

**INTRODUCTION TO
SULFURIC ACID ALKYLATION
UNIT PROCESS DESIGN**

Presented By

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INTRODUCTION TO SULFURIC ACID ALKYLATION UNIT PROCESS DESIGN

I. INTRODUCTION

Alkylation, first commercialized in 1938, experienced tremendous growth during the 1940s as a result of the demand for high octane aviation fuel during World War II. During the mid 1950s, refiners' interest in alkylation shifted from the production of aviation fuel to the use of alkylate as a blending component in automotive motor fuel. Capacity remained relatively flat during the 1950s and 1960s due to the comparative cost of other blending components. The U.S. Environmental Protection Agency's lead phase-down program in the 1970s and 1980s further increased the demand for alkylate as a blending component for motor fuel. As additional environmental regulations are imposed on the worldwide refining community, the importance of alkylate as a blending component for motor fuel is once again being emphasized. Alkylation unit designs (grassroots and revamps) are no longer driven by only volume, but rather a combination of volume and octane requirements. Lower olefin, aromatic, sulfur, Reid vapor pressure (RVP) and drivability index (DI) specifications for finished gasoline blends have also become driving forces for increased alkylate demand in the U.S. and abroad. Additionally, the phaseout of MTBE in the U.S will further increase the demand for alkylation capacity.

The alkylation reaction combines isobutane with light olefins in the presence of a strong acid catalyst. The resulting highly branched, paraffinic product is a low vapor pressure, high octane blending component. Although alkylation can take place at high temperatures without catalyst, the only processes of commercial importance today operate at low to moderate temperatures using either sulfuric or hydrofluoric acid catalysts.

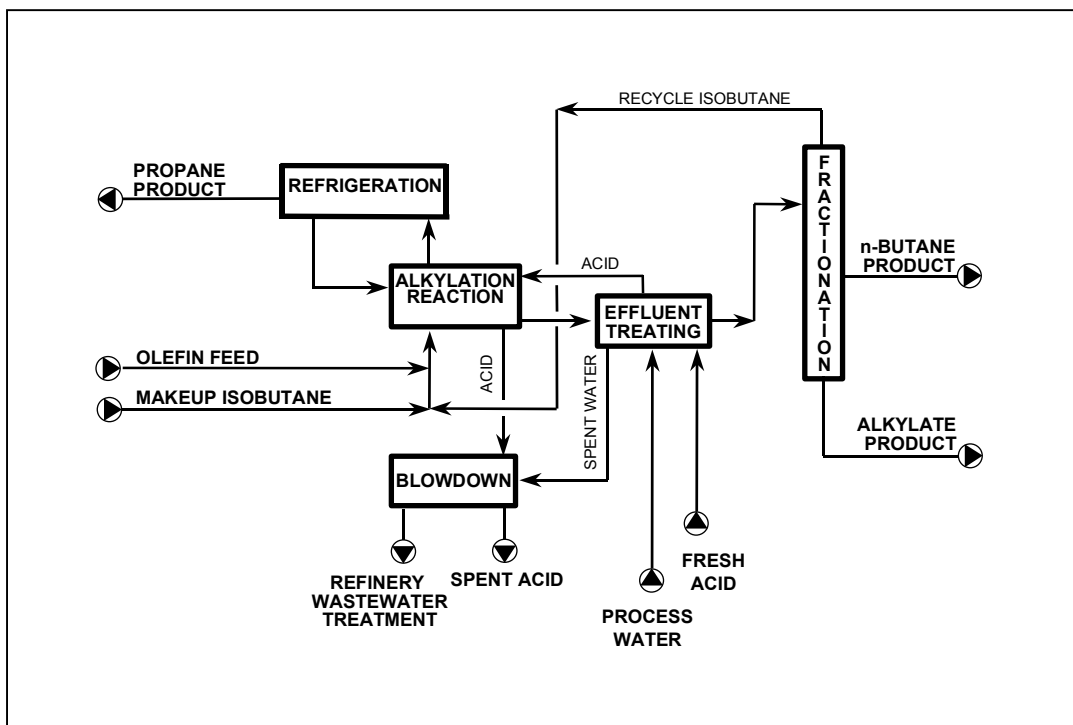
The reactions occurring in the alkylation process are complex and produce an alkylate product that has a wide boiling range. By optimizing operating conditions, the majority of the product is within the desired gasoline boiling range with motor octane numbers (MON) up to 95 and research octane numbers (RON) up to 98. For the purposes of this paper, only sulfuric acid catalyzed alkylation is considered.

This paper will discuss the technical issues involved in the design of a sulfuric acid alkylation unit. More specifically, the design of a STRATCO[®] Effluent Refrigerated Sulfuric Acid Alkylation Process will be discussed.

I. INTRODUCTION (Cont'd)

This paper will discuss the main sections in the STRATCO effluent refrigerated sulfuric acid alkylation unit. A sulfuric acid alkylation unit can be divided into five major sections (Figure 1).

Figure 1
Block Flow Diagram of a STRATCO Effluent Refrigerated
Sulfuric Acid Alkylation Unit



Each section is described below.

- A. **Reaction Section** — Where the reacting hydrocarbons are brought into contact with sulfuric acid catalyst under controlled conditions.
- B. **Refrigeration Section** — Where the heat of reaction is removed and light hydrocarbons are removed from the unit.
- C. **Effluent Treating Section** — Where the free acid, alkyl sulfates, and di-alkyl sulfates are removed from the net effluent stream to avoid downstream corrosion and fouling.
- D. **Fractionation Section** — Where isobutane is recovered for recycle to the reaction section, and remaining hydrocarbons are separated into the desired products.
- E. **Blowdown** — Where spent acid is degassed, waste water pH is adjusted, and acid vent streams are neutralized before being sent off site.

I. INTRODUCTION (Cont'd)

STRATCO's technology and all of the features of the Contactor reactor are designed to promote the alkylation reaction and to inhibit competing reactions. Competing reactions, such as polymerization, result in the production of a lower octane product with a high distillation end point and higher overall acid consumption.

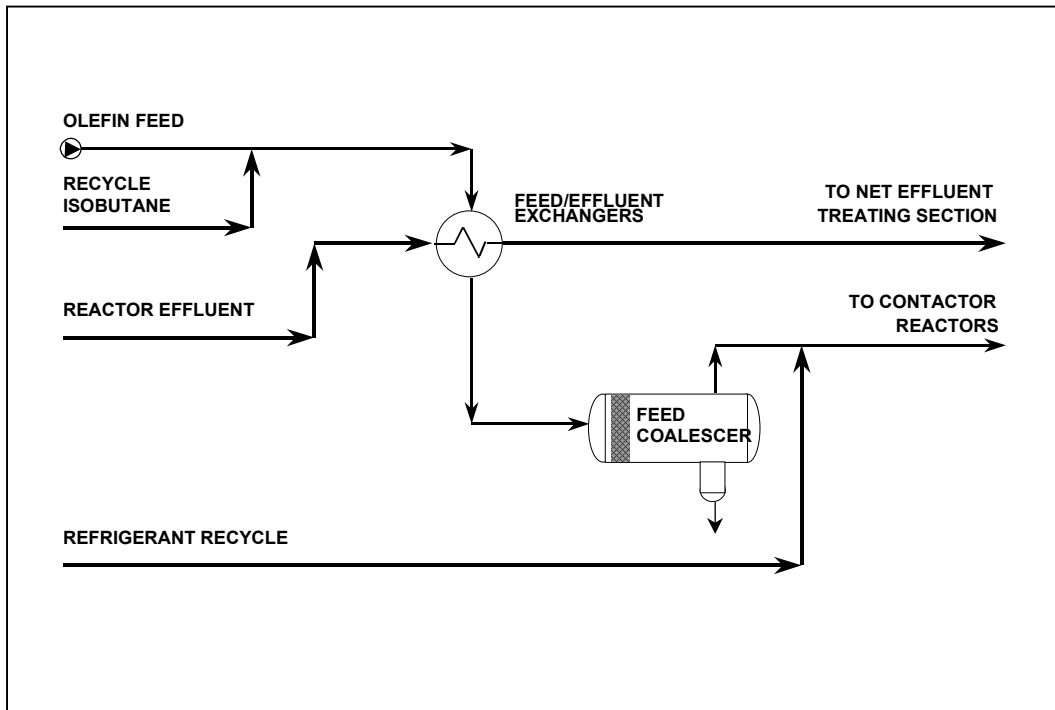
Proper design and operation of all of the sections in the alkylation unit is vital to the safe and efficient production of high quality alkylate.

II. REACTION SECTION

A. Feed Mixing and Cooling

In the reaction section, olefins and isobutane are alkylated in the presence of sulfuric acid catalyst. As shown in Figure 2, the olefin feed is initially combined with the recycle isobutane. The olefin and recycle isobutane mixed stream is then cooled to approximately 60°F (15.6°C) by exchanging heat with the net effluent stream in the feed/effluent exchangers.

Figure 2
Single Train Feed Coalescer



II. REACTION ZONE (Cont'd)

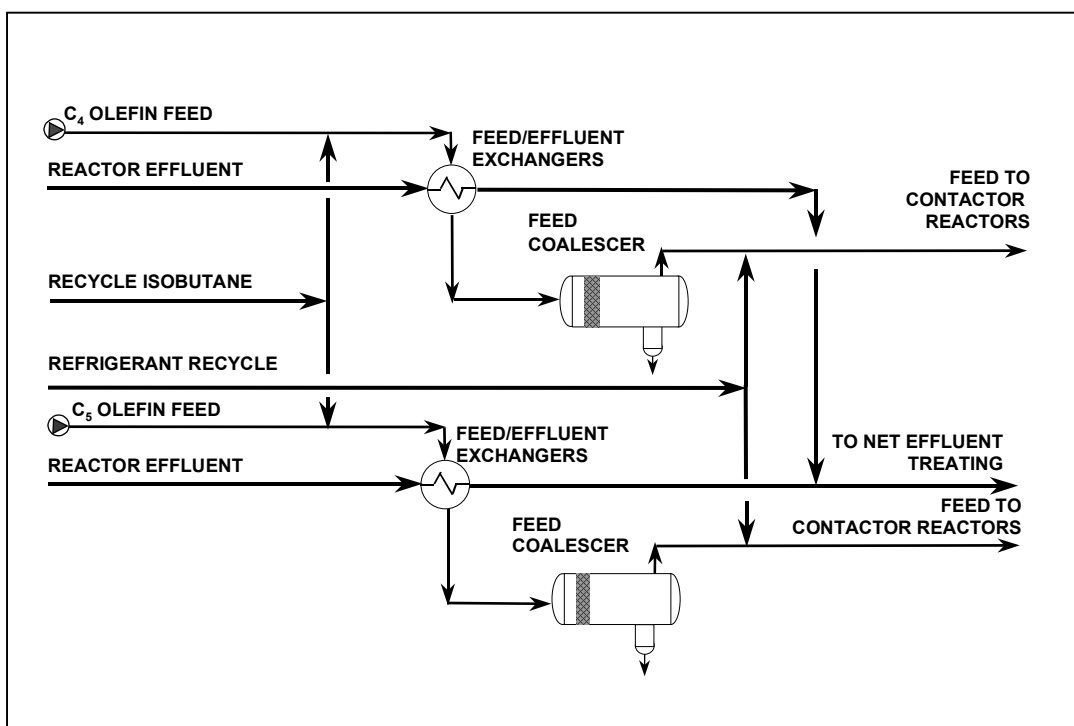
A. Feed Mixing and Cooling (Cont'd)

Since the solubility of water in the feed stream is reduced at lower temperatures, water is freed from the hydrocarbon to form a second liquid phase. The feed coalescer removes this free water in order to minimize dilution of the sulfuric acid catalyst.

