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The Separation of *n*-Paraffins from Paraffin Mixtures

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INTRODUCTION

The choice of the preferred operative phase for a separation system is determined by many factors, which ultimately affect process practicality as well as the capital and operating costs. Practical considerations, such as the temperature and pressure required to operate in a specific phase or the reactivity and stability of feed and desorbent components at elevated temperature, may dictate the preferred processing strategy. When no such controlling factors exist, the decision becomes less obvious and is, in simplest terms, governed by which phase requires the least adsorbent and desorbent.

In general, the liquid-phase process offers the advantage of higher adsorbent capacity as well as greater flexibility in designing a system that takes maximum advantage of desorbent–desorbate interactions. However, the interaction of such factors as selectivity and capacity, the influence of the nonselective volume on the separation, and the mass transfer efficiency in the operative phase may in some cases shift the decision in favor of the vapor-phase process. Each separation system must be evaluated on a case-by-case basis. In fact, the choice of the preferred process must consider not simply the separation unit, but also an evaluation of the total production complex, and it may include nontechnical as well as technical considerations.

UOP* has long held a dominant position in the area of liquid-phase separations with its Sorbex technology. The formation of the joint venture between UOP and the CAPS unit of Union Carbide Corporation added the vapor-phase IsoSiv process to the list of UOP licensed technologies.

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To properly position the technologies in the marketplace, considerable thought was given to the incentives and ramifications of pursuing one processing strategy over another. This paper does not intend to make generalized comparisons of vapor- versus liquid-phase operation. Rather, two commercially proven and successful processes for the separation of *n*-paraffins from paraffin mixtures are compared and contrasted. The liquid-phase Molex process is a continuous simulated countercurrent operation; the vapor-phase IsoSiv process is a semibatch operation. This paper discusses the commercial history, general process description, processing steps, and the influence of feed properties on process performance and design for both processes. The incentives for choosing one option over the other and the implications of the choices are elaborated for both naphtha- and kerosine-range feedstocks.

The commercialization of molecular-sieve-based *n*-paraffin separation technologies that depend on differences in molecular critical diameters was made possible by the synthesis of molecular sieves in the early 1950s by the Union Carbide Corporation. The use of such technology has found application across a wide range of feedstocks, including naphtha at the light end for octane enhancement and solvent production, kerosine in the intermediate carbon range for the production of detergent intermediates, and gas oils at the other extreme for single-cell protein and wax production. Since the invention of molecular sieve synthesis, a number of competing technologies that use somewhat different approaches have been developed and commercialized to meet the market demand in each of the areas cited. In the naphtha range, these technologies include the UOP gasoline Molex and naphtha IsoSiv processes and the British Petroleum MS2 process. In the kerosine and gas oil range, the list is somewhat longer and includes the UOP Molex and IsoSiv processes, the British Petroleum MS1 process, the Texaco TSF process, Shell technology, the paraffin extraction process developed in what was formerly East Germany, and the Exxon Ensorb process. Both the Molex and IsoSiv processes obtained dominant positions at an early stage and consolidated those positions through licensing of these and other complementary technologies.

COMMERCIAL HISTORY OF THE IsoSiv AND MOLEX PROCESSES

The first naphtha-range IsoSiv units that were designed and built in the late 1950s were pressure swing adsorption (PSA) units. In these units, adsorption and desorption took place at high and low pressures, respectively. Although PSA-type units do have some interesting modern applications in refinery octane-enhancement strategies, the vast majority of naphtha IsoSiv units today are based on adsorption–desorption cycles

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driven by the *n*-paraffin concentrations in the bulk phase. Almost all have been built in conjunction with a zeolitic isomerization catalyst in the Total Isomerization process, in which the isomerate is separated into a high-octane stream lean in *n*-paraffins and a normals-rich stream that is recycled to the reactor section. The primary incentive for the Total Isomerization process is octane enhancement of the light straight-run naphtha. The 50 units licensed to date have a capacity in excess of 310,000 BPSD.

The commercialization of the first kerosine IsoSiv unit was accomplished in 1961 as a revamp of the South Hampton Company's naphtha IsoSiv unit. In 1964 the Union Carbide Texas City facility came on-stream at a capacity of 100,000 MTA of *n*-paraffin product. Since that time, a total of 10 kerosine and gas oil units have been licensed. These units have an *n*-paraffin product capacity in excess of 1.2 MM MTA. Of these 10 units, five are currently operating, one is a revamp of a German paraffin extraction unit now in progress, and one is a standalone grass-roots unit currently under construction. The remaining three have been decommissioned. Most of the product from these units is used for detergent production. However, feed properties vary significantly. The molecular weights of the feeds range from 164 to 240. The *n*-paraffin content of the feeds range from 20 to 43 wt%. Feed sulfur levels vary from less than 1 wppm to more than 2000 wppm.

The Molex process was invented for the processing of gasoline-range feedstocks; the intent was to separate low-octane *n*-paraffins from gasoline. However, the commercial demand for high-octane gasoline was limited in the 1960s, and the first commercial application for the Molex process was destined to be a kerosine-range unit for Continental Oil at West Lake, Louisiana. The first of the gasoline Molex units came on-stream at Kuwait Petroleum in The Netherlands in early 1990, and the second began operating early in 1991. Since 1964, when the Continental unit came on-stream, 23 other Molex units for heavy ($C_{10}+$) feedstocks and nine others for light feedstocks (C_5–C_6) have been licensed. The combined capacity of these units exceeds 1400 KMTA *n*-paraffins in the kerosine range and 115,000 BPSD of light naphtha in the gasoline range. The Molex process continues to play a dominant part in *n*-paraffin separation technology in the liquid phase.

THE KEROSINE IsoSiv PROCESS

General Description

The kerosine IsoSiv process is a vapor-phase, semicontinuous process that separates *n*-paraffins from a mixture of normal, cyclic, branched-chain paraffins and aromatics. The kerosine IsoSiv process can be characterized as having two primary sections:

- *Adsorption Section:* The adsorption section is the heart of the process and is composed of several chambers containing the adsorbent central to the separation.
- *Desorbent Recovery Section:* The desorbent recovery section is composed primarily of dehexanizer columns in which the *n*-hexane desorbent is stripped from the nonnormal and *n*-paraffin products and then recycled to the adsorption section.

Figure 1 provides a schematic of these sections for a typical kerosine IsoSiv unit. When a particularly sulfurous feed is processed, H_2S stripper and depentanizer columns are added to maintain the purity and quality of the circulating *n*-hexane desorbent and minimize acid destruction of the adsorbent. These sections are present in most of the units licensed, although they are seldom used continuously. In addition to these sections, a regeneration section is added because of the need to burn off carbonaceous material that accumulates and reduces capacity as the adsorbent ages. A typical regeneration section is depicted in Fig. 2.

The primary process equipment used in the kerosine IsoSiv unit consists of the standard furnaces, heat exchangers, pumps, compressors, fractionation columns, flash drums, adsorbers, and solenoid control valves that are generally found in a refinery (Table 1). The required metallurgy is carbon steel. Auxiliary process equipment is designed to provide vaporized feed and desorbent to the adsorption section at an operating temperature above the feed capillary condensation point and slightly above atmospheric pressure.

During the operation of the six-adsorber system depicted in Fig. 1, five vessels are always cycling through the adsorption, copurge, and desorption steps. Two chambers are performing in the adsorption mode, one in the copurge mode, and the remaining two are operating in the desorption mode. The time required to complete a full processing sequence is defined as the cycle time and varies as a function of molecular weight. A typical cycling sequence is shown in Fig. 3. As shown in this figure, the sixth chamber is always allocated to a regeneration step. The following discussion of the processing steps through which an operating kerosine IsoSiv unit cycles provides additional insight into the process configuration and operation.

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Adsorption Step

During the adsorption step, the vaporized feed from the charge heater is directed upflow through the adsorbers at elevated temperature and

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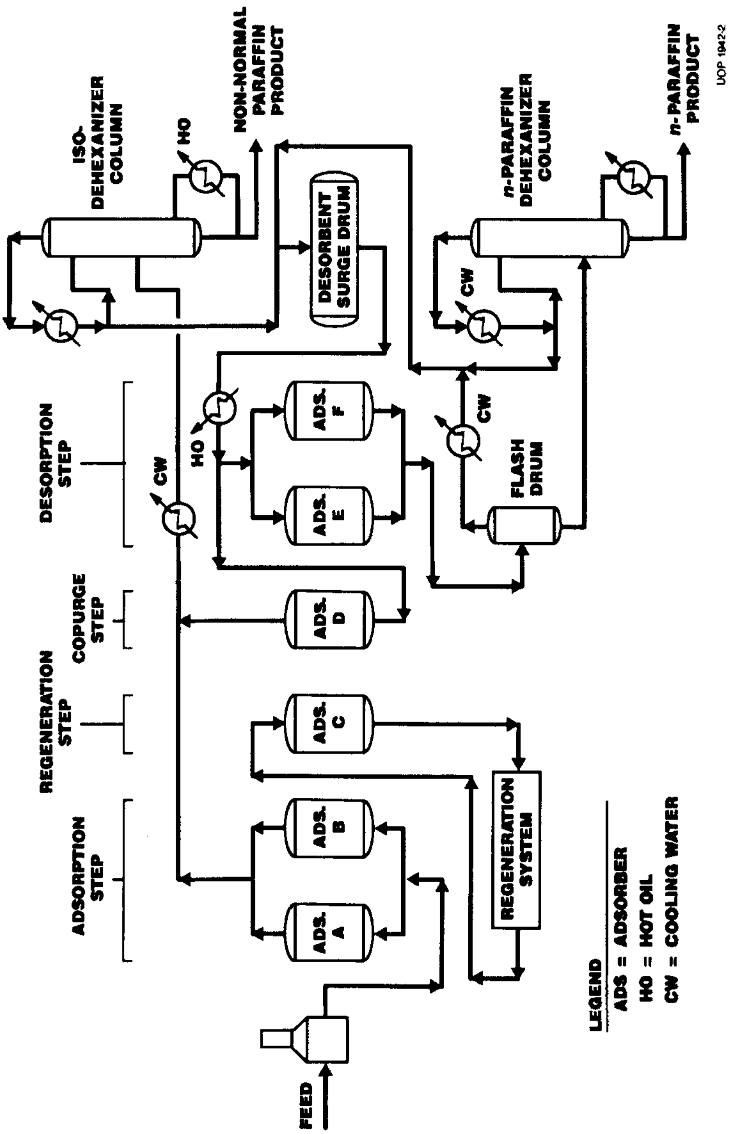

FIG. 1. Simplified kerosine IsoSiv process flow sheet.

