Research Project

The substitution of hydrofluoric acid with sulfuric acid in the alkylation unit in refineries.

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2nd December 2021

CHE 597 Process Safety

Executive Summary

Hydrofluoric Acid (HF) is extensively used as a catalyst in the alkylation units of refineries. However, the HF is an extremely volatile and toxic acid, which can cause deep severe burns and damage the eyes, skin, throat, nose, and the respiratory system. As of 2013, it was estimated that there are 50 refineries in the U.S. These refineries are located close to major cities such as Houston, Philadelphia, Memphis and Salt Lake City. Thus, 26 million Americans are at risk of being exposed to HF.

Some of the prominent issues associated with HF release accidents are as follows:

1. Absence of enforceable regulations and non-compliance of safe practice guidelines.
2. Inefficient release mitigation and containment systems.
3. Lack of Emergency Response Planning involving all stakeholders.
4. No PHA studies, safety audits, or Risk Management Plan.

The pressure on refiners to replace HF with sulfuric acid as the catalyst has been increasing in the past few years due to increased public scrutiny. Sulfuric acid is less toxic and volatile than HF and it is easier to contain sulfuric acid spills since it exists as a liquid at ambient conditions. However, refiners are hindered by the expensive conversion costs and long shutdown times of the plant. The process conditions for the sulfuric acid alkylation unit differ significantly from the HF unit. Thus, the installation of expensive new equipment such as a refrigeration unit are required. The cost of conversion for a 25,000 BPD plant was estimated to be $120 million. Studies are being conducted to reduce the costs by up to 20% by reusing some of the equipment.

The following recommendations are discussed in the report.

1. OSHA should establish legally enforceable PSM standards.
2. Refiners should focus on improving process integrity and following inherently safer practices.
3. Refiners should regularly conduct PHA studies and safety audits. Risk Management Plans should also be updated regularly.
4. An Emergency Response Plan should be established involving all stakeholders.
5. Capital should be invested in the research and development of alternate technologies.

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Introduction

Alkylation process is a vital process present in refineries. It is used to convert low value refineries products (C_3s, C_4s) into valuable high-octane products. Nowadays, most refineries' plants use acid catalyst, such as sulfuric acid (H_2SO_4) or hydrofluoric acid (HF) in alkylation process. However, these acid catalysts are hazardous and the processes are very environmentally unfriendly, especially for those refineries' plants utilizing hydrofluoric acid (HF) as main catalyst.

Both H_2SO_4 and HF are corrosive and toxic. HF is extremely toxic and the cost of risk mitigation for HF units is very high. Even though the Alkylation units that use HF usually have higher yields than those that use H_2SO_4, the size of the fraction equipment and effluent piping of HF alkylation unit is approximately two times the size of H_2SO_4 alkylation unit. When HF is released into the atmosphere, it rapidly forms a vapor cloud that hovers near the ground and can travel great distances. HF is a powerful acid and can cause deep severe burns. It can also damage the eyes, skin, throat, nose, and the respiratory system. The fluoride ion by itself is also very poisonous and can damage the lungs. Therefore, HF requires much stricter precautions because of its greater potential for harm. Moreover, OSHA and EPA have classified HF as highly toxic. Due to the hazardous nature of HF, the ideal solution to reduce risk is by substituting HF with a less hazardous chemical such as H_2SO_4.

Over the past 20 years, the pressure on refiners to abandon the use of HF in their alkylation units has been increasing. This is caused by the high risk of HF release in refineries accompanied by the potential damage than can be caused to the plant personnel as well as the neighboring communities. On 19th July 2009, a hydrocarbon gas release had occurred in the alkylation unit of Citgo's Corpus Christi refinery in Texas. The release resulted in a fire that burned for several days causing extensive damage. The hydrocarbon gas release was caused by the rupturing of a recycle piping. A control valve failed which completely blocked the flow of hydrocarbons in the pipe. This caused the pipe to violently shake and consequently broke two threaded connections in the pipe. One CITGO employee was critically injured by the fire and another employee was treated for possible exposure to HF.

Initially, the hydrocarbons were released in the form of a vapor cloud. The vapor cloud ignited when it reached the adjacent unit and caused an explosion. This resulted in multiple failures in the plant and the release of HF. CITGO reported to the Texas Commission that approximately 21 tons (42,000 lbs.) of HF was released from the alkylation unit. The emitted

HF was captured by a water mitigation system that is used by refineries to capture HF emissions. However, these systems only have 90% efficiency in field applications. Thus, 2 tons (4,000 lbs.) of HF was not captured by the mitigation system.