The feed stream is then combined with the refrigerant recycle stream from the refrigeration section. The refrigerant recycle stream provides additional isobutane to the reaction zone. This combined stream is fed to the Contactor reactors.

If a segregated olefin feed scheme has been chosen, the unit will have parallel trains of feed/effluent exchangers and feed coalescers as shown in Figure 3.

Figure 3
Parallel Train Feed Coalescers



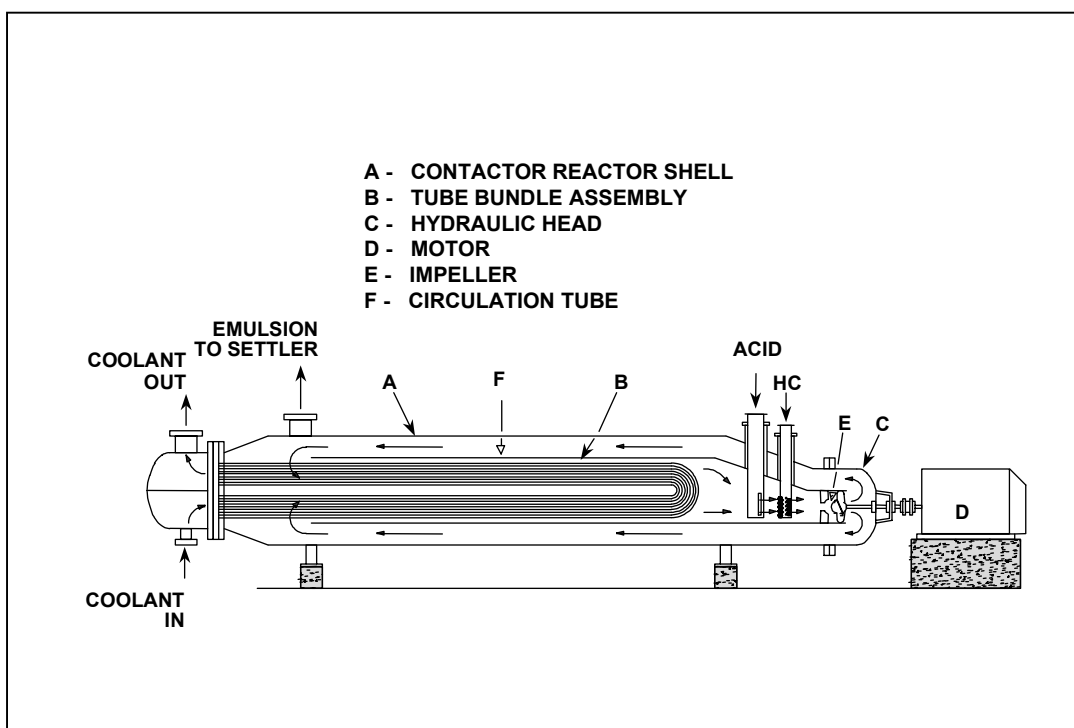
II. REACTION ZONE (Cont'd)

B. Contactor Reactor and Acid Settlers

At the “heart” of STRATCO’s Effluent Refrigerated Alkylation Technology is the Contactor reactor (Figure 4). The Contactor reactor is a horizontal pressure vessel containing an inner circulation tube, a tube bundle to remove the heat of reaction, and a mixing impeller. The hydrocarbon feed and sulfuric acid enter on the suction side of the impeller inside the circulation tube. As the feeds pass across the impeller, an emulsion of hydrocarbon and acid is formed. The emulsion in the Contactor reactor is continuously circulated at very high rates.

The superior mixing and high internal circulation of the Contactor reactor minimizes the temperature difference between any two points in the reaction zone (less than 1°F (0.6°C)). This reduces the possibility of localized hot spots that lead to degraded alkylate product and increased chances for corrosion. The intense mixing in the Contactor reactor also provides uniform distribution of the hydrocarbons in the acid emulsion. This prevents localized areas of non-optimum isobutane to olefin ratios and acid to olefin ratios, both of which promote olefin polymerization reactions.

Figure 4
STRATCO Contactor Reactor



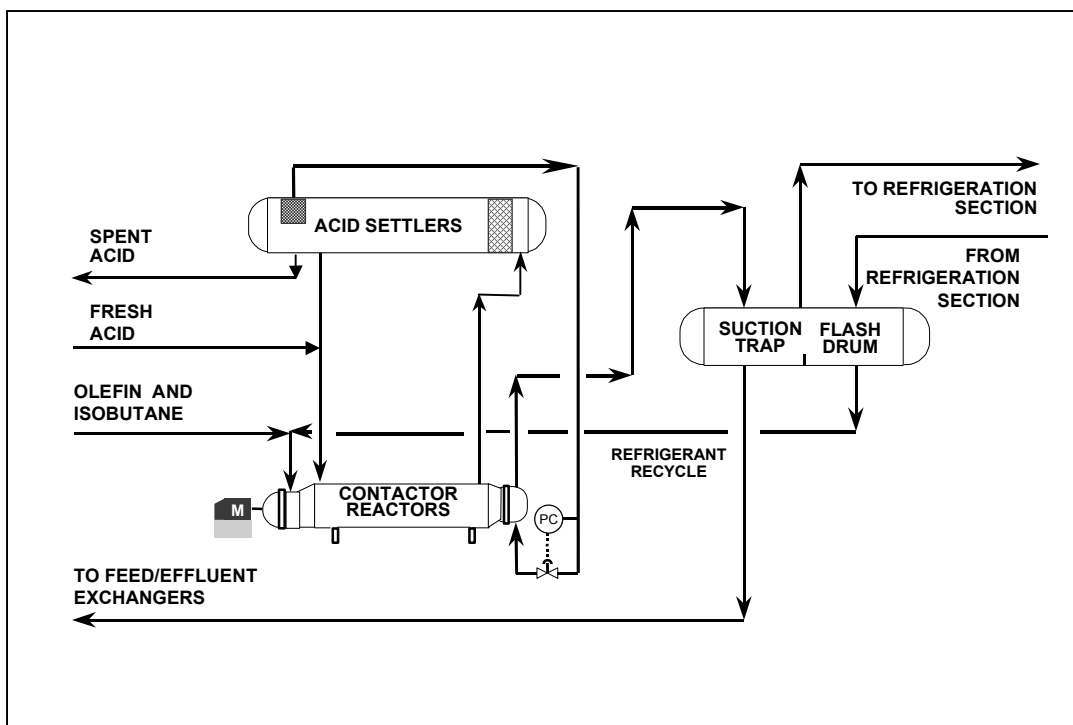
II. REACTION ZONE (Cont'd)

B. Contactor Reactor and Acid Settlers (Cont'd)

Conversion of olefins to alkylate in the reactor is essentially 100% regardless of the feed rate. However, the alkylate quality degrades and catalyst costs increase, as the feed rate is increased beyond certain limits. The limit is specific to the type of olefin feed processed.

Figure 5 shows the typical Contactor reactor and acid settler arrangement. A portion of the emulsion in the Contactor reactor, which is approximately 50 LV% acid and 50 LV% hydrocarbon, is withdrawn from the discharge side of the impeller and flows to the acid settler. The hydrocarbon phase (reactor effluent) is separated from the acid emulsion in the acid settlers. The acid, being the heavier of the two phases, settles to the lower portion of the vessel. It is returned to the suction side of the impeller in the form of an emulsion, which is richer in acid than the emulsion entering the settlers.

Figure 5
Contactor Reactor/Acid Settler Arrangement



In the STRATCO process, acid rich emulsion rather than flat acid is recycled to the Contactor reactor. Emulsion recycle minimizes undesirable side reactions, such as polymerization, in the acid settler by keeping the olefins and reactive alkyl sulfates (commonly referred to as “esters”) in contact with isobutane. This results in improved alkylate quality with reduced acid consumption.

II. REACTION ZONE (Cont'd)

B. Contactor Reactor and Acid Settlers (Cont'd)

Flat acid recycle reduces alkylate quality by increasing the acid residence time in the acid settler, providing an opportunity for the reaction intermediates in the acid phase to react with each other (polymerize). A heavy alkylate with low octanes and a high distillation end point is produced. A temperature difference of greater than 3°F (1.7°C) between the emulsion line from the Contactor reactor to the acid settler and the acid recycle line from the acid settler to the Contactor reactor could indicate the occurrence of undesirable side reactions in the settler.

Emulsion recycle is accomplished by lowering the residence time of the acid in the acid settler so that the hydrocarbon does not have time to completely separate from the emulsion. To operate with emulsion recycle, STRATCO recommends low acid levels in the acid settlers and high circulation rates (acid recycle valves wide open). This level should be adjusted to yield a 45 - 60 LV% acid concentration in the Contactor reactor.

In an effort to further reduce the residence time and the acid level in the acid settler, STRATCO has been working in conjunction with Koch-Otto-York to re-design the acid settler. The new acid settler design incorporates two stages of coalescing to separate the hydrocarbon product from the acid phase. The first stage results in a 90 vol% H₂SO₄ stream that is recycled back to the Contactor reactor. The second stage reduces the acid carryover rate to only 15 vol ppm. This is at least a three fold decrease in acid carryover in comparison to simple gravity settling with a typical 50-100 vol ppm of acid in the hydrocarbon stream.

The first stage coalescing media is a polypropylene Flexichevron type which occupies the diameter of the acid settler at the inlet nozzle from the Contactor reactor. The second stage of coalescing employs a 316 stainless steel Fleximesh type of coalescing media and will be located at the hydrocarbon outlet nozzle.

The new acid settler design not only reduces the residence time and acid level in the acid settler, but reduces the actual vessel dimensions as well. Based on the effect of reduced residence time alone, the new acid settler size can be reduced to less than 10% of the old acid settler size. Research is currently being conducted at our lab facility to determine the optimum vessel dimensions. The new acid settler design is presently being offered in proposals for grassroots alkylation unit designs and a commercial application is expected within two years time.

II. REACTION ZONE (Cont'd)

B. Contactor Reactor and Acid Settlers (Cont'd)

The STRATCO alkylation process utilizes an effluent refrigeration system to remove the heat of reaction and control the reaction temperature. With effluent refrigeration, the hydrocarbons in contact with the sulfuric acid catalyst are maintained in the liquid phase. The hydrocarbon effluent flows from the top of the acid settler to the tube bundle in the Contactor reactor. A control valve located in this line maintains a back pressure of about 60 psig (4.2 kg/cm²G) in the acid settler. This pressure is usually adequate to prevent vaporization in the reaction system. In plants with multiple Contactor reactors, the acid settler pressures are operated about 5 psi (0.4 kg/cm²) apart to provide adequate pressure differential for series acid flow.