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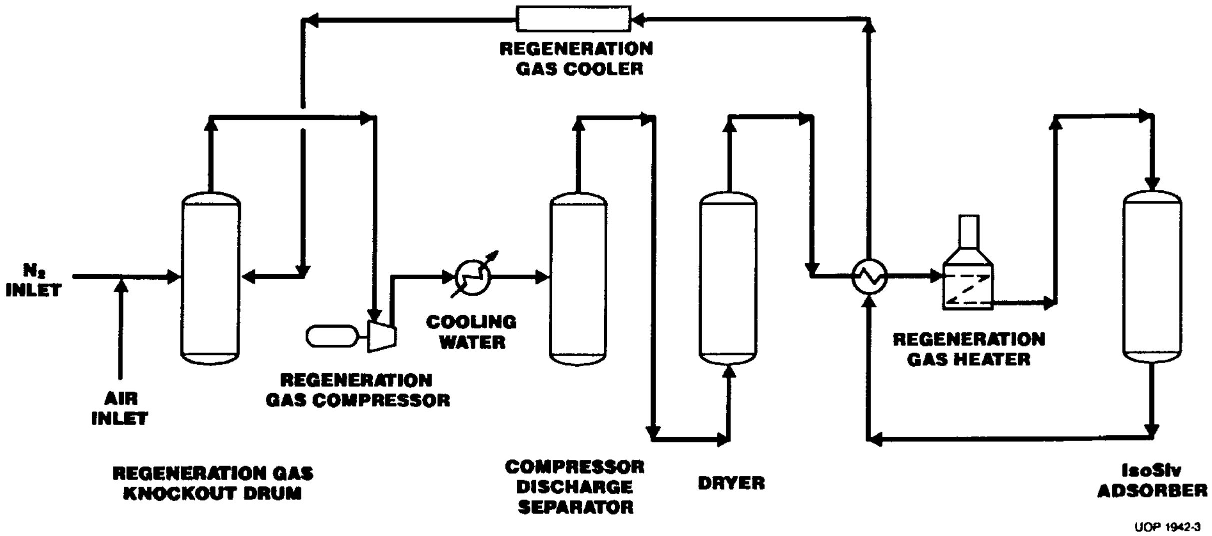

FIG. 2. Simplified kerosine IsoSiv regeneration section.

TABLE 1
Equipment Summary

Equipment	*n*-Paraffin separation: Molex	*n*-Paraffin separation: IsoSiv
Fired heaters	—	4
Valves (major)	1RV	31
Compressors	—	2
Adsorbers	2	8 (6 + 2)[a]
Vessels	6	9
Fractionation columns	3	6
Exchangers	10	19
Pumps	22	23

[a] 6-Adsorber configuration.

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slightly above atmospheric pressure. As the feed *n*-paraffins are selectively adsorbed in the micropores, they displace the *n*-hexane remaining from the previous desorption step. The nonnormal components remain in the nonselective volume. The driving force for adsorption is the concentration gradient between the bulk and adsorbed phases. The displaced desorbent, as well as a portion of the nonadsorbed feed materials, exits the top of the chamber and is combined with the effluent from the copurge step, which is discussed later. The heat of adsorption released as the *n*-paraffins are preferentially adsorbed produces a temperature front that follows closely behind the mass transfer front and provides a means of tracking the movement of the normals through the bed. The amount of *n*-paraffins charged to the bed is halted before breakthrough occurs so that product is not lost from the top of the chamber. In a commercial unit the actual temperature front is not easily defined, and a timer is used to limit the normals loading of the chamber.

The actual number of adsorbers at a unit is set by the *n*-paraffin production rate, the capacity of the adsorbent, and the adsorbent deactivation rate associated with the specific feed being processed. Pressure drop considerations may also govern the number of adsorbers. Systems having four, six, and eight adsorbers have been designed, with six being the most typical.

Copurge Step

The purification of the desired *n*-paraffin fraction is performed during the copurge step. During this step, vaporized *n*-hexane desorbent is directed upflow through the adsorber loaded with *n*-paraffins to flush the void of the undesired nonnormal feed components. The typical relationship between the copurge rate, purity, and recovery is illustrated in Fig. 4. In

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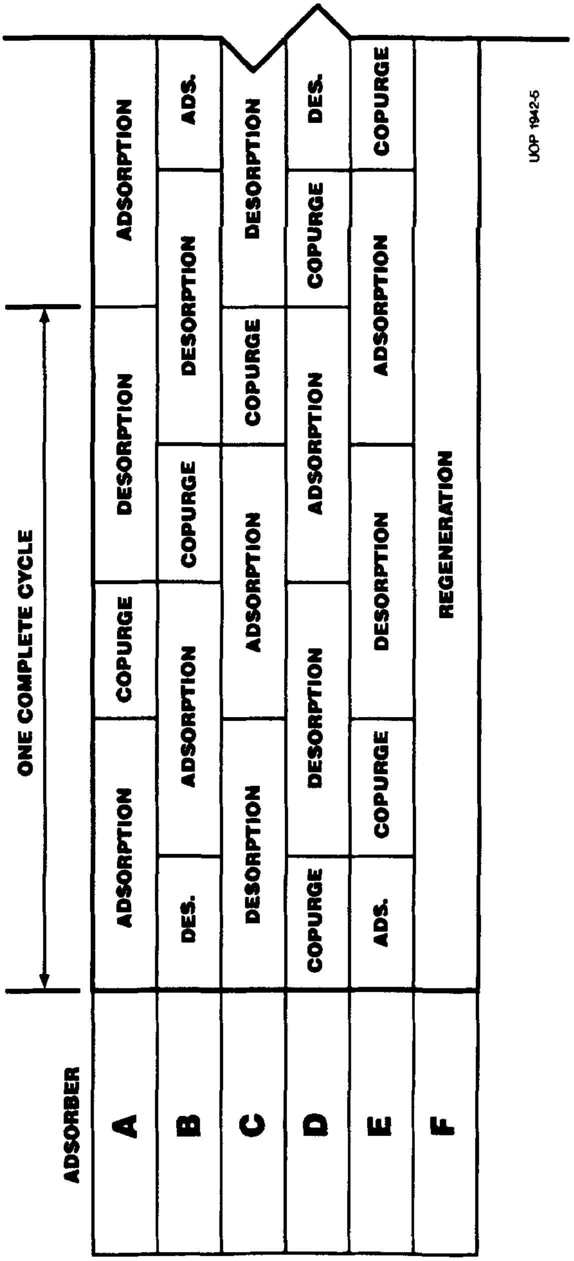

FIG. 3. Adsorber sequencing diagram.

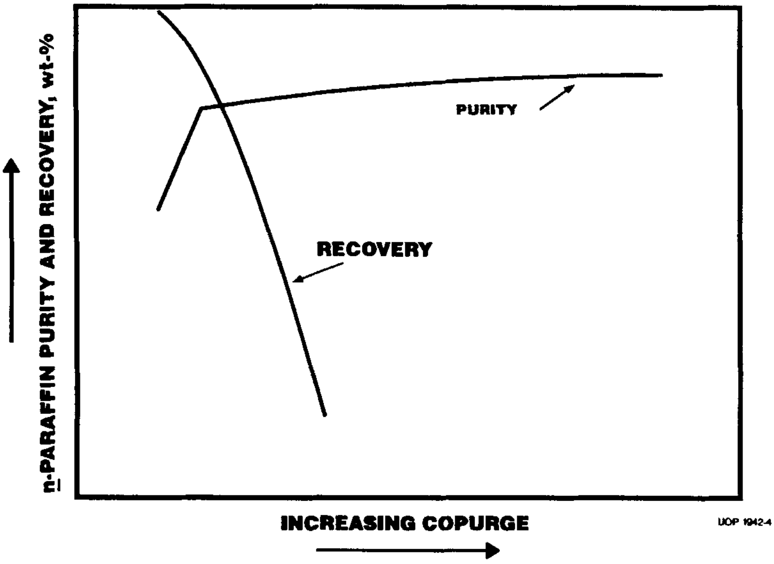

FIG. 4. Copurge rate vs purity and recovery.

a properly operated unit, the copurge quantity is adjusted to thoroughly purge the void without losing *n*-paraffins from the top of the adsorber. As shown in Figure 4, an inadequate copurge results in unacceptable product purity. Excessive copurge results in low recovery. As the nonnormal feed components exit the top of the chamber, they are combined with the effluent from those chambers operating in the adsorption mode. The combined effluent is charged to the isodehexanizer column, where the desorbent is recovered as an overhead fraction and recycled to the adsorption section.

Desorption Step

The *n*-paraffins are recovered from the adsorbent micropores during the desorption step. During this step, *n*-hexane desorbent is directed downflow through the adsorbers. The concentration gradient between the adsorbed and bulk phases drives the desorption process. The process is also facilitated by the physical removal of the heavier feed *n*-paraffins from the pores by the entering *n*-hexane desorbent. Not all of the feed *n*-paraffins are removed from the adsorbent, and the decision as to the quantity of residual *n*-paraffins is based on economic considerations. The more residual *n*-paraffins that remain, the less selective pore volume that is available for the next adsorption cycle, and the greater the coke formation and frequency

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of regeneration. As a result, the size and capital cost of the adsorption section required to accomplish the desired production target increases. The increased capital costs of the adsorption section are offset by the reduced operating and capital costs associated with the desorbent recovery section. A balance between these two considerations must be made in designing the unit. The *n*-paraffin-rich desorbent stream exiting the bottom of the adsorber is directed to the *n*-paraffin dehexanizer column, where the desorbent is recovered as an overhead product and recycled to the adsorption section.

Regeneration Step

Unlike the lighter *n*-paraffin separations systems, the kerosine or gas oil IsoSiv process experiences adsorbent deactivation, which necessitates oxidative regeneration on a regular basis. The deactivation of the adsorbent results from the accumulation of carbonaceous materials on the adsorbent. This accumulation is a natural consequence of processing heavy feeds at elevated temperature. The accumulated materials reduce the available selective pore volume until the process suffers from either lost recovery or reduced purity as the copurge quantity is lowered to compensate for the lost capacity and increased bed utilization. The frequency of regeneration is a function of numerous factors, which include feed molecular weight, sulfur level, operating temperature, and residual *n*-paraffin loading. For a kerosine feedstock, the frequency of regeneration ranges from 15 to 30 days depending on the above parameters. More frequent regenerations are required for gas oil feeds.

In performing the regeneration, desorbent purge, hydrocarbon removal, and oxidative burn steps are carried out to ensure a safe and relatively complete regeneration of the adsorbent. Not all of the capacity is recovered after the carbon burn. Unlike the Molex process and the lighter *n*-paraffin recovery systems, the kerosine IsoSiv unit processes feeds that can contain significant levels of sulfur. Some of the feed sulfur becomes bound on the adsorbent in the residual coke. During the regeneration step, the adsorbent capacity is permanently reduced by the formation of calcium sulfate salts. The rate at which this decline occurs is related to the amount of sulfur in the feed processed and the frequency of regeneration.