Prevailing winds carried the uncaptured HF towards the Corpus Christi ship channel and Nueces Bay. During the following investigations, it was found that CITGO had never conducted a safety audit of HF alkylation unit. Therefore, the API Recommended Practice 751, Safe Operation of Hydrofluoric Acid Alkylation Units, was introduced. This recommended that refiners should conduct a safety audit of their HF alkylation operations once every 3 years.

Another prominent incident occurred on 27th September 2012, in South Korea. An accident occurred in Hube Global HF production plant in Gumi, a city located 125 miles southeast of Seoul. The incident occurred when the workers were unloading HF at the plant. This incident resulted in the fatality of 5 Hube employees and sickened more than 3,000 people within the vicinity of the plant site. The released HF also damaged crops and affected livestock. Given the magnitude of the incident, the central South Korean region was declared as a "special disaster zone". Based on security camera footage, it was determined that the plant personnel were not following proper safety guidelines. The local authorities were unprepared to handle the release of HF. Their response was so haphazard that the Prime Minister's Office became involved in handling the accident response. The plant had been operating since 2008 and had a production capacity of 9,000 metric tons.

Due to the rising number of fatalities of workers in refineries, the United Service Workers International Union (USW), initiated a Refinery Alkylation Research Action project. The union conducted a survey of the refineries in U.S. that has HF alkylation units. The results of the survey were summarized in a report released in 2013. The results showed that alkylation units that used HF posed the most risk to human lives than any other industrial process.

Most of the fifty refineries the U.S. that use HF are located close to major cities including Philadelphia, Houston, Memphis and Salt Lake City. Therefore, 26 million Americans faced the risk of being exposed to HF. The survey also found that between 2008 and 2013, there were 131 HF releases or near misses and refiners had committed hundreds of violations with regards to OSHA's rules. Therefore, it is increasingly becoming important for us to study the prevalence of HF in refineries and minimize, if not eliminate its use.

Literature Review

A Risk Too Great – Hydrofluoric Acid in Refineries, United Steelworkers, 2013

This report was released by the United Steelworkers union in 2013 to highlight the hazards faced by the operators working in close proximity to HF in refineries. The report summarized the results of a survey conducted across 50 refineries in the United States that used HF in their process. The report also discussed recent incidents of HF release, alternate technologies and the current regulations.

Safer with Sulfur, McDermott, 2010

This report includes a general description of the alkylation process as well as a comprehensive comparison of the HF and sulfuric acid alkylation processes. The report also highlights the challenges faced by refiners who use the HF alkylation process. The conversion of an HF alkylation unit to a sulfuric acid alkylation unit is discussed in detail. The report explores the possibility of reducing the cost of conversion by up to 20% by reusing certain equipment from the original alkylation unit.

Alkylation Technology Study – Final Report, Norton Engineering, 2016

Norton Engineering Consultants Inc. released this report in 2016 when they were commissioned by the South Coast Air Quality Management District (SCAQMD) to research and analyze the commercially available alternatives to HF alkylation units. The alternate processes were evaluated on the basis of efficiency and effectiveness, chemical hazards, commercial viability, storage & transportation requirements, and current development status. The processes studied in the report are sulfuric acid alkylation, Ionic Liquid Alkylation, Sodium Onium Poly Alkylation, Fixed Bed Alkylation, and Slurry Catalyst Alkylation.

CSB Calls on EPA to Update HF Study, CSB News Release, 2019

The U.S. Chemical Safety Board (CSB) released a letter than it had sent to the Environmental Protection Agency (EPA) calling for the agency to update its HF study that it had conducted in 1993. The letter was sent in the wake of 2017 Husky Energy Refinery Fire in Lake Superior, WI & 2015 ExxonMobil Refinery Explosion in Torrance, CA. This action was taken in response to the concerns raised by members of the communities surrounding the refineries and their demand to eliminate the use of HF. The CSB strongly encouraged the

EPA to update its previous study, evaluate the risk management plans of those refineries, and determine any inherently safer alkylation technologies for petroleum refineries.

