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DuPont is frequently asked what can be done to lower an alkylation unit’s fresh acid consumption. Literature on alkylation implies that lowering the target spending strength is one way to lower acid consumption. The same literature may mention the risk of acid runaway if the spending strength is too low. Acid runaway can be described as very high acid consumption that occurs if the acid strength gets too low. How are these two statements reconciled? What is the optimum spending strength for your alkylation unit?

In this paper, acid consumption will be shown to reach a minimum as a function of spending strength. Reducing acid consumption by lowering spending strength is only effective above the minimum acid consumption strength. Near the minimum, acid consumption is insensitive to changes in spending strength. At spending strengths below the minimum, acid consumption is higher. Acid runaway is an extrapolation of that trend. At some lower than normal acid strength, acid consumption exceeds the hydraulic capacity of the acid delivery system. Acid strength then drops uncontrollably or “runs away”.

There is also a perception that the type of olefin feed (propylene, butylene, amylene) determines the optimum spending strength and strength at which an acid runaway begins. It will be shown that the type of olefin feed does have an impact on the optimum and acid runaway strength but only in context with operating conditions and the hydraulic capacity of the acid delivery system.

I. ACID CONSUMPTION FUNDAMENTALS

The alkylation reaction can be considered as occurring in three steps: First the olefin absorbs into the acid forming an alkyl sulfate or cation intermediate (olefin absorption). Second, isobutane reacts with the intermediate to form an alkylate cation (isobutane reaction). The alkylate cation may isomerize to a more stable cation, depending on the acid strength. Third, the alkylate cation undergoes hydride transfer to become alkylate.

At high acid strengths, the isobutane reaction occurs quickly. As a result, the concentration of intermediates in the acid is low. However, the strong acid will fragment some of the alkylate resulting in some production of acid soluble oils (ASO) that consume (dilute) the acid.

At low acid strengths, the isobutane reaction is slower. As a result, the concentration of intermediates in the acid phase increases. Although there is less fragmentation of alkylate, side reactions of the intermediates in the acid phase increase the production of ASO.

Acid consumption due to reaction can be considered acid dilution by intermediates and ASO. In the remainder of this paper, the intermediates and ASO that dilute the acid will be referred to collectively as acid diluents.

At some intermediate acid strength, acid diluents production is minimized by limiting both fragmentation of alkylate and acid phase side reactions. Figure 1 is an example of acid diluent production as a function of acidity as measured in a DuPont alkylation pilot plant.
Figure 1 is typical of data plotted from many pilot and commercial tests. The acid diluent production is typically lowest at intermediate acid strengths and higher at typical spending strengths. As the acid strength drops below typical spending strengths, the diluent production increases at an increasing rate. In terms of reaction steps, the isobutane reaction continues to slow while olefin absorption continues. A high concentration of olefin intermediates leads to more side reactions increasing acid diluent production.

At very low acid strengths, the isobutane reaction will eventually stop. Typically, long before this point, the flow of acid required to maintain an abnormally low spending strength exceeds the hydraulic capacity of the system. This is the definition of an acid run away. Without intervention, the acid strength will continue to drop until olefin absorption also stops.

II. MINIMUM ACID CONSUMPTION

It is a popular concept that acid consumption can be reduced by lowering acid spending strength. It is logical to assume that extending the dilution range for acid by reducing spending strength should reduce acid consumption. However, the trend in diluent production indicated in Figure 1 offsets that benefit. The trend in diluent production combined with the effect of the dilution range produces the actual acid consumption curve shown in Figure 2. This curve assumes three acid stages in series.
The curve in Figure 2 indicates that, for 40/60 C₃/C₄ feed at typical operating conditions, acid consumption reaches a minimum at a spending strength of around 91 wt%. At spending strengths significantly below the minimum, more acid is required to maintain the acidity. Any reduction in acid flow in this regime of the curve will cause the acidity to drop continuously until either the acid flow is increased or the olefin feed is reduced or stopped.

The minimum acid consumption for the alkylation of a butylene feed is shown in Figure 3. There are two different curves representing two different operating conditions. Again, the assumption is three acid settlers in series. At design conditions, the acid consumption reaches a minimum near 86 wt%. At extreme conditions, higher space velocity, higher temperature and lower isobutane to olefin ratio, the minimum occurs at a lower acidity. However, since acid runaway is technically a hydraulic limit, the higher acid consumption at extreme conditions (dashed line) could result in a runaway at a higher acid strength (sooner) than the system at more ideal operating conditions (solid line).
In Figure 4, the acid consumption trend is shown for different numbers of acid stages. Acid consumption is always highest in the low acid strength stage. Adding stages in front of the low strength stage dilutes the impact of the low strength stage on acid consumption.

