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ALKYLATION UNIT MONITORING

I. INTRODUCTION

Recent changes in gasoline reformulation legislation demand that alkylate producers maximize unit efficiencies at ever increasing throughput rates. This extra burden on the alkylation process requires that refiners develop a more thorough understanding of unit performance and operating trends through a complete monitoring and surveillance program. The knowledge obtained from such a program will allow for a greater degree of plant optimization and control, ensuring that efficiencies are maintained at peak levels while unit downtime is minimized.

This paper is a precursor to any consulting or unit operation enhancement program. The effectiveness of this type of program is greatly dependent upon the ability of a refiner to monitor, track, and understand normal alkylation unit operating performance. Implementation of the basic monitoring and troubleshooting programs outlined in this paper will improve operating efficiency, and allow for a greater understanding of unit performance and trends. This will enable a refiner to increase the effectiveness of STRATCO's alkylation consulting programs, resulting in improved alkylate quality and plant reliability.

STRATCO continues to pursue on-line alternatives to the traditional technologies used to monitor acid strength, acid to hydrocarbon ratio, and acid settler levels. STRATCO would like to be involved in any projects where refiners are seeking a greater degree of control over the critical process parameters in an alkylation reaction zone.
II. ALKYLATION UNIT FEED STREAMS

Figure 1 shows a block flow diagram for an alkylation unit. The two main feed streams, olefin feed and makeup isobutane, are highlighted.

![Diagram of Alkylation Unit Feed Streams]

A. Olefin Feed

The olefin feed to an alkylation unit generally originates from a Fluid Catalytic Cracking Unit (FCC), and will contain butylenes, isobutane, and possibly propylene and/or amylenes. The olefin feed is also likely to contain diluents (propane, n-butane, and n-pentane), noncondensables (ethane and hydrogen) and contaminants, which are discussed in detail on the following pages.
II. ALKYLATION UNIT FEED STREAMS (Cont'd)

A. Olefin Feed (Cont'd)

To properly monitor feedstock quality, most refiners perform a daily gas chromatographic (GC) analysis on the olefin stream. To minimize laboratory analytical costs and GC operator time, some refineries run incomplete GC analyses, checking only for C3, C4, and C5 constituents. To properly monitor the feedstock components, the refinery should perform a complete GC analysis at least once a month. This provides a reliable baseline of olefin feed impurity data, so that any changes in alkylation or upstream unit operating performance may be properly addressed. The olefin feed impurities discussed in this section can significantly affect alkylation unit performance and operating efficiency.

1. Diluents

Diluents in the feed, propane, n-butane and n-pentane, do not react, but simply pass through the alkylation unit. Diluents are undesirable compounds because they simply take up space in the reaction zone and fractionation systems. High levels of diluents in the reaction zone tend to decrease the probability that the desired alkylation reactions (olefin with isobutane) will occur and tend to increase the probability of polymerization reactions (olefin with olefin). Refiners should routinely monitor diluent levels in the olefin feed and adjust propane and/or n-butane product rates to compensate for increases in these levels. High diluent concentrations can cause an increase in alkylate endpoint and a decrease in alkylate octane.

2. Noncondensables

Noncondensables are compounds which are similar to diluents in that they do not react in the alkylation process, but differ in that they build up because they do not condense at normal plant operating conditions. Noncondensables typically originate from a selective hydrogenation unit upstream of the alkylation unit or distillation tower upsets in the FCC. Ethane and hydrogen are examples of these noncondensable compounds.

Noncondensables concentrate in the refrigerant and depropanizer overhead accumulators. The pressure within these vessels increases to a point that it must be vented. If a significant amount of noncondensables enter the unit, an increase in the compressor discharge pressure will result. The suction trap/flash drum pressure may also increase which raises the Contactor reactor temperature. If noncondensables are present in the olefin feed, monitor upstream processing units closely to minimize the level of these impurities.
II. ALKYLATION UNIT FEED STREAMS (Cont'd)

A. Olefin Feed (Cont'd)

3. Contaminants

Contaminants in the olefin feed are compounds that react with and/or dilute the sulfuric acid catalyst. They increase acid consumption (dilution), produce undesirable reaction products, and in some instances, increase polymer formation. Certain contaminants also cause undesirable emulsion characteristics in the reaction and treating sections of the alkylation unit. Table 1 on the following page provides factors for estimating the sulfuric acid consumption (dilution) for common feed contaminants.
II. ALKYLATION UNIT FEED STREAMS (Cont'd)

A. Olefin Feed (Cont'd)

3. Contaminants (Cont'd)

Table 1
Sulfuric Acid Dilution Factors

<table>
<thead>
<tr>
<th>Contaminant</th>
<th># Acid/# Contaminant*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>9.8</td>
</tr>
<tr>
<td>Ethyl Mercaptan</td>
<td>15.7</td>
</tr>
<tr>
<td>Ethyl Disulfide</td>
<td>11.8</td>
</tr>
<tr>
<td>Hydrogen Sulfide</td>
<td>~29.3</td>
</tr>
<tr>
<td>Methanol</td>
<td>26.1</td>
</tr>
<tr>
<td>Ethanol</td>
<td>19.4</td>
</tr>
<tr>
<td>t-Butyl Alcohol</td>
<td>9.8</td>
</tr>
<tr>
<td>Diethanolamine</td>
<td>24.0</td>
</tr>
<tr>
<td>Dimethyl Ether</td>
<td>12.5</td>
</tr>
<tr>
<td>Diethyl Ether</td>
<td>10.5</td>
</tr>
<tr>
<td>MTBE</td>
<td>9.2</td>
</tr>
<tr>
<td>ETBE</td>
<td>15.0</td>
</tr>
<tr>
<td>TAME</td>
<td>12.8</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>8.3</td>
</tr>
<tr>
<td>3-Methyl-1,2-Butadiene</td>
<td>12.6</td>
</tr>
<tr>
<td>2-Methyl-1,3-Butadiene (isoprene)</td>
<td>11.4</td>
</tr>
<tr>
<td>1,3-Pentadiene (piperylene)</td>
<td>12.4</td>
</tr>
<tr>
<td>1,4-Pentadiene</td>
<td>8.1</td>
</tr>
<tr>
<td>Cyclopentadiene</td>
<td>~18.5</td>
</tr>
<tr>
<td>Ethylene</td>
<td>28.2</td>
</tr>
<tr>
<td>Acetylene</td>
<td>11.1</td>
</tr>
<tr>
<td>1-Butyne (Ethyl Acetylene)</td>
<td>12.9</td>
</tr>
<tr>
<td>1-Pentyne</td>
<td>17.4</td>
</tr>
<tr>
<td>Cyclopentene</td>
<td>3-5</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>12.5</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>16.8</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>10.0</td>
</tr>
</tbody>
</table>

* The factors provided in Table 1 are approximate for an acid dilution range of 99.2-90.0 wt% H₂SO₄. To apply these values to other acid strengths, the formula below can be used to calculate acid consumption:

\[
\text{Acid Consumption} = \frac{(\text{Value From Table 1}) \times (\text{Spent Acid Wt\%})}{(9.8) \times (\text{Fresh Acid Wt\%} - \text{Spent Acid Wt\%})}
\]
II. ALKYLATION UNIT FEED STREAMS (Cont'd)

A. Olefin Feed (Cont'd)

3. Contaminants (Cont'd)

a. Water

Water in the olefin feed is a major source of sulfuric acid dilution. Almost all the free water present in the feed can be removed via a properly operating feed coalescer. New units are designed for less than 15 ppm free water in the coalescer outlet. Operate this vessel at the lowest possible temperature to minimize water solubility in the hydrocarbon and maximize water removal in the coalescer.

Monitor the feed coalescer operating temperature along with the feed/effluent exchanger heat transfer coefficients. Record and periodically check the rate of water removal against water saturation tables to insure proper operation. If the existing coalescing element is ineffective or plugs easily, STRATCO recommends Koch’s Fleximesh 316SS elements (or equivalent). This type of element resists plugging, and is not subject to the hydroxyl ion attack (from steam or high pH water) that decomposes fiberglass and phenolic resin based elements.

Periodically monitor the pH and iron content of the water drained from the coalescer. If the pH drops, a possible cause is a problem with an upstream unit. This commonly occurs with MTBE units. If the pH of the DIB overhead accumulator water is normal (above 6.0), it is more likely that an upstream unit is the culprit. If you have an MTBE unit, check the methanol extraction column water pH. If the water is not changed out often enough, the pH will drop and increase corrosion in the alky feed system.

Another cause of low coalescer water pH is a leak in one of the feed/effluent heat exchanger tubes bundles. If a leak occurs, the higher pressure net effluent will flow into the lower pressure feed side. The traces of acid in the net effluent will lower the pH of the water in the feed and accelerate corrosion. The leaking tube bundle should be repaired/replaced immediately to avoid further damage to the unit.
II. **ALKYLATION UNIT FEED STREAMS** (Cont'd)

A. Olefin Feed (Cont'd)

3. Contaminants (Cont'd)

b. Oxygenates

Oxygenates in the olefin feed originate from either an MTBE, TAME or ETBE process upstream of the alkylation unit. Methanol, ethanol and dimethyl ether (DME) react with sulfuric acid and produce water. MTBE and tertiarybutyl alcohol (TBA) can also be present. **Some oxygenates also act as cosolvents which significantly increase the solubility of water in the alkylation unit feed.** Since water in sulfuric acid makes the acid more corrosive, these contaminants are also costly in terms of acid consumption and reaction zone corrosion. If the oxygenate unit performance cannot be improved to lower these contaminants, an oxygenate removal process can be installed to reduce acid consumption and corrosion. Oxygenate carryover in the raffinate olefin stream to the alkylation unit is not uncommon when upsets in the oxygenate unit occurs.

c. Dienes

Dienes are contaminants that have become increasingly important to alkylate producers. Butadiene is produced in greater quantities as refiners increase FCC reaction temperatures to achieve higher conversions. Pentadiene levels are also on the rise for refiners that are feeding amylene to their alkylation units. Pentadiene in amylene feeds are typically at a higher concentration than butadiene in butylene feeds. Dienes are undesirable compounds because they increase acid consumption and produce higher molecular weight alkylate. The higher molecular weight alkylate produces a higher distillation (ASTM D86) end point. Several refineries have installed selective hydrogenation processes upstream of the alkylation unit to convert these dienes to olefin compounds.
II. **ALKYLATION UNIT FEED STREAMS** (Cont'd)

A. Olefin Feed (Cont'd)

3. Contaminants (Cont'd)

   d. Aromatics

   Aromatics in the olefin feed will cause foaming problems in the effluent treating system. These compounds will sulfonate in the presence of sulfuric acid, and will then form a sodium detergent in the presence of caustic. Aromatics stabilize emulsions in the acid settler(s) as well as in the alkaline water wash vessel (or caustic wash). Aromatics typically become a concern when processing amylenes or during a unit startup when there is no alkylate available and another gasoline boiling range material must be substituted. Typically, aromatic content as low as 100 ppm(wt) can cause emulsion problems.

   e. Sulfur Compounds

   Typically, sulfur compounds (such as H₂S and mercaptans) are removed upstream of the alkylation unit by amine and caustic treaters. If these treaters are not operated correctly, break through of H₂S and mercaptans to the alkylation unit are possible. The compounds do consume acid. Perhaps more important than the increased acid consumption are the emulsion problems caused by mercaptans. The mercaptans when sulfonated in the presence of sulfuric acid and neutralized by caustic form surfactants. These surfactants cause emulsion separation problems in the alkaline water wash.

