse.

### Nickel Carbonyl Formation

Nickel carbonyl ( $\text{Ni}(\text{CO}_4)$ ) is known to be an extremely toxic gas. Its primary effect is to cause lung damage with a lesser effect on the liver. The maximum average exposure to nickel carbonyl recommended by NIOSH is a TLV of 0.001 ppm (1 ppb), and a maximum spot exposure of 0.04 ppm (40 ppb). In the methanator, the potential for forming nickel carbonyl exists during regeneration or during the handling of unregenerated catalyst. Care must be exercised to insure that the procedures used will prevent the formation of nickel carbonyl. Data has been published showing the equilibrium concentration of  $\text{Ni}(\text{CO})_4$  versus temperature, pressure, and CO concentration in a gas. The nickel carbonyl concentration drops rapidly with increasing temperature and decreasing CO concentration.

At 100 psig (7kg/cm<sup>2</sup>g) with 0.5 mole % CO in the gas, the nickel carbonyl concentration is at the maximum permissible spot level of 0.04 ppm at 300°F (149°C), and it is 0.001 ppm at 360°F (182°C). The following practices should be followed to prevent the formation of nickel carbonyl:

- a) Once a reactor containing a nickel catalyst has been exposed to oxidizing conditions (regeneration), a measurable concentration of oxygen must be maintained until the combustion of all carbon ceases and all  $\text{CO}_2$  has been purged.
- b) Once a reactor containing a nickel catalyst is in a reducing atmosphere and regeneration is not desirable, maintain the system in a reducing or nitrogen atmosphere until all the catalyst has been cooled to at least 150°F (66°C). Unregenerated catalyst should be unloaded with a  $\text{N}_2$  purge at the reactor inlet, and each empty drum should be  $\text{N}_2$  purged before receiving used catalyst. Oxidation (burning) must be avoided.

There are many published techniques for determining the concentration of nickel carbonyl in air (such as a vessel to be entered for maintenance), and several direct reading instruments are available commercially.

**\*DO NOT USE** an inert gas which has been produced by the controlled combustion of natural gas (or similar) and air for purging the methanator at any time. This gas can contain carbon monoxide.

## II. METHANATOR OPERATIONS

### Introduction

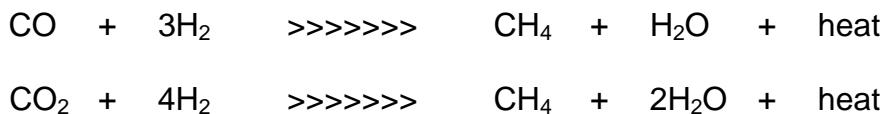
A methanator is utilized for treating the makeup hydrogen gas to an Isomerization Unit because of the catalyst's extreme sensitivity to oxygenated compounds. Any amount of CO or CO<sub>2</sub> in the makeup hydrogen gas will affect the life of the catalyst. A methanator can prolong the catalyst life by reducing the CO/CO<sub>2</sub> concentration to low ppm levels that in the case of CO<sub>2</sub> will be further reduced to essentially nil by the Isomerization Unit's molecular sieve driers.

### CO/CO<sub>2</sub> Sources

There are two principal sources of CO and CO<sub>2</sub> in the makeup hydrogen. One source is a catalytic reformer which periodically has one of its reactors taken off line, regenerated and put back on stream. CO and CO<sub>2</sub> generated during the regeneration will be present in the net hydrogen from this type of reformer and may find its way to the Isomerization Unit. Another type of reformer (those with continuous catalyst regeneration) also can have moderately high levels of CO/CO<sub>2</sub> depending on the operating conditions. The other source of CO and CO<sub>2</sub> in H<sub>2</sub> is a hydrogen plant. The product gas from a hydrogen plant may contain as much as one mole percent CO plus CO<sub>2</sub>, although many hydrogen plants have their own methanators that will reduce the CO/CO<sub>2</sub> concentration to lower levels. However, most H<sub>2</sub> plant methanators are not designed to assure low enough CO/CO<sub>2</sub> levels to be acceptable to an Isomerization Unit. Even concentrations of 5-10 ppm CO/CO<sub>2</sub> may be sufficient for justifying a separate methanator for the makeup gas to the Isomerization Unit.