The pressure of the hydrocarbon stream from the top of the acid settler is reduced to about 5 psig (0.4 kg/cm²G) across the back pressure control valve. A portion of the effluent stream is flashed, reducing the temperature to about 35°F (1.7°C). Additional vaporization occurs in the Contactor reactor tube bundle as the net effluent stream removes the heat of reaction. The two phase net effluent stream flows to the suction trap/flash drum where the vapor and liquid phases are separated.

The suction trap/flash drum is a two compartment vessel with a common vapor space. The net effluent pump pumps the liquid from the suction trap side (net effluent) to the effluent treating section via the feed/effluent exchangers. Refrigerant from the refrigeration section flows to the flash drum side of the suction trap/flash drum. The combined vapor stream is sent to the refrigeration section.

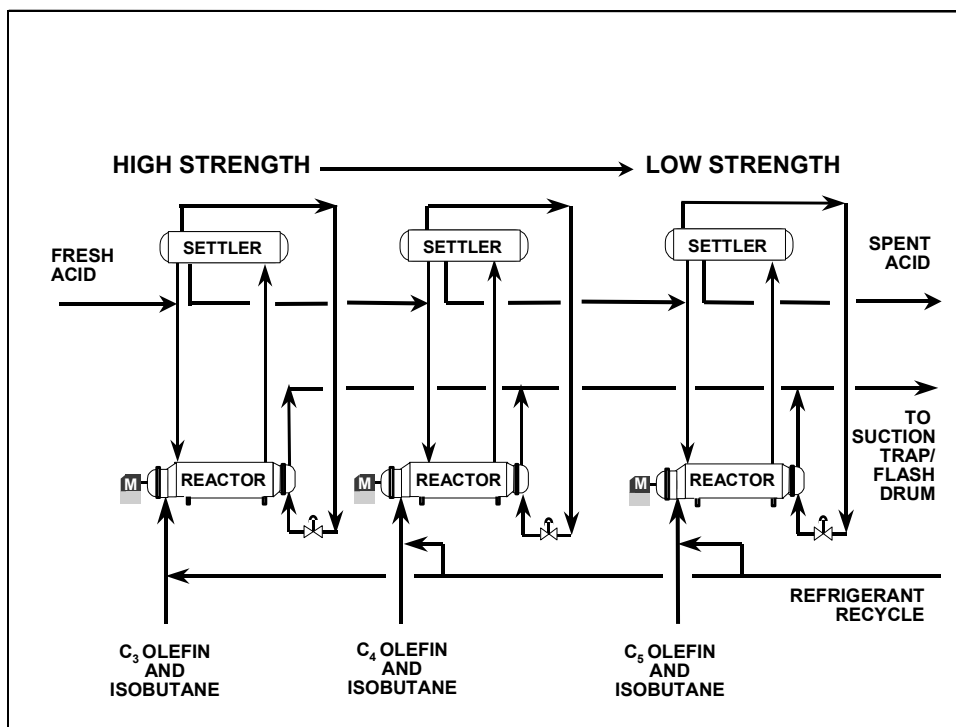
The sulfuric acid present in the reaction zone serves as a catalyst to the alkylation reaction. Theoretically, a catalyst promotes a chemical reaction without being changed as a result of that reaction. In reality, however, the acid is diluted as a result of the side reactions and feed contaminants. To maintain the desired spent acid strength, a small amount of fresh acid is continuously charged to the acid recycle line from the acid settler to the Contactor reactor and an equivalent amount of spent acid is withdrawn from the acid settler.

II. REACTION ZONE (Cont'd)

C. Acid Staging

In multiple Contactor reactor plants, the reactors are usually operated in parallel on hydrocarbon and in series/parallel on acid, up to a maximum of four stages (Figure 6). Fresh acid and intermediate acid flow rates between the Contactor reactors control the spent acid strength. The acid strength of the intermediate stages are not controlled but should be monitored for potential problems.

Figure 6
Series Acid Staging



The spent acid strength is generally monitored by titration, which is done in the laboratory. In response to our customer requests, STRATCO has developed an on-line acid analyzer that enables the operators to spend the sulfuric acid to lower strengths with much more accuracy and confidence.

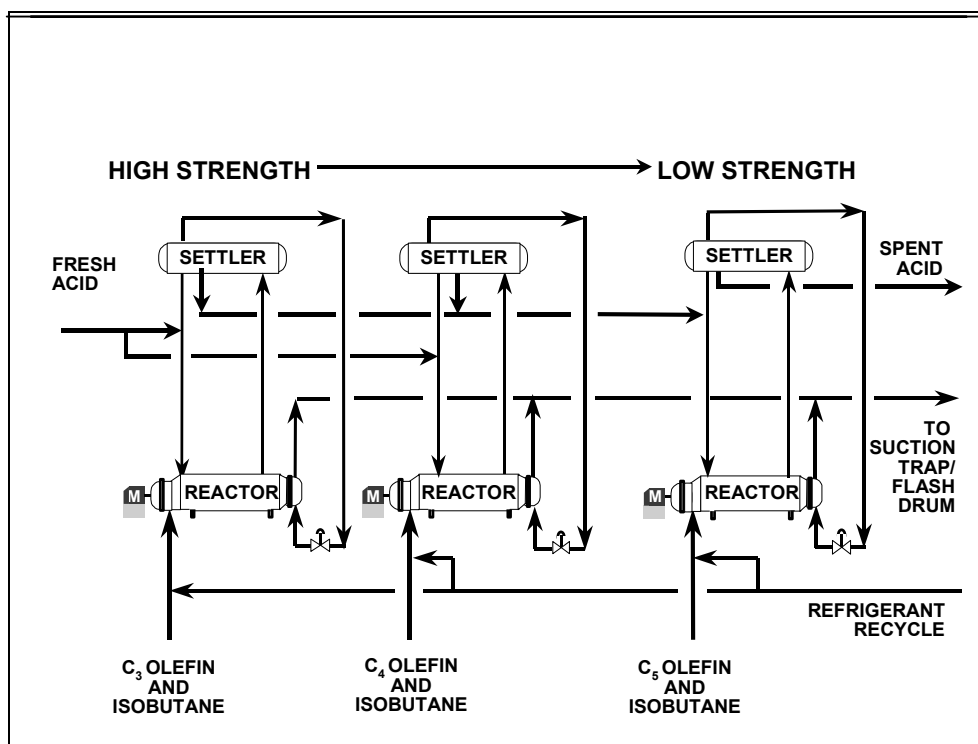
By staging the acid, STRATCO's alkylation process takes advantage of alkylating a portion of the olefins in the optimum acid strength range for octane. A maximum of four acid stages is recommended. The problem of controlling acid flows, and therefore acid strengths, becomes difficult with additional acid stages. Additional stages can also increase the potential for coating of the tubes in the Contactor reactor, because of the viscous nature of high strength sulfuric acid.

II. REACTION ZONE (Cont'd)

C. Acid Staging (Cont'd)

When alkylating segregated olefin feeds, the optimum acid settler configuration will depend on the olefins processed and the relative rates of each type of feed. Generally, STRATCO recommends processing the propylene in the high strength Contactor reactor, butylenes in the intermediate reactor and amylenes in the low strength reactor (Figure 7). The optimum configuration for a particular unit may involve operating some reaction zones in parallel, then cascading to additional reaction zones in series. STRATCO considers several acid staging configurations for every design in order to provide the optimum configuration for the particular feed.

Figure 7
Parallel Acid Staging



When alkylating propylene, STRATCO recommends operating with acid emulsion cascading versus flat acid cascading. Research indicates that the alkyl sulfates (reaction intermediates) formed when alkylating propylene are more stable and remain in the acid phase longer than those sulfates formed when alkylating butylene or amylenes. In order to prohibit polymerization reactions between the propyl sulfates in the acid phase, the acid residence time in the acid settler is reduced and hydrocarbon and acid is cascaded to the lower strength reaction zones. Continuous contact of the propyl sulfates and isobutane improves alkylate quality and yield. The propyl sulfates in the acid phase will react to form alkylate in the downstream reaction zone.

II. REACTION ZONE (Cont'd)

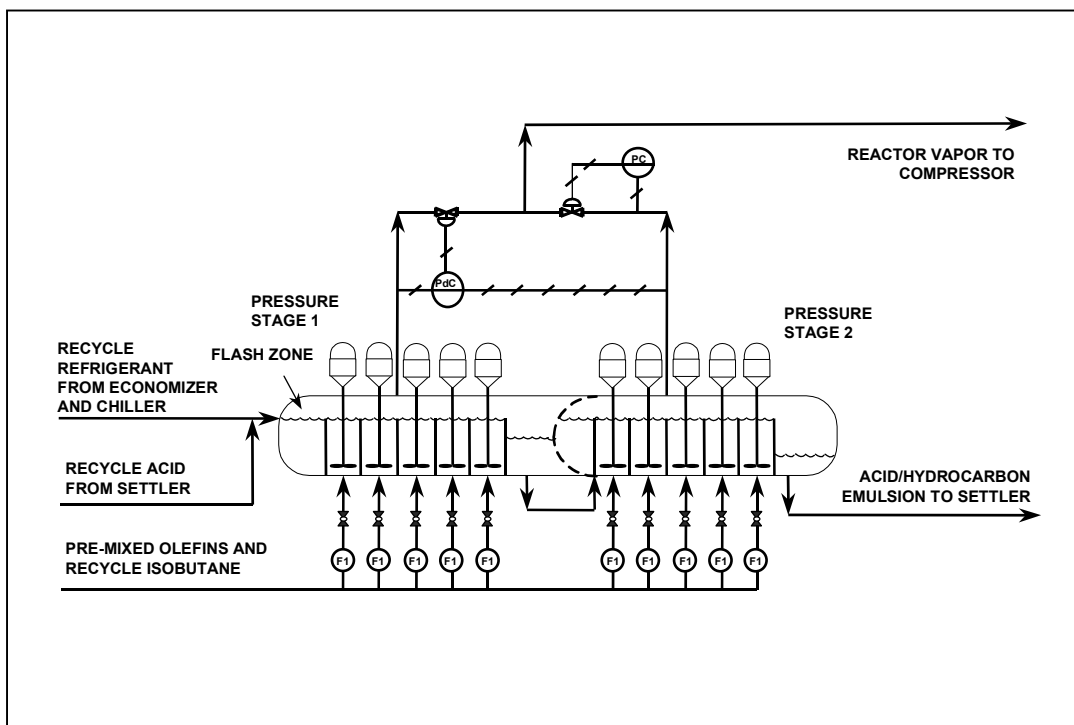
C. Acid Staging (Cont'd)

Accurate measurement of acid flow is vital to controlling spent acid strength and maintaining a steady operation. STRATCO recommends using coriolis meters in the acid lines to accurately control the acid flows through the unit. Although magnetic flow meters are equally accurate, coriolis meters offer the added feature of providing the stream density. The density information can be correlated to acid strength and used to trend interstage and spent acid strengths. Coriolis meters should be used to effectively process propylene so that the acid strength of the acid/hydrocarbon emulsion can be monitored. Orifice plates tend to erode over time and therefore are less precise than magnetic flow meters and coriolis meters.

D. Auto-Refrigerated Reaction Zone Equipment

In an auto-refrigerated alkylation unit (technology previously licensed by M.W. Kellogg and now by Exxon), the reaction zone consists of a horizontal vessel divided into a series of “compartments” or reaction zones (Figure 8). Some designs may involve dividing the vessel into two pressure stages, each with several compartments.