   An upset in the caustic treater can lead to carryover of caustic and mercaptans. Both caustic and mercaptans will lead to increased acid consumption. An upset in an upstream amine treater can lead to carry over of amine. The amine will react with sulfuric acid to form a sulfonated compound which when neutralized with caustic forms a surfactant. This surfactant can cause emulsion problems in the alkaline water wash.
II. ALKYLATION UNIT FEED STREAMS (Cont'd)

B. Makeup Isobutane Feed

The makeup isobutane feed to an alkylation unit can be either low or high purity. Low purity makeup isobutane feedstock (typically <70 vol% isobutane) usually originates from a saturate gas plant, and is fed to the alkylation unit deisobutanizer (DIB) tower for separation of the isobutane from the n-butane. High purity feedstock (>70 vol% isobutane) normally originates from an external DIB, and is fed directly to the alkylation unit reaction zone.

Contaminants in the makeup isobutane are normally not as significant as those in the olefin feed. However, sulfur compounds, particularly hydrogen sulfide, can be troublesome. This contaminant has a high acid consumption value as shown in Table 1, so the level of hydrogen sulfide in the makeup isobutane should be closely monitored. If hydrogen sulfide levels are high, a caustic or amine treater for the makeup isobutane can be installed.

Additionally, monitor mercaptan concentrations in the low purity makeup isobutane feed to the DIB. Mercaptans can cause the alkylate product to fail corrosion tests. Mercaptans fed to the reaction zone will decompose upon contact with H₂SO₄ and can lead to emulsion problems in the reaction section and alkaline water wash. Odorants such as t-butyl mercaptan (if fed to the DIB) will exit the unit with alkylate and can cause the product to fail copper strip or doctor tests.

Take caution when processing purchased isobutane. The transportation and handling of this material increases the potential for contamination. To avoid problems, analyze each shipment for impurities. As is the case with the olefin feed, perform a full analysis by gas chromatography on the makeup isobutane on a regular basis. This baseline will allow for a more timely response to any variances in alkylation unit operating performance due to impurities in the makeup isobutane.
III. ALKYLATION UNIT PRODUCT STREAMS

Figure 2 is a block flow diagram of an alkylation unit. The three main product streams, alkylate, n-butane and propane, are highlighted.

**Figure 2**
Typical Alkylation Unit Product Streams

A. Alkylate

Alkylate product quality is a direct result of the reaction zone and distillation operation. The alkylate product should be tested daily to monitor distillation characteristics (through D-86 distillation), octane level, and Reid vapor pressure (RVP). Sulfur content and copper strip or doctor tests should be checked periodically to avoid potential corrosion in the alkylate product storage tank.
III. ALKYLATION UNIT PRODUCT STREAMS (Cont’d)

A. Alkylate (Cont’d)

1. Distillation Results

The distillation end point provides a good indication of the extent of olefin polymerization. These polymerization reactions produce high-boiling products. An end point below 400°F (205°C) is typical of most well-run butylene feed units. Alkylate product with a high end point can usually be traced to the following reaction zone problems.

a. Insufficient Mixing

The degree of emulsification of the hydrocarbons with the acid controls the mass transfer rate of the reactants with the acid catalyst. Increasing the dispersion of the hydrocarbon droplets in the acid-continuous emulsion increases the interfacial surface area and improves product quality and lowers acid consumption. Insufficient mixing increases the potential for polymerization reactions. The Contactor reactor mixing performance can be monitored by the impeller differential pressure, motor amperage and emulsion break time observed in the ratio glass (discussed in Section VII-A). Typically, the impeller pressure differential should be 7 to 11 psi (0.5-0.8 kg/cm²) with approximately a 50/50 acid to hydrocarbon volume ratio in the Contactor reactor.

b. Low Isobutane to Olefin Ratio

Maintain a high ratio of isobutane to olefin in the reaction zone to force the reaction between isobutane and the olefins and to reduce olefin to olefin polymerization reactions. Keep isobutane to olefin ratios in the composite feed to the reaction zone within the range of 7:1 to 10:1 (volume) for an optimum balance between product quality and utility usage.

c. High Reaction Temperature

Reducing reaction temperature lowers polymerization reaction rates, resulting in higher alkylate octane and lower acid consumption. The potential for corrosion increases with higher reaction temperatures. Reaction temperature should optimally fall within the range of 42-55°F (5.6-12.8°C) for butylenes and amylene.
III. ALKYLATION UNIT PRODUCT STREAMS (Cont’d)

A. Alkylate (Cont’d)

1. Distillation Results (Cont’d)
   
d. High levels of dienes and diluents in the feed

   Excessive concentration of either dienes or diluents can result in a higher endpoint alkylate product.

2. Octane Results

   Alkylate octane levels will be reduced if polymerization in the Contactor reactor(s) is significant. If low alkylate octane values are being reported, investigate the aforementioned reaction zone problems. Excessive amounts of n-pentane in the feed lower the octane since this diluent is a low octane isomer that passes through the unit and dilutes the alkylate product. This compound generally is of concern only when amylenes are fed to the alkylation unit.

3. Reid Vapor Pressure Results

   The alkylate RVP is an indication of the amount of light hydrocarbons remaining in the alkylate. Compounds such as isobutane, n-butane and isopentane in the alkylate will increase the RVP. When this parameter is higher than targeted, increase the debutanizer (DEB) bottoms temperature, (in a DIB/DEB system or the DIB bottoms temperature when used alone) to drive the lighter components up the tower and lower the alkylate RVP. Increase the n-butane product rate to compensate for this change.

Employ statistical data tracking methods to properly monitor alkylate quality. Statistical Process Control (SPC) charting of alkylate end point, octane, and RVP is ideal. The use of a simple spreadsheet to track and plot these parameters is also helpful. The alkylation unit operating personnel should undertake such a program so that they may better understand variances in unit performance and properly respond to changes.
III. ALKYLATION UNIT PRODUCT STREAMS (Cont’d)

B. Propane Product

Test the propane product via gas chromatography several times a week to ensure proper operation of the depropanizer tower. New alkylation units are designed with the propane product containing less than 2 vol% isobutane. Excessive amounts of isobutane in the propane indicate a fractionation problem. Sulfur content or doctor tests should be performed periodically on the propane product to ensure proper operation of the depropanizer feed treating.

C. n-Butane Product

Test the n-butane product several times a week via gas chromatography to monitor its purity and to help monitor operation of the DIB and DEB. Analyze this stream periodically in units with continuous on-line chromatographic analyzers to verify analyzer accuracy. New units are designed with the n-butane product containing less than 5 vol% isobutane and the DIB overhead recycle containing approximately 13 vol% n-butane. Several scenarios that may occur and the corrective actions that should be taken are listed below:

1. If the concentration of isobutane is high in the n-butane product and is low in the DIB overhead, increase the steam to the DIB reboiler to drive more isobutane up the tower and increase the DIB reflux rate.

2. If the n-butane product and the DIB overhead both contain too much isobutane, then there is too much isobutane in the feeds to the DIB. Reduce the makeup isobutane rate and increase the steam to the DIB reboiler. This will temporarily result in a high isobutane purity in the DIB overhead. The excess isobutane can be sent to storage until the isobutane purity returns to normal as a result of the reduction in the makeup isobutane rate.

3. If the n-butane product contains too much C₅+ material, then increase the DEB reflux rate and/or reduce the DEB bottoms temperature until the n-butane product purity is improved.

In general, it is desirable to lose as little isobutane to the n-butane product as possible. Depending upon the specifications for the n-butane product, it may also be desirable to lose as little isopentane to the n-butane product as possible. There is usually a trade-off between DIB reboiler steam usage and product purity.
III. **ALKYLATION UNIT PRODUCT STREAMS** (Cont’d)

C. n-Butane Product (Cont’d)

Units that do not have a DEB produce n-butane through a vapor side draw on the DIB. The above scenarios may still occur, and the actions that should be taken are the same (however, substitute “DIB” wherever the word “DEB” occurs). Operators have a very limited control over the C₅⁺ content of the n-butane side draw from a DIB. This stream will typically contain a minimum of 1.5-2.0 LV% C₅⁺ material.

IV. **INTERNAL ALKYLATION RECYCLE STREAMS**

Figure 3 shows a typical alkylation unit block flow diagram. The two main internal recycle streams, recycle isobutane and refrigerant recycle, are highlighted.

**Figure 3**

*Typical Alkylation Unit Recycle Streams*
IV. INTERNAL ALKYLATION RECYCLE STREAMS (Cont’d)

A. Recycle Isobutane from Deisobutanizer

The quality of the recycle isobutane stream from the DIB overhead accumulator can significantly affect alkylation unit operations. Therefore, monitor this stream closely so that maximum isobutane purity is maintained. A high isobutane concentration in the DIB overhead will increase the isobutane to olefin ratio and decrease the diluents (n-butane) in the reaction zone, thereby decreasing the potential for polymerization reactions.

Use the recycle isobutane composition to determine if the unit is in n-butane balance. New DIBs are designed for overhead stream compositions of approximately 85 vol% isobutane, 12 vol% n-butane, and 3 vol% propane. The levels of propane and n-butane should be minimized since these compounds are diluents in the reaction zone. If the amount of n-butane in the recycle isobutane increases over time, then there is probably an increase of n-butane in the feed to the unit. Adjust DIB reflux rate and bottoms temperature to compensate for such changes.

Any propane present in the DIB feed will recycle back to the reaction zone with the DIB overhead. If significant levels of propane in this stream occur, then the feed rate to the alkylation unit depropanizer should be increased. Increasing levels of propane in the DIB overhead is an indication that the unit is not in propane balance and that propane is building up in the unit.

Due to the impact of the composition of the DIB overhead on alkylation plant performance, many refiners have installed on-line analyzers to monitor the composition of this stream. Verify the accuracy and reliability of these instruments on a periodic basis by gas chromatography of stream samples.

Monitor the amount of water in the recycle isobutane stream via the DIB water boot. The quantity of water being drawn from the boot should be recorded. Knowing the temperature and composition of the DIB feed(s) and overhead, use water saturation tables to predict the amount of water that should accumulate in the overhead accumulator boot. If more water is present in the accumulator boot than predicted, water is likely carrying over from the effluent treating section. Monitoring the pH and iron content of this water is important as well. The pH of this water should be in the range of 6.0-7.0. A water pH outside this range indicates effluent treating problems. The effluent treating section is discussed in Section X.
IV. INTERNAL ALKYLATION RECYCLE STREAMS (Cont’d)

A. Recycle Isobutane from Deisobutanizer (Cont’d)

For the ease of operation, the recycle isobutane stream rate should be fixed once an optimum rate and composition is found. During extended turndown of 50% or more, this stream may need to be adjusted downward to ensure the Contactor reactor seal flush does not become lean in C5+ material. (This is only applicable for Contactor reactors with single seals since the flush provides lubrication to a Teflon sleeve bearing).

