

Petroleum Refiners & Inherently Safer Technology

The Realities of Hydrofluoric and Sulfuric Acid



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Introduction

Refining operations have been targeted by certain groups as being ripe for the application of “inherently safer technology” (IST). These groups are, in reality, demanding the substitution of hydrofluoric acid with sulfuric acid. Few terms in chemistry are as misunderstood as inherently safer technology. IST is a conceptual approach to engineering involving chemical processing procedures, equipment, protection and, when feasible, the use of less hazardous substances in these processes.¹ There is any number of challenges for applying IST to existing processes. Dr. M. Sam Mannan, professor of chemical engineering at Texas A&M and one of the world’s leading authorities on inherently safer technology, has repeatedly warned of the difficulties in applying IST to existing facilities, stating that “[e]xisting equipment and processes impose restrictions on changes toward inherently safer technologies.”²

This analysis does not intend to favor one process over another; rather, it proves that this type of complex decision-making is best left to highly-trained, professional practitioners from the appropriate scientific disciplines.

Many outside the engineering discipline have been led to believe that the only road to inherent chemical safety is by way of reducing the number of hazardous substances used in chemical manufacturing and processing. IST, however, is limited by the laws of physics and nature. A simple reduction in the use of hazardous chemicals is often not possible within the confines of a particular reaction or process. *Such reductions can even result in transferring risk to other points in a chemical process or somewhere else along the supply chain, without actually reducing the risk.* Because of the potential for risk-shifting, refining operations typically conduct a Quantitative Risk Analysis (QRA), which addresses potential releases, the consequences of each type of release and, very importantly, the estimated likelihood that a particular release could occur. This rigorous and complex analysis requires a high degree of expertise in several scientific disciplines. The results of the analysis allow the facility to apply the appropriate measures to mitigate the identified risks. QRA is just one example of the many approaches used when evaluating inherently safer technologies.

IST is not a technique or procedure; it is an engineering philosophy. *There is no valid method for objectively characterizing whether a process is as inherently safe as it can be.*

How Refineries Use Hydrofluoric Acid and Sulfuric Acid

To achieve superior performance and cleaner burning fuels, gasoline blends use a specialized mixture of chemical compounds called alkylate, the components of which have a distinct molecular structure. The process by which this specialized product is made is called alkylation. A catalyst is used to allow the process to occur at much lower temperatures and pressures than is otherwise possible, greatly reducing safety risks. Without the catalyst, alkylation would be unfeasible and gasoline blends would suffer, both in terms of performance and environmental quality. Because there are no commercially available solid acid catalysts for use in alkylation units, contrary to some claims, this analysis will focus only on hydrofluoric acid and sulfuric acid.

A desirable feature of an alkylation catalyst is the strength of its negative electrical charge, which lowers the reaction’s energy requirements. Hydrofluoric acid has an *exponentially greater* negative electrical charge than sulfuric acid. Additionally, *sulfuric acid degrades during the alkylation process at a much higher rate than hydrofluoric acid*, which can be fed right back into the alkylation unit. Sulfuric acid, on the other hand, must be removed from the system and undergo treatment before it can be used again. Therefore, *the amount of sulfuric acid consumed in*

¹ See Appendix A for an explanation on the concepts and principles of IST.

² Dr. M. Sam Mannan, White Paper, *Challenges in Implementing Inherent Safety Principles in New and Existing Chemical Processes (2002)*, Texas A&M University, p. 3.

the process is approximately 250 times greater than the amount of hydrofluoric acid. For a 10,000 barrel per day alkylation unit, this equates to one to two truckloads of hydrofluoric acid delivered to the site each month compared to 140 to 200 truckloads of regenerated sulfuric acid coming in, and 140 to 200 truckloads of spent sulfuric acid going out each month.³