![Figure 4 - Acid Consumption vs. Spending Strength – Butylene Feed](image1)

Figure 5 shows the acid consumption for an amylene feed at design conditions and assuming three acid stages. Cyclopentene, a high acid consuming olefin, was excluded from the amylene feed. The acid consumption for an amylene feed, free of cyclopentene, does not come to a minimum in the range shown. Additional experiments at lower acid strengths suggest that the minimum occurs at a spending strength around 80 wt%. As spending strength is lowered, the alkylate properties from amylene feed decline, especially D-86 T90 and end point. At strengths approaching 80%, yield also begins to decline.

![Figure 5 - Acid Consumption vs. Spending Strength – C5 Feed](image2)
Figure 6 presents a hypothetical case of running an 80% propylene feed in a three stage system. Two different reaction temperatures are represented. The acid consumption for this hypothetical case is very high, but appears to be lower at the higher reaction temperature. However, this figure is misleading. Most of the acid consumption shown in Figure 6 occurs in the low strength stage. At low acid strength the propylene intermediate is very slow to react with isobutane. Raising the temperature makes the propylene intermediate more reactive thus lowering the acid consumption in the low strength stage. However, raising the temperature also results in the production of more ASO.

As shown in Figure 7, the acid consumption in the lower strength stage is much higher at the lower reaction temperature. The implication for separate olefin processing is that acid consumption for the low strength propylene stage is higher at lower reaction temperatures.
An alkylation unit designed to separately alkylate propylene, butylene, and amylene feeds can take advantage of the acid consumption trends for all three olefins. The high strength stage would run the 80% propylene feed followed by the butylene feed in the mid strength stage followed by the amylene feed in the low strength stage. The acid consumption trend for this hypothetical case is shown in Figure 8.

![Figure 8 - Acid Consumption vs. Spending Strength – Separate Olefin Processing](image)

### III. Acid Consumption Estimate

The data presented in Figure 1 was developed from pilot plant experiments at constant feed and operating conditions but varying acid strength. In an operating unit, this curve can be approximated using settler acid strengths and overall acid consumption data. Consider a three settler alkylation unit processing the same feed at the same conditions used to generate the pilot plant data shown in Figure 1. Predicted acid strengths for each settler are given in Table 1 for a spending strength of 89.5 wt%. The acid consumption, from Figure 2, or from operating data, is 0.74 lb/gal of true alkylate. This consumption is proportioned to each settler according to the drop in acidity from the stage ahead or the fresh acid.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Acid Strength wt% H₂SO₄</th>
<th>Drop</th>
<th>lb/gal True Alkylate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh Acid</td>
<td>98.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>High Strength</td>
<td>96.2</td>
<td>2.3</td>
<td>0.57</td>
</tr>
<tr>
<td>Mid Strength</td>
<td>94.5</td>
<td>1.7</td>
<td>0.42</td>
</tr>
<tr>
<td>Low Strength</td>
<td>89.5</td>
<td>5.0</td>
<td>1.23</td>
</tr>
<tr>
<td>Total / Average</td>
<td>9.0</td>
<td></td>
<td>0.74</td>
</tr>
</tbody>
</table>
The calculated stage consumption can be fit to a quadratic equation. To estimate the actual acid consumption requires the solution of two equations with two unknowns (for three stages). The assumption built into these equations is based on mass conservation of sulfuric acid. This is an approximation because some acid is consumed by breaking down to SO₂ or combining with hydrocarbons to a stable form. However, an estimate of the amount of acid lost through these mechanisms will confirm that this amount is small compared to the total acid flow and the approximation is reasonable. The two equations can be developed from the following relationship:

\[
\begin{align*}
A_0 - A_1 &= A_1 - A_2 = A_2 - A_3 \\
\text{Eqn}(A1) &= \text{Eqn}(A2) = \text{Eqn}(A3)
\end{align*}
\]

\(A_0\) = Fresh acid strength  
\(A_1\) = High acid strength  
\(A_2\) = Mid acid strength  
\(A_3\) = Spending strength

\(\text{Eqn}(A1,A2,A3) = \) stage consumption equation fit to data in Table 1

Example:

Let \(A_0 = 98.5\) (fresh acid strength)  
Let \(A_3 = 90.0\) (spending strength)

Stage Consumption Equation = 331.613 - 7.03413*\(A\) + 0.037349*\(A^2\)

\[
\begin{align*}
A_2 - 90 &= A_1 - A_2 \\
1.065 &= \text{Eqn}(A2) \\
98.5 - A_1 &= A_2 - 90 \\
\text{Eqn}(A1) &= 1.065
\end{align*}
\]