Objective

The objective of this report is to analyze the Hydrofluoric Acid (HF) based alkylation process in refineries. The report discusses the potential hazards of using HF in refineries and evaluates its substitution with sulfuric acid. Furthermore, the cost of conversion of HF based alkylation units to sulfuric acid based alkylation units is also estimated. The report also discusses the limitations of other alkylation processes that are currently in the development stages. Lastly, the current regulatory status of HF use in refineries is highlighted. The analysis of the report is then used to recommend future steps to minimize the potential hazards of HF in refineries.

Analysis

Hydrofluoric Acid Alkylation Process

The hydrofluoric acid alkylation unit is composed of three main units, including reaction unit, fractionation unit and defluorination / alumina treating unit. In order to produce alkylate, an olefin feed with isobutene is reacted in the reactor with the help by the presence of hydrofluoric acid, which acts as catalyst in this process. A general version of the HF alkylation process is shown below in Figure 1.

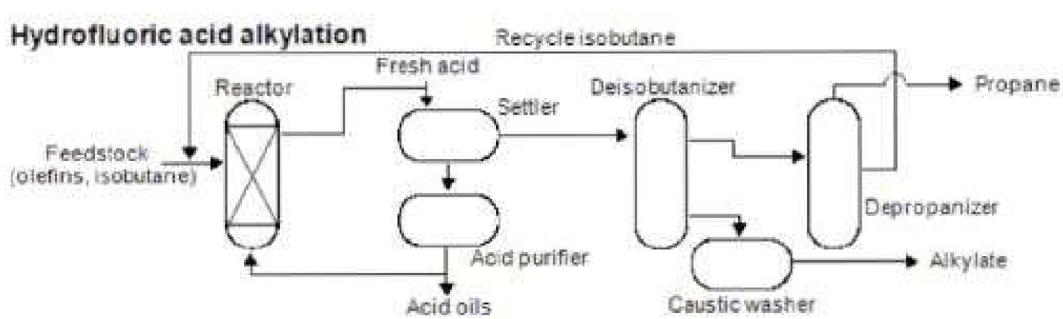

Figure 1. Hydrofluoric Acid Alkylation Process. (MIE Maverick Engineering)

Before entering the reactor, the olefin and isobutane feed should pass through a coalescer to remove and filter water, sulfur and other contaminants. To maintain the feeds in the liquid state, temperature is required to control at 60 to 100 °F. In the fractionation unit, the separation takes place in the distillation tower to separate the reaction products from isobutene and hydrofluoric acid. Unreacted isobutane is recovered and recycled back to the reactor to react with the olefin feed. Propane is one of major products of the distillation process. Some amount of n-butane that has entered with the feed is also withdrawn as a side product.

Sulfuric Acid Alkylation Process

The sulfuric acid alkylation unit is composed of five units, including reactor unit, refrigeration unit, effluent unit, fractionation unit and blowdown unit. In the reactor, the olefin feed with isobutene is reacted under specific conditions and at a temperature of 60 °F. Without the presence of sulfuric acid, which acts as catalyst in this reaction, the reaction will never occur. The sulfuric acid alkylation process is illustrated in Figure 2 below.

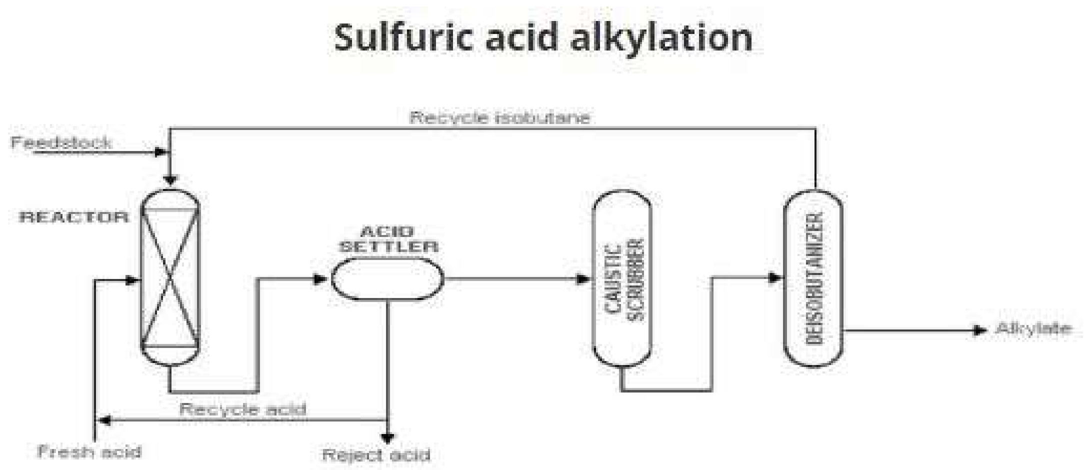

Figure 2. Sulfuric Acid Alkylation Process. (MIE Maverick Engineering)