Run the DIB at the lowest possible pressure at which the overhead condenser will operate. The DIB is a major energy consumer and it will use less reboiler steam for the same fractionation when operating at a lower pressure.

B. Refrigerant Recycle

Analyze the refrigerant recycle stream periodically by gas chromatography to determine its isobutane content. It is necessary to know this isobutane content, and also the isobutane content of the DIB recycle & makeup isobutane streams, to determine the isobutane to olefin ratio in the reaction zone. Maintain the isobutane to olefin ratio at a high level (between 7:1 and 10:1) to reduce polymerization reactions. Note that the composition of the refrigerant recycle stream cannot be controlled directly. It is controlled by adjusting the overall unit propane and n-butane balances via the depropanizer and DIB.

V. ACID STREAMS

The alkylation process involves the reaction of isobutane with olefin compounds in the presence of sulfuric acid catalyst to form a gasoline blending component called alkylate. Ideally, the sulfuric acid should promote the alkylation reaction without being consumed. In actuality, however, olefins and certain feed impurities dilute the catalyst through competing reactions, producing acid soluble components. As a result, it is necessary to continuously add fresh acid and remove spent acid to maintain optimum catalyst strength.

A. Fresh Acid

The fresh acid makeup to the reaction section is typically a slip stream that is pulled off the acid circulation line of the acid wash drum on newer units. Sample this stream as well as the fresh acid to the unit at least once per week. It should have a titratable acidity between 98 and 99.5 wt%. The highest alkylate octane is achieved when there is 0.5-1.0 wt% water present to ionize the acid. If the acid strength is higher than 99.5 wt%, then there is a greater chance of having free SO3 present in the stream, which is both corrosive and toxic. The fresh acid flow rate to the reaction section should be adjusted to control spent acid strength.
V. ACID STREAMS (Cont’d)

B. Intermediate and Spent Acid

If an alkylation unit employs more than one Contactor reactor with acid flow in series (from one Contactor reactor to the next), the acid stream from one settler to another Contactor reactor is generally referred to as intermediate strength acid (typically 93-96 wt%), while the acid from the final settler is called spent acid (typically 89-90 wt%). Refer to Figure 4. By operating with series acid flow, the spent acid strength can be minimized to reduce acid consumption. Since maximum octane is achieved at acid strengths between 92 and 96 wt% depending on olefin feed type, a portion of the olefin is alkylated at optimum acid strengths. For these reasons, series acid flow increases alkylate product quality at lower acid regeneration costs than with a parallel acid flow design.

Acid spending is critical to plant performance, economics, and product quality. Increased polymerization reactions occur at lower acid strengths. However, due to the high cost of acid regeneration, it is desirable to maintain the acid spending strength from the final settler as low as possible. However, at low strengths, polymerization reactions become so predominant that the acid strength and stable plant operation cannot be adequately maintained. Below these strengths, the plant is said to be in an “acid runaway” which results in a temporary, but costly loss in alkylation capacity and a potential for equipment damage condition. In order to provide a sufficient safety margin to avoid “acid runaway” conditions, STRATCO recommends maintaining the spent acid strength at a sufficiently high strength to avoid an acid runaway condition.

Figure 4
Series Acid Flows
V. **ACID STREAMS** (Cont’d)

B. Intermediate and Spent Acid (Cont’d)

Vary the fresh acid flow rate to the first Contactor reactor to hold the strength of acid leaving the final settler at about 90 wt%. Adjust the flow rates of spent acid from each acid settler to hold a constant inventory of acid in that settler as shown on its overall gauge glass. Under stable operating conditions, the fresh acid and spent acid flow rates should be nearly the same. The volume of acid in the Contactor reactors and settlers is very large relative to the fresh and spent acid rates, so any changes that are made will take a long time to observe.

Measure the spent acid strength at least three times per day in the refinery laboratory to insure that optimum strengths are maintained, and to avoid an “acid runaway” condition. Also check intermediate and fresh acid strength on a periodic basis. Table 2 (in Section XI) outlines STRATCO’s recommended sampling schedule for these acid streams.

If you measure the density of acid to infer the strength (acid analyzer or hydrometer), be aware that correlation between strength and gravity is not always constant. Therefore, validate density readings with lab titrations periodically.

Experience has shown that MTBE raffinate can produce a different balance of water and red oils (organic contaminants) in the spent acid than a mixed FCC butylene feed. MTBE does not contain much isobutylene, so red oil production is reduced. However, MTBE raffinate can contain oxygenates (primarily dimethyl ether and methanol) which break down to form water on contact with sulfuric acid. Oxygenates also act as cosolvents which significantly increase the solubility of water in the alkylation unit feed. Since the densities of water and red oil differ, any changes in their relative amounts will change the density-acid strength correlation.

Some refiners “spike” the final settler with fresh acid when the spending strength drops too low. STRATCO recommends doing this only in an emergency situation and not on a regular basis. The reason for this is that spent acid contains some acid-soluble hydrocarbons, which when contacted with fresh acid, are oxidized. \( \text{SO}_2 \) is formed as a byproduct of this oxidation reaction. This additional \( \text{SO}_2 \) will eventually build up in the refrigeration section and will ultimately consume more caustic in the depropanizer feed caustic wash. “Spiking” with fresh acid also consumes more acid.
V. **ACID STREAMS (Cont’d)**

C. Acid Flow Meters

Accurate measure of acid flow is vital to controlling spent acid strength and maintaining a steady operation.

1. Orifice Plates

Orifice plates tend to erode over time and therefore are less accurate than other forms of instrumentation. In our first worldwide alkylation survey conducted in 1988, 60% of the respondents used orifice plates and 30% used magnetic flow meters. In our 1995 survey, the results were reversed with 30% using orifice plates and 59% using magnetic flow meters.

2. Magnetic Flow Meters

Magnetic flow meters have been the instrument of choice in new units and in replacing orifice plates. These meters offer much better accuracy and durability than orifice plates in measuring fresh, spent, and intermediate strength acid. However, they can not measure acid density.

3. Coriolis Meters

STRATCO currently recommends coriolis mass flow meters for measuring acid flow rates. The coriolis meters offer the accuracy of the magnetic flow meters but also provide a density output. The density information can be correlated to acid strength and used to trend interstage as well as spent acid strengths.

Since the flow through these meters is comprised of a mixture of acid, water, and hydrocarbon components (except for fresh acid), these meters only provide a strength trend and should be used along with laboratory titration results. Excess hydrocarbon carryunder from the acid settler, a slug of water in the feed, or a change in the olefin feed type can affect the density/acid strength correlation. If the meter is not tracking the titration results closely, hydrocarbon carryunder may be occurring or there may be excessive water or oxygenates in the feed.

STRATCO recommends specifying these meters with acid velocities of less than 2 ft/sec (0.6 m/s). Higher velocities may lead to excessive erosion/corrosion and premature failure of the instrument.
VI. ON-LINE ACID STRENGTH MONITORING

A. Continuous Acid Strength Measurement

Traditionally, acid strength has been measured by lab titration of alkylation unit acid samples. The spent acid stream is sampled at regular intervals, typically once per shift. The titration provides a true measure of spent acid strength, which is used to make intermittent changes to the makeup acid rate.

Why Monitor Acid Strength Continuously?

STRATCO guidelines call for sampling spent acid for titration three times per day. Also, alkylation units have been running with similar amounts of acid data for decades. Why, then, is continuous monitoring of acid strength so important? Figure 5 below demonstrates a common scenario faced by operators that must rely solely on spent acid titration results.

Based on the data in the figure above, the unit was operating at the target spent acid strength of 90% for the previous day. However, the most recent titration result indicates a severe drop in spent acid strength to 88.1%. Hopefully, the board operator’s first response is to call for an immediate resample. Unfortunately, it may take an hour or two before the next result is called in from the laboratory. Will the result of the resample be 90% as expected? Or will it be a confirming 88% or be an even lower 86%? Rather than waiting for the results of the retest, the board operator will probably increase the fresh acid flow as insurance against an acid runaway. When the new sample result is found to be 89.8%, it is very unlikely that the operator will reduce the acid flows to the original rates. Because of the clear operating penalties associated with an acid runaway, the tendency to increase acid flow is much stronger than the willingness to reduce acid flow.
VI. ON-LINE ACID STRENGTH MONITORING (Cont’d)

A. Continuous Acid Strength Measurement (Cont’d)

This is a common scenario in any sulfuric alkylation unit that does not have the advantage of continuous acid monitoring. With some indication that the strength was more stable than the sample indicated, the board operator would likely have waited for a confirming titration result before making any changes to acid flow. This provides two conclusions regarding acid strength monitoring:

- Continuous data from on-line acid measurement can prevent the “panic” between titration measurements.
- Continuous data from on-line acid measurement can promote more gradual changes in acid flow control, which generally reduces unit acid consumption.

Depending on the existing operation and the type of instrumentation technology chosen, the economic payback for instituting a continuous monitoring system can typically be measured in weeks or months.

Before discussing any of the methods used to provide continuous acid strength, it is important to understand the following fact:

**Acid titration is the only TRUE measure of acid strength.**

All of the continuous acid strength measurement techniques are based on mathematical correlations and fundamental scientific principles. However, unlike acid titration they do not provide a direct measure of acidity. STRATCO does not recommend using on-line analysis as a replacement for routine sample titration, but rather as a supplement to titration analysis.

The most common relationship used to infer acid strength is its correlation with density. Below, we discuss several of the complications that arise when a density correlation is developed for spent acid strength.

Figure 6 on the following page shows the relationship between sulfuric acid strength and density when water is the only diluent.
In the typical range of alkylation spent acids, the density curve is relatively linear, allowing acid strength to be accurately inferred. The non-acid diluents in alkylation acid include acid soluble oils (red oils) and other chemical species in addition to water.

Figure 7 shows how the hydrocarbon/water diluent content of the spent acid can impact the resulting density. The dark curve to the far right is the well-documented sulfuric acid/water density curve. The other curves have been calculated for specific percentages of hydrocarbon (red oils) in the diluents blended with the original acid and are based on simplified blending assumptions. In each curve it is assumed that 99% sulfuric acid (1% water) is the original acid starting point.
VI. ON-LINE ACID STRENGTH MONITORING (Cont’d)

A. Continuous Acid Strength Measurement (Cont’d)

Figure 7
“Red-Oil” Adjusted Sulfuric Acid Strength vs. Density

For a given acid strength, it is clear from the Figure 7 graph that the spent acid density decreases as the hydrocarbon/water ratio increases. Obviously, any strength correlation based on acid density will deviate as the relative amounts of water and red oils vary. The production rates of water and red oils in the reaction zone can be affected by the configuration and operation of the alkylation unit.

The production of water, for example, can be significantly affected by feed stream contaminants. Alkylation units that run MTBE raffinate feeds tend to show higher levels of water in the spent acid due to significant amounts of methanol and DME in the feed. If the feed to an alkylation unit is changed from an ether plant raffinate to a conventional mixed butylene feed, this will impact acid water contents and ultimately the acid density correlation.