This paper assumes that facilities using sulfuric acid as a catalyst do not have sulfuric acid regeneration units on-site. This assumption presents more of a worst-case scenario with respect to risk. However, while some refineries do have regeneration capability, *the majority of facilities do not.*

Safety Risks Associated with Alkylation

An overly simplistic view of risks associated with alkylation units would highlight the lower probability of sulfuric acid to form mists or vapors when released into the atmosphere. In a fire situation, however, which is probable in a terrorist attack scenario, it is reasonable to expect that both sulfuric acid and hydrofluoric acid would form mists and eventually undergo thermal decomposition. Sulfuric acid decomposes into various oxides of sulfur, which are toxic. Hydrofluoric acid decomposes into its gaseous state, hydrogen fluoride, which is also toxic.

A compounding factor in a fire is the fact that concentrated sulfuric acid can react violently with water, which would in turn generate substantial amounts of mist, *even in the absence of actual contact with flame.* According to NIOSH, OSHA and other government agency guidelines, the inhalation exposure threshold values for sulfuric acid are noticeably less than for hydrofluoric acid, which indicates that sulfuric acid mists are expected to be more toxic than hydrofluoric acid vapors.⁴ Therefore, it is difficult to make a conclusive judgment as to which acid is “inherently safer” in a fire scenario.

The risks associated with either acid are not confined to the alkylation unit or storage facility. There are also safety risks associated with the transport and transfer of the acids. While switching from hydrofluoric to sulfuric acid may appear to be “inherently safer”, *the operators who must transport and transfer the catalysts may disagree.* As previously discussed, the equivalent of one or two truckloads of hydrofluoric acid would have to be delivered and transferred each month. A sulfuric acid unit, on the other hand, requires anywhere from 140 to 200 truckloads per month, dramatically increasing safety risks during transport and transfer of the fresh acid, and another 140 to 200 loads taking out the spent acid. As the number of deliveries, pickups and transfers increase, the likelihood of an accident increases. Vehicular transport is only one option, however, and many facilities may choose to ship and receive via rail or barge. This, too, can impact the overall transportation and transfer risk profile. Shipping by rail or barge would reduce the number of shipments, which would reduce the likelihood of an accident, although the quantity that would be released in an accident scenario would increase.

Comparison of Direct and Fugitive Emissions for Different Alkylation Units

The two main factors affecting the amount of carbon dioxide released into the environment due to alkylation are energy requirements for heating or cooling during alkylation and energy requirements for transport of the catalyst. The alkylation processes that use hydrofluoric and sulfuric acid catalysts are different and operate under different conditions, both of which require energy. According to experts in alkylation, the energy requirements, although for different reasons, *are comparable between the two alkylation systems.*

³ Art Gardner, *Refining Details Alkylation Process Comparison, Today's Refinery*, August 1994, pp. 16-17.

⁴ Exposure limit values for sulfuric acid are typically expressed in mg/m³, which can be converted to parts per million at ambient temperature and pressure using formulas provided by the American Conference of Governmental Industrial Hygienists (ACGIH). This allows for a more direct comparison of toxicity between mists and gases.

The carbon dioxide emissions resulting from transportation of each catalyst depend on the number of truckloads shipped into and out of the refinery. As previously stated, for a 10,000 barrel per day alkylation unit, there is an exponential difference (280 to 400 truckloads of sulfuric acid moving in and out, compared to one or two of hydrofluoric) between alkylation units. It is reasonable to conclude that the amounts carbon dioxide, nitrogen oxides, sulfur oxides and other emissions related to diesel fuel combustion will be exponentially greater for shipments to sulfuric acid units than for hydrofluoric acid units. For those facilities using sulfuric acid as a catalyst and transporting it in and out of the facility by rail or barge, the emissions scenarios may be different. For those that have sulfuric acid regeneration capability on-site, the emissions associated with transportation will be greatly reduced.