Before entering the reactor, the olefin and isobutane feed should pass through a coalescer to remove and filter water and other impurities in order to reduce corrosion. In the refrigeration unit, the heat of reaction is balanced, and the light hydrocarbons are purged from the unit. The free acid, alkyl sulfates and di-alkyl sulfates are removed from the net effluent stream to prevent downstream corrosion in the effluent treating unit.

In the fractionation unit, the separation takes place in the distillation tower to separate the reaction products from isobutene and sulfuric acid. Besides, the unreacted isobutane is recovered for recycle to the reactor. To maintain the desired spent acid strength, it is recommended to continuously input a small amount of fresh sulfuric acid.The spent acid is degassed in an acid blowdown drum, wastewater pH is adjusted, and acid vent streams are neutralized with caustic in a scrubber before being flared. Spent acid goes to storage and periodically removed.

Transportation & Storage

The fresh hydrofluoric acid used in the alkylation process is stored in a specially designed storage tank. When the acid unit shutdowns, this tank is also using for storage. The fresh hydrofluoric acid is almost transported by chemical trucks. Truck delivery frequency is low because of the low consumption in hydrofluoric acid. It is recommended to 1 to 2 times/month for an average sized 10 to 15 kBPD unit.

The fresh sulfuric acid is required to be stored on-site in a new tank. Additional plot space is necessary for this tank in order to provide space for delivery trucks. Moreover, on hundred percent of containment walls are also required to prevent the leak or release. Acid purged from the process contains a small number of light hydrocarbons which need to be removed. These light hydrocarbons can vaporize and form flammable vapor mixture. For safety reasons, CO2 or N2 should serve as inert gas in the spent acid tank.

For a nominal 25,000 BPD sulfuric acid alkylation unit, estimated truck traffic is 10-15 trucks per day for fresh acid imports, and a slightly higher number for exports of spent acid (for a total of 20-30 trucks/day). Total truck traffic of 900-1300 trucks/month for Sulfuric Acid Alkylation compared to 2-4 trucks/month for HF Alkylation

Significant Risk Scenario for Release

In a typical refinery there are many process units working situated close to each other. Consequently, there are many sources of ignition and other incidents that can trigger a release of HF or sulfuric acid from the alkylation unit. As evidenced in the CITGO Corpus Christi incident in 2009, the HF release was the result of a secondary incident caused by the ignition of the vapor cloud rather than being the primary incident itself. Therefore, it is important to analyze some potential sources of incidents that are commonly seen in such accidents. Some of the most prevalent scenarios that pose a significant risk of release are discussed below.

1. <u>High temperature in the acid regenerator</u>: The possible cause of this scenario is a failure in the flow control valve. While the flow control valve is accidentally closed, the inlet flow of the hydrofluoric acid will decrease. Due to the decrease of hydrofluoric acid, the removal of soluble pollutants in the acid will be influentially decreased. Even though there isn't any significant effect in the short term, a higher

overhead temperature in the regenerator and a loss of acid purity will eventually turn into a runaway reaction in the long term. Moreover, in the long term the corrosion will cause leaks, which are definitely dangerous to workers. Another consequence would be an undesirable increase in the production of organic fluorides and polymerization in the reaction section.

2. <u>Low pressure in the acid regenerator</u>: The possible cause of this scenario is that the manual valve at the top of the regenerator is left open. The consequences for this scenario are probable fire explosion due to hydrocarbon spill, air pollution due to the organic chemical leak and fatalities or injuries due to the acid spill and exposure to high concentration of hydrofluoric acid. Not to mention the repair cost for the ruined equipment and public evacuation from the high concentration of hydrofluoric acid.
3. <u>High pressure in the closed drain drum:</u> The possible cause of this scenario is that the bypass system of PCV is left open, which causes an increase in the nitrogen flow rate. The consequences for this scenario would be full nitrogen pressure on the drum and