THE NAPHTHA IsoSiv PROCESS

The naphtha IsoSiv process can be considered a simplification of the kerosine IsoSiv process that takes advantage of the low molecular weight of the feedstock as well as its quality. Except where the IsoSiv unit is a standalone or front-end unit, the process derives its feedstock from a cat-

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alytic isomerization unit. The most widely used catalyst in such a scheme is zeolite based. When this type of catalyst is used, the contaminant specifications for the isomerization feedstock are always stringent and so the naphtha IsoSiv unit, unlike the kerosine-range unit, receives relatively contaminant-free feedstock. Therefore, adsorbent deactivation is not of prime concern, and naphtha IsoSiv units can be designed with fewer beds than in kerosine units and without the requirement for one bed to be in a regeneration step. Additionally, the lower molecular weight of the feed in naphtha IsoSiv units lends itself to lower cycle times than kerosine units have. Figure 5 shows an overall flow diagram, including the conventional unit operations and equipment used to move, heat, cool, and separate the process streams.

A simplified cycle description of a naphtha IsoSiv unit is shown in Fig. 6. Four beds loaded with adsorbent are shown. At any given moment, either one adsorber is on each of the four steps, A-1, A-2, D-1, or D-2; or two adsorbers are on the A-2 step and two on the D-2 step. Each of these steps is shown in Fig. 6. In a manner comparable to that used with the kerosine IsoSiv process, these four steps are repeated in sequence with each of the four adsorbent beds. The integrated cycle and sequencing diagram are shown in Figs. 7 and 8, respectively.

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A-1 Step

During the A-1 step, a slipstream of adsorber feed is introduced into the bed to bring hydrocarbon into a hydrogen-purged adsorber. The normal components of the feed (called "n" in Fig. 6) are adsorbed in the adsorbent pores and the nonnormals (called "ISO'S" in Fig. 6) remain in the void spaces of the bed. These nonnormals displace the purge gas (retained during the previous D-2 step and called "H_2" in Fig. 6) out through the top of the bed. The A-1 step is terminated before the nonnormals and purge gas interface breaks through the top of the adsorber, thereby ensuring that the exiting gas, which is internally recycled, is not excessively diluted by feed nonnormal components.

A-2 Step

During the A-2 step, heated adsorber feed from the feed furnace is sent to the adsorber beginning the A-2 step and to a second adsorber already on the A-2 step. When only one adsorber is on the A-2 step, the adsorber feed is mixed with the D-1 effluent from another bed, and this combined feed is sent to the single adsorber on the A-2 step. As A-2 feed flows up through the bed, the normals continue to be adsorbed to an extent determined by the partial pressure and molecular weight of the normals and

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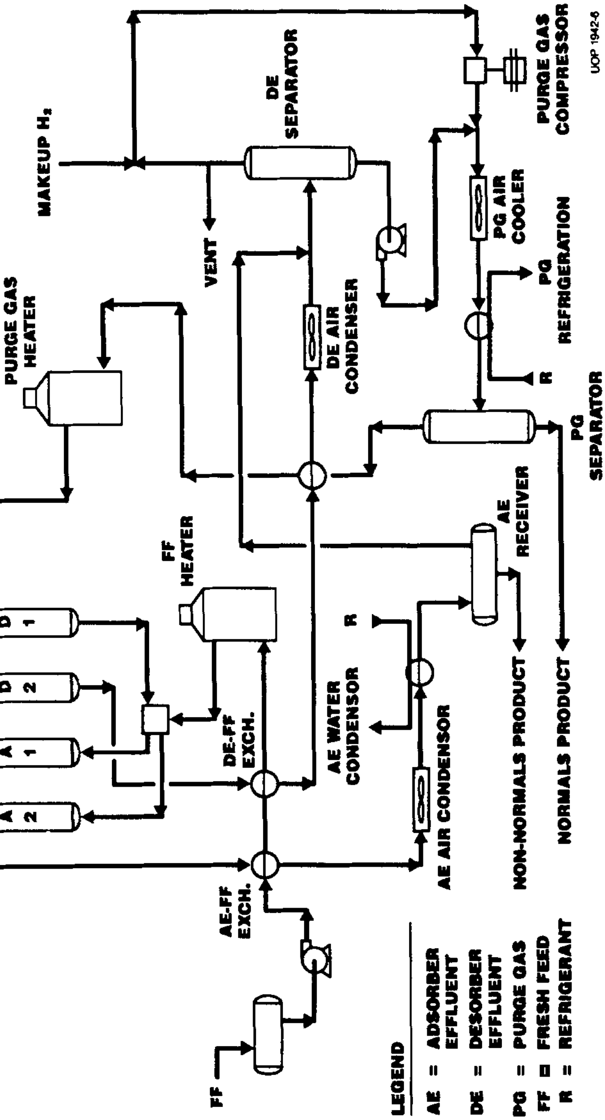

FIG. 5. Flow diagram of the naphtha IsoSiv process.

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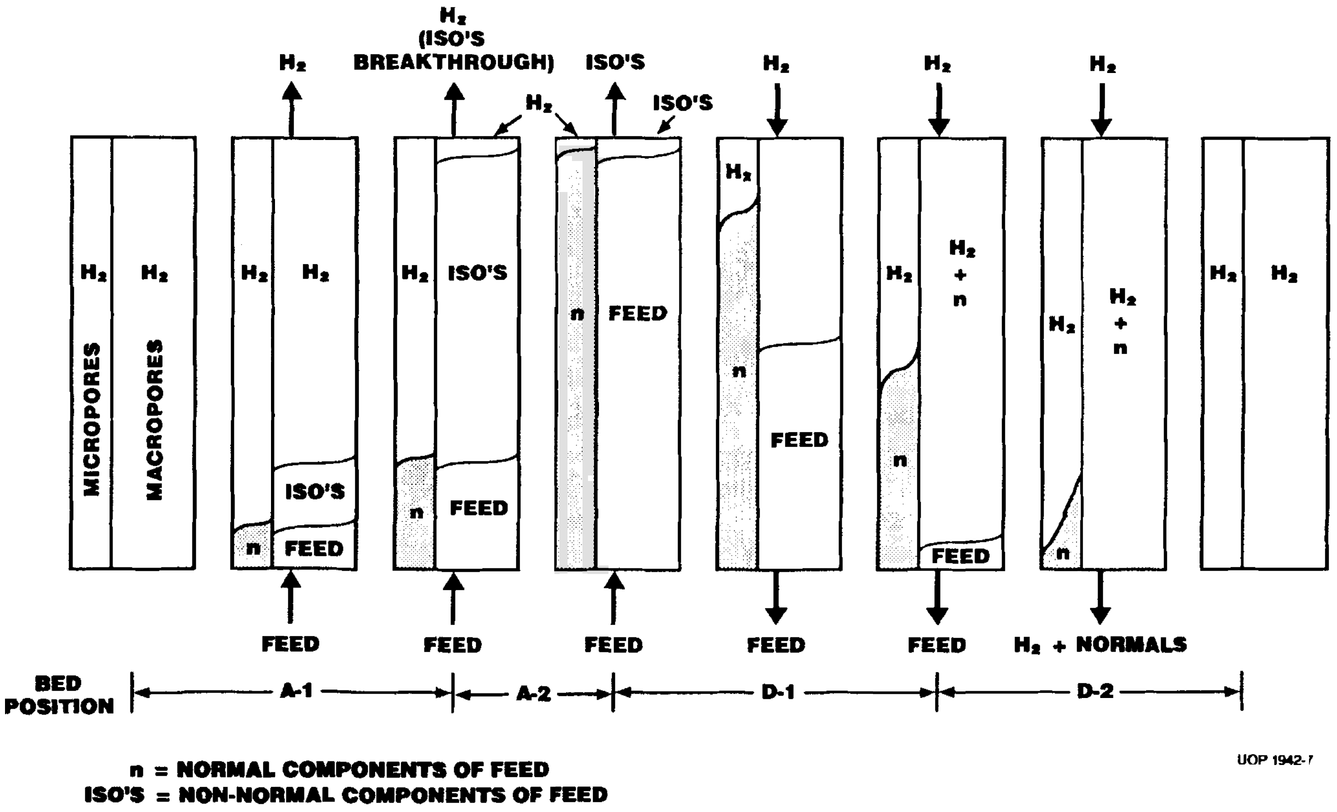

FIG. 6. Naphtha IsoSiv cycle description.

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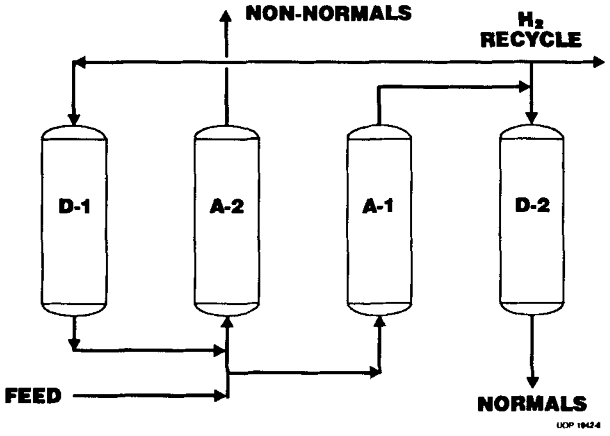

FIG. 7. Naphtha IsoSiv cycle integration.

operating temperature. The nonnormals, together with some purge gas and a small quantity of normals, exit the adsorber at the top and are recovered as product. As shown in Fig. 6, the A-2 step is terminated before the mass transfer front between the normals and purge gas reaches the top of the bed, thereby ensuring that normals breakthrough is minimized and nonnormals purity is maximized.

D-1 Step

During the D-1 step, the nonadsorbed C_4+ hydrocarbons retained in the bed after the completion of the A-2 step are displaced with hydrogen purge gas. The displaced hydrocarbon, along with some purge gas, is

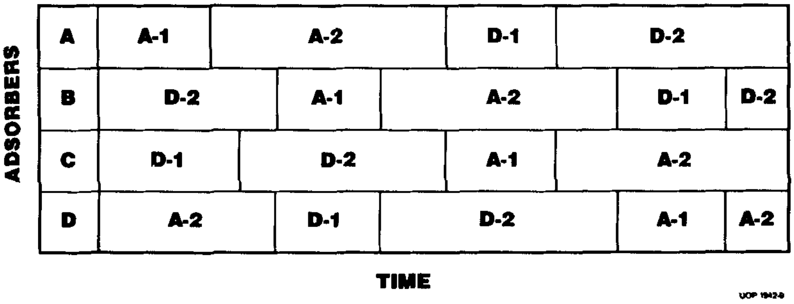

FIG. 8. Adsorber sequencing diagram.

blended at the bottom of the bed with adsorber feed for the A-1 and A-2 steps. The step is terminated when the concentration of nonnormals in the effluent reaches a low level.