The hazardous properties of hydrofluoric acid and sulfuric acid are well-characterized and understood by professionals who work with the substances. Rigorous, quantitative risk analyses are conducted to determine the appropriate risk reduction and mitigation measures. The engineering and mitigation standards, legal requirements and emergency procedures for both acids minimize the potential for release and off-site consequences. Sulfur dioxide is known to be released in very small quantities during transfer from sulfuric acid transport vessels to storage tanks at the alkylation facility and, for spent sulfuric acid, from storage tanks to transport vessels and then back to storage tanks at the regeneration facility.⁵ Because the number of catalyst transfers substantially increases for sulfuric acid alkylation units, versus hydrofluoric acid units, *it is reasonable to conclude that releases of sulfur dioxide will be greater than releases of hydrofluoric acid on a per-barrel-of-alkylate basis.*

Comparison of Emissions During Manufacture of Different Catalysts

Most sulfuric acid is now produced by what is called the contact process, which converts elemental sulfur or some other starting material to a gas called sulfur trioxide. The sulfur trioxide is then reacted with water to form concentrated sulfuric acid. The concentrated sulfuric acid is no longer water and sulfur trioxide. In fact, if water is added to concentrated sulfuric acid, a tremendous amount of heat is generated. Regeneration of spent sulfuric acid employs a similar process, the main difference being the starting material, spent sulfuric acid, which is heated to combustion and passed through a gas cleaning and mist removal system before oxidation to sulfur trioxide. Other sulfuric acid manufacturing plants, such as those using sulfide ores or smelter gas, use mechanical means to purify the gases before they are scrubbed in a drying tower. After the drying tower stage, the process is similar to the elemental sulfur burning plants, which produce sulfur from raw materials.

Releases of sulfur dioxide can be found in facility exit stack gases, the amount depending on the efficiency of conversion from sulfur dioxide to sulfur trioxide. According to the Environmental Protection Agency (EPA), the “conversion is always incomplete.”⁶ Most modern elemental sulfur burning plants employ a technique called dual absorption and achieve an efficiency rate of roughly 99.7percent, so the amount of sulfur dioxide released into the environment is greatly reduced, compared to older plants that use single absorption and have efficiencies ranging from 95 to 98percent.⁷

Sulfuric acid mist is typically released with absorber exit gases. The amount and particle size of the mist are dependent on several different physical factors, especially impurities such as water vapor and hydrocarbons. Sulfuric acid mist releases from acid regeneration processes are anywhere from two to four times greater than releases from elemental sulfur burning processes.⁸

⁵ U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emission Factors, Volume I: Stationary Point and Area Sources*, EPA-AP-42, Fifth Ed., Research Triangle Park, NC, January 1995, Section 8.10-5.

⁶ U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emission Factors, Volume I: Stationary Point and Area Sources*, EPA-AP-42, Fifth Ed., Research Triangle Park, NC, January 1995, Section 8.10-3.

⁷ *Ibid* Section 8.10-5

⁸ *Ibid* Section 8.10-8

Hydrofluoric acid is manufactured by reacting acid-grade fluorspar (calcium fluoride) with sulfuric acid, resulting in the formation of hydrogen fluoride and calcium sulfate, which are separated by a series of steps. According to EPA, emissions at hydrofluoric acid manufacturing facilities “are suppressed to a great extent” by the recovery and purification steps used in the process.⁹ Because of the hazardous nature of hydrofluoric acid, “all but small amounts” of hydrofluoric acid, silicon tetrafluoride, sulfur dioxide and carbon dioxide are removed from the tail gas before being released into the environment.¹⁰ The tail gas is then sent to caustic scrubber, which further reduces the level of these pollutants.