Figure 8
Auto-Refrigerated Reactor System



II. REACTION ZONE (Cont'd)

D. Auto-Refrigerated Reaction Zone Equipment (Cont'd)

Each reaction zone contains a dedicated mixer to provide mixing that favors the alkylation reaction. Liquid can flow from one reaction zone to the next while light vapors generated by evaporative cooling of the exothermic alkylation reaction are collected and sent to the refrigeration section. Fresh acid and refrigerant enter the reactor at one end and flow through each compartment in series. A portion of the olefin feed, mixed with the deisobutanizer (DIB) recycle isobutane, is injected to each reaction zone in parallel. The hydrocarbon and acid emulsion flows to a settling vessel. The hydrocarbon phase from the settling vessel flows to the DIB and the acid is pumped back to the first stage of the reaction zone.

III. REFRIGERATION SECTION

STRATCO's current design uses effluent refrigeration, which uses acid settler effluent as the refrigerant. This configuration makes maximum use of all the isobutane recycled to the reaction section since all the isobutane remains in the liquid phase during the reaction process as opposed to the competing auto-refrigerated technology.

In some older designs, STRATCO utilized Contactor reactors with a closed cycle refrigerant. Closed cycle refrigeration uses a pure refrigerant such as Freon or propane as the cooling medium in the tube bundles as opposed to the process fluids themselves, as is the case for effluent and auto-refrigerated units. Closed cycle refrigeration often enjoys the advantage of slightly lower power requirements due to the higher heat of vaporization associated with Freon refrigerants. However, a larger deisobutanizer (DIB) and higher unit steam usage is required in a closed cycle refrigeration process, as all of the effluent is sent to the tower as opposed to being split between a refrigeration section and a fractionation section.

Recent legislation has banned the use and manufacture of traditional Freon refrigerants in the U.S. after 1995. Replacement refrigerants do not possess as pronounced a heat of vaporization advantage as their predecessors and therefore require increased compressor capacity and power.

In the auto-refrigerated process, the vapors evaporated in the reaction vessel are compressed, condensed, flashed, purged of light ends, and sent back to the reaction zone. Because the vapors from the reaction zone are feeding the compressor at a higher pressure than the vapors in an effluent refrigerated process, the compressor horsepower requirements are lower. However, to achieve a reaction zone isobutane concentration comparable to STRATCO's technology, the DIB recycle rate and/or purity must be increased to compensate for the flashed isobutane in the auto-refrigerated reactors. Therefore, the DIB operating costs will be higher for the auto-refrigerated process.

III. REFRIGERATION SECTION (Cont'd)

STRATCO, in conjunction with its customers, has developed three refrigeration section configurations. In all three configurations, a portion of the refrigerant condensate is purged from the unit. Depending on the level of light ends in the feed streams to the unit, this purge is directly from the refrigeration section or is in the form of a propane product from a depropanizer. A description of the three refrigeration configurations follows.

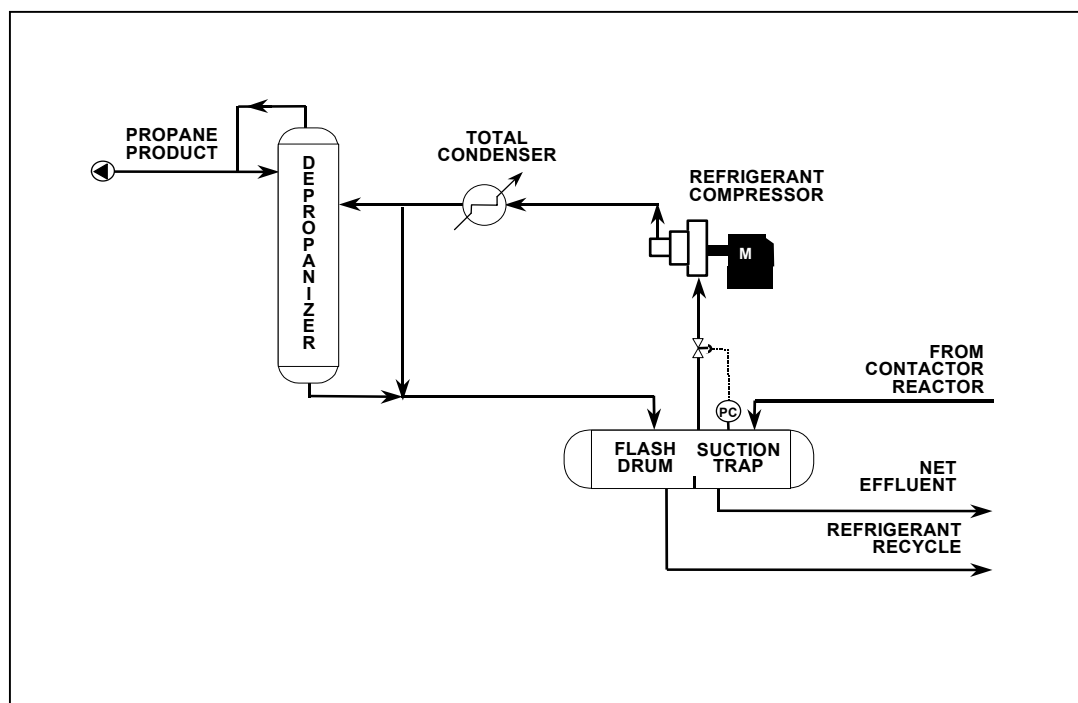
A. Simple Refrigeration

Figure 9 is a diagram of the simple refrigeration configuration. The partially vaporized net effluent stream from the Contactor reactor flows to the suction trap/flash drum where the vapor and liquid phases are separated. The vapor stream from the suction trap/flash drum is compressed by a motor or turbine driven compressor and then condensed in a total condenser.

A portion of the refrigerant condensate is purged or sent to a depropanizer. The remaining refrigerant is flashed across a control valve and sent to the flash drum side of the suction trap/flash drum. If a depropanizer is included in the design, the bottoms stream from the tower is also sent to the flash drum side of the suction trap/flash drum.

During normal operation, changing the pressure of the suction trap controls the reactor temperature. For a fixed speed motor driven compressor, a pressure controller, which adjusts the flow through the compressor, maintains the suction trap pressure. Varying the compressor speed controls the suction trap pressure for a steam turbine or variable motor driven compressor.

Figure 9
Simple Refrigeration System



III. REFRIGERATION SECTION (Cont'd)

A. Simple Refrigeration (Cont'd)

Opening the suction pressure control valve or increasing the compressor speed, depending on the type of compressor, will lower the suction trap/flash drum pressure. Decreasing the suction trap pressure will decrease the bubble point temperature of the refrigerant. As the bubble point of the refrigerant is lowered the Contactor reactor temperature is lowered. Typically, a 1 psi (0.1 kg/cm^2) change in pressure will change the reaction temperature about 2 to 3°F (1.1 to 1.7°C).

The composition of the refrigerant also has an effect on the effluent vaporization temperature. STRATCO typically designs alkylation units to have 10-15 mol% propane concentration in the depropanizer charge or propane purge. During normal operation, the depropanizer feed or propane purge rate is adjusted to maintain a constant propane concentration in this stream. By doing this, the refrigerant composition is held fairly constant and the unit is maintained in propane material balance. The higher the propane concentration in the refrigerant loop, the higher the compressor discharge pressure required to condense the stream in the total condenser. The lower propane concentration in the loop, the higher the bubble point temperature of the effluent flashing in the Contactor reactor tube bundle and the higher the reactor temperature.

STRATCO's technology does not require the installation of a dedicated compressor suction knockout drum. STRATCO has rigorous design standards for the vessel and internal design of the suction trap/flash drum which have proven to be adequate for liquid knock-out. A compressor knock-out drum introduces a pressure drop between the suction trap and the compressor due to the entrance and exit effects. This pressure drop will make it more difficult to maintain a positive pressure at the compressor suction. The suction trap pressure could be increased to account for this increase in pressure drop, but this may increase the reaction temperature. The propane content in the refrigeration loop could be increased, but this may increase the compressor power requirements. Installation of a dedicated compressor suction knock-out vessel is unnecessary and may pose operational challenges.

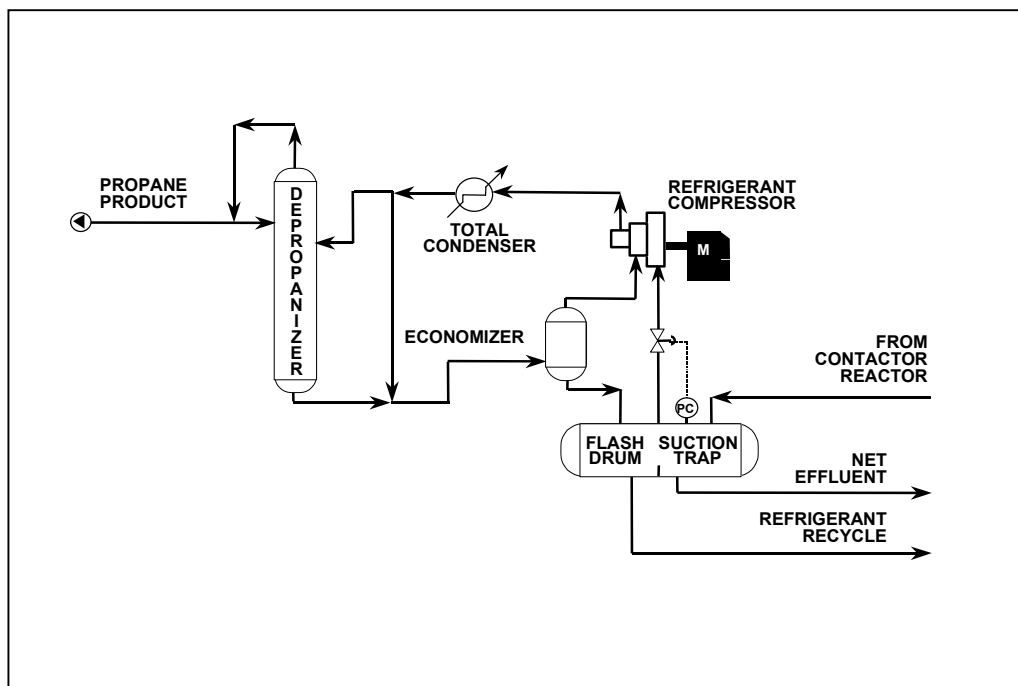
B. Refrigeration with Economizer

The principal difference between this configuration and the simple configuration is the economizer (Figure 10). The economizer operates at a pressure between the condensing pressure and the compressor suction pressure. Refrigerant condensate and depropanizer bottoms are flashed and sent to this vessel. The economizer vapor flows to an intermediate stage of the compressor. The economizer liquid is flashed and sent to the flash drum side of the suction trap/flash drum. Incorporation of an economizer results in approximately 7% savings in compressor horsepower requirements.