Solution:

\(A_1 = 96.16\) \(\text{Eqn}(A1) = 0.564\)  
\(A_2 = 94.42\) \(\text{Eqn}(A2) = 0.418\)

\[
\text{Acid Consumption} = \text{Average Stage Consumption} \times \frac{\text{Initial Dilution Range}}{\text{New Dilution Range}} = 0.682 \times \frac{9}{8.5} = 0.722 \text{ lb/gal true alkylate}
\]

**IV. OPTIMUM SPENDING STRENGTH**

The proceeding analyses are based on three acid settlers in series. The results would be different for two settlers or four settlers in series. It would also be different if the acid flow were other than series or if the feed rate or composition varies significantly between Contactor reactor/settler systems.
The optimum spending strength for alkylation takes into consideration both operational and economic considerations. First, the spending strength should be higher than the minimum spending strength. This prevents the acidity from going below the minimum in an upset situation. A careful analysis of historical spending strengths should give guidance as to how much above the minimum to operate. Secondly, an economic analysis could suggest an even higher spending strength. Alkylate properties improve at higher acid strengths providing a trade-off to higher acid consumption. An example of this trade-off is shown in Table 2. Acid consumption is reduced by lowering spending strength in this limited range, but alkylate properties will suffer slightly. Economic calculations are needed to determine the optimum for a specific alkylation unit.

### Table 2 - Acid Consumption and True Alkylate Properties versus Spending Strength

<table>
<thead>
<tr>
<th>Spending Strength</th>
<th>Butylene Alkylation</th>
<th>Amylene Alkylation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Consumption (lb/gal)</td>
<td>90 wt%</td>
<td>87 wt%</td>
</tr>
<tr>
<td>Acid Consumption (lb/gal)</td>
<td>0.23</td>
<td>0.21</td>
</tr>
<tr>
<td>Research Octane</td>
<td>96.5</td>
<td>96.2</td>
</tr>
<tr>
<td>Motor Octane</td>
<td>93.2</td>
<td>93.0</td>
</tr>
<tr>
<td>D-86 T_{90}, °F</td>
<td>276</td>
<td>284</td>
</tr>
<tr>
<td>End Point, °F</td>
<td>407</td>
<td>410</td>
</tr>
</tbody>
</table>

An alkylation unit running at a spending strength below the minimum acid consumption strength would be at significant risk of an acid runaway. A sudden, temporary increase in the olefin feed to the low strength Contactor reactor, for example, would result in a decrease in acid strength. The acid strength would then continue to fall, even if the olefin feed rate returned to normal. How is this condition recognized?

### V. ACID RUNAWAY RECOGNITION

If the acid strength of a Contactor reactor/settler drops below the minimum acid consumption strength, due to normal or upset conditions, the acid strength will continue to drop until acid flow is increased or the olefin feed is decreased. Without an on-line method of measuring acid strength, it is unlikely that falling acid strengths would be the first indication of an acid runaway. Although there is very little commercial data available, indications are that a runaway can occur within a few hours. Therefore, a lab titration that is completed every eight hours would not be frequent enough to indicate an acid runaway.

One key to recognizing an acid runaway is observing the reaction temperature. By definition, during a runaway, the rate of olefin absorption exceeds the rate of the isobutane reaction. Both steps are exothermic but since the isobutane reaction is suppressed, less heat is generated, causing the Contactor reactor temperature to drop. The temperature can drop to as low as 30°F (-1.0°C) in a runaway condition. Adding olefin feed does not increase the Contactor reactor temperature; it simply increases the rate of olefin absorption and reduces the rate of the isobutane reaction.
One cautionary note: A temperature loss in the low strength Contactor reactor does not prove that an acid runaway is underway. Be certain that the olefin feed rates and the refrigerant recycle rates are balanced between reactors. If a runaway is suspected, check that the feed control valve positions and the back pressure control valve positions agree with the indicated flow rates to verify that the Contactor reactors are balanced.

An online method of measuring acid density would also give an indication of an ensuing runaway. Density correlates with acid strength at a fixed water concentration. The quickest response would be with, for example, a coriolis meter installed in parallel with the ratio glass in the Contactor reactor. This method of measuring density is currently being tested in the field but is yet unproven. Measuring the acid density of the spent acid will also give an indication, but the lag time is on the order of 2 hours because of the residence time in the baffle of the settler.