Also, there is a second source of hydrocarbon in the spent acid, besides acid soluble oils. Typically, a small amount of hydrocarbon carryunder is entrained in the acid phase leaving the acid settler. This hydrocarbon’s density is likely to be different from the red oils that must be factored into the acid density correlation. If the entrained hydrocarbon content is too high and too variable (due to emulsion separation problems), an accurate correlation may not be possible. In this case, the hydrocarbon phase must be removed from the batch sample or bypass sample stream before a useful on-line density can be measured.
A. Continuous Acid Strength Measurement (Cont’d)

As shown in Figure 8, temperature is another complicating process variable that must be addressed.

**Figure 8**  
**Sulfuric Acid Density vs. Temperature**
VI. ON-LINE ACID STRENGTH MONITORING (Cont’d)

A. Continuous Acid Strength Measurement (Cont’d)

Although sulfuric acid density varies significantly with temperature, this effect is often ignored when acid strength is correlated with density. Given the relatively consistent temperature in the reaction zone, this is not an unreasonable simplifying assumption. However, if there is a considerable amount of uninsulated piping between the acid settler and the density monitor, a temperature correction should be included in the correlation to account for ambient effects. Using the above graph, a temperature change of 10°F (6°C) for 90 wt% acid translates to a specific gravity change of about 0.006. This corresponds to a change in apparent acid strength of more than 1 wt%.

In summary, before any correlation can be made between acid strength and density, the following three issues must be considered.

- Water content in the spent acid will have a major impact on the resulting density. Changes in unit feed streams may require changes in the correlation.

- Variations in the free hydrocarbon content of the spent acid will result in a less reliable correlation. Preferably, the on-line measurement should be performed on “flat” acid, free of entrained hydrocarbon.

- Temperature of the spent acid at the density monitoring location will have an impact on acid density, and any significant variation in temperature must be factored into the correlation.

B. On-Line Instrument Options

Having outlined the complications associated with density measurement techniques, we now discuss several commercial technologies available for continuous acid strength monitoring. The first three technologies relate acid strength to density, while the fourth option provides a more direct measure of acidity.

1. Nuclear Source Density Detector [STRATCO Acid Analyzer Pre-1997]

In the STRATCO Acid Analyzers built before 1997, a nuclear density meter was used to infer acid strength. The key to success with this device is a feed conditioning system which helps produce consistently accurate analyzer data. Figure 9 shows a simple schematic of the STRATCO Acid Analyzer system.
VI. ON-LINE ACID STRENGTH MONITORING (Cont’d)

B. On-Line Instrument Options (Cont’d)

1. Nuclear Source Density Detector (Cont’d)

In the STRATCO Acid Analyzer [Pre-1997] the acid sample is fed on level control into the settling pot. There is a 30 minute residence time to allow any free hydrocarbons to float to the top and out through the overflow line.

Figure 9
STRATCO Acid Analyzer [Pre-1997]

A heating jacket on the pot maintains the temperature at about 100°F (38°C). Vaporized hydrocarbon exits through the vent, while the remaining flat acid is sent through the nuclear device where the density is measured. Acid exits the nuclear device and flows to the blowdown drum.

The advantage of this system is in feed conditioning, which provides a consistent testing basis. Any free hydrocarbon is separated before the sensor, and a constant feed temperature is maintained. This makes the measurements relatively independent of acid settler operations, where an upset can cause significant hydrocarbon carryunder. However, if the monitored acid stream composition is very consistent, the cost of the feed conditioning system within the STRATCO Acid Analyzer may not be economically justified.
VI. ON-LINE ACID STRENGTH MONITORING (Cont’d)

B. On-Line Instrument Options (Cont’d)

1. Nuclear Source Density Detector (Cont’d)

   One disadvantage of this system is the presence of a nuclear device, which requires special administrative efforts during procurement and installation. After installation, the perception of a potential radioactive danger must also be addressed. Another disadvantage with the older STRATCO Acid Analyzer design was repeated plugging problems in the needle valve used to control feed rate to the analyzer. For these older systems, STRATCO offers upgrade services to replace the original hand operated needle valve with the level control automated valve shown in Figure 9.

2. Coriolis Meter

   A Coriolis meter measures the mass flow and density of a fluid by monitoring the vibration characteristics of flow through a tube. Because these meters provide very precise flow and density measurements, they have historically been used in services where precise measurement of mass flow is critical (custody transfer, product blending, chemical additives). Figure 10 shows a very simplified schematic of a Coriolis meter flow tube.

![Figure 10: Coriolis Meter Flow Tube](image_url)

   In service, the Coriolis meter’s flow tube is vibrated by an electromagnetic drive coil located at the center of the bend in the flow tube. When flow is forced through the tube, the fluid takes on the vertical momentum of the vibrating tube. As the fluid exits the tube it causes the tube to twist. This phenomenon is called the Coriolis effect. According to Newton’s Second Law of Motion ($F = ma$), the amount of twist is directly proportional to the mass flow through the tube.\(^1\)

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\(^1\) Micro Motion, Inc. Product Catalog, “Theory of Operation,” 1995
VI. ON-LINE ACID STRENGTH MONITORING (Cont’d)

B. On-Line Instrument Options (Cont’d)

2. Coriolis Meter (Cont’d)

Similar to a weight on a spring, the flow tube will vibrate at the natural frequency that corresponds to the mass of the flow tube. Since the fluid inside the tube constitutes part of the vibrating mass, and because the tube volume is constant, the natural frequency of vibration is directly proportional to the fluid density.²

Starting with the STRATCO Acid Analyzers built in 1997, a Coriolis meter has been used in place of the nuclear source density detector to infer acid strength. The same general system shown in Figure 9 is used to provide a consistently conditioned feed for the Coriolis meter. As with the nuclear design, valve plugging problems are avoided by use of an automated feed control valve. However, because the Coriolis meter provides both flow and density, the level control shown in Figure 9 is replaced with flow control based on the Coriolis meter’s flow output signal. This reduces the cost of the analyzer system compared to the nuclear design by eliminating the need for a level indicator/transmitter.

STRATCO also recommends Coriolis meters for flow measurement in acid process lines, as an improvement over the magnetic flow meters specified in older designs. Because they provide an accurate and reliable measurement of both mass flow and density, STRATCO has specified the Coriolis meter as the standard acid flow meter to be used in all grassroots designs.

Some refiners have attempted to use a Coriolis meter to infer acid strength directly from the spent acid process line. This method affords a low cost solution and avoids the testing complications associated with batch or slip-stream analysis. However, to give successful results, this method can only be used on an acid stream with a relatively consistent hydrocarbon carryunder and requires a continual update of the on-stream correlation.

Without inlet stream conditioning, variations in the stream temperature and hydrocarbon content make calibration more difficult. Depending on the settler design and operation, scatter produced by variations in hydrocarbon carryunder flow from the acid settler may be too great to provide a reliable indication of spent acid strength. We know of one refiner that installed a Coriolis meter on the spent acid line in each of its

² Ibid
VI. ON-LINE ACID STRENGTH MONITORING (Cont’d)

B. On-Line Instrument Options (Cont’d)

2. Coriolis Meter (Cont’d)

two plants. One plant has been successful at correlating acid strength with density. However, the other plant has an older (non-STRATCO) settler design that does not provide sufficient settling time for flat acid separation. The meter in this plant could not even provide a stable flow measurement.

Another complication with in-line density measurement is hydrocarbon buildup inside the Coriolis tube. Hydrocarbon polymers in the process line may slowly coat the inside of the tube, thereby changing the available tube volume and distorting the calculated density. Although this drift in measured density can be continuously corrected, it adds another degree of complication to the control process.

As long as the acid quality is consistent in both temperature and hydrocarbon content, the Coriolis meter is a cost effective and reliable in-line device for providing acid strength via density. For systems with significant process variation, a STRATCO Acid Analyzer system will ensure that the Coriolis meter receives a conditioned feed that will allow consistently accurate acid strength results.

3. Sonic Velocity Meter

The fundamental principle behind a sonic velocity meter is that the speed of sound in a fluid is a function of the fluid density and bulk modulus. Since it has already been established that acid strength is related to density, a relationship can be made between the speed of sound in the acid and its strength.

Historically, this technology has been used in “fresh” sulfuric acid applications where the only diluent is water. When it was first applied to alkylation acids, the correlation was not found to be repeatable. The problem facing the developers was that the speed of sound in alkylation acid is not stable with respect to time. Figure 11 on the following page shows an example of how the speed of sound in alkylation acid changes with sample storage time.
VI. ON-LINE ACID STRENGTH MONITORING (Cont’d)

B. On-Line Instrument Options (Cont’d)

3. Sonic Velocity Meter (Cont’d)

Through additional research, the developers found that the shape of the speed of sound vs. time curve could be used to correlate acid strength. Regardless of the hydrocarbon diluent components in the acid, the general shape of the curve is consistent for a given acid strength. The developers also found that if water content is independently measured via conductivity that a single correlation can be used even if the water content of the acid varies. Therefore, using only the first 10-20 minutes of the curve, a speed at $t=\infty$ can be estimated. This estimated speed is combined with the measured conductivity and temperature of the acid sample to determine acid strength.

The system works by collecting a batch sample of acid and allowing it to settle. The sonic velocity is measured, along with temperature and conductivity, over a fixed period of time. Once the analysis is complete, the sample is drained and the cycle is repeated. The system can be automated using solenoid valves and a programmable logic controller (PLC) so that the system can run itself after an initial calibration phase conducted by the vendor. Using this system, a single testing device can be used to sequentially sample and test any number of acid streams in the alkylation unit. Because the PLC is required for the calculation routines and single stream valve sequencing, the incremental cost to sample additional acid streams is minimal.

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3 NuSonics Division Model 86 APM Product Data Sheet, 1997
VI. ON-LINE ACID STRENGTH MONITORING (Cont’d)

B. On-Line Instrument Options (Cont’d)

3. Sonic Velocity Meter (Cont’d)

To provide reliable on-line acid strength data, a significant amount of up-front calibration is required by the vendor. It may take several weeks of work (some of which may be performed off site) before the system is ready to be turned over to the refiner. Once in operation, the vendor can make adjustments via modem, if necessary.

This is a new and developing technology for acid strength measurement. The company developing this technology currently has two applications in operation with good results. The systems are fully automated and a data point is generated every 15 minutes. STRATCO is willing to provide the necessary contacts to any licensee interested in the sonic velocity device.

4. NMR Analyzer

Nuclear magnetic resonance (NMR) technology has historically been limited to operating in a laboratory environment. However, STRATCO knows of one refiner that has comprehensively tested a prototype in-line NMR analyzer. The system uses a flow-through probe to eliminate potential for plugging and does not use any moving parts or consumable materials. The analyzer is now being offered commercially, packaged with ongoing calibration and maintenance services.

NMR technology identifies chemical components by their molecular nature, providing temperature independent process data. From NMR raw output data, acid strength, I/O ratio, and acid/hydrocarbon ratio can be monitored in the reaction zone. More academic parameters such as paraffin and acid soluble oil content can also be monitored. The analyzer measures the ionizing effect of acid on water in the system, enabling a more direct indication of acid strength. If the analysis is performed on the reactor emulsion, NMR output will show changes in acid strength hours before other detectors that analyze the spent acid stream. Although on-line NMR technology allows numerous parameters to be monitored simultaneously, this an expensive option compared to a combination of less flexible devices.
VII. REACTION ZONE

A. STRATCO Contactor Reactor Emulsion Monitoring

Intimate contact of the feed hydrocarbons with the acid catalyst is an extremely important step in the alkylation process. In the reaction zone, an olefin molecule will combine with an isobutane molecule in the presence of sulfuric acid catalyst. Olefinic compounds are readily soluble in the acid phase unlike isobutane, which is only slightly soluble. Therefore, intense mixing is required to provide the interfacial surface area needed to allow alkylate production.