D-2 Step

During the D-2 step, purge gas is either combined with A-1 effluent purge gas and passed downflow through the one adsorber on the D-2 step or distributed evenly between the two adsorbers on this step. If the latter is true, the total D-2 effluent also includes bypassed D-1 feed. In this desorption step, the purge gas desorbs normals from the adsorbent pores by reducing the partial pressure of the normals in the vapor phase, thereby shifting the equilibrium loading to a lower value. The rate of desorption continually decreases as the pore concentration of the normals declines. The D-2 step is terminated before the normals concentration reaches that of the purge gas.

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FEED PROPERTIES

As emphasized earlier, the naphtha IsoSiv unit can be viewed as a simplification of the kerosine IsoSiv unit. Much of the simplification is a direct result of differences in feed properties and reduced contaminant levels which obviate the need for regular adsorbent regeneration. In the case of a kerosine IsoSiv process, feed properties such as sulfur content, *n*-paraffin content, and molecular weight have a surprisingly significant impact and are pivotal in the design and performance of the process. Specifically, these feed properties drive such basic decisions as adsorber sizing, desorbent requirement, and placement of a hydrotreater upstream or downstream of the separation process.

Contaminant Levels

Commercial kerosine IsoSiv units have processed feeds with sulfur levels ranging from less than 1 wppm to as great as 2000 wppm. The impact of such extremes in sulfur levels on adsorbent life is equally extreme. The decision to process such a sulfurous feedstock or to hydrotreat the feed prior to the separation step hinges on an economic balance between the cost of the replacement adsorbent and downtime against the cost of a hydrotreater. Although complicated by such factors as feed *n*-paraffin content and normal and nonnormal product quality requirements, the decision is generally made to hydrotreat feeds containing more than 2000 wppm sulfur prior to the separation step. For feeds containing less than 500 wppm sulfur, the hydrotreating is typically performed downstream of the IsoSiv process.

n-Paraffin Content and Molecular Weight

The *n*-paraffin content of the kerosine is an important consideration and influences such factors as the adsorbent capacity and the deactivation rate. In the case of adsorbent capacity, the driving force for the adsorption of feeds rich in *n*-paraffin is increased by the greater *n*-paraffin concentration in the bulk phase during the adsorption step. The deactivation rate observed for feeds rich in *n*-paraffins is less than that for leaner feeds simply because the adsorbent is exposed to less hydrocarbon to make the same amount of product, and as a result, less carbonaceous material is deposited on the adsorbent per unit of time.

Although most of the kerosine feeds processed in IsoSiv units are in the C_{10} to C_{14} carbon range, some feeds having molecular weights as great as 240 have been processed. As illustrated in Figs. 9 and 10, increased molecular weight has a pronounced negative effect on both absorbent capacity and desorbent requirement. These considerations and the associated increased capital and operating costs make the relative rarity of such an operation understandable.

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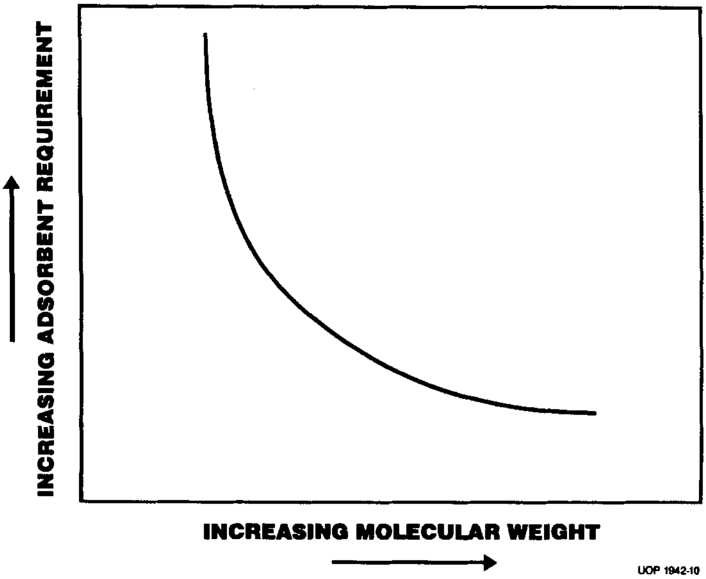

FIG. 9. Adsorbent requirement vs feed molecular weight for kerosine IsoSiv.

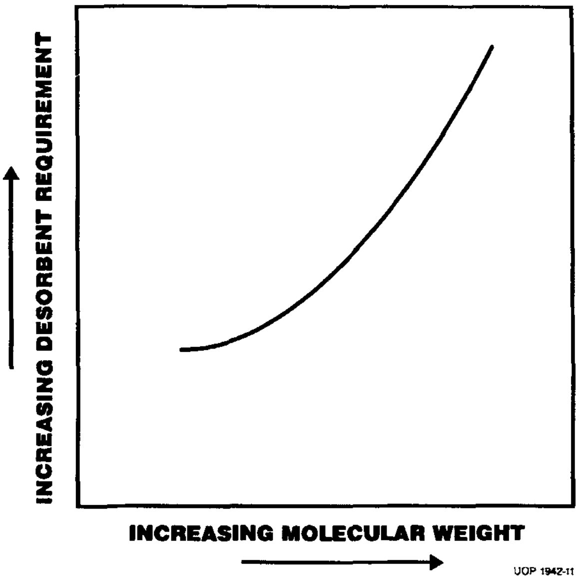

FIG. 10. Desorbent requirement vs feed molecular weight for kerosine IsoSiv.

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THE KEROSINE MOLEX PROCESS

The Molex process is an application of the UOP liquid-phase Sorbex technology and enjoys wide acceptance and application in the production of detergent-range and, to a lesser extent, heavier *n*-paraffins. Figure 11 shows a simplified schematic of a Sorbex process unit which uses a desorbent that is lighter than the feed components and consists of more than one component. Therefore, the process configuration includes a desorbent splitter for splitting the desorbent components. Such a configuration is typical of kerosine-range Molex units. In its most evolved configuration, the Molex process is capable of producing extract at 99.8 wt% *n*-paraffin purity with less than 300 wppm aromatics at >95% recovery for kerosine-range feedstocks.

Primary Sections

Although zone configuration and desorbent changes have been made several times since it was first commercialized in 1964, the Molex process has, in general, been characterized as having three primary sections: feed pretreatment, adsorption (with two chambers and a rotary valve), and desorbent recovery.

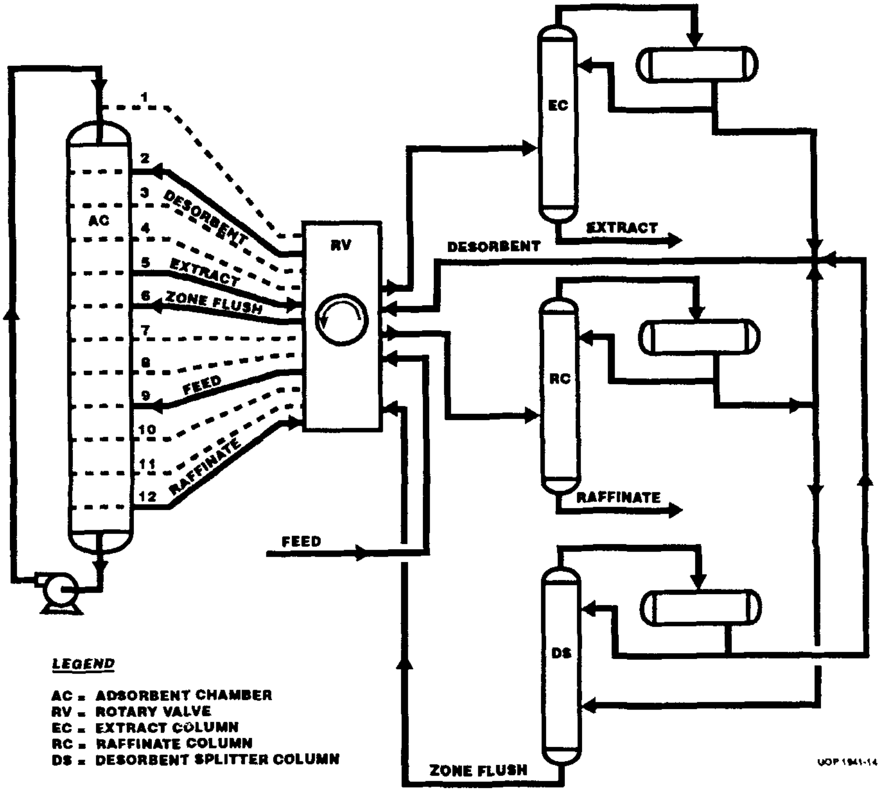

FIG. 11. Sorbex simulated moving bed for adsorptive separations.

Feed Pretreatment Section

Unlike the kerosine IsoSiv unit, Molex does not rely on routine *in-situ* regeneration to maintain stable adsorbent performance. Instead, emphasis is placed on pretreatment of the feed prior to processing across the adsorbent. The kerosine, which contains native oxygenates, nitrogenates, olefins, and sulfur compounds, is hydrotreated at rather severe conditions to reduce the contaminants essentially to extinction. The importance of this pretreatment step cannot be overemphasized, and every Molex unit is preceded by a hydrotreater. When the feed quality is maintained at the desired pristine quality, Molex adsorbent life in excess of 4 years is not uncommon. When a significant contaminant ingress has been allowed, performance has declined precipitously. The hydrotreated kerosine exiting the reactor is stabilized in a stripper column. The bottoms fraction, which

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is typically either a C_{10} to C_{13} or C_{11} to C_{14} fraction, is then charged to the Molex adsorption section through the rotary valve.

Adsorption Section

The adsorption section can be envisioned to comprise two parts. The rotary valve directs process flows to different sections of the adsorption section, and the adsorbent chambers physically hold the adsorbent in a multitude of beds.