III. REFRIGERATION SECTION (Cont'd)

B. Refrigeration with Economizer (Cont'd)

Figure 10
Refrigeration System with Economizer



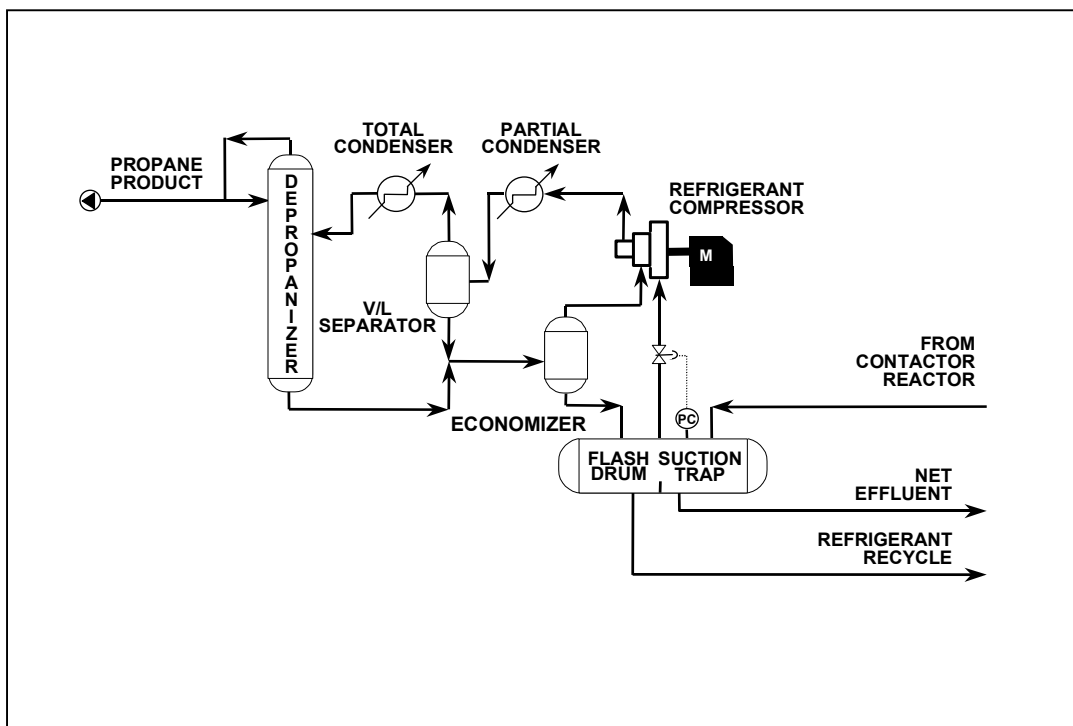
C. Refrigeration with Economizer and Partial Condensers

Incorporation of partial condensers to the economizer configuration effectively separates the refrigerant from the light ends and allows for propane enrichment of the depropanizer feed stream (Figure 11). As a result, both depropanizer capital and operating costs can be reduced. The partial condenser design is most cost effective when feed streams to the alkylation unit are high (typically greater than 40 LV%) in propane/propylene content.

III. REFRIGERATION SECTION (Cont'd)

C. Refrigeration with Economizer and Partial Condensers (Cont'd)

Figure 11
Refrigeration System with Economizer and Partial Condenser



D. Depropanizer Feed/ Propane Purge Treating

For all of the refrigeration configurations, the purge from the refrigeration loop is treated to remove impurities prior to flowing to the depropanizer or leaving the unit. These impurities can cause corrosion in downstream equipment. The main impurity removed from the purge stream is SO₂. SO₂ is produced from sulfuric acid degradation in the reaction section and decomposition of sulfur bearing contaminants in the unit feeds.

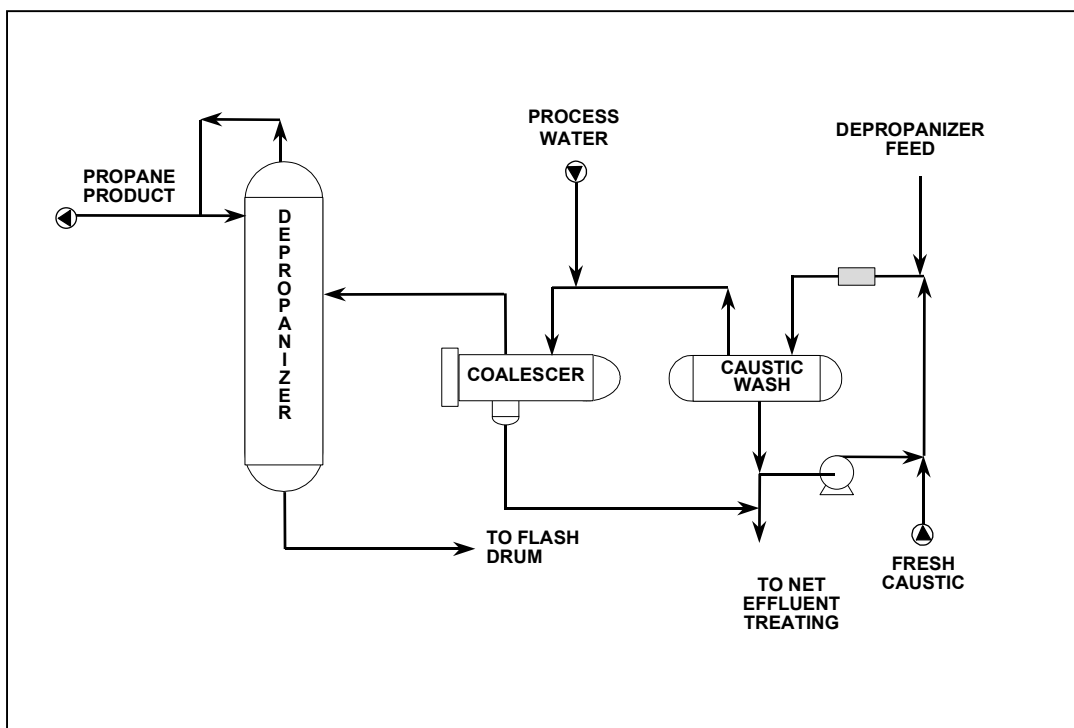
The purge is contacted with strong caustic (10-12 wt%) in an in-line static mixer and is sent to the caustic wash drum. The caustic wash is designed to remove trace acidic components in the depropanizer feed stream. STRATCO specifies the mixer as a five element Koch SMV type static mixer with a drop size of 300-400 microns. Typical differential pressure across the mixer is 8 to 15 psi (0.5 to 1.1 kg/cm²). The caustic wash drum is designed to provide sufficient hydrocarbon residence time (30 minutes) for gravity settling.

III. REFRIGERATION SECTION (Cont'd)

D. Depropanizer Feed/ Propane Purge Treating (Cont'd)

The separated hydrocarbon stream from the caustic wash drum then mixes with process water and is sent to a coalescer (Figure 12). The coalescer reduces the carryover caustic in the hydrocarbon stream that could cause stress corrosion cracking or caustic salt plugging and fouling in downstream equipment. The injection of process water upstream of the coalescer was added recently to the STRATCO standard design. This process change was made to enhance the removal of caustic carryover in the coalescer.

Figure 12
Depropanizer Feed Treating



IV. NET EFFLUENT TREATING SECTION

The net effluent stream from the reaction section contains traces of free acid, alkyl sulfates, and di-alkyl sulfates formed by the reaction of sulfuric acid with olefins. These alkyl sulfates are commonly referred to as “esters.” Alkyl sulfates are reaction intermediates found in all sulfuric acid alkylation units, regardless of the technology utilized. If the alkyl sulfates are not removed they can cause corrosion in downstream equipment.

STRATCO's net effluent treating section design has been modified over the years in an effort to provide more effective, lower cost treatment of the net effluent stream. STRATCO's older designs included caustic and water washes in series. Up until recently, STRATCO's standard design included an acid wash with an electrostatic precipitator followed by an alkaline water wash. Now STRATCO alkylation units are designed with an acid wash coalescer, alkaline water wash and a water wash coalescer in series or with an acid wash coalescer followed by bauxite treating. Although all of these treatment methods remove the trace amounts of free acid and reaction intermediates (alkyl sulfates) from the net effluent stream, the acid wash coalescer/alkaline water wash/water wash coalescer design and acid wash coalescer/bauxite treater design are the most efficient.

A. Acid Wash Coalescer/ Alkaline Water Wash/ Water Wash Coalescer

With the acid wash coalescer/alkaline water wash/water wash coalescer design (Figure 13), the net effluent stream is contacted with fresh acid in an in-line static mixer. The mixed stream is sent to the acid wash coalescer to separate. STRATCO specifies the in-line mixer as a five element Koch SMV type static mixer with a drop size of 300-400 microns. Typical differential pressure across the mixer is 8 to 15 psi (0.5 to 1.1 kg/cm²).

In earlier designs, the acid wash drum was sized based only on gravity settling and an electrostatic precipitator provided insurance against acid carry over to the alkaline water wash. In STRATCO's current design, coalescing media is used in the acid wash allowing an appreciably smaller vessel to be used without the aid of an electrostatic precipitator.

The acid wash utilizes the normal fresh acid supply to the reaction zone to extract both free acid and alkyl sulfates from the net effluent stream. The acid recovered in the bottom of the acid wash drum contains acid esters transferred from the net effluent. A portion of this acid is sent to the reaction section where the reaction intermediates can form alkylate and where the steam serves as a fresh acid supply to the Contactor reactors. The rest of the acid continuously circulates to mix with the incoming net effluent. Fresh acid is pumped from storage at a continuous rate to maintain the acid level in this drum.

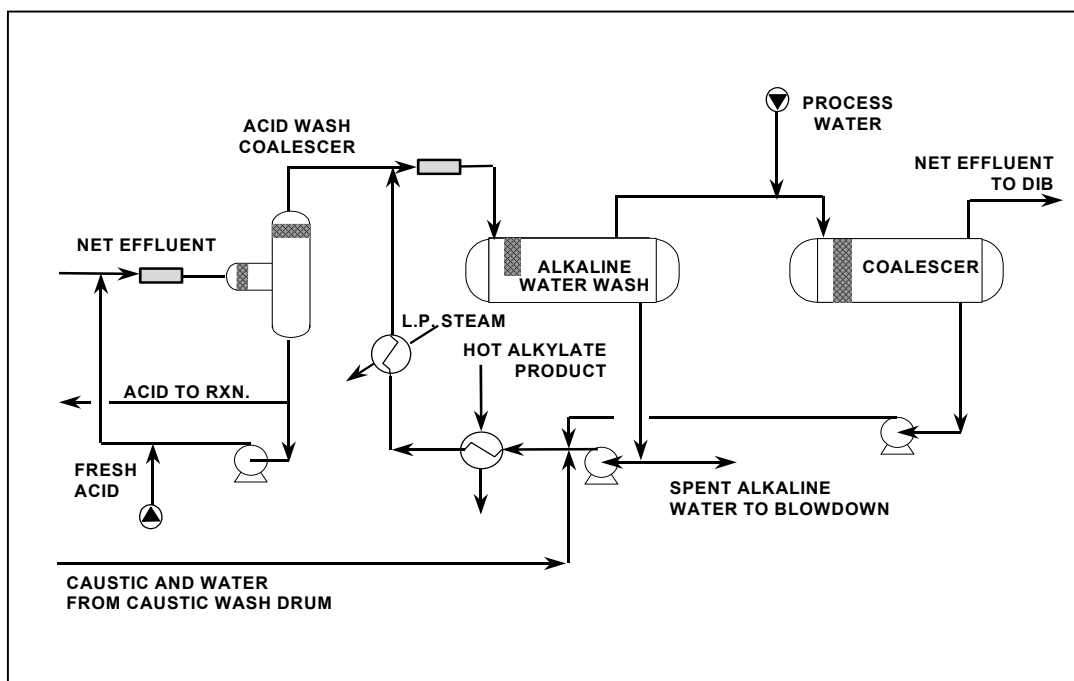
The hydrocarbon flows from the top of the acid wash drum to the alkaline water wash drum, where any residual free acid, alkyl sulfates and di-alkyl sulfates are decomposed or neutralized. Effluent from the acid wash drum is combined with the hot recirculated alkaline water and passed through an in-line static mixer before entering the alkaline water wash drum.