The excellent mixing and internal circulation properties of the STRATCO Contactor reactor promotes contact of isobutane with olefins in the acid phase. The uniform Contactor reactor temperature, coupled with this intense mixing, produces a fine dispersion of hydrocarbon droplets in the acid phase. This fine emulsion of hydrocarbon in acid creates a high mass transfer rate of isobutane into the acid catalyst, resulting in a high quality alkylate product.

The relative volume of hydrocarbon in the acid emulsion is an important parameter in the alkylation process. To promote the alkylate reaction and minimize undesirable side reactions, the olefin and isobutane must be dispersed in a large volume of acid. Therefore, STRATCO recommends that a relatively high volume of acid (45-60 vol%) be maintained in the Contactor reactor. It is particularly important that the Contactor reactor emulsion be acid continuous with hydrocarbon droplets dispersed within the acid phase, as opposed to being hydrocarbon continuous (acid droplets dispersed in a hydrocarbon phase). In a hydrocarbon continuous emulsion, the acid will not form small droplets, but rather larger globs of acid, providing far less interfacial surface area for contact between acid and isobutane. The resulting increase in olefin-olefin polymerization leads to higher acid consumption and lower alkylate octane and yield.

Several methods to monitor the acid to hydrocarbon ratio and the emulsion characteristics in the Contactor reactor are listed on the following pages. STRATCO recommends using as many methods as possible, since each one can provide information about reaction conditions.

1. Ratio Glass Monitoring

The acid to hydrocarbon ratio should be monitored to insure that the emulsion in the reaction zone remains acid continuous. In a STRATCO alkylation unit, the Contactor reactor ratio glass is used to measure the ratio. STRATCO recommends that the ratio be checked at least once per day. Figure 12 shows the configuration of a typical ratio glass assembly.
VII. REACTION ZONE

A. STRATCO Contactor Reactor Emulsion Monitoring (Cont’d)

1. Ratio Glass Monitoring (Cont’d)

Figure 12
Typical Contactor Reactor Ratio Glass Configuration

Follow the procedure outlined below to collect a representative Contactor reactor acid/hydrocarbon emulsion reading:

a. Open all valves on the ratio glass flow loop. The impeller differential pressure will cause the emulsion to flow downward through the ratio glass.

b. After the emulsion appears homogenous, close the lower valve (Valve A in Figure 12) to trap the sample. Keep the upper valves open to prevent thermal expansion from overpressuring the ratio glass.

c. Record how long it takes for the emulsion to completely break. The hydrocarbon phase should not be evident for several minutes. A good acid/hydrocarbon emulsion should take 20 to 40 minutes to resolve. If the emulsion characteristics are poor (i.e., not enough mixing, etc.), the emulsion may begin to separate immediately and completely break within 10 minutes. This can also be indicative of a hydrocarbon continuous emulsion rather than the desirable acid continuous emulsion. Product quality will suffer under these conditions because of insufficient contacting. Long break times (50 minutes or
VII. REACTION ZONE

A. STRATCO Contactor Reactor Emulsion Monitoring (Cont’d)

1. Ratio Glass Monitoring (Cont’d)

...are an indication of “tight” emulsions possibly caused by feed contaminants or rust particles. “Tight” emulsions can lead to acid carryover in the hydrocarbon from the acid settler and/or hydrocarbon carryunder in the spent acid.

d. Once the emulsion completely breaks, record the position of the interface as a percentage of the total calibration range (see Figure 12). The settled acid phase should fill 45-60% of the total calibration range. This reading will determine if there is too much or too little acid in the Contactor reactor. To adjust the amount of acid in the Contactor reactor, the acid settler levels will need to be adjusted. This procedure is discussed in Section VIII-C of this paper.

Take ratio glass readings at least once per day.

Assuming the acid from the acid settler to the Contactor reactor is not throttled, it should be possible to adjust the acid inventory in the settler to maintain an emulsion containing 45-60% of acid. If your ratio glass provides readings consistently outside of this range, check the installation and calibration of the ratio glass.

If the ratio glass provides consistently low readings, its calibration may be inaccurate. It is best to have the ratio glass centered within the calibration range. The center of the top “tee” and the center of “Valve A” should be equidistant from the ratio glass. A 50% reading on this type of installation will correspond to an emulsion containing 50% acid. Installations with the ratio glass not centered within the calibration range will need to account for unequal volumes above and below the sight glass to be calibrated properly.

If the ratio glass readings tend to increase over time, the likely cause is leakage of acid into the sight glass after the outlet valve is closed. Please note that Figure 12 shows the ratio glass inlet line with a 5° slope to prevent this from occurring.

Some characteristics of the ratio glass system inhibit proper monitoring of the acid to hydrocarbon ratio. The first is a perception that it requires a fair amount of operator time. In reality, the operator only needs to close a single valve (Valve “A” shown previously) and then wait about an hour. However, because an operator’s time is often spent addressing immediate issues, the valve may not be closed. If the valve is often closed and then
VII. REACTION ZONE

A. STRATCO Contactor Reactor Emulsion Monitoring (Cont’d)

1. Ratio Glass Monitoring (Cont’d)

Forgotten, the ratio glass begins to plug and foul without fresh circulation, and eventually renders the system useless.

Another ratio glass operating issue concerns the use of ball check valves. Because continuous circulation is required to keep the system clean, ball checks prevent the system from working properly. However, many refiners have standardized requirements that prevent the removal of ball checks from any sight glass assembly. In this case, the ball checks have to be rigged open to allow circulation through the glass. Even then, these check valves provide a place for plugging to begin.

Finally, the 5 degree slope on the top connection to the glass is often an issue. We have seen a unit where the construction group did not understand the need for the slope and proceeded to bend the nozzle down to horizontal. Also, the slope often makes for a less than elegant installation if the glass is also allowed to slope 5 degrees from vertical. However, please note that the slope of the glass will have little or no impact on the accuracy of the measurement.

B. On-Line Instrument Options

Why Monitor Acid : Hydrocarbon Ratio Continuously?

Because of the consistent operator effort required to measure the acid to hydrocarbon ratio, this critical data may not be recorded on a regular basis. Although continuous ratio data is not required to properly operate the unit, on-line analysis provides a regular stream of data to ensure that the acid to hydrocarbon ratio of the emulsion in the Contactor reactor is maintained in the most effective alkylation range. The on-line ratio data also provides a record of this important reaction zone parameter and may benefit the operator by showing subtle trends and abrupt changes in the reaction zone.

We now discuss three standard and two alternative technologies that are available to continuously monitor the acid to hydrocarbon ratio in the Contactor reactor.
VII. **REACTION ZONE**

B. **On-Line Instrument Options (Cont’d)**

1. **Overall Contactor Reactor Sight Glass / Level Indicator**

The overall Contactor reactor sight glass and/or level indicator is a new addition to our designs. It can give an immediate but rough indication of the amount of acid in the Contactor reactor emulsion. The overall Contactor reactor level indication is most useful when filling or emptying the Contactor reactor during startup or shutdown so the liquid level can be detected at all times. This level bridle is tied into the Contactor reactor relief line and the Contactor reactor drain line, so it can be installed without adding new nozzles to the Contactor reactor. STRATCO incorporates a net effluent flush to the sight glass on new alkylation units to prevent plugging of taps.

2. **Contactor Reactor Motor Amperage**

Monitor the Contactor reactor motor amp level to provide a rough indication of any acid/hydrocarbon ratio changes in the Contactor reactor. If the acid content of the Contactor reactor emulsion increases by a significant amount, the Contactor reactor motor amperage level will increase due to the increased load on the motor. Therefore, if an amp meter is available, check and track the amperage of the motor periodically.

3. **Contactor Reactor Impeller Pressure Differential**

Monitor and track the pressure differential across the Contactor reactor impeller. The pressure differential will gradually decrease over time due to normal wear on the impeller blades. If the pressure differential changes over a short period of time, there may be a change in the acid/hydrocarbon ratio in the Contactor reactor.

An increase in impeller pressure differential indicates an increase in the amount of acid in the Contactor reactor (due to the higher density of the acid). Typically, the pressure differential should be 7 to 11 psi (0.5-0.8 kg/cm²).

4. **Coriolis Meter**

STRATCO is currently pursuing an alternative to the ratio glass that will provide continuous measurement of the acid to hydrocarbon ratio. As discussed earlier, a Coriolis meter will measure density in addition to mass flow. Since acid and hydrocarbon have such different densities, the density of the emulsion can be directly correlated to the acid to
hydrocarbon ratio in the mixture. Figure 13 shows the proposed changes in the ratio glass system to allow an on-line indication of ratio.

**Figure 13**

New Ratio “Glass” System Configuration

In the system shown above, the ratio glass has been replaced with a Coriolis meter. The drawback to having the ratio glass removed is an inability to monitor the settling time of the emulsion by watching how long it takes for the emulsion to break in the ratio glass. This capability is useful for troubleshooting operating problems such as acid carryover. Therefore, a refiner should weigh the advantages before installing a Coriolis meter in series or parallel, or as a replacement for the existing
VII. REACTION ZONE
   B. On-Line Instrument Options (Cont’d)

4. Coriolis Meter (Cont’d)

   ratio glass. In 1998, STRATCO worked with a refiner that successfully calibrated the output from a Coriolis meter to provide on-line acid to hydrocarbon ratio data.

5. AGAR Probes

   These instruments have an extensive history in the crude desalter emulsion detection service. They work by measuring the amount of energy absorbed by each phase (i.e., acid and hydrocarbon) in an emulsion. The hydrocarbon is a low absorber of energy and the acid is a high absorber of energy. Thus, these probes can measure the volume percentage of a particular phase at a specific point in the system. STRATCO believes that it may be possible to install an AGAR probe on the Contact reactor to measure the acid to hydrocarbon ratio in the emulsion. Calibration is required.

6. NMR Analyzer

   As mentioned previously, an NMR analyzer can provide the acid and hydrocarbon content of the emulsion in the Contact reactor. Using this data, one refiner successfully monitors the acid to hydrocarbon ratio in their Contact reactors.

C. Contactor Reactor Temperature

   Maintain the STRATCO Contact reactor temperature between 42 and 50°F (5.6 and 10.0°C) if possible. Excessively high temperatures will result in excessive olefin-olefin polymerization, fragmentation, olefin oxidation, acid dilution, corrosion, and the increased production of hydrocarbon-soluble sulfur compounds. The exception to this is when running high concentrations of propylene (>40% of total olefins), STRATCO recommends temperatures up to 60°F (15°C). Contact reactor temperatures below 40°F (4.4°C) should be avoided to prevent freezing (high viscosity) of the sulfuric acid, poor emulsion resolution in the acid settler, and subsequent acid carryover.