Like all Sorbex applications, the Molex process simulates the countercurrent movement of the liquid and adsorbed phases without actual movement of the solid phase. This approach eliminates difficulties associated with mechanical abrasion and flow distribution resulting from actual movement of the adsorbent. The simulation is achieved using an indexing device developed by UOP and known as a rotary valve. A simplified schematic of a rotary valve is shown in Fig. 12. The process streams, such as feed,

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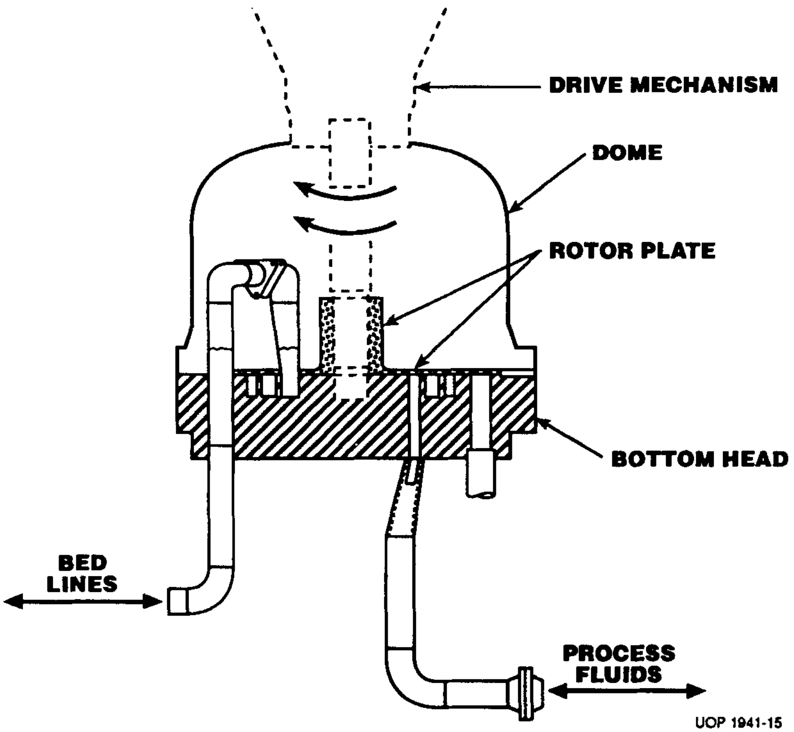

FIG. 12. Rotary valve.

desorbent, extract, raffinate, and zone flush, are introduced into and withdrawn from the chambers by the rotary valve. As these streams are being introduced into and withdrawn from the adsorbent chambers, the rotary valve shifts all stream positions simultaneously and in the same direction as liquid flow, one bed at a time. The stream flows are maintained continuously as the valve moves through the 24 beds typically found in a Molex unit. The relative positions of the process streams are fixed by the rotary valve configuration and define zones in which, among others, the adsorption, purification, and desorption steps of the separation occur. These steps are discussed in more detail later.

The adsorption section typically consists of two chambers, each containing 12 beds loaded with adsorbent. The beds are separated by grids which serve as both liquid distributors and collectors. Liquid is pumped from the bottom of the second chamber to the top of the first chamber and from the bottom of the first chamber to the top of the second chamber at flow rates set to establish the desired concentration profiles in the adsorbent chambers. The flow rates vary and are regulated by control systems. The overall effect of the streams entering and exiting the chamber at changing positions determined by the rotary valve configuration and step time and the continuous downward liquid flow through the chambers is a simulated countercurrent movement of the adsorbent relative to the liquid.

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Desorbent Recovery Section

The extract and raffinate streams exiting the chambers are diluted with *n*-pentane and *i*-octane desorbent. The dilute streams are directed to a desorbent fractionation and recovery system as depicted in Fig. 13. The *n*-paraffin and nonnormal paraffin product streams are recovered as the extract and raffinate column bottoms, respectively. A portion of the desorbent is taken as side cuts from the extract and raffinate columns and directed to the desorbent splitter column, where the nC_5 is split from the iC_8 as an overhead fraction and sent to the desorbent surge drum. The iC_8-rich splitter bottoms stream is used as Zone II flush and chamber head flushes. The overhead fractions from the extract and raffinate columns are directed to the desorbent surge drum for recycle to the rotary valve and chambers.

Molex Zone Definitions

As indicated, the relative positions of the process streams are fixed by the rotary valve configuration and define zones in which the adsorption, purification, and desorption steps of the separation occur. An understand-

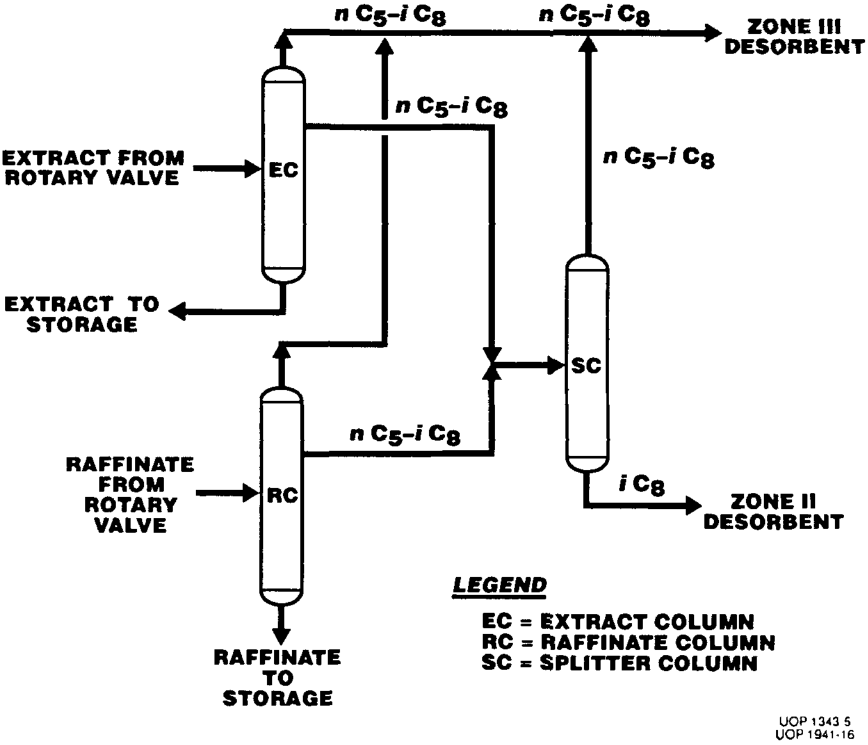

FIG. 13. Split desorbent fractionation system in a Molex unit.

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ing of the zones and their definition as well as the associated chamber concentration profiles is central to understanding how the Molex process functions (Fig. 14).

- *Zone I—Adsorption Zone:* The adsorption zone is designated as Zone I and is defined as the region between the feed injection point and the raffinate withdrawal point. In this zone the feed *n*-paraffins are adsorbed in the micropores by displacing *n*-pentane desorbent. The feed nonnormals remain in the macropore and interstitial voids and are removed from the system in the raffinate.
- *Zone II—Purification Zone:* The purification zone, designated Zone II, is defined as the region between the extract-out and feed-in streams. The nonnormals are flushed from the nonselective void volume in this zone.
- *Zone III—Desorption Zone:* The region between the desorbent-in and extract-out streams is defined as the desorption zone, designated Zone

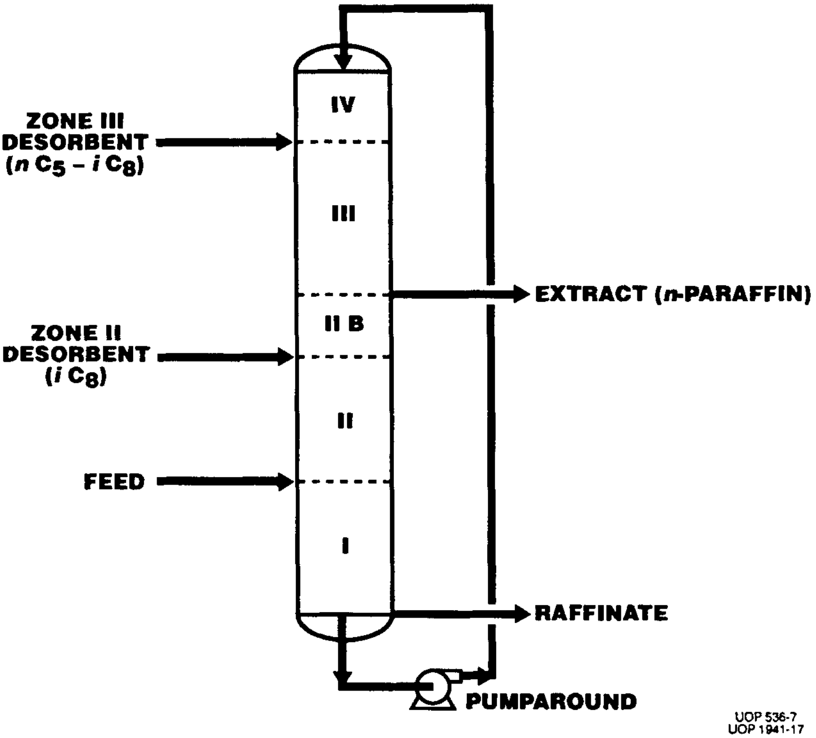

FIG. 14. Zone definitions in a split-desorbent Molex unit.

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III. The *n*-paraffins adsorbed in Zone I are recovered from the adsorbent micropores in Zone III and are withdrawn in the extract.

- *Zone IV—Zone III Buffer Zone:* The region between the desorbent inlet and raffinate withdrawal points is defined as Zone IV, the Zone III buffer zone. Zone IV provides a buffer between the raffinate stream at the bottom of Zone I and the desorption zone, and it serves to prevent contamination of the extract by nonadsorbed feed components.

Operating Parameters

The maintenance of proper concentration profiles in each of the zones is central to achieving consistent operation at high purity and recovery at minimal operating cost. Zone reflux ratios are the operating parameters that are adjusted to establish the proper concentration profiles in each of the zones and are used to compensate for either adsorbent aging or changes in feed composition:

- A/F_n: This parameter is defined as the ratio of the simulated adsorbent pore circulation rate to the flow rate of *n*-paraffins in the Molex feed. It quantifies the chamber size for a given throughput and is typically increased to compensate for adsorbent aging and capacity loss. An optimum A/F_n is the minimum required to perform the desired separation and defines the purity–recovery curve (Fig. 15).
- L_{2B}/W: This parameter is defined as the ratio of the gross liquid flow in the Zone II buffer zone relative to the rate of the nonselective voids circulation. The L_{2B}/W ratio minimizes *n*-pentane flow from the desorption zone into Zone II to maximize *n*-paraffin recovery (*1*). Figure 16 illustrates the effect of this variable on *n*-paraffin recovery.
- L_2/W: This zonal reflux ratio is defined as the ratio of the gross liquid flow in the purification zone, Zone II, to the nonselective voids circulation rate. The L_2/W ratio is the primary variable used to control extract purity. Increases in L_2/W ratio result in higher purity and lower recovery. Figure 15 illustrates the effect of changing L_2/W on unit performance.

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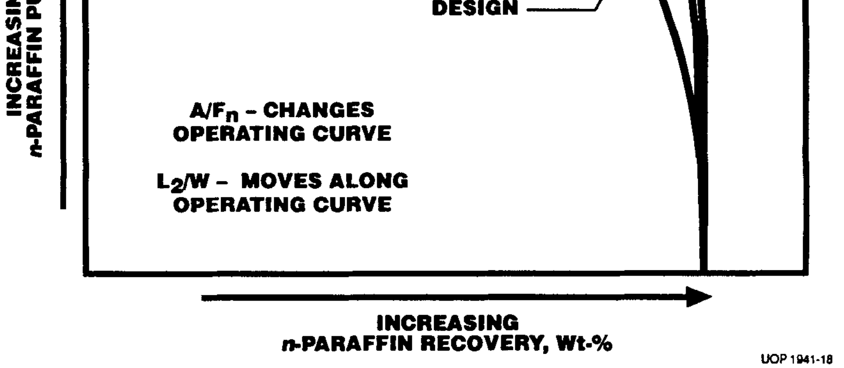

FIG. 15. Effect of A/F_n and L_2/W on *n*-paraffin purity and recovery.