Modern processing plants, in general, emit far fewer pollutants on a per-unit basis than in the past. Because of the amount of sulfuric acid required to achieve catalytic alkylation, versus hydrofluoric acid, *it is reasonable to expect that emissions associated with manufacturing of the catalysts will be greater for sulfuric acid than for hydrofluoric.*

Release Mitigation

Mitigation strategies for acids and vapors they emit focus on vapor knockdown and immediate isolation and containment followed by neutralization of runoff and any other remaining liquid.¹¹ The refining and petrochemical industry has taken substantial steps to mitigate the risk of an accidental spill or vapor release. Extremely specialized techniques have been developed and deployed for this purpose, and highly trained professionals are tasked with executing these techniques in any emergency situation.

The primary concern with a sulfuric acid release is the potential for misting in a spill scenario, due to potential churning and its reactivity with water. An enormous amount of heat is generated when concentrated sulfuric acid comes into contact with water. The heat can be sufficient to cause the acid to form mists. The usual mitigation strategy includes containment and neutralization. Polyacrylamides, an ingredient added to specialized fire extinguishers, are now used to blanket the surface of the liquid spill and minimize the potential for misting during neutralization or pumping. Some facilities employ rapid acid dump systems, which are systems designed to isolate and contain the sulfuric acid to minimize the potential for exposures.¹²

Hydrofluoric acid requires specific mitigation equipment. Remotely controlled isolation valves are typical in hydrofluoric acid alkylation systems, as are rapid acid dump systems. In addition, most systems also utilize water curtain or water cannon systems to immediately knock down vapors.

Comparative Costs of Alkylation Units

The Center for American Progress believes that all refineries should be forced to use sulfuric acid or a solid acid catalyst in their alkylation units.¹³ What they fail to address, however, is the fact that a company would be forced to completely replace its alkylation unit at a cost of \$45 million to \$150 million dollars.¹⁴ This figure only represents capital and design costs and assumes at the low end that no rearrangement of existing piping and equipment in the facility is necessary, which is usually not the case. The annual operating costs for the sulfuric acid catalyst are typically twice that of hydrofluoric acid, primarily because of maintenance and regeneration requirements.¹⁵ However, this cost is only relevant to facilities that have sulfuric acid regeneration units on site. The cost of a sulfuric acid regeneration unit is expected to range from \$30 million

⁹ *Ibid* Section 5.8, p. 5

¹⁰ *Ibid*

¹¹ *Hazardous Substances Data Bank*, TOXNET Toxicology Data Network, National Library of Medicine, URL <http://toxnet.nlm.nih.gov/cgi-bin/sis/search/fp./temp/~K9413V:1>

¹² *Hazardous Substances Data Bank*, TOXNET Toxicology Data Network, National Library of Medicine, URL <http://toxnet.nlm.nih.gov/cgi-bin/sis/search/fp./temp/~ReKGzg:1>

¹³ Center for American Progress, *Chemical Security 101: What You Don't Have Can't Leak, or Be Blown Up By Terrorists*,

¹⁴ NPRA conducted a series of interviews with specific refineries to obtain cost estimates.

¹⁵ Art Gardner, *Refining Details Alkylation Process Comparison, Today's Refinery*, August 1994, pp. 16-17.

to \$60 million.¹⁶ If the refinery must ship the sulfuric acid offsite for regeneration, then the operating costs *and safety risks* increase substantially.¹⁷

Conclusion

It should be readily apparent that the decision to use a particular alkylation process requires careful deliberation. Both catalysts have advantages and disadvantages in areas such as environmental impact, safety and cost. While the intent of this analysis is not to demonstrate a preference for one alkylation process over another, it does prove there are the real-world challenges facing refiners when confronted with potentially mandated inherent safety requirements in the context of security. *Therefore, decisions on alkylation techniques other facility processes are best left to the scientific disciplines that ensure safety and security at the refining facilities.*

¹⁶ This figure is derived from consultations with the leading experts in sulfuric acid alkylation technology.

¹⁷ Cal Hodge, *AM-04-13 Comparison of Existing and Emerging Alkylation Technology*, presented at the NPRA Annual Meeting, San Antonio, TX, March 21-23, 2004.