   Control the Contact reactor temperature by adjusting the suction trap pressure. If the Contact reactor temperature drops below 40°F (4.4°C), increase the suction trap pressure by closing down on the compressor suction throttling valve (for an electric driven compressor), or by decreasing the speed of the compressor
VII. REACTION ZONE

C. Contactor Reactor Temperature (Cont’d)

(for a turbine driven compressor). This increases the vaporization temperature of the refrigerant passing through the tube bundle which increases the Contactor reactor temperature.

Temperature variations between identical Contactor reactors with equal flows may be the result of a reduction in the overall heat transfer coefficient of the Contactor reactor tube bundle. This is more common in the higher acid strength Contactor reactor due to viscosity characteristics of higher strength acid at lower temperatures. A reduction in the overall heat transfer coefficient of the high acid strength Contactor reactor may indicate that acid carryover from the acid settler is coating the inside of the Contactor reactor(s) tubes. Acid carried over into the lower acid strength Contactor reactors will typically pass through and not significantly affect the overall heat transfer coefficient since it is less viscous.

STRATCO recommends periodically calculating the Contactor reactor superficial heat transfer coefficients (U) as follows:

\[
U_{\text{superficial}} = \frac{Q}{A \cdot \Delta T}
\]

The duty, \( Q \), is determined by adding the heats of reaction of the olefins, mechanical heat, and atmospheric heat. Approximate values for olefin heats of reaction are as follows: Propylene, 840 BTU/lb olefin (467 Kcal/kg); Butylenes, 615 BTU/lb (342 Kcal/kg); and Amylenes, 500 BTU/lb (278 Kcal/kg). Combined mechanical and atmospheric heat input varies but a conservative approximation is 1.30 MM BTU/hr per Contactor reactor (328 Mcal/hr).

The area of the tube bundle, \( A \), is known, and the temperature difference, \( \Delta T \), can be estimated by taking the temperature differential of the suction trap liquid and the Contactor reactor. A superficial heat transfer coefficient of 50 BTU/hr\( \cdot \)\( ft^2 \cdot °F \) (244 Kcal/hr\( \cdot \)\( m^2 \cdot °C \)) is typical for new Contactor reactor tube bundles.

If the tube bundle in the high strength Contactor reactor is fouled, flush the viscous acid from the tubes by temporarily increasing the temperature of the Contactor reactor. The most common practice is to increase the olefin feed to the fouled Contactor reactor, which increases its temperature and reduces the viscosity of the acid so it can be washed away with the settler effluent. If this is not successful, shut off the hydrocarbon feeds (except seal flush) to the affected Contactor reactor and keep the impeller running. Since the refrigerant flow through the tube bundle will cease, the tube wall temperature will quickly increase to the Contactor reactor temperature. The Contactor reactor will also gradually warm up due to the mechanical heat provided by the impeller.
When the Contactor reactor temperature reaches approximately 60°F (15°C), restart the feeds to the Contactor reactor. The refrigerant flow will flush the acid from the tube bundle to the suction trap and into the acid knock out drum.

Monitor the Contactor reactor temperature and minimize fluctuations. In addition, make plant operating personnel aware of the controlling factors of the Contactor reactor temperature, and the impact upon unit performance of good/poor temperature control.

There are several circumstances that can cause unbalanced temperatures among Contactor reactors. A few of the more common ones include inaccurate flow meters, poor Contactor reactor mixing, and tube bundle fouling. Plugged tubes and unsymmetrical piping are other possible causes, but less common.

STRATCO recommends using Contactor reactor temperatures to detect and compensate for inaccuracy in feed flow meters for individual Contactor reactors since, the accuracy of thermocouples is generally better than flow meters. If the olefin feeds are in balance, the Contactor reactor temperatures should be in balance as well. However, STRATCO recommends using Contactor reactor temperatures only to fine tune olefin feed rates. Do not adjust olefin feed rates drastically to balance temperatures or an acid runaway may result.

Adjusting olefin feeds or refrigerant recycle rates to achieve equal Contactor reactor temperatures when the temperature imbalance is caused by reasons other than inaccurate olefin flow meters can affect alkylate quality to a greater extent than the temperature difference alone. STRATCO does not recommend balancing Contactor reactor temperatures with refrigerant recycle since it is a key component of the Contactor reactor feed isobutane to olefin ratio.

Poor Contactor reactor mixing will cause the temperature to increase. Over time, as the clearances between impeller and wear ring increase, short circuiting of flow occurs and the internal circulation rate decreases. Short circuiting of flow can also occur due to a mechanical failure of the circulation tube or feed nozzle. The heat transfer rate of the Contactor reactor tube bundle will decrease as the circulation rate decreases. A new Contactor reactor should have an impeller ΔP between 7 and 11 psi (0.5 - 0.8 kg/cm²) at a 50/50 acid to hydrocarbon volume ratio.

The Contactor reactor tube bundle will experience erosion and corrosion over time. Rather than replacing the bundle, refiners usually plug the leaking tubes. As
VII. REACTION ZONE (Cont’d)

C. Contactor Reactor Temperature (Cont’d)

the number of plugged tubes increases, the temperature within the Contactor reactor will increase due to reduced surface area. Also, older tube bundles generally have more pitting and rough areas where the viscous acid emulsion can adhere. As a result, older tube bundles generally have a lower overall heat transfer coefficient than newer ones. Typically, the lowest strength Contactor reactor bundle will experience erosion and corrosion at a greater rate than the higher strength bundles. Higher reaction temperatures (>55°F, 13°C) increase the rate of corrosion.

D. Contactor Reactor Pressure

Relatively, acid-free hydrocarbon flows from the top of the acid settler, through a back pressure control valve, then back into the Contactor reactor tube bundle. Set the back pressure control valve at a high enough pressure, generally 50-60 psig (3.5-4.2 kg/cm²g), to prevent vaporization in the acid settler. With multiple acid stages, set the settler pressures approximately 5 psi (0.35 kg/cm²) apart to allow acid flow between stages.

VIII. ACID SETTLER

The acid settler is a large vessel that allows for separation of the acid/hydrocarbon emulsion created in the Contactor reactor. The hydrocarbon reaction effluent is removed from the top of the acid settler and should be virtually free of acid. The acid recycled back to the Contactor reactor(s) from the bottom of the settler should contain 20-40 vol% entrained hydrocarbon. This mode of operation is referred to as “emulsion recycle” and is recommended by STRATCO. Some older alkylation units are not equipped for emulsion recycle and operate with “flat acid recycle,” in which there is no hydrocarbon present in the acid. This mode of operation is undesirable because it increases the residence time of the acid in the settler which promotes polymerization. If your acid settlers cannot be operated in “emulsion recycle” mode, contact STRATCO and we can propose a solution.

A. Monitoring the Settler Emulsion

Correctly reading and controlling the acid settler emulsion is of critical importance in optimization of alkylation plant performance. The emulsion is monitored by two types of sight glasses on the settler. The first of these gauge glasses is referred to as the overall sight glass, and extends from the bottom to the top of the vessel as shown in Figure 14.
A. Monitoring the Settler Emulsion (Cont’d)

Figure 14
Acid Settler Sight Glass Layout

The level observed in the overall sight glass shows the total acid inventory in the
acid settler. Under normal operating conditions, however, the emulsion in the
acid settler is not resolved (as indicated by the overall sight glass), so a method is
required to determine the emulsion level in the acid settler. This is accomplished
by a series of short, staggered “split” glasses that are used for determining the
acid content of the emulsion at various intervals in the settler.

Each split glass will indicate an individual acid/hydrocarbon ratio. The specific
ratio seen in a particular split glass is representative of the emulsion existing at
the height in the settler between the taps of the split glass. Typically, acid should
only be observed in the bottom two or three glasses.

Whenever the emulsion becomes “tight” and acid is present in the upper split
glasses, the potential for physical acid carryover becomes more pronounced.
Remedial action should be taken to correct the situation, see Section VII-D,E of
this paper.

Monitor the settler emulsion frequently. It is imperative that the gauge glasses be
flushed with net effluent once every one to two weeks to clean the glass and to
keep the taps open so that an accurate emulsion reading is obtained. Acid in the
bottom of the gauge glasses will polymerize over time and cause plugging if it is
not flushed out. Monitor and track both the overall acid level in the settler and
the tightness of the emulsion by noting the highest split glass where acid is found.
VIII. ACID SETTLER (Cont’d)

B. Continuous Acid Settler Level Monitoring

The primary problem with the split glass is that, unlike the Contactor reactor ratio glass, there is essentially no flow through the instrument. As a result, the split glasses are very susceptible to plugging. In order to keep the glasses in useful condition, a diligent flushing program is required. Even if they are flushed at regular intervals, the glass tends to discolor from constant exposure to the dark acid. The final result is that the glasses are very difficult to read and monitoring is often abandoned.

Because of the problems associated with the split glass assembly, acid settler level data may often go unrecorded. Although continuous data is not required to properly operate the unit, on-line analysis would provide a regular stream of data to help the operator monitor the results of adjusting acid flow rates to and from the settler. The recorded level data may point out trends in the unit operation and may help the operator to minimize acid carryover to the suction trap/flash drum.

C. On-Line Instrument Options

STRATCO is in a continuous process of improving the design of the alkylation unit. To this end, we are investigating alternatives to the settler split glasses that will provide a more reliable reading as well as a continuous reading. In order to find a suitable replacement, a test in an operating facility is required. We have a few options to consider if a refiner is interested in pursuing other alternatives.

1. AGAR Probes

As mentioned previously, these instruments work by measuring the amount of energy absorbed by each phase in an emulsion. The probes can be placed at a few locations in the acid settler to determine the percentage acid and hydrocarbon (not level) at those points. It is critical that the probes be placed at an angle in the vessel in order for them to work properly. This may require a retrofit of existing nozzles or new nozzles being installed in the vessel. STRATCO is aware of a few refiners who have used AGAR probes in their acid settlers with varying degrees of success.

2. Capacitance Meters

Capacitance meters, depending on configuration, have the capability of determining the level of acid similar to the split glasses. Each installation would require an individual settling zone, so plugging could still be an
VIII. ACID SETTLER (Cont’d)

C. On-Line Instrument Options (Cont’d)

2. Capacitance Meters (Cont’d)

issue. Historically, capacitance probes have been used to determine the overall emulsion level with varying degrees of success.

3. Magnetic Floats

STRATCO is aware of two refiners that use magnetic floats to determine acid levels in the settler. Although this is not a new technology, we mention it here because it is possible to use the float device to send a signal to the control room to allow continuous monitoring. To confirm the on-line data, a local indicator is needed. STRATCO believes that the “flapper” type of indicator is preferable to the “follower” type.

D. Monitoring the Settler Temperature

The acid in the settler contains intermediate reaction compounds, such as alkyl sulfates, that can react with each other to form polymers. If significant polymerization is occurring in the settler, the acid recycled to the Contact reactor will be more than 3°F (1.7°C) warmer than the emulsion entering the settler. This is due to the exothermic properties of these reactions. Therefore, monitor the temperature of the settler and compare it to that of the Contact reactor.

In order to lower the potential for polymerization, minimize the acid residence times in the settler. Do this by maintaining low acid inventories in the settlers (between 18-24 inches (460-610 mm) on most new units), and maximizing emulsion recirculation rates between the settlers and the Contact reactors (i.e., the acid recycle valves should remain completely open).