### Chemistry of Methanation

The CO and CO<sub>2</sub> are consumed in the following reactions:



The water produced is subsequently removed in the makeup gas driers. The methanation of CO occurs readily at 400°F (204°C), but the methanation of CO<sub>2</sub> requires 600°F (316°C). Any CO<sub>2</sub> not methanated will generally be removed by the Isomerization Unit's makeup H<sub>2</sub> molecular sieve driers.

The methanation catalyst is a nickel catalyst and it will hydrogenate any olefins in the makeup gas as well as crack C<sub>2+</sub> hydrocarbons. The catalyst can be permanently deactivated by sulfur so pretreatment for H<sub>2</sub>S removal is recommended for gas streams containing H<sub>2</sub>S.

The methanation reaction is exothermic as are the side reactions, hydrogenation and cracking. The methanation of a feedstream with 1 mole percent CO or 1 mole percent CO<sub>2</sub> can generate a delta T of hundreds of degrees. There is danger of a temperature excursion in circumstances where a sudden increase in CO/CO<sub>2</sub> concentration can occur, or where C<sub>2+</sub> hydrocarbons, benzene, or olefins can enter the methanator.

For reformer H<sub>2</sub>, there are usually enough hydrocarbon impurities in the H<sub>2</sub> supply that it is not possible to run hot enough to remove the CO<sub>2</sub> in the methanator without risking a temperature excursion. Where reformer H<sub>2</sub> is being methanated, it is normal to operate at reduced temperatures in the 400-500°F (204-260°C) range to get the CO in the methanator then to remove the CO<sub>2</sub> by diligent operation of the driers.

### Loading

Since the methanation catalyst is normally in the oxidized state when it is shipped to the refiner it will be possible to use standard sock loading practices. The catalyst vendor's loading and unloading instructions as well as the MSDS sheet for the catalyst must be obtained and followed. The procedures below are meant as a guide and should be altered as needed to match the vendor instructions.

- 1) Isolate the reactor by blinding the inlet and outlet and properly purge any hydrocarbons per the refinery safety standards.

- 2) Install the reactor outlet basket and secure in place.
- 3) Place the appropriate amounts of catalyst support material in the reactor and level it. Refer to the methanator reactor loading diagram in the UOP Project Specifications book. Care should be taken not to disturb the position of the reactor outlet basket.
- 4) Install a hopper with a canvas sock at the top of the reactor and adjust the sock length so that the catalyst will fall no more than five feet.
- 5) The canvas sock must be grounded.
- 6) Dress in proper safety clothing and clear all non-essential personnel from tie area.
- 7) Load the catalyst into the reactor and adjust the length of the canvas sock as needed. Record the lot number and drum number from each catalyst drum and the total weight loaded. Load catalyst to the height indicated on the loading diagram.
- 8) Level the catalyst bed and measure the distance from the catalyst to the top of the reactor top manway flange.
- 9) Install the ceramic holddown material and level. (Per the methanator reactor loading diagram.)
- 10) Close the reactor. The reactor can be air-freed either by purging with nitrogen or by repeated evacuation and nitrogen pressuring.
- 11) Remove the isolation blinds.

## Methanator Procedures

**Important:** No CO/CO<sub>2</sub> containing hydrogen should be introduced to the methanator below 300°F (149°C) because nickel carbonyl will form and can damage the catalyst by depleting the nickel from the catalyst.

### Startup

1. Introduce nitrogen upstream from the pressure control valve and pressure the methanator system up to header pressure.
2. Start a nitrogen flow through the system by opening the vent to the flare downstream of the makeup gas knock out drum.
3. Immediately commission the reactor heater and raise the outlet temperature to 400°F (204°C) or the design inlet temperature at the rate of 200°F (110°C)/hour. Commission downstream coolers if present.
4. When the reactor outlet temperature reaches 300°F (149°C), slowly introduce hydrogen from the hydrogen plant. As the catalyst is normally supplied in an oxidized state, the introduction of hydrogen will start to reduce the catalyst and a temperature rise will occur. A temperature wave will pass through the catalyst. Limit the hydrogen to control a 50°F (28°C) delta temperature rise. Hold 400°F (204°C) or the design inlet temperature on the reactor inlet until the reduction has been completed. Block in the nitrogen and pressure up the system slowly with hydrogen from the hydrogen plant. (The vent to the flare is, of course, blocked in.)
5. Open up the vent to the flare and establish a minimal hydrogen flow rate. Check for CO at the reactor outlet. If <0.5 ppm, proceed. If not, raise the reactor inlet by 10°F (6°C), equilibrate and check again.
6. Close the warm-up vent to the flare and begin hydrogen flow to the Isomerization Unit.

7. When the Isomerization Unit is at operating pressure, the pressure control should be switched from the make-up gas knock out drum to the product separator.

With the specified hydrogen gas flow, the delta T across the reactor may be very low or in the case of H<sub>2</sub> plant H<sub>2</sub> could be as high as 100°F (55°C). If there is no delta T, check for CO conversion.

- (a) If CO is present at the outlet, raise the reactor temperature again by 10°F (6°C) and check the CO conversion again.
- (b) If no CO is present at the reactor outlet, check the CO at the inlet. The lack of delta T may be due to a lack of carbon oxides in the makeup hydrogen gas.

### Shutdown

If the shutdown is temporary and expected to last less than 2 hours:

1. As soon as there is no more hydrogen demand in the Isomerization Unit, switch pressure control to the make-up gas knock out drum.
2. Open the vent to the flare and keep the hydrogen flow to a minimum.
3. Lower the reactor inlet temperature to 400°F (204°C) and maintain this temperature until there is a demand for hydrogen in the Isomerization unit.

If the shutdown will be more than just a few hours:

4. Stop makeup gas flow and depressurize the methanator system through the vent to the flare while maintaining a 400°F (204°C) reactor inlet. Depressurize to 20 psig (1.5 kg/cm<sup>2</sup>g) less than the nitrogen header pressure.

5. Introduce nitrogen to the methanator and cool down to 150°F (66°C) at the reactor outlet by cutting out the heating medium to the heater and purging nitrogen through the reactor to the flare.
6. At a reactor outlet temperature of 150°F (66°C), block in the vent to the flare and the nitrogen source and maintain under nitrogen pressure.

### Temperature Excursion

In some cases where high delta T is expected due to the high carbon oxides in the feed, there is a control system designed to prevent temperature excursions by cutting out the hydrogen gas feed.

For low levels of carbon oxides there may be only a high temperature alarm which alerts the operator that attention is needed. In either case, the operator should make sure the feed is stopped manually and reduce the methanator heater outlet temperature to compensate for the increase in heat generated. As soon as the temperature is under control, the feed may be introduced slowly and the reactor inlet temperature controlled accordingly.

If the reactor temperature approaches the vessel limit, take the following actions:

1. Block in the hydrogen gas feed to the reactor.
2. Block in the heating medium to the methanator heater.
3. Block in the methanated gas to the makeup gas dryers.
4. Open the warm up vent to the flare and reduce the methanator reactor pressure to 20 psig (1.5 kg/cm<sup>2</sup>g) less than the nitrogen header.
5. Introduce nitrogen to the reactor at a maximum rate to cool the catalyst bed to a safe temperature.

## (A) Catalyst Unloading

Spent catalyst is in the reduced state and it must be unloaded cool under an inert atmosphere since contact with oxygen may result in combustion and/or the formation of nickel carbonyl. Nickel carbonyl is extremely toxic and is dangerous at parts per billion levels so precautions taken to exclude air must be thorough. Fire extinguishers and steam hoses or water should be available for immediate use.

- 1) Isolate the cooled reactor (150°F, 66°C) by blinding the inlet and outlet lines. Maintain the nitrogen purge (if possible) and in any case, the nitrogen blanket must be maintained.
- 2) Monitor the methanator bed thermocouples on a routine basis and record. The board operator must notify the field operator of any temperature increase. The use of a portable potentiometer may also be used. A temperature increase could indicate air entry to the catalyst bed that could possibly initiate the formation of nickel carbonyl.
- 3) The reactor will normally have unloading nozzles and the following procedure can be used.
- 4) Non-essential personnel should not be permitted in the area while the catalyst is being dumped.
- 5) Personnel involved in handling spent catalyst or those working near the unloading operations must wear full protective clothing and self-contained or air-supplied respiratory equipment.
- 6) Attach a nitrogen line to the top of the reactor. There should be a valve or a regulator on the line so that the nitrogen purge can be controlled.
- 7) Remove the unloading nozzle blind flange and replace it with a short pipe that has a slide valve in it. The slide valve should have a large enough opening so that the key can be pulled through it.

- 8) A screening device should be set up below the dumping spout. It should be equipped with a fitted canvas top to exclude air and must have a connection so that it can be continually purged with nitrogen. It must be grounded.
- 9) The screened catalyst should empty into a drum that is being purged with nitrogen.
- 10) The next drum to be filled should also be purged with nitrogen.
- 11) Ground the drum being filled.
- 12) Put the tops on the drums immediately.
- 13) When the reactor has been emptied, the reactor top manway can be opened and the hold down grating removed. This work should be done while wearing self-contained air supply safety equipment.
- 14) Have the refinery safety department check the unloading area and if their review indicates no safety hazards present, then discontinue the use of the air supplied equipment.
- 15) Clearly identify all drums containing the used unregenerated methanator catalyst. The identification of these drums should include a note of caution relating to the nickel contents of the drum.

**(B) Catalyst Unloading (no unloading nozzle on reactor)**

Spent catalyst is in the reduced state and it must be unloaded cool under an inert atmosphere since contact with oxygen may result in combustion and/or the formation of nickel carbonyl. Nickel carbonyl is extremely toxic and is dangerous at parts per billion levels so precautions taken to exclude air must be thorough. Fire extinguishers and steam hoses or water should be available for immediate use.

- 1) Isolate the cooled reactor (150°F, 66°C) by blinding the inlet and outlet lines. Maintain the nitrogen purge (if possible) however, the nitrogen blanket must be maintained.
- 2) Monitor the methanator bed thermocouples on a routine basis and record. The board Operator must notify the field operator of any temperature increase. A portable potentiometer may also be used. A temperature increase could indicate air entry to the catalyst bed that could possibly initiate the formation of nickel carbonyl.
- 3) If the reactor does not have an unloading nozzle, then the following procedure can be used.
- 4) Non-essential personnel should not be permitted in the area while the catalyst is being dumped.
- 5) Personnel involved in handling spent catalyst or those working near the unloading operations must wear full protective clothing and self-contained or air-supplied respiratory equipment.
- 6) Attach a nitrogen line to the top of the reactor. There should be a valve or, a regulator on the line so that the nitrogen purge can be controlled.
- 7) Remove all but three bolts in the bottom side vessel unloading blankoff. Connect a rigid metal chute from the bottom of the vessel unloading blankoff to a point where it will terminate over a drum that will receive the spent catalyst. Remove the bottom two remaining bolts in the bottom side unloading blankoff and slowly loosen the top bolt. This will start a flow of catalyst down the chute as the blankoff plate is moved sideways.
- 8) The catalyst should empty into a drum that is being purged with nitrogen.
- 9) The next drum to be filled should also be purged with nitrogen.

- 10) Ground the drum being filled.
- 11) Put the tops on the drums immediately.
- 12) When the reactor has been emptied, the reactor to manway can be opened and the hold down grating removed. This work should be done while wearing self-contained air supply safety equipment.
- 13) Have the refinery safety department check the unloading area and if their review indicates no safety hazards present, then discontinue the use of the air supplied equipment.
- 14) Clearly identify all drums containing the used unregenerated methanator catalyst. This identification of these drums should include a note of caution relating to the nickel contents of the drum.

### **(C) Catalyst Unloading (oxidized)**

If it is desired to oxidize the methanator catalyst prior to dumping, the following guidelines can be followed:

- 1) Use nitrogen to purge the isolated methanator reactor circuit of all hydrocarbons. The refinery Safety Department should verify this has been accomplished.
- 2) Maintain the methanator reactor inlet is at 300-350°F (149-177°C).
- 3) Maintain a nitrogen purge of the methanator venting to a safe location. (Not to flare as oxygen may enter this system later in the procedure.)
- 4) Introduce a small quantity of air to give a 0.6 mol percent oxygen in the nitrogen passing through the methanator. The oxygen will oxidize the methanator catalyst. Also a temperature rise will be encountered in the catalyst bed due to this oxidation. Do not permit the bed temperatures to

exceed 750°F (400°C) or the temperature limits of the equipment, whichever is lesser. If the temperature starts to become excessive, reduce the air rate to the methanator.

- 5) When the bed temperatures start to decrease, this will indicate that the oxidation has been completed. Cool down the reactor with the nitrogen/oxygen gas mix. Depressurize the system.
- 6) Follow the methanator catalyst dumping procedures as outlined in either of the previous two unloading guidelines.