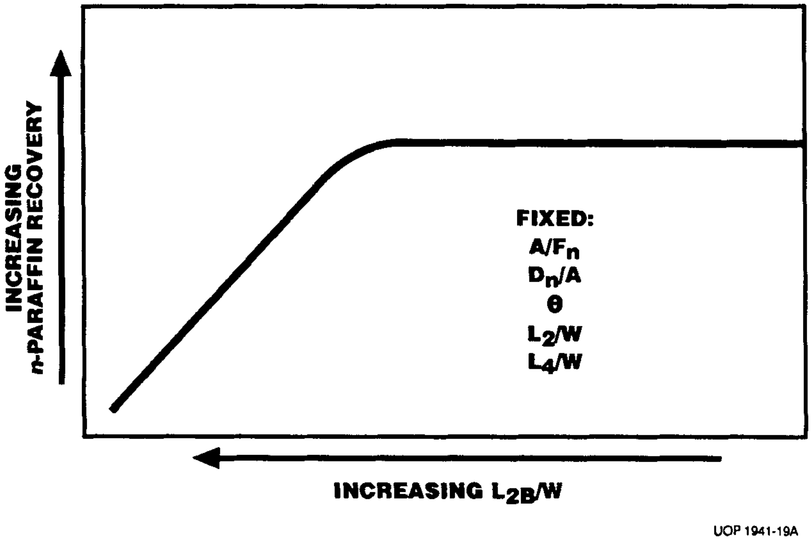

FIG. 16. Effect of L_{2B}/W on *n*-paraffin recovery.

- D_n/A: This zone ratio is defined as the ratio of the desorbent normals flow rate in the desorption zone, Zone III, to the selective pore circulation rate. The optimum ratio is the minimum required to desorb the feed components across this zone. Higher values of D_n/A result in increased desorbent flow to the chambers and higher utilities in the desorbent recovery columns. In the Molex process, operation at too low a D_n/A results in lowered *n*-paraffin recovery (Fig. 17).
- L_4/W: This parameter is defined as the ratio of the gross liquid flow in the buffer zone, Zone IV, to the rate of the nonselective voids circulation. This parameter is set to prevent breakthrough of raffinate components from Zone I to Zone III. Such a breakthrough reduces the purity of the *n*-paraffin extract product. However, operation at too low an L_4/W results in more desorbent circulation and higher operating costs. The two requirements must be balanced, and this balance determines the optimum value (Fig. 18).

The cycle time (θ) is defined as the time required to complete one complete revolution of the rotary valve. During that time, the position of the feed changes 24 times as the valve steps through 24 beds. The ability to operate at faster cycle times reduces chamber volume for a given throughput. Lower limits for the cycle time are set by the mass transfer characteristics of the system. Operation below this minimum results in impaired performance. Generally, Molex units processing heavier or full-

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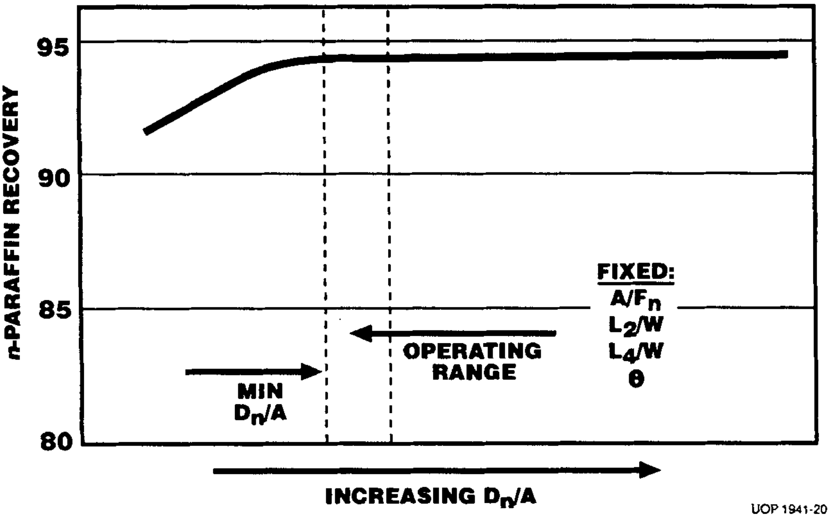

FIG. 17. Effect of D_n/A on *n*-paraffin recovery.

range feedstocks are designed with cycle times that are three to six times longer than those used for naphtha-range feeds.

The correct adjustment of each of these parameters is critical to achieving the optimum process performance and producing a product that meets specifications. In addition to the zone reflux ratios, temperature and pres-

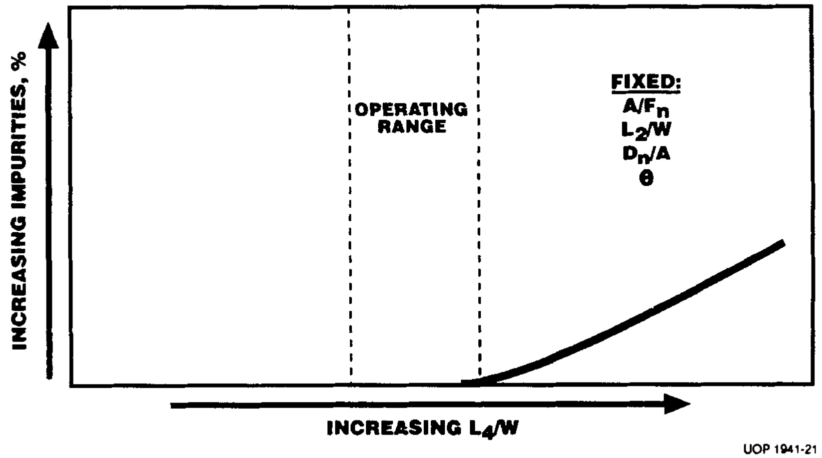

FIG. 18. Impurities from Zone IV in extract.

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sure are also considered to be important design and, to a lesser extent, operating variables. The operating pressure is set to maintain the circulating streams in the liquid phase and, once set, is typically not adjusted further. The operating temperature is a function of feed carbon number range. Increases in temperature may be used to compensate for mass transfer limitations encountered when processing heavy, full-range feeds.

THE GASOLINE MOLEX PROCESS

Just as the naphtha IsoSiv process can be looked upon as a simplification of the process used for kerosine-range feedstocks, so can the gasoline Molex process be thought of as a simpler version of the kerosine Molex process. The gasoline Molex process is typically downstream of a UOP Penex unit. The Molex unit recovers and recycles unconverted low-octane normal C_5 and C_6 components in the naphtha-range isomerate to increase its octane number. Octane numbers of *n*-pentane and *n*-hexane are much lower than those of the other components of light naphtha isomerate (Table 2), and significant increases in the octane number of isomerate can be achieved by recycling the normals back for isomerization. Several recent publications and presentations have dealt extensively with the gasoline Molex process (*2*, *3*). These publications have included commercial performance data for the isomerization of light straight-run naphtha and the production of high-octane gasoline in conjunction with a liquid-phase isomerization process using a chlorided catalyst and the Molex separation process. This section concentrates on discussing the major simplifications that

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TABLE 2
Octane Numbers of Some Pure Components

	ASTM	
	RON-C	MON-C
C_5:		
i-Pentane	92.3	90.3
n-Pentane	61.7	62.6
C_6:		
2,2-Dimethylbutane	91.8	93.4
2,3-Dimethylbutane	103.5	94.3
2-Methylpentane	73.4	73.5
3-Methylpentane	74.5	74.3
n-Hexane	24.8	26.0
Methylcyclopentane	91.3	80.0
Cyclohexane	83.0	77.2
Benzene	120.0	115.0

were made to the kerosine Molex process to adapt it to the specific needs of processing naphtha-range feedstocks for gasoline production.

A summary of the major differences is shown in Table 3. The most important of these differences are:

- *Reduction of the Number of Beds and the Number of Chambers:* The lower volume of adsorbent typically required for a gasoline Molex unit and the less-stringent extract-quality requirements mean that a gasoline Molex unit needs only an 8-bed, 1-chamber design compared with the 24 beds and 2 chambers that are normally used in a kerosine Molex unit.
- *Operating Temperature Reduction:* The gasoline Molex process operates at lower temperatures, typically less than 250°F, because it processes feedstock with lower molecular weight and diffusivity limits are not reached. The ability to operate the unit at lower temperatures also helps keep design pressures sufficiently low, even for an operation involving C_4 to C_6 hydrocarbons.
- *Reduction of Cycle Time:* The gasoline Molex process is able to operate at cycle times that are two to four times lower than kerosine units simply because of the higher diffusion rates of the lower-molecular-weight feed components.
- *Desorbent Makeup:* The kerosine Molex process requires some desorbent makeup to compensate for fractionation and mechanical losses. The gasoline Molex process derives its makeup desorbent, which is a blend of nC_4 and iC_4, from the feed. The recirculating desorbent is recovered from an intermediate tray in either the extract or raffinate columns. Its composition is kept constant by dragging an iC_4-enriched stream from the overhead receiver of that fractionator (*3*).
- *Elimination of Flushes:* Flushes were deemed to be unnecessary because a high-purity normals stream is not critical in this application. Although extract normals purities of 98 + % are routinely expected in petrochemical

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TABLE 3
Simplifications to Kerosine Molex Design for Naphtha Applications

	Kerosine Molex	Naphtha Molex
Beds, no.	24	8
Adsorbent chambers, no.	2	1
Temperature, °F	<450	<250
Cycle time, min	Base	(0.25 − 0.5) × Base
Desorbent makeup	Required	None

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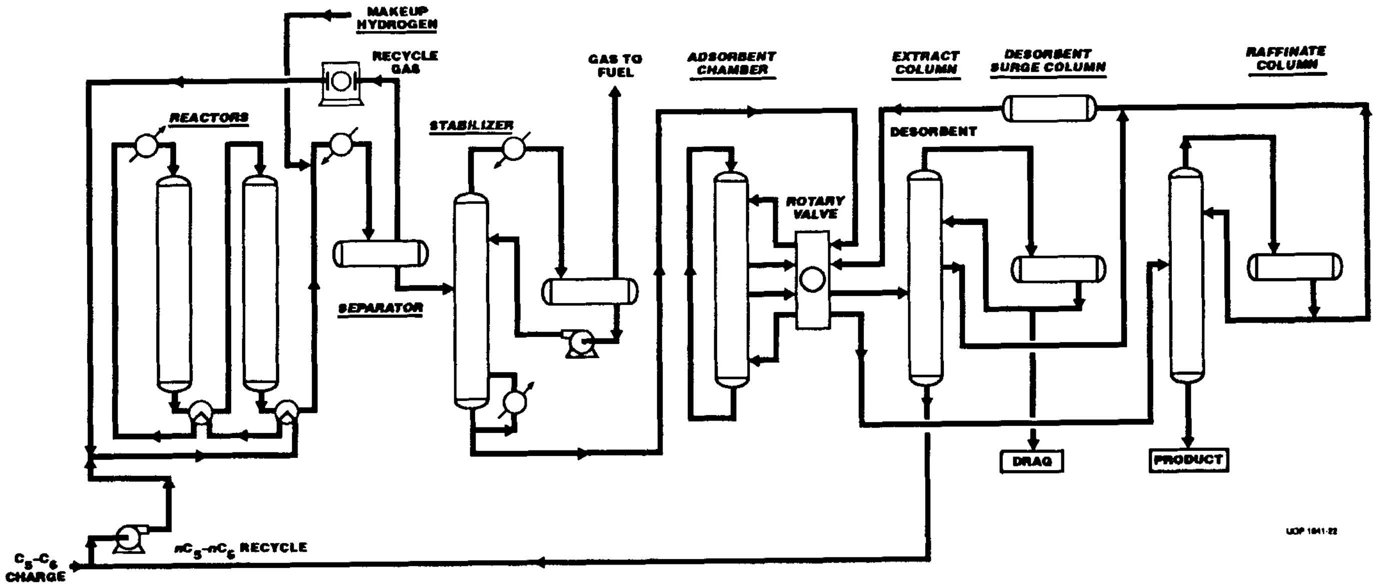

FIG. 19. Schematic of a Penex-Molex complex.

