

## **H<sub>2</sub>SO<sub>4</sub> vs. HF**

A process comparison of H<sub>2</sub>SO<sub>4</sub> and HF alkylation processes shows that neither has an absolute advantage over the other. From a safety and environmental standpoint, H<sub>2</sub>SO<sub>4</sub> has a clear advantage over HF. Economics of the processes are sensitive to base conditions for feedstocks and operating conditions, as well as refined product pricing. Thus, the actual choice for a particular location is governed by a number of site-specific factors that require a detailed analysis. The following table provides an overall comparison between H<sub>2</sub>SO<sub>4</sub> and HF.

Commercial alkylation catalyst options for refiners today consist of hydrofluoric (HF) and sulfuric (H<sub>2</sub>SO<sub>4</sub>) acids. In some areas of the world, HF is no longer considered an acceptable option for a new unit due to concerns over safety; however, this is not the case everywhere.

Due to site-specific differences in utility economics, feed and product values, proximity to acid regeneration facilities, etc., both H<sub>2</sub>SO<sub>4</sub> and HF alkylation technologies should be evaluated. The evaluation criteria can be divided into the following categories: Feed Availability and Product Requirements. Safety and Environmental Considerations. Operating Costs. Utilities. Catalyst and Chemical Costs. And Capital Investment Maintenance.

### **A. Feed Availability and Product Requirements**

Historically, butylenes from the FCC were the traditional olefins fed to the alkylation unit. Today, alkylation units are using a broader range of light olefins including propylene, butylenes and amylenes. Alkylate composition and octane from pure olefins are quite different for each catalyst as shown in Table 1.

**Table 1.** Light Olefin Alkylate Octanes

	RON		MON	
	HF	H <sub>2</sub> SO <sub>4</sub>	HF	H <sub>2</sub> SO <sub>4</sub>
Propylene	91-93	91-92	89-91	90-92
Butene-1	90-91	97-98	88-89	93-94
Butene-2	96-97	97-98	92-93	93-94
Isobutene	94-95	94-95	91-92	92-93
Amylenes	90-92	89-92	88-89	88-90

## B. Safety & Environmental Considerations

Safety and environmental concerns are extremely important when choosing an alkylation technology. A huge concern is the large volume of LPG present within the unit. Refineries must protect against conditions that could lead to LPG releases and potential fire hazards. All of the alkylation technologies being evaluated have similar volumes of hydrocarbon within the unit. In addition, neither acid catalyst impacts the flammability of LPG; therefore, no one technology has an advantage over another in this regard.

Another major safety concern is the acid catalyst used to promote the reaction. Both HF and H<sub>2</sub>SO<sub>4</sub> acids are hazardous materials, however, HF is considerably more dangerous. In the United States, HF has been identified as a hazardous air pollutant in current federal and state legislation. Sulfuric acid has not.

HF and H<sub>2</sub>SO<sub>4</sub> represent an ever-present danger to personnel working on alkylation units. Contact with either HF or H<sub>2</sub>SO<sub>4</sub> can result in chemical burns. However, HF burns tend to be more severe, since the fluoride ion penetrates the skin and destroys deeper layers of tissue. If not treated, it may even cause dissolution of the bone. In addition, inhalation of HF vapors may cause pulmonary edema and, in severe cases, may result in death.

The volatility of the acid at ambient conditions is a chief concern. HF is a toxic, volatile gas at these conditions, while H<sub>2</sub>SO<sub>4</sub> is a toxic liquid. Therefore, H<sub>2</sub>SO<sub>4</sub> is much easier to contain in the event of an accidental release. The hazardous nature of both materials has been known and respected for years. In more densely populated areas of the world, safety and environmental concerns of HF usage have given H<sub>2</sub>SO<sub>4</sub> alkylation a notable advantage.

In 1986, tests were conducted in the Nevada desert to determine the dangers of a possible HF liquid release. Under conditions similar to those that exist in an alkylation unit, lethal concentrations of an HF aerosol were present up to 8 km (5 miles) from the release points. It was during these tests that HF releases were observed to be much more dangerous than anticipated.