Each Contact reactor/settler system will have its own optimum acid settler acid inventory. This optimum is based on obtaining an acid/hydrocarbon ratio in the range of 45-60 vol% and obtaining flat acid for the intermediate and/or spent acid transfer. It is possible to operate with an intermediate acid stream which contains significant amounts of hydrocarbon. However, it is more difficult to transfer equal volumes of acid in and out of each stage when the acid contains varying amounts of hydrocarbon. Flat acid is critical for the spent acid stream to minimize hydrocarbon losses to flare.
D. Monitoring the Settler Temperature (Cont’d)

Acid recycle valves should be opened as wide as possible to achieve maximum acid recirculation rates. With some settler configurations it may not be possible to maintain the desired acid to hydrocarbon ratio, minimize acid inventory, and transfer flat acid at the same time. In these cases, STRATCO can assist with acid settler modifications.

E. Controlling the Contactor Reactor Emulsion Ratio

The desired acid/hydrocarbon ratio target in the Contactor reactor is 45-60 vol%. In current STRATCO alkylation designs, this ratio is controlled through acid settler acid inventory levels. Some refiners control the ratio by adjusting the valve position in the acid recycle line, thereby changing the amount of acid being recycled through the Contactor reactor. This practice is not recommended, as STRATCO has determined that maximum acid recycle rates and minimum acid residence time promote better alkylate product quality, and decrease the potential for polymerization.

Adjust the Contactor reactor ratio by changing the overall settler acid inventory. Increasing the acid level (as shown by the overall sight glass) will cause more acid to be returned to the Contactor reactor, and will increase the relative volume of acid in the Contactor reactor. Therefore, when the Contactor reactor acid ratio is below 45 vol%, increase the inventory in the acid settler, as depicted by the overall sight glass. Conversely, when the ratio is above 60 vol%, lower the settler level. Make changes in settler acid levels by adjusting the acid flow rate out of the settler. When controlling the ratio through adjustment of the settler acid levels, make gradual changes and keep the levels close to the targets discussed previously. Also, do not allow the spent acid strength to decrease below about 89 wt% when making inventory adjustments.

Controlling Contactor reactor acid/hydrocarbon ratios with two or more settlers is slightly more complex than in a single vessel system. Figure 15 shows a two Contactor reactor/settler configuration. If the ratio in Contactor reactor A is high, then decrease the level of Settler A, as measured by the overall sight glass, to cause less acid to be returned to the Contactor reactor. Accomplish this by increasing the intermediate acid flow rate (FC-2) out of Settler A. However, this will increase the amount of intermediate strength acid sent to the second Contactor reactor (Contactor reactor B in Figure 15).
VIII. ACID SETTLER (Cont’d)

E. Controlling the Contactor Reactor Emulsion Ratio (Cont’d)

Therefore, to maintain the ratio of acid/hydrocarbon in Contactor reactor B, increase the rate of spent acid flow (FC-3) such that the flow as measured by FC-3, equals that of FC-2. In this situation, the fresh acid flow as measured by FC-1 should not be adjusted (as long as acid strengths are at optimum levels).

On the other hand, if the ratio in Contactor reactor B is low, then the level of Settler B should be increased by temporarily decreasing the spent acid flow to storage. The intermediate strength acid rate as measured by FC-2 should not be adjusted, unless the spent acid strength decreases below 89 wt%.

Figure 15
Contactor Reactor/Settler Acid Flows

Over the long term, the flow rates through the acid flow control valves should be approximately equal. One or more flow controllers can be temporarily adjusted to adjust acid inventory within the associated stage. However, be sure to watch the spent acid strength closely when making significant changes and reset the acid flow controllers back to their normal set points when the inventories are at their target values.

F. Physical Acid Carryover

Every alkylation unit will have some physical acid carryover in the reactor effluent (approximately 50 ppm). For this reason, an acid knockout pot is installed below the suction trap/flash drum. The prewarning for excessive acid carryover is the appearance of acid in the upper acid settler split glasses. The next indication of acid carryover is excessive acid accumulation in the suction trap.
VIII. **ACID SETTLER** (Cont’d)

F. **Physical Acid Carryover** (Cont’d)

knockout pot. The acid can and will find its way into the net effluent which can severely affect units with caustic/water washes due to the increased acid neutralization requirements.

The effects of acid carryover with units that have fresh acid washes is greatly reduced since the acid is recovered in the acid wash and does not require neutralization. The majority of physical acid carryover incidents can easily be prevented and corrected through proper monitoring of the settler split glasses and suction trap acid knockout pot. On unit startup, however, it is fairly common to experience carryover problems. This is due to the amount of solids, such as rust, present in the unit during turnaround. These solids tend to stabilize the settler emulsion, increasing the amount of acid present in the hydrocarbon effluent. During alkylation unit turnarounds, proper cleaning and vessel washing procedures can minimize carryover concerns.

During normal alkylation unit operation, the following factors can lead to acid carryover:

1. **Cold Acid**

   Alkylation is generally favored at low reaction temperatures. However, at temperatures below 40°F (4.4 °C), the settling rate of the acid in the settler is reduced, occasionally resulting in acid carryover.

2. **Acid Settler Levels**

   An inaccurate settler level indication is one of the most frequent causes of physical acid carryover. Flush the settler split glasses with net effluent frequently to minimize this concern. STRATCO incorporates a net effluent flush to all of the settler gauge glasses on new alkylation units.

3. **Contactor Reactor Pressure Control**

   Unusually low Contactor reactor operating pressures can cause entrainment of acid. A high propane content in the system or a high Contactor reactor reaction temperature also may lead to acid carryover. Poor control of these parameters will cause vaporization in the acid settler. This increased agitation can inhibit settling. To determine if the carryover is caused by this phenomenon, increase the settler pressure. This should stop any vaporization. Fluctuations of the settler pressure also can lead to initiation of acid carryover.
VIII. ACID SETTLER (Cont’d)

F. Physical Acid Carryover (Cont’d)

4. Contactor Reactor Tube Bundle Leak

A leak in a Contactor reactor tube bundle will allow acid from the Contactor reactor to combine with settler effluent, resulting in excessive acid carryover to the suction trap knockout pot. If this should occur, check the strength of the acid in the knockout pot and use this as an indication of which Contactor reactor has a tube leak. Then remove the suspected Contactor reactor(s) from service one at a time until the acid carryover to the suction trap subsides. The Contactor reactor removed from service is the likely culprit.

G. Tight Emulsions

Tight emulsion problems are more common on startups due to solid particulates in the system. However, some feed contaminants, such as aromatics or ethylene, can lead to a tight emulsion during normal operation. Seal oils leaks on the compressor or Contactor reactor may also cause a tight emulsion since seal oils typically contain aromatics or polyolefins. The acid settler overall and split glasses along with the Contactor reactor ratio glass will detect a tight emulsion problem if monitored.

Tight emulsion can lead to hydrocarbon carryunder in intermediate and spent acid streams. The hydrocarbon in the intermediate acid streams will affect transfer rates and acid inventories. The acid inventory may eventually increase since the volume of acid taken out of the system is less than the fresh acid coming in. Hydrocarbon in the spent acid may be lost to flare.

Remedial action is to detect and remove the contaminant(s) from the feed. Removal of the contaminant is a dilution process since it is likely distributed throughout the entire volume of the reaction zone. The acid inventory may need to be reduced. To lower the acid inventory, increase the spent acid rate if possible without excessive hydrocarbon carryunder to the acid blowdown drum. To maintain acid spending strengths, adjust the olefin feed rates as necessary. An alternate approach is to take the affected Contactor reactors/acid settlers off line, allow the acid to settle, and replace the acid in the system with fresh acid.
G. Tight Emulsions (Cont’d)

The figures on this page provide a comparison of the emulsion characteristics. Figure 8 shows an acid settler with normal emulsion characteristics:

**Figure 8**

*Acid Settler with Normal Emulsion*

![Diagram of acid settler with normal emulsion characteristics.](image)

Figure 9 shows an acid settler with tight emulsion characteristics. Note that the upper gauge glasses contain acid and the acid in the stilling well is not settled.

**Figure 9**

*Acid Settler with Tight Emulsion*

![Diagram of acid settler with tight emulsion characteristics.](image)
IX. REFRIGERATION SYSTEM

A. Suction Trap/Flash Drum

The pressure of the suction trap controls the Contactor reactor average temperature. A rule of thumb is that a 1 psi increase in suction trap pressure corresponds to a 3°F increase in reaction zone temperature and vice versa (0.1 kg/cm² → 2.4°C). If the suction trap is operating in slight vacuum at the desired reaction zone temperature, STRATCO recommends increasing the propane content of the refrigerant (see Section VIII-C) to increase the suction trap pressure at the same Contactor reactor temperature. STRATCO recommends avoiding vacuum operation to insure that oxygen (air) cannot enter the system and form an explosive mixture.

As previously stated, monitor the suction trap acid knockout pot regularly so that acid carryover problems can be detected and corrected.

B. Compressor

The refrigeration compressor increases the pressure of the refrigerant vapor to produce condensation in the refrigerant condensers. The compressor maintains a low suction trap pressure to vaporize the refrigerant and cool the reaction zone. The refrigeration compressor discharge pressure is a function of composition and condensing temperature of the refrigerant.

With a turbine drive or variable speed motor the speed is adjusted to control the suction trap pressure which in turn controls the Contactor reactor(s) temperature. This type of system is very energy efficient since the compressor will spin only as fast as required to condense the refrigerant. Increasing the speed of the compressor will decrease the suction trap pressure for the same discharge pressure.

A constant speed motor driver for the compressor is more common, and uses a suction throttle valve to control the suction trap pressure. Opening the valve will reduce the suction trap pressure. This will increase vaporization in the Contactor reactor tube bundles and thus reduce the temperature of the Contactor reactor. Therefore, the Contactor reactor reaction temperature can be controlled by throttling the compressor suction valve. A suction throttle valve is a much more efficient method of pressure control in comparison to “spilling back” the compressor discharge to the suction trap. Spillback should only be utilized for compressor surge protection.
IX. REFRIGERATION SYSTEM (Cont’d)

C. Depropanizer

Monitor the depropanizer tower feed composition (or refrigerant recycle composition) and adjust the feed rate to maintain an optimum propane content in the refrigerant and to maintain an overall propane balance. Increase the feed to the depropanizer to lower the level of propane in the refrigerant and reduce the compressor discharge pressure required for condensation (and vice versa). The optimum propane level in the refrigerant is a balance between reaction zone temperature, compressor and depropanizer utility consumption, and keeping the suction trap above atmospheric pressure. The optimum propane concentration determined during the design phase is typically 10 to 15 wt% in the depropanizer feed (3-7 wt% in refrigerant recycle).

X. EFFLUENT TREATING

The reactor effluent from a H₂SO₄ alkylation unit will contain reaction intermediates (alkyl sulfates) and traces of acid. Optimum reaction zone conditions will minimize these components. In general, the reactor effluent from a propylene feed is the most difficult to treat since propyl sulfates are more stable and harder to decompose than butyl sulfates. The reactor effluent from an amylene feed is the easiest to treat.