Another indication of an acid runaway can be found by monitoring the Contactor reactor operating parameters. Because the acid strength falls during an acid runaway, the acid phase density and viscosity decrease as well. This reduces both the impeller differential pressure and the horsepower (amps) required by the Contactor reactor. Motor amperage, if tracked, could be used as an indicator.

During an acid runaway the acid becomes “wild” due to the high concentration of reactive intermediates. With reduced density, the acid does not settle out readily and can be carried throughout the unit. Another example of the properties of runaway acid can be demonstrated in a “heat up” test. If a sample of acid is warmed to ambient temperature and then shaken, oxidation of polymeric hydrocarbons will produce SO₂ with heat. Usually, the sample will foam over the flask as well. A “heat up” test is a simple way to test the stability of the acid.

An additional indication of an acid runaway is that the alkylate can turn purple. As the concentration of the olefin intermediates increase, more hydrocarbon soluble acid-complexes are formed and extracted into the hydrocarbon phase. A high concentration of neutral esters in the alkylate can also be expected. These neutral esters can overload the effluent treating system and end up decomposing in the deisobutanizer.

VI. **ACID RUNAWAY RESPONSE**

If you have firmly established that you are experiencing an acid runaway, stop olefin feed. You may have no idea how the problem started. It may have been contaminants such as caustic, butadiene, or sulfur compounds that originally started the runaway. However, once an acid runaway is in progress, the olefins can be considered to be nothing more than contaminants that consume acid. DuPont recommends the following procedure when responding to an acid runaway:

1. Block in olefin feed at the runaway Contactor reactor(s). Keep cooling and flushing the reaction mass with refrigerant recycle. Do not block in the refrigerant recycle stream in an attempt to heat the Contactor reactor to a normal operating temperature.
2. Continue operating the Contactor reactor to provide intimate contact with isobutane. The goal is to maximize the isobutane reaction and thus remove the olefin intermediates from the acid phase. This will stabilize the runaway acid as the acid strength is restored.

3. **DO NOT PRESSURE THE ACID TO A BLOWDOWN DRUM OR TO A SPENT ACID TANK UNLESS IT IS REQUIRED TO DEPRESSURE THE SYSTEM DUE TO AN EMERGENCY.** Runaway acid will continue to react and produce a heavy tar, SO₂ and water in a stagnant vessel.

4. Feed fresh acid directly through the acid spike line to increase the runaway acid strength. The strength has to be restored to a minimum of 90 wt% before the Contactor reactor can be placed back in service.

5. Acid samples should be obtained from the Contactor reactor. Do not obtain acid samples from the spent acid line. The spent acid (or withdrawal line) is no longer flowing and would not yield a representative sample.

6. The acid sample should be checked for both strength and with a “heat up” test to establish whether the Contactor reactor is ready for olefin feed.

7. Find out what precipitated the acid runaway before introducing olefin feed again.

The last item can be puzzling; about two out of three incidents that are reported do not list a cause for what initiated the runaway.

The point to remember is that runaway acid has to be handled carefully and cautiously. It continues to react for days after the runaway in the unit is completed.

The corrosivity of runaway acid depends on how much water is produced due to hydrocarbon oxidation. It is best to assume the worst and inspect the equipment after an acid runaway situation has been resolved.

One should also note that with the production of sulfur dioxide gas, the caustic wash for the depropanizer feed is subject to caustic depletion and subsequent corrosion. In fact, all of the points where the process changes from an acidic system to an aqueous system, such as the mixing point to the alkaline water wash drum, may be a point of corrosive attack.

**VII. HANDLING OF RUNAWAY ACID**

Runaway acid also presents a problem for the regenerator because it contains a significant amount of hydrocarbon. The regeneration of acid is accomplished by burning the spent acid to remove the acid soluble hydrocarbons. Significant changes in the hydrocarbon content causes significant temperature swings in the decomposition furnace.
Some refiners have tried blending fresh acid with runaway acid in a storage tank to achieve a hydrocarbon concentration that the regenerator can use. However, this has some problems associated with it as well. Strong sulfuric acid will oxidize the runaway polymer releasing heat and SO$_2$ fumes. Because the storage tank has no means of agitation, the acid will become stratified and probably cause more temperature fluctuations for the regenerator. However, we would strongly recommend against agitating runaway acid with fresh acid to produce a homogeneous mixture because that would also initiate further reactions.

DuPont recommends slowly blending the runaway acid into the other operating Contactor reactors as the safest way of getting rid of the wild acid. This has to be done in a careful manner. If too much runaway acid is added, this could initiate a runaway in the operating system. For example, a blend of 10% runaway acid with 90% fresh acid results in a make-up acid strength of only 92 wt%. This is clearly another accident waiting to happen. A little runaway acid goes a long way.