IV. NET EFFLUENT TREATING SECTION (Cont'd)

A. Acid Wash Coalescer/ Alkaline Water Wash/ Water Wash Coalescer (Cont'd)

Figure 13

Acid Wash/ Alkaline Water Wash/ Water Wash Coalescer



In the alkaline water wash drum, the hydrocarbon and aqueous phases are separated by gravity settling aided by coalescing media. In previous designs, hydrocarbon residence time was critical to the successful gravity phase separation in the alkaline water wash drum. This required very large vessels, which increased the capital cost of the grassroots facility. With STRATCO's new coalescer aided settling vessel, residence time is reduced drastically as performance is based on much higher hydrocarbon velocities. This allows the unit to be designed with a much smaller vessel.

The design of the alkaline water wash system is based on the olefin feed to the unit. When alkylating propylene, the alkyl sulfates formed are more stable than those formed when alkylating butylenes and amylenes. Therefore, many enhancements are made to the treating design when processing a high level of propylene.

IV. NET EFFLUENT TREATING SECTION (Cont'd)

A. Acid Wash Coalescer/ Alkaline Water Wash/ Water Wash Coalescer (Cont'd)

The specification of the alkaline water wash in-line static mixer is based on the type of olefin feed processed. For units alkylating mostly butylenes and amylenes, STRATCO specifies the in-line mixer as a five element Koch SMV type static mixer with a drop size of 300-400 microns. Typical differential pressure across the mixer is 8 to 15 psi (0.5 to 1.1 kg/cm²). For units alkylating propylene, STRATCO specifies the five element in-line static mixer to have three spacers, one before each of the final three elements. The specified drop size and differential pressure drop specification is not modified for propylene designs. The propylene design enhancements were developed in order to increase the contact time of the alkaline water and net effluent stream.

The operating temperature of the alkaline water wash also depends on the olefin feed type processed. When processing butylenes and amylenes, STRATCO designs the alkaline water wash to operate at a temperature of 120°F (49°C) to facilitate decomposition of the remaining alkyl sulfates. However, STRATCO designs the alkaline water wash to operate at 160°F (71°C) for units processing a high level of propylene. Hot alkylate product is used in the alkylate/alkaline water exchanger to maintain this temperature. Medium pressure steam can be used in the stress relieved circulating alkaline water heater to supplement the heat addition.

Upstream of the alkylate/alkaline water exchanger, process water is added to the circulating alkaline water stream. Spent alkaline water is withdrawn and replaced by process water to control the conductivity of the alkaline water between 5,000 and 8,000 µmho/cm. Conductivity is a function of total dissolved solids (TDS) concentration. Excessive TDS (>10,000) can cause a tight emulsion which can result in carryover. Caustic is added continuously to the circulating alkaline water to maintain an alkaline water pH of 11 ± 1 .

The design caustic and process water makeup rates for the unit depend on the olefin feed processed. Units processing propylene are designed with twice as much process water makeup and caustic makeup to account for the higher difficulty encountered in treating operations. STRATCO's design values for these rates are very conservative, even for butylene or amylene operation.

The hydrocarbon from the alkaline water wash flows to the water wash coalescer where traces of caustic from the alkaline water wash drum are removed with the aid of a coalescer. Fresh water make-up is added to the hydrocarbon feed to this drum to absorb alkaline water droplets that carried over from the alkaline water wash drum.

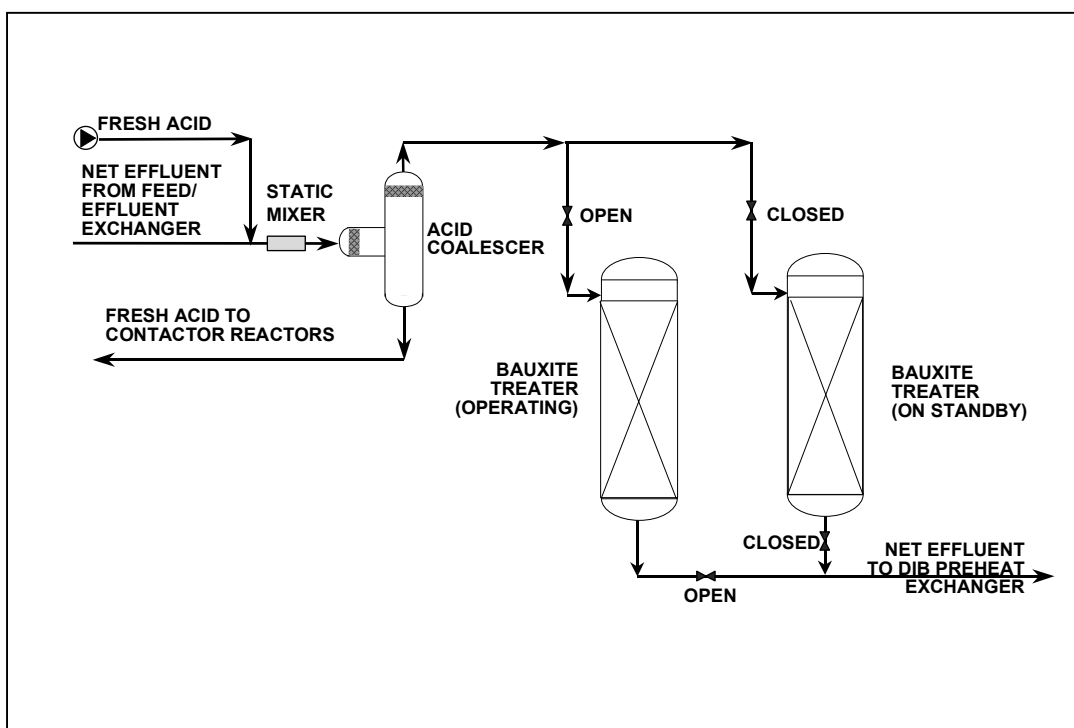
Retrofits may be possible for existing units to reduce carryover problems or increase throughput. Design information is available from STRATCO.

IV. NET EFFLUENT TREATING SECTION (Cont'd)

B. Bauxite Treating

Another type of treating available for net effluent involves the use of a bauxite treater (Figure 14). The bauxite treater uses alumina (bauxite) as an adsorbent to remove all sulfate contaminants. Bauxite treating can operate as a stand alone unit or in conjunction with an acid wash. It is generally accepted that an upstream acid wash will unload the bauxite treater resulting in fewer regenerations of the bed, which will give longer cycle times. Because acid carryover will cause pressure drop problems in the bauxite bed, an acid coalescer should be installed upstream of the bauxite treaters for protection. After the acid coalescer, the effluent stream flows down one of the bauxite treaters where the remaining acid and sulfate bearing materials are adsorbed onto the activated alumina.

Figure 14
Acid Wash Coalescer/ Bauxite Treating



Depending on a plant's preference, regeneration of the bauxite beds can be timed strictly on the basis of pressure drop through the bed, or may be set on a designated cycle length. In the regeneration of a bed, the spent bed is taken off line and its parallel twin is placed in service. The spent bed is drained of hydrocarbon and depressurized to the suction trap and flare. Initially, copious amounts of water are flushed into the bed to begin regeneration.

IV. NET EFFLUENT TREATING SECTION (Cont'd)

B. Bauxite Treating (Cont'd)

Because bauxite absorbs water, there is an initial heat of reaction that tends to heat the bed. In addition, water is heated by steam injection to slowly raise the water temperature. Elevated temperatures are required to enhance the removal of the organic sulfate contaminants from the bauxite adsorption sites.

As the bed regenerates, the organic sulfates are hydrolyzed to alcohol and sulfuric acid. After the water washing, the water that was absorbed by the alumina must be removed with a drying cycle. Either natural gas or vaporized isobutane can be heated and used to dry the bed which reactivates the alumina sites. Then the bed is cooled to ambient conditions and filled with net effluent awaiting its turn in the cycle.

A bauxite treater competes economically with a traditional aqueous treating system and several advantages and disadvantages exist when evaluating each system. Although it is believed that bauxite treating is superior in removing contaminants from the effluent stream, the real advantage is that water or caustic streams are no longer in contact with the reaction effluent at any time. Therefore, the streams are dry so that corrosion and fouling problems in the unit are virtually eliminated. In addition, free water in the recycle isobutane stream is eliminated which results in lower acid consumption and a slight increase in octane. Finally, operating with a dry system eliminates tight emulsions in alkaline water systems due to contaminants, and consequent tower fouling from salt and entrainment in the tower.

Other advantages exist for bauxite treating over the more common aqueous treating. For example, when bauxite treating is used, aviation fuel copper strip problems, due to inadequate effluent treating, are eliminated. Failures in the copper strip test typically result from trace sulfur dioxide that forms as a result of inadequate treating in the effluent stream.

Disadvantages also exist when comparing the bauxite system to the aqueous system. One disadvantage is that the bauxite system is a batch system and more labor intensive. Secondly, the regeneration of the beds creates a surge in the water treating system demand. Based on STRATCO's calculations, the total amount of water used during regeneration is approximately equal to that used for the alkaline water wash in a continuous system. The rate of water from the alkylation unit is much higher during the short washing cycle, which puts a higher load on the waste water treating system, but drops to nearly zero, when regeneration is completed. Additionally, energy costs for regeneration increase the overall unit costs slightly. Also, the regeneration water is hot and has a low pH, which may lead to corrosion. Finally, the bauxite must be replaced sometime after thirty-five to fifty regenerations and topped off after every four regenerations.