Due to the risk, many refiners are implementing water mitigation and detection devices in an effort to remove any HF that would vaporize in the event of a release. With water/HF ratios of 40:1, nearly 90% of the HF can be removed. However, these systems are expensive and there is the concern that the water sprays could become inoperative as a result of an accident. In addition, details have not yet been obtained, or at least reported, on the fate of the HF that is not removed by the water sprays. For a major leak (200 lb/s 100 kg/s) that might result from a 4 inch (10 cm) hole at process conditions, water systems are thought to be less effective. Major HF leaks have been rare in the industry, and when they have occurred, there has usually been a major fire event that has dissipated the HF cloud as it formed. However, the impact of a major HF release should always be considered.

Following a number of HF incidents in the 1980s, and in view of the impact that the Bhopal and Valdez calamities had on the companies concerned, many refiners have carried out Quantified Risk Assessment studies to identify the risk associated with specific HF units. In terms of offsite impact, an unmitigated HF unit will usually generate by far and away the largest element of the risk associated with the site.

Tests conducted in 1991 by Quest Consultants, Inc. showed that the potential for a H<sub>2</sub>SO<sub>4</sub> aerosol formation from an alkylation unit release is highly unlikely. Several tests were performed under a variety of conditions resembling those observed in an alkylation unit. The tests provided conditions favorable to the formation of airborne particles. However, the released acid did not remain airborne, and an aerosol was not formed. It is apparent, based on these tests, that a sulfuric acid aerosol formation will not

occur under conditions similar to those present in a STRATCO<sup>®</sup> Effluent Refrigerated Alkylation Unit.

## **C. Operating Costs**

Operating costs for H<sub>2</sub>SO<sub>4</sub> technologies tend to be spread equally amongst steam, electric power and acid costs. With the HF process, most operating costs are associated with high pressure steam or fuel requirements for the isostripper reboiler. This reboiler provides thermal defluorination of the alkylate product, in addition to providing the required reboiler duty.

### **1. Utility Costs**

Utility costs tend to favor the H<sub>2</sub>SO<sub>4</sub> systems. Many HF units require isobutene-to-olefin ratios on the order of 13 - 15/1 to produce an acceptable octane product. Other HF units and many H<sub>2</sub>SO<sub>4</sub> units develop conditions of mixing and recycle optimization such that they produce similar octane products with isobutane to olefin ratios on the order of 7 - 9/1. Clearly the latter, better-designed units operate with significantly lower fractionation costs. Today, many HF units are operating below the design isobutene-to-olefin ratio, but to obtain the required octane, due to increasingly tight gasoline specifications, these ratios will need to be increased back to design ratios. The H<sub>2</sub>SO<sub>4</sub> process employs either electric or turbine drives for the reactors and compressor to optimize refinery utilities.

Horsepower input to the HF reaction zone is lower than to the H<sub>2</sub>SO<sub>4</sub> reaction zone. In addition, the HF process does not require refrigeration. Therefore, power costs are less for HF units. Normally, the difference in fractionation costs outweighs this advantage when comparing overall utility costs. However, HF units may show a utility advantage if fuel cost is low relative to power cost.

### **2. Catalyst and Chemical Costs**

Catalyst and chemical costs favor HF units, with the main difference being acid cost. Although HF is more expensive, much less is used, and, can be regenerated on site. The operating cost of H<sub>2</sub>SO<sub>4</sub> alkylation depends heavily on reactor design, feed pretreatment, residual contaminants, and the cost and availability of H<sub>2</sub>SO<sub>4</sub> regeneration. Presently, refiners can either regenerate the catalyst on site or send it to an outside regenerator. The latter choice is

very common in the United States, where most refiners are not too distant from H<sub>2</sub>SO<sub>4</sub> manufacturers who can regenerate spent acid at a reasonable cost.

On-site acid regeneration is much more common outside the U.S., due to the lack of regional commercial acid regeneration facilities. Over 25% of the new alkylation units built outside the United States in the last five years have elected to build on-site regeneration facilities. Some regenerators have greatly reduced acid regeneration cost by providing total sulfur handling facilities for refiners.