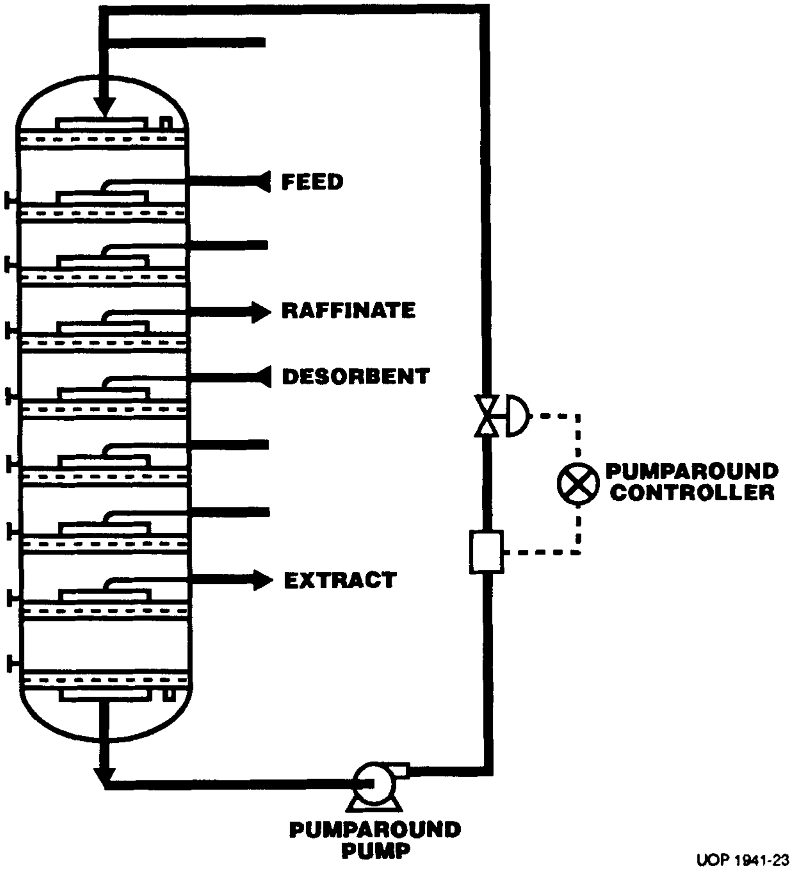

FIG. 20. Gasoline Molex adsorbent chamber.

applications, a target purity of 90% (at high recovery) is typical of gasoline units.

For the sake of completeness, a process flow diagram of a gasoline Molex unit in a Penex-Molex process configuration as well as a diagram of a gasoline Molex adsorbent chamber are shown in Figs. 19 and 20.

COMPARISON OF KEROSINE MOLEX AND IsoSiv TECHNOLOGIES

This section compares and contrasts the liquid-phase Molex and vapor-phase IsoSiv processes for the kerosine range to provide insight into the

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incentives for and implications of pursuing one processing strategy over another. Both the kerosine Molex and IsoSiv processes are commercially proven technologies capable of producing high-purity *n*-paraffin products that are used primarily for the production of detergent intermediates. Furthermore, the two processes undergo fundamentally similar adsorption, purification, and desorption steps; both can be characterized as having adsorption and desorbent recovery sections which provide additional common elements.

In contrast, the two kerosine processes differ in that the IsoSiv process is a semicontinuous, vapor-phase application and the Molex process is a continuous, liquid-phase application. These basic differences, rather than the similarities, characterize the processes and are reflected in virtually every aspect of the process design and operation and to a significant extent determine which process is best in a particular situation. The areas in which such differences are manifested include feed pretreatment, adsorbent requirements, product quality, recovery profile, process equipment requirements, chamber internals and metallurgy, and capital and operating costs.

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Feed Pretreatment

As discussed earlier, commercial IsoSiv units process feeds with sulfur levels ranging from 1 to 2000 wppm. Polar compounds such as oxygenates, nitrogenates, and, to some extent, olefins pose little problem for an IsoSiv unit. The process is able to handle such contaminants because it is configured to easily allow *in-situ* regeneration.

A different strategy is used for the Molex process. Rather than contend with frequent adsorbent replacement or regeneration, the feed is hydrotreated to extremely low contaminant levels upstream of the Molex unit. This approach has been successful, particularly with detergent-range units, and adsorbent lives of several years have been routinely observed commercially. However, without the flexibility to easily perform *in-situ* regeneration, the implications of premature adsorbent deactivation in a Molex unit are more serious.

Adsorbent Requirement

The two technologies differ with regard to adsorbent requirements, both in terms of the absolute quantity required to produce a fixed quantity of *n*-paraffins as well as the processing demands and adsorbent properties. In general, two times more adsorbent is required for an IsoSiv application than for a Molex application. This greater adsorbent requirement is a reflection of the higher selective pore volume of the Molex adsorbent as well as the greater staging efficiency of the countercurrent Sorbex technology, which is the dominant effect.

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The adsorbents used for the two applications also differ markedly. The differences include shape, size, capacity, and mass transfer rate. Both adsorbents are highly engineered materials. Although the Molex adsorbent can be either granular or spherical in form, the IsoSiv adsorbent is typically a 1⁄16-inch pellet. A granular adsorbent sized for a Molex unit is unsuitable for the vapor-phase application because of pressure drop considerations. Although adsorbent stability is a critical concern in an IsoSiv unit operating at elevated temperature, the lack of an easily implemented *in-situ* regeneration in a Molex application as well as the longer turnaround time pose more significant limitations for Molex. This processing concern is addressed by the stringent feed pretreatment upstream of a Molex unit as well as in the design of the Molex adsorbent.

Although adsorbent capacity is critical for both liquid- and vapor-phase applications, mass transfer rate is significantly more important for the liquid-phase Molex process, which is more subject to diffusion limitations. The smaller size of the granular or beaded Molex adsorbent, as well as other elements of the product design, facilitates mass transfer in the liquid phase. Diffusional properties of the IsoSiv adsorbent are less critical as a consequence of the relatively faster diffusion rates in the vapor phase at elevated temperature.

Recovery Profile

As a moderately low-temperature, liquid-phase application, the Molex process is much more subject to mass transfer rate limitations than the vapor-phase IsoSiv process. As a result, the recovery pattern observed as a function of carbon number differs significantly for the two processes. As indicted in Fig. 21, the *n*-paraffin recovery decreases with increasing carbon number in a Molex unit, whereas the recovery pattern observed in an IsoSiv unit is relatively independent of carbon number. In most detergent applications that process relatively narrow carbon range feeds, this pattern has not been an impediment, and the Molex process functions exceptionally well. The trend toward lighter detergents and away from less biodegradable C_{14} alkylbenzene sulfonates plays to a Molex strength. However, when heavy, wide-carbon-range feedstocks are processed, the problem is more pronounced, and the processing choice must be evaluated on a case-by-case basis.

Product Quality

Both kerosine Molex and IsoSiv technologies are capable of producing *n*-paraffins at high purity and recovery. However, the aromatic content of the products can differ considerably, depending on the feed being processed. In a high-purity Molex application, extract purities in excess of

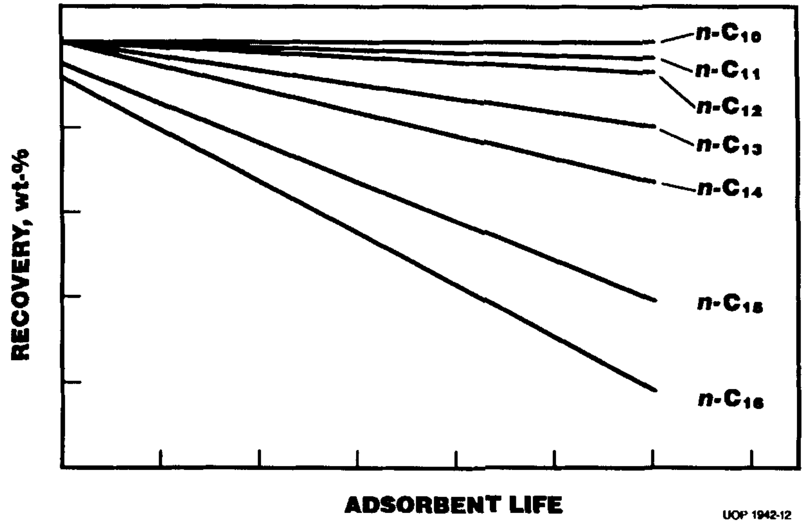

FIG. 21. Molex component recovery.

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99.8 wt% with less than 300 wppm aromatics have been produced commercially. In the standard design, purities of 99.5 wt% with less than 0.3 wt% aromatics are routine. The aromatics content of IsoSiv extracts, while generally low, tends to be more feed dependent. Units are typically designed with a downstream hydrotreating unit for aromatics and sulfur reduction, and great care must be exercised to avoid *n*-paraffin isomerization. The two processes also differ in the quality of the by-product streams. The Molex strategy of hydrotreating the feed prior to the separation step sweetens and improves the smoke point of the raffinate product, which can then be used as a high-grade blending component. The quality of the IsoSiv nonnormals product is extremely feed dependent.

Process Equipment Requirements

As shown in Table 1, which summarizes the equipment requirements for a six-adsorber IsoSiv unit and a comparable Molex unit, the IsoSiv unit has more equipment components. This summary shows only equipment for the separation section. The associated hydrotreater and prefractionation sections are not considered.