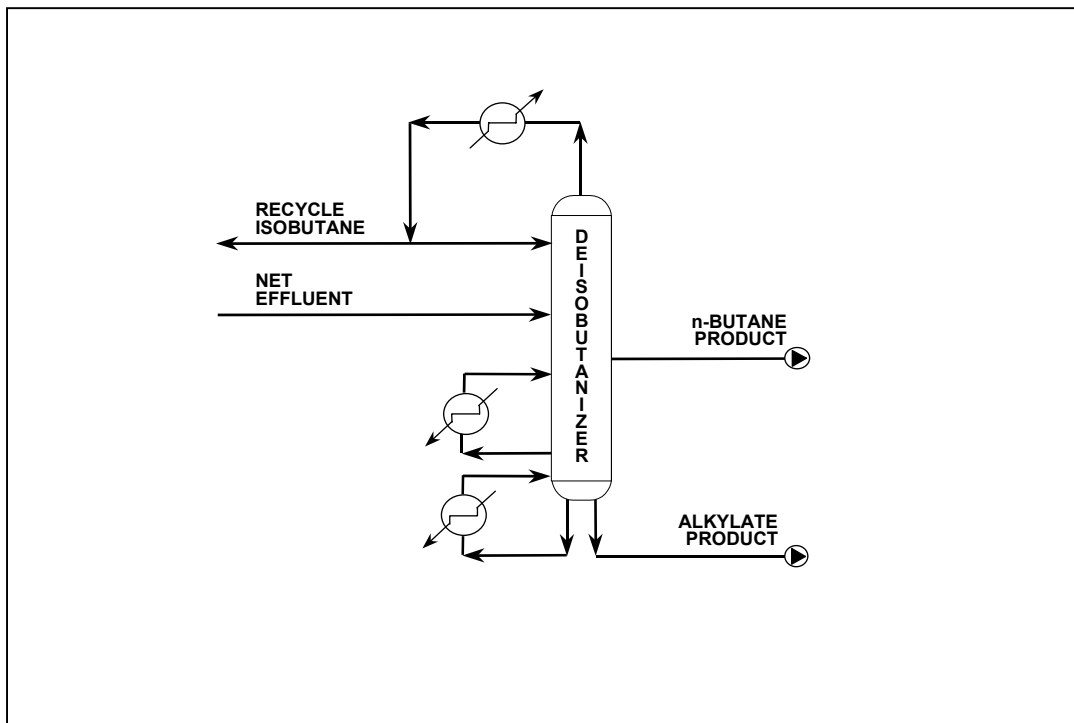
V. FRACTIONATION SECTION

The fractionation section configuration of grassroots alkylation units, either auto-refrigerated or effluent refrigerated, is determined by feed composition to the unit and product specifications. As mentioned previously, the alkylation reactions are enhanced by an excess amount of isobutane. In order to produce the required I/O volumetric ratio of 7:1 to 10:1 in the feed to the Contactor reactors, a very large internal recycle stream is required. Therefore, the fractionation section of the alkylation unit is not simply a product separation section; it also provides a recycle isobutane stream.

A. Base Case Fractionation Design

STRATCO's base fractionation section design consists of a DIB with an n-butane side draw (Figure 15). This configuration minimizes capital costs but provides the least amount of control over n-butane product quality. The n-butane product will contain isobutane and isopentane. The amount of isopentane is dependent on olefin feed type (e.g., propylene, butylene, amylene) and Reid vapor pressure (RVP) of the alkylate product. It is often cost effective to add an upper reboiler to the column to take advantage of the lower cost of low pressure steam.

Figure 15
Fractionation System with a DIB with n-Butane Side Draw

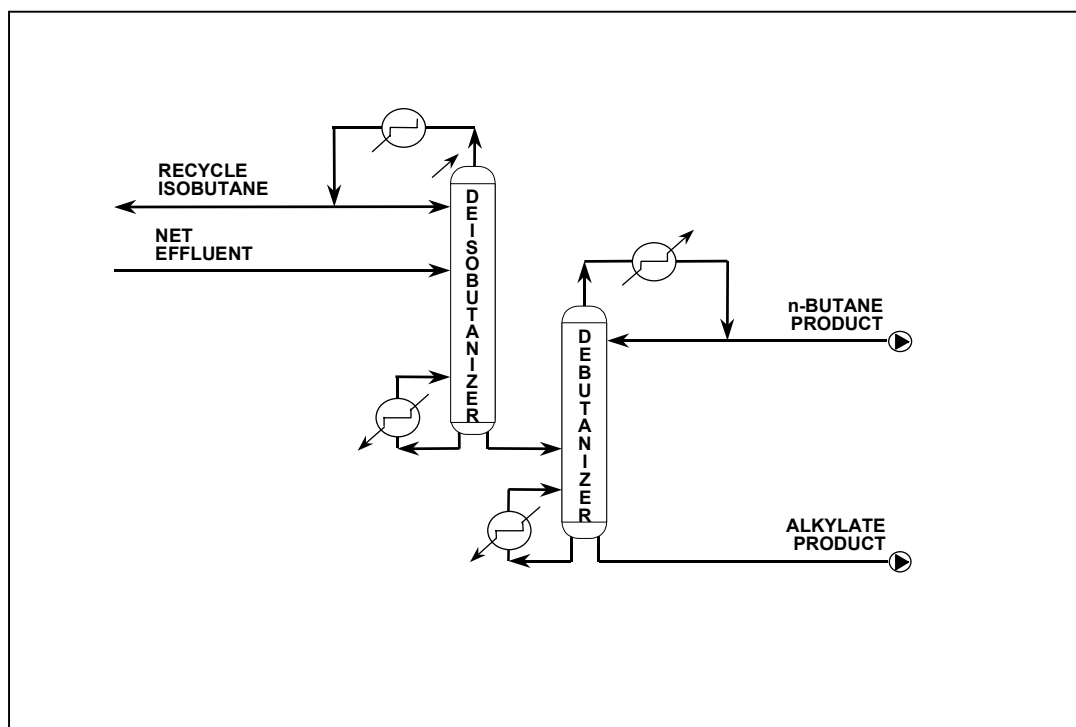


V. FRACTIONATION SECTION (Cont'd)

B. n-Butane Quality Fractionation Design

To meet overall gasoline pool RVP requirements, many of the recent alkylation designs require an alkylate RVP of 4-6 psi (0.28-0.42 kg/cm²). To reduce the RVP of the alkylate, a large portion of the n-butane and isopentane must be removed. Low C₅⁺ content of the n-butane product is difficult to meet with a vapor side draw on the DIB and requires the installation of a debutanizer tower (Figure 16). Typically, a debutanizer is required when the specified C₅⁺ content of the n-butane product must be less than 2 LV%.

Figure 16
Fractionation System with a DIB and Debutanizer

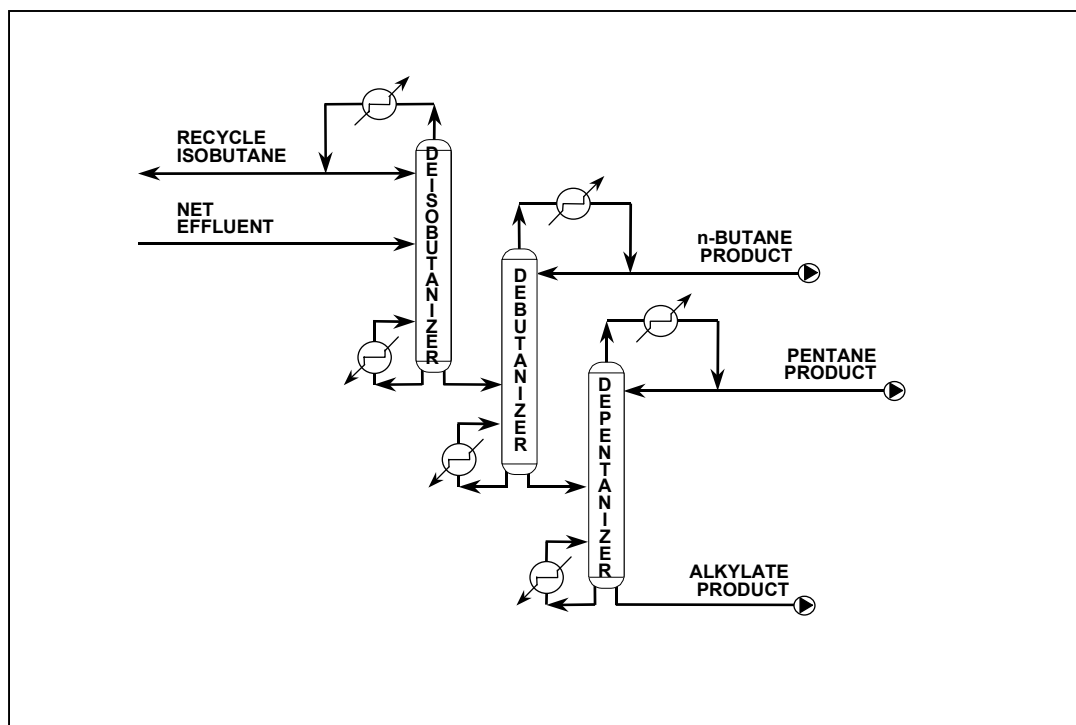


V. FRACTIONATION SECTION (Cont'd)

C. Amylene Feed Fractionation Design

To meet olefin and RVP limitations on finished gasoline, more U.S. refiners have decided to feed amylene to the alkylation unit. This results in significant quantities of isopentane being fed to the unit. A depentanizer, in addition to a debutanizer, may be required to produce a low RVP alkylate and meet n-butane quality specifications (Figure 17). With this configuration, a pentane product stream is produced which provides for more flexibility in gasoline blending.

Figure 17
Fractionation System with Deisobutanizer,
Debutanizer and Depentanizer



VI. BLOWDOWN SECTION

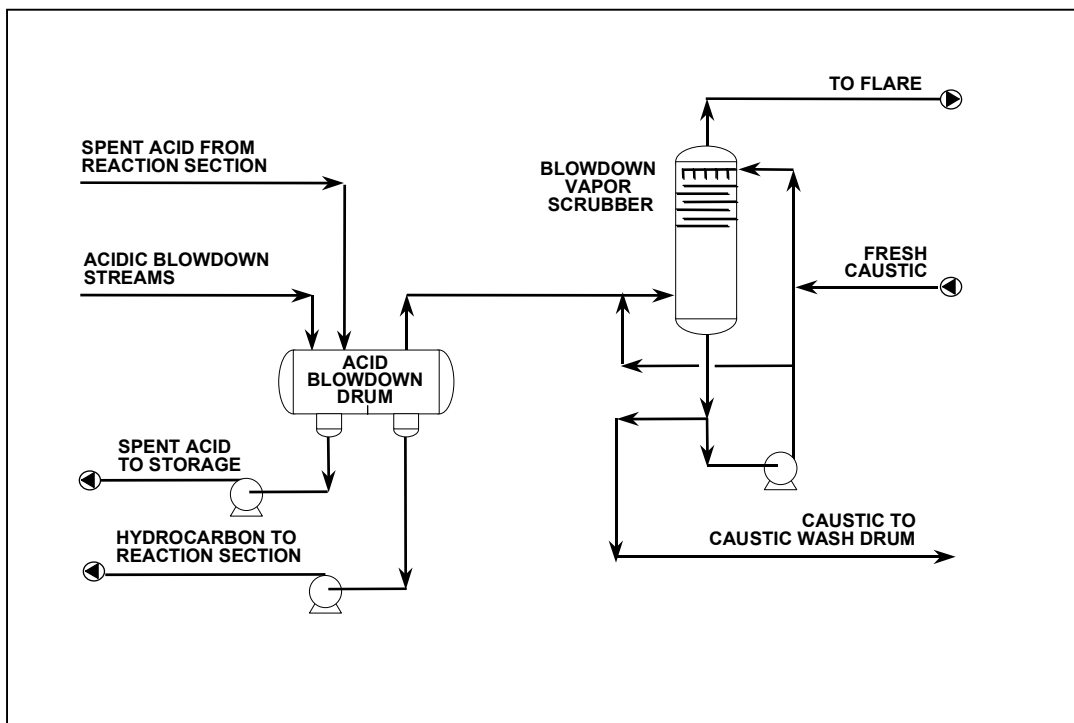
STRATCO has conservative design standards for the required blowdown facilities for an alkylation unit. Refiners frequently customize this area to meet their own internal design criteria and local regulations. The blowdown section is an integral part of a well-designed alkylation unit. This section includes blowdown facilities, acid handling, and caustic handling.