A properly operating effluent treating system can have a significant impact on overall alkylation plant efficiency and reliability by preventing corrosion, fouling and plugging of the DIB tower and auxiliaries. If fouling or plugging occurs, fractionation efficiency will decrease, potentially lowering the reaction isobutane to olefin ratio and decreasing the quality of the alkylate product.

A. Caustic/Water Wash

The purpose of the caustic wash is to neutralize any free acid carried over from the reaction zone and to break down and neutralize the alkyl sulfates (esters) in the net effluent. The purpose of the water wash is to (thermally) decompose any remaining esters and remove caustic and salts carried over from the caustic wash. Typical caustic/water wash reactions are shown below for butyl sulfates:

**Saponification of monoalkyl sulfates (acid esters)**

\[
(C_4H_9)HSO_4 + NaOH \rightarrow NaSO_4(C_4H_9) + H_2O
\]

**Hydrolysis of monoalkyl sulfates (acid esters)**

\[
(C_4H_9)HSO_4 + H_2O \rightarrow C_4H_9OH + H_2SO_4
\]
X. **EFFLUENT TREATING** (Cont’d)

A. **Caustic/Water Wash (Cont’d)**

**Hydrolysis of dialkyl sulfates (neutral esters)**

\[
(C_4H_9)_2SO_4 + 2 \text{H}_2\text{O} \rightarrow 2C_4H_9\text{OH} + \text{H}_2\text{SO}_4
\]

**NOTE:** Temperatures above 120°F (49°C) promote this reaction.

**Neutralization**

\[
\text{H}_2\text{SO}_4 + 2 \text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + 2 \text{H}_2\text{O}
\]

Alkyl sulfates remaining in the feed to the DIB can thermally decompose in the tower (or in DIB feed preheaters) to form SO₂ and tars. The SO₂ will rise in the tower, combine with water, form acid, and corrode the DIB overhead system. The tars will foul the DIB and/or DEB reboiler. Low pH water collected in the DIB overhead accumulator water boot indicates a poorly operating effluent treating system. The pH should be monitored and remain above 6.0 (preferably 6.5 to 7.5).

To prevent erroneously low pH indication, collect the water samples in a plastic container purged with nitrogen to prevent any sulfurous acid in the water from oxidizing to sulfuric acid (stronger). Refiners have reported this phenomena. The initial pH reading is approximately 6.0 and subsequent readings for the same sample exposed to oxygen can go as low as 3.0 due to oxidation.

Salts or caustic remaining in the feed to the DIB will deposit on or near the feed tray as the water vaporizes and goes overhead in the column. Tray plugging and flooding near the feed tray results from salt buildup. For this reason, it is important to avoid carryover from the water wash since the water contains salts. Excess water in the DIB overhead accumulator water boot is an indication of water carryover. If the recommended treating parameters are followed and salt buildup continues to occur, consider adding a coalescing element or electrostatic precipitator in (or downstream of) the final wash drum.

To improve caustic/water wash effluent treatment, the following parameters should be monitored:

1. **Circulation Rates**

   The caustic and water circulation rates should be maintained between 20 and 30% of the net effluent volume rate. Higher rates can lead to carryover and lower rates can reduce the interfacial surface area where the reactions occur.
X. **EFFLUENT TREATING** (Cont’d)

A. Caustic/Water Wash (Cont’d)

2. Static Mixers

The static mixer pressure drop should typically be 10-15 psi (0.7-1.1 kg/cm²) for both the caustic and water wash. Lower pressure drop can be a sign of mixer deterioration or improper sizing. Many units install a globe valve in series with the static mixer to increase ΔP (mixing) during turndown or to compensate for mixer wear.

Koch type SMV static mixers are recommended. An average drop size of 300-400 microns (per Koch correlation) should be specified. These mixers typically have five Alloy 20 mixing elements.

3. Temperature

Many refiners operate their caustic and water washes at 65-80°F (18-27°C). However, a temperature of approximately 120°F (49°C) in either the caustic or water wash is required for the decomposition of dialkyl sulfates in the net effluent. Most refiners choose to heat the water wash to 120°F (49°C) by heating the circulating water stream.

4. Interface Level and Caustic/Water Addition

STRATCO recommends that the interface level in both the caustic and water washes be kept at 25% of the drum height. Higher levels can lead to carryover of caustic or water. Lower levels can lead to hydrocarbon carryunder.

Fresh water should be added to the caustic wash to maintain a constant interface level and/or specific gravity reading between 1.10 and 1.15. This replaces the water that is absorbed by the dry net effluent.

Add fresh water to maintain the conductivity of the water wash between 5,000 and 8,000 µmhos (µSiemens). If the water wash is heated, add caustic to the water wash, if needed, to maintain the pH between 10 and 12 so that any acid formed in the decomposition reactions can be neutralized. Monitor the water and caustic addition rates.
X. **EFFLUENT TREATING** (Cont’d)

A. Caustic/Water Wash (Cont’d)

4. Caustic Change-Outs

Spend caustic batch-wise when the caustic wash strength falls to 3 wt%. Refill with fresh caustic having a strength of 10-15 wt%. Avoid using makeup caustic with strength greater than 15 wt% as salt precipitation and plugging of the caustic circulation circuit can occur. Monitor the frequency of caustic change-outs to provide an indication of acid carryover and/or poor reaction zone conditions.

B. Acid/Alkaline Water Wash

Newer alkylation units use a fresh acid/alkaline water wash process to treat the net effluent. This type of system consumes less caustic and is generally more effective. As with the caustic/water wash system, the purpose of a fresh acid/alkaline water wash is to remove alkyl sulfates and free acid from the net effluent to prevent DIB corrosion and fouling.

The acid wash uses fresh acid to absorb monoalkyl sulfates (acid esters) and a portion of the dialkyl sulfates (neutral esters) and sends them back to the Contactor reactor, instead of neutralizing them as the caustic wash does. The acid wash typically includes an electrostatic precipitator to remove acid (<10 ppm residual acid) from the feed to the alkaline water wash.

The alkaline water wash decomposes any remaining alkyl sulfates not extracted by the acid wash and removes any acid carried over from the acid wash or formed in the alkyl sulfate decomposition reactions (see Section IX-A for typical reactions).

Low pH water in the DIB overhead accumulator water boot indicates that not all of the alkyl sulfates were absorbed in the acid wash or decomposed in the alkaline water wash. To improve effluent treatment, the following parameters should be monitored and controlled.

1. Circulation Rates

The acid circulation rate should be controlled between 3 and 5% of the net effluent rate. The alkaline water circulation rate should be maintained at 20-30% of the net effluent rate. Higher rates can lead to carryover and lower rates can reduce the interfacial surface area where the reactions occur.
X. **EFFLUENT TREATING** (Cont’d)

B. Acid/Alkaline Water Wash (Cont’d)

2. **Static Mixer Pressure Drop**

The static mixer pressure drop should typically be 10-15 psi (0.7-1.1 kg/cm²) for both the fresh acid and alkaline water wash. Lower pressure drop can be a sign of mixer deterioration or improper sizing. Many units install a globe valve in series with the static mixer to increase ΔP (mixing) during turndown or to compensate for mixer wear.

Koch type SMV static mixers are recommended. An average drop size of 300-400 microns (per Koch correlation) should be specified. These mixers typically have five Alloy 20 mixing elements.

3. **Interface Level**

STRATCO recommends that the interface level in the acid wash and alkaline water wash be kept at 15% and 25% of the drum height, respectively. Higher levels can lead to carryover of acid or water. Lower levels can lead to hydrocarbon carryunder. Also a low acid level is required to keep the level below the electrostatic precipitator grid.

4. **Alkaline Water Wash Temperature**

The temperature of the alkaline water wash should be kept above 120°F (49°C). This temperature is required to decompose the remaining dialkyl sulfates in the net effluent.

5. **pH Level**

Add caustic to the alkaline water wash to maintain a pH in the range of 10 to 12. An alkaline environment is required to neutralize the acid that is formed as a byproduct of the dialkyl sulfate decomposition (i.e., hydrolysis) reactions, and to neutralize any acid carryover. Monitor the caustic addition rates.

6. **Alkaline Water Conductivity**

Add fresh water and spend alkaline water to maintain the water’s conductivity between 5,000 and 8,000 µmhos (µSiemens). Monitor the amount of water required. Note that some water will be absorbed by the dry effluent from the acid wash.
X.  **EFFLUENT TREATING (Cont’d)**

B.  Acid/Alkaline Water Wash (Cont’d)

7.  Electrostatic Precipitator Amp and Volt Readings

Monitor the electrostatic precipitator voltage and amperage readings. The volts should be high (20,000 - 30,000 V) and the amps low (< 8 mA). If this is not the case, then there is probably poor emulsion resolution. If a stable emulsion is present, decrease the acid recirculation rate to 2% of the net effluent and also check for a high interface level. As with the acid settlers, the gauge glasses should be flushed on a regular basis to keep the gauge glass taps clean. Also maintain flush to the precipitator bushing housing(s). The bushing flush should be clean and dry. Most refiners use depropanizer feed (before caustic treating) or n-butane product. The bushing flush should be at least 10°F (6°C) warmer than the acid wash so the clean hydrocarbon flush will pool in the bushing housings and prevent acid from entering. Traces of acid in the bushing area can cause arcing, which will short out the electrostatic precipitator.

XI.  **LABORATORY SAMPLING SCHEDULE AND PROCEDURES**

Table 2 on the following page outlines recommended alkylation laboratory analyses and provides a list of sample frequency, while Table 3 lists recommended laboratory testing procedure information. STRATCO’s procedure for titration of sulfuric acid is also included.
Table 2: Laboratory Sampling Schedule

<table>
<thead>
<tr>
<th>Stream</th>
<th>Test</th>
<th>Samples Per 7 Days</th>
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<tbody>
<tr>
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## Table 3: STRATCO Recommended Lab Methods

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<td>Spent Acid</td>
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<td>Wt.%</td>
<td>STRATCO TITRATION</td>
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</table>
XI. LABORATORY SAMPLING SCHEDULE AND PROCEDURES (Cont’d)

A. Alkylation Sulfuric Acid Titration Procedure

1. **Centrifuge acid for 15 minutes in a sealed centrifuge tube.**

2. Weigh about 0.5 g (+/-0.1 mg) of acid into a 250 ml beaker containing a magnetic stirring bar. Add ~25 ml of water and 5 drops of 0.1% methyl red indicator.

3. Fill an 80 ml plastic syringe with 0.25 N standardized NaOH, attach a needle, and weigh on an analytical balance. Tare before removing the syringe.

4. Add caustic to the diluted acid sample while stirring until the color changes to orange (pH 5.8).

5. Reweight the syringe. The negative weight displayed is the weight of caustic used in the titration.

6. Calculate the wt. % H₂SO₄ as follows:

\[
\text{wt. % H}_2\text{SO}_4 = \frac{(\text{g NaOH sol’n used})(98.0)(100)(Y)}{(\text{g acid sample})(2)(40)}
\]

Where \( Y = \frac{\text{g NaOH}}{\text{g NaOH sol’n}} \) as determined by the normality and density of the NaOH solution.

Standardize NaOH with dried potassium acid phthalate to the phenolphthalein end point. Convert grams of NaOH solution used to milliliters before calculating normality.