#### **D. Capital Investment**

It has been over ten years since a comparative cost analysis was conducted between HF and H<sub>2</sub>SO<sub>4</sub> alkylation technologies. For purposes of this discussion, alkylation technology will refer only to the ISBL of the alkylation unit itself. Changes in peripheral equipment to both technologies have changed dramatically in the past ten years, and the impact of these on capital investment will be discussed later in this section. When the above-referenced cost estimate was performed there was objectively no real difference in installed costs between the two technologies. Since that time, there have been no improvements in either technology that would warrant a significant change in the cost advantage of one technology over the other. The separate studies performed by independent consulting firms (Pace Engineering and Chem Systems) found that the cost for H<sub>2</sub>SO<sub>4</sub> and HF alkylation units were comparable.

<b>Installed Capital Costs (\$MM)</b>		
<b>Alkylate Production (BPD)</b>	<b>H<sub>2</sub>SO<sub>4</sub></b>	<b>HF</b>
5,000	14.9	14.5
7,000	18.8	18.2

These cost estimate (Gulf Coast, 1983 basis) differences are negligible given the accuracy of estimating methods.

It is not surprising that the two processes are competitive on a capital cost basis, when one considers the basic process differences. The  $\text{H}_2\text{SO}_4$  process has a more expensive reactor section and requires refrigeration. However, equal costs are realized in the HF unit by the need for feed driers, product treating, regeneration equipment and more exotic metallurgy. In addition, most refiners will require a dedicated cooling system for an HF unit, to remove the risk of site-wide corrosion in the case of an HF leak.

It should be noted that these capital cost estimates do not account for the additional safety and mitigation equipment now required in HF units. Due to the possible hazardous aerosol formation when the HF catalyst is released as a superheated liquid, expensive mitigation systems are now required in many locations throughout the world where HF is used as an alkylation catalyst. Consequently, capital costs for a grassroots HF unit are greater by \$2-5 million (U.S.) depending upon the degree of sophistication of the mitigation design.

## **E. Maintenance**

Maintenance costs and data are difficult to obtain on a comparable basis. HF units have much more peripheral equipment (feed driers, product treaters, acid regeneration column and an acid-soluble oil neutralizer); thus, more pieces of equipment to operate and maintain.  $\text{H}_2\text{SO}_4$  units have larger pieces of equipment, such as the compressor and reactor, but maintenance costs are generally lower. Unit downtime to prepare for a full unit turnaround can take longer for HF units, since the reactor-settler system and all the fractionators must be neutralized before maintenance work can proceed. In  $\text{H}_2\text{SO}_4$  units, only the reactor-settler system requires neutralization. In addition, extensive safety equipment (breathing apparatus, etc.) is required whenever maintenance is performed with a potential of HF release. Once work is completed, the maintenance worker must go through a neutralization chamber to cleanse the safety equipment. A face shield and gloves are the only typical requirements when performing maintenance on an  $\text{H}_2\text{SO}_4$  unit.

## F. H<sub>2</sub>SO<sub>4</sub> vs. HF Summary

A process comparison of the alkylation processes shows that neither has an absolute advantage over the other. From a safety and environmental standpoint, H<sub>2</sub>SO<sub>4</sub> has a clear advantage over HF. Economics of the processes are sensitive to base conditions for feedstocks and operating conditions, as well as refined product pricing. Thus, the actual choice for a particular refinery is governed by a number of site-specific factors, which require a detailed analysis. The following table provides an overall comparison between H<sub>2</sub>SO<sub>4</sub> and HF.

**Table 2.** OVERALL COMPARISON H<sub>2</sub>SO<sub>4</sub> VS. HF

	FAVORABLE FOR	
	H <sub>2</sub> SO <sub>4</sub>	HF
UNIT INVESTMENT	X	X
UTILITY COSTS	X	
CATALYST & CHEMICALS		X
SAFETY/ENVIRONMENTAL CONSIDERATIONS	X	
PRODUCT QUALITY	X	X
FEED TYPE/ISOBUTANE AVAILABILITY	X	X

As a result of these factors, nearly 90% of new units licensed since 1990 have selected H<sub>2</sub>SO<sub>4</sub> alkylation technology over HF.