A. Blowdown Facilities

Potential pressure relief valve releases are divided into two classifications: acidic blowdown and hydrocarbon blowdown. Hydrocarbon blowdown releases are routed directly to the refinery's flare system. Acidic blowdown vapors are scrubbed with caustic within the alkylation unit battery limits before being routed to the refinery flare system.

The acidic blowdown vapors are routed to the acid blowdown drum to knock out any entrained liquid sulfuric acid. Additionally, spent acid from the last Contactor reactor/acid settler system(s) in series is sent to the acid blowdown drum. This allows any residual hydrocarbon in the spent acid to flash and provides surge capacity for spent acid. The acidic vapor effluent from the acid blowdown drum is sent to the blowdown vapor scrubber. The acidic vapors are counter-currently contacted with a circulating 12 wt% caustic solution in a six tray scrubber (Figure 18).

Figure 18
Acid Blowdown System



VI. BLOWDOWN SECTION (Cont'd)

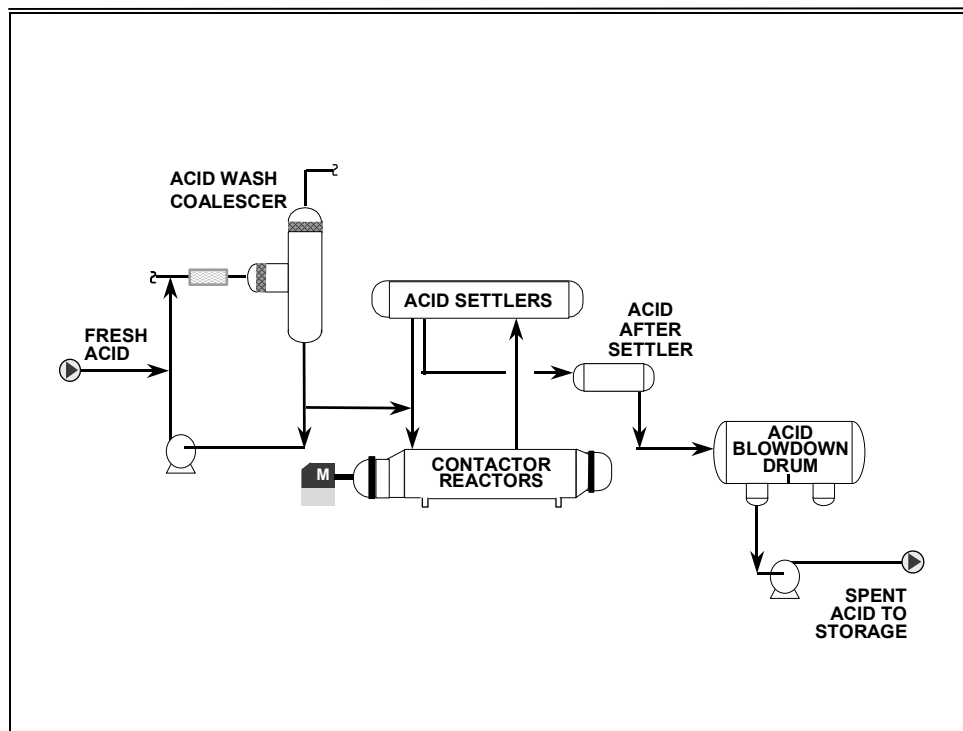
A. Blowdown Facilities (Cont'd)

During the design phase, the caustic inventory/hold-up in the scrubber is set based on the quantity of caustic required to neutralize the maximum vapor (e.g., acid) load from the acid blowdown drum with the caustic strength decreasing from 12 wt% to 1 wt% over a one hour period. This criteria was chosen so that the refinery flare system would be protected during the maximum acid-containing vapor relief without makeup caustic.

B. Acid Handling

In current designs, acid enters the process in the acid wash system (Figure 19). The acid cascades from stage to stage within the reaction zone until it leaves the process flowing to the acid aftersettler. The entrained hydrocarbon separates from the acid in the liquid full acid aftersettler and hydrocarbon is returned to the reaction section. The acid stream is sent to the acid blowdown drum, which operates close to flare header pressure allowing the light hydrocarbons dissolved in the acid to flash. The acid in the acid blowdown drum is pumped batch-wise to spent acid storage and then on to loading or acid regeneration facilities.

Figure 19
Cascaded Flow of Sulfuric Acid in the Alkylation Unit



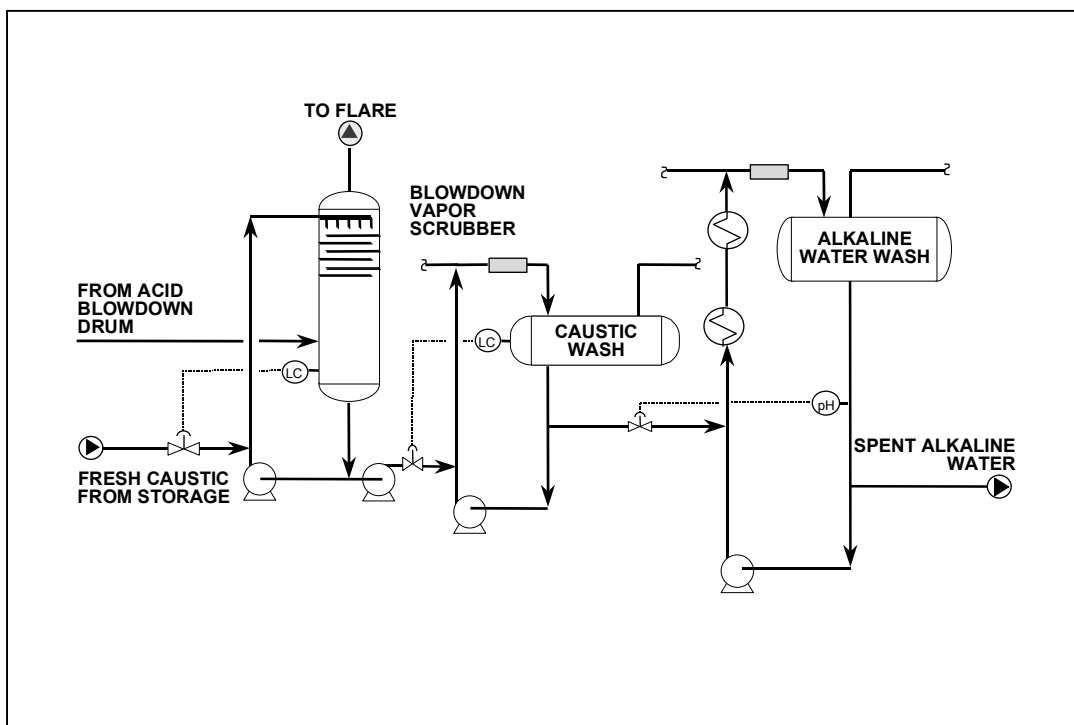
VI. BLOWDOWN SECTION (Cont'd)

C. Caustic Handling and Process Water Flow

In older alkylation units, the blowdown vapor scrubber is operated with batch caustic. However, in STRATCO's current designs it is the first stage in a continuous cascade caustic system (Figure 20). Makeup caustic flows in series through the blowdown vapor scrubber, the depropanizer caustic wash drum and the alkaline water wash drum. This system reduces caustic consumption and eliminates a strong caustic effluent stream compared to operation of separate batch systems.

Makeup caustic (12 wt%) from outside battery limits is supplied to the blowdown vapor scrubber on level control. The makeup caustic pump pumps caustic from the blowdown vapor scrubber to the depropanizer caustic wash drum. The level controller on the caustic wash drum sets the flow from the blowdown vapor scrubber to the caustic wash drum. Caustic from the depropanizer caustic wash drum is sent to the alkaline water wash for pH control. The pH controller on the alkaline water wash sets the overall caustic demand.

Figure 20
Cascaded Flow of Caustic in the Alkylation Unit

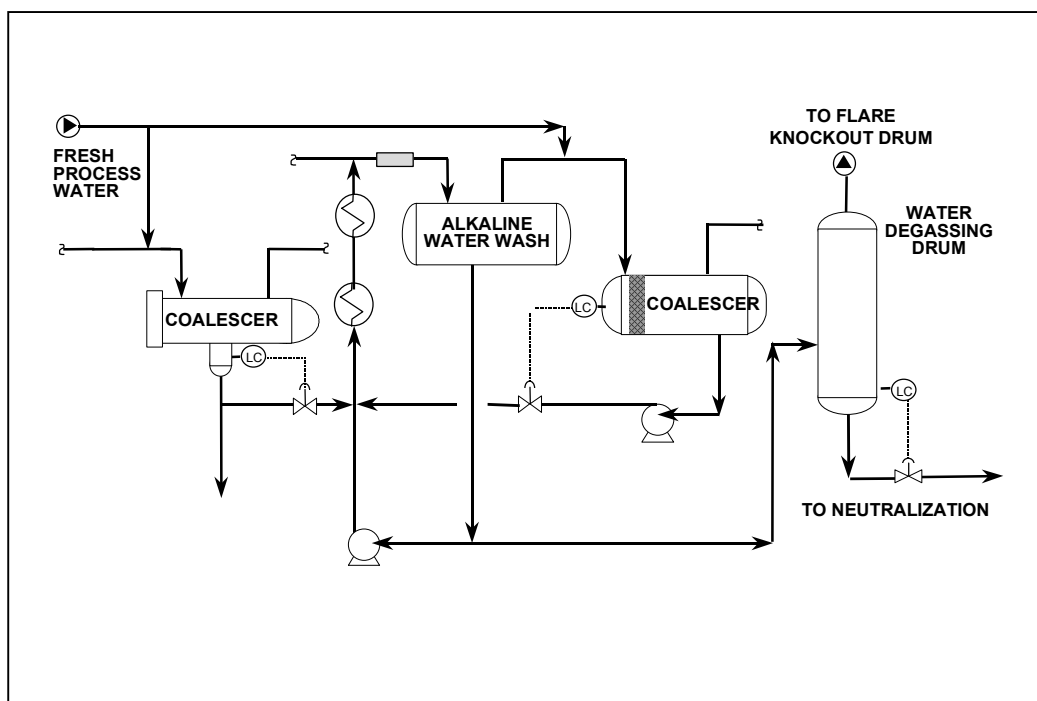


VI. BLOWDOWN SECTION (Cont'd)

C. Caustic Handling and Process Water Flow (Cont'd)

With the addition of water washes to the depropanizer feed treating and net effluent feed treating sections, STRATCO has developed a cascaded flow scheme for the unit process water. Makeup water is sent to both the net effluent water wash coalescer and depropanizer feed coalescer feed lines (Figure 21). Water collected from both of these vessels is sent to the discharge of the circulating alkaline water pump. Spent alkaline water from the alkaline water wash is sent to the water degassing drum to remove entrained and dissolved hydrocarbons. The water from the degassing drum is then routed to the neutralization system.

Figure 21
Process Water Flow in the Alkylation Unit



VII. SUMMARY

The design of a sulfuric acid alkylation unit is dependent on many factors including:

- the composition of the unit olefin feed(s)
- diluent and light end content of the unit feed(s)
- product specifications.

The five major sections of the alkylation unit include the reaction zone, refrigeration section, effluent treating, fractionation and blowdown. The proper design of each of the processing areas is imperative to the safe and efficient operation of the alkylation unit.