The differing equipment requirements directly reflect the divergent processing strategies. The two-chamber configuration and use of the rotary valve in the Molex process are contrasted with the multiple chambers and valves used in the IsoSiv process. The need for a regeneration section also adds to the IsoSiv equipment list and makes the unit significantly larger. Such considerations add to the capital cost and become significant when limited plot space is available. However, a complete evaluation must include the total process needs. Conclusions based solely on the separation section may be countered by considerations associated with other process units.

Chamber Internals and Metallurgy

In a Molex application, the adsorbent is typically loaded into two chambers, each containing 12 beds. The beds are separated by collector-distributor grids which aid in establishing the concentration profiles that enable the process to function. The IsoSiv process uses a rather different strategy: it has far simpler chamber internals but more chambers. Both approaches function equally well. However, as a result of the simpler internal configuration of the IsoSiv process, the time required to reload the chambers with adsorbent is significantly less than for a Molex unit. IsoSiv and Molex adsorbers can be turned around in approximately 2 and 4 weeks, respectively, assuming 12-hour shifts in both cases. Carbon steel is the required metallurgy for both processes.

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Capital and Operating Costs

In general, the capital costs for the IsoSiv unit tend to be 1.3 to 1.9 times greater than for a comparable Molex unit. This cost differential is consistent with the amount of equipment needed for the IsoSiv process. However, the higher costs associated with the IsoSiv unit may be offset by lower costs in other sections of the total complex. For example, when a low-sulfur, low-aromatics feed is processed, a hydrotreater is not needed.

As a result of the need to vaporize both the feed and desorbent streams, the operating costs associated with an IsoSiv unit proper are 1.5 to 2.0 times greater than for a Molex unit. As with the capital costs, when the operating cost of the hydrotreating and prefractionation sections of the complex are considered in the evaluation, the operating cost difference between the technologies may narrow somewhat, and the conclusion depends on the specific case evaluated.

COMPARISON OF NAPHTHA MOLEX AND IsoSiv TECHNOLOGIES

This section compares IsoSiv and Molex technologies for processing naphtha-range feedstocks. The effect of the operative phase and processing strategy on performance and costs is discussed.

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The Molex process operates in the liquid phase at relatively low temperatures; the IsoSiv process operates in the vapor phase at a higher temperature. Molex operation is also more continuous in nature than is an IsoSiv operation. Therefore, the compositions and flow rates of the normals-rich and nonnormals-rich stream from an IsoSiv unit vary much more than do those from a Molex unit. In the IsoSiv process, desorption of the adsorbed normal paraffins is effected by reducing their concentration in the bulk phase by the introduction of hydrogen-rich purge gas. In the Molex process, desorption is effected by displacement with an adsorbed hydrocarbon of a different molecular weight. These facts alone do not translate into a purity–recovery performance advantage for either process.

The temperature of operation does have a bearing on the choice of technology downstream of the Penex isomerization unit, which uses a chlorided alumina catalyst. In the isomerization reactor, the organic chlorides introduced with the fresh feed are virtually instantaneously converted to hydrogen chloride at Penex temperatures. Some dissolved hydrogen chloride is present in the Penex separator bottoms and is removed overhead in the Penex stabilizer column during normal operation. However, olefins present in any makeup hydrogen that is introduced to either the separator or stabilizer can easily react with the hydrogen chloride to reform organic chlorides. These organic chlorides, unlike hydrogen chloride, cannot be removed overhead and enter a downstream separation process unit via the stabilizer bottoms.

At IsoSiv operating temperatures and in the presence of hydrogen, these organic chlorides can decompose into hydrogen chloride, which damages the adsorbent. Such decomposition of organic chlorides into hydrogen chloride and subsequent adsorbent damage does not occur in a Molex unit because it operates at a lower temperature and no hydrogen is present in Molex chambers. Organic chlorides themselves have been shown to cause no damage to the Molex adsorbent in repeated experiments. Because hydrogen chloride can form within IsoSiv units from organic chlorides that could be present in the feed, a Molex unit, rather than an IsoSiv unit, is a logical choice downstream of Penex units. A chloride guard bed placed on the Molex feed stream provides additional protection against the inadvertent introduction of chlorides into the Molex unit as a result of stabilizer operation that is not at design conditions. When the separation section is integrated with an isomerization unit that uses a zeolitic catalyst that is less active and operates at higher temperatures in the vapor phase, an IsoSiv unit that also uses hydrogen (as the purge gas) becomes the logical process of choice. Such an integrated processing scheme is widely commercialized as the Total Isomerization process.

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When a standalone unit is being considered, choosing a processing strategy is not easy. The following factors can play important roles in the ultimate choice (Table 4).

- *Major Equipment:* In addition to such items as pumps and heat exchangers, the Molex unit primarily consists of a single adsorbent chamber and two fractionators. The IsoSiv unit requires the use of four adsorbent beds, two furnaces, and one compressor in addition to the basics (exchangers, pumps, and separators). The routing of process streams is done using the rotary valve in the Molex unit and multiple valves in the IsoSiv unit. Therefore, personal preferences and plot space can play an important role in choosing between the two options.
- *Adsorbent Requirement:* For the same throughput, the IsoSiv process requires more adsorbent than does the Molex process. The comparison shown in Table 4 assumes operation at commercial cycle times. The adsorbent volume in an IsoSiv unit can be somewhat reduced at the expense of increasing the purge gas compressor duty. Nevertheless, differences in the adsorbent required for the two processes relate generally to the more continuous nature of the Molex process compared with the semicontinuous operation of the IsoSiv process and the mechanism of desorption. The first fact also means that the mass transfer zone in the IsoSiv process remains unused. Both factors lead to a more complete utilization of the adsorbent in the Molex process than in the IsoSiv process, thereby causing

TABLE 4
Comparison of IsoSiv and Molex Processes in Naphtha-Range Processing

	IsoSiv	Molex
Adsorption	Shape-selective adsorbent	Shape-selective adsorbent
Desorption	Hydrogen-rich purge gas	*n*-Paraffin desorbent
Flow distribution	Multiple valves	Rotary valve
Utilities	More electric power and fired fuel	More low- and medium-pressure steam
Major equipment	4 Beds 2 Heaters 3 Separators and receiver 1 Compressor	1 Adsorbent chamber (8 beds) 1 Rotary valve 2 Fractionators
Adsorbent requirements	(1.5 − 2.0) × base	Base
Operations and general	Easier to replace adsorbent and turnaround Adsorbent regenerable *in situ*	More difficult to replace adsorbent and turnaround Adsorbent not regenerable *in situ*

the adsorbent volume in the Molex process to be lower than that in the IsoSiv process.

- *Chamber Internals and Metallurgy:* The adsorbent in the Molex chamber is loaded into several beds. These beds are separated by grids which serve as distributors and collectors. As a result of the liquid-phase operation, care must be taken to ensure that sharp composition profiles are maintained through the height of the chamber. Thus, the grids are specially designed to achieve and maintain plug flow. Similar concerns apply to the IsoSiv process as well, but the fact that the adsorbent is distributed in four separate vessels in the IsoSiv unit leads to easier adsorbent changeouts and unit turnarounds. Neither process requires the use of special alloy steels in any equipment.
- *Operations:* Neither process has any special operating requirements or needs. Both IsoSiv and Molex units have routinely operated around the clock. Adsorbent lives are long, provided that routine care is taken to keep adsorbent poisons out of the feed. The chances of introducing contaminants into either the IsoSiv or Molex unit, which operate downstream of isomerization units, without first causing damage to the catalyst are small. As standalone units, known adsorbent poisons to both Molex and IsoSiv processes include sulfur, nitrogen, oxygenates, chlorides, fluorides, olefins, and diolefins. Therefore, the feed to standalone Molex and IsoSiv units should be adequately treated to remove these poisons. However, acceptable levels of each contaminant are different for the two processes. Again, the IsoSiv process design lends itself more readily to both adsorbent regenerations as well as adsorbent changeouts, should the need arise, than does the Molex process design.
- *Capital and Operating Costs:* Capital costs for IsoSiv and Molex process units are comparable. Excluding offsites, cost estimates for units sized for the same throughput are usually within 10% of one another. The IsoSiv process consumes more electric power and fired fuel than the Molex process, which primarily consumes more steam, both low and medium pressure. Thus, utility costs at specific locations can become quite important. As a rough estimate, about 75% of the utility costs of a Molex unit are steam costs and 25% are electric power costs. In contast, the utility costs of an IsoSiv unit are roughly equally divided between fired fuel and electric power. Based on typical values for utilities, these costs translate to about $0.02 per barrel of raffinate per day more in utility costs for the IsoSiv process.

When the feedstock being processed is free of contaminants, site-specific considerations related to plot space and utility costs usually dictate which of the two processes, IsoSiv or Molex, is better suited to the specific

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application. When the feed is not relatively clean, the IsoSiv process is usually better suited as a standalone unit. An example is in the recovery of *n*-paraffins from the raffinate of an aromatics extraction unit for recycle to a cracking unit for increased ethylene yields.

SUMMARY AND CONCLUSIONS

This paper has provided descriptions of the IsoSiv and Molex processes and a comparison of the two processes for the recovery of *n*-paraffins from kerosine- and gasoline-range feedstocks. Both technologies are commercially proven and significant. In the case of both the IsoSiv and Molex processes, the designs for naphtha processing are simplifications of the designs for operation with kerosine and gas oil feedstocks. The simplifications take advantage of the less stringent performance requirements of gasoline processing compared to those of petrochemical applications.

The choice of a vapor- or liquid-phase operation is governed by a combination of practical considerations and fundamental adsorption properties. Examples of practical considerations that dictate the preferred operative phase are the temperature and pressure required to operate in a specific phase and the reactivity and stability of feed and desorbent components at elevated temperature. Adsorption system properties, such as selectivity, capacity, influence of nonselective volume on the separation, and mass transfer efficiency, become pivotal when no controlling practical considerations exist. In simplest terms, the adsorbent and desorbent requirements are determined by these properties. In rare instances, such as in *n*-paraffin separations, both liquid- and vapor-phase processes are practical and efficient.

Regardless of feed boiling range, both the IsoSiv and Molex processes take advantage of differences in critical molecular diameters of the feed components. In both processes, adsorption of the *n*-paraffins takes place because of their linearity, and the *i*-paraffins are unadsorbed because they are too large to fit in the pores. However, the two processes use different means of desorption and recovery of the *n*-paraffins. This difference is reflected in every aspect of process design and operating philosophy for the two processes. More important, the difference causes variations in the yield structure between IsoSiv and Molex processes, particularly in the kerosine range.

A determination of which technology is best suited in a particular situation is based on such factors as feed quality, product requirements, the nature of the naphtha isomerization catalyst (if any), plot space, and site-specific utility costs. These considerations emphasize the need to evaluate each project on a case-by-case basis. The evaluation must include not

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simply the separation section, but also the total production complex, and it must consider the product needs of the customer and the equipment and feed quality available. One operative phase is not always better than the other, and every choice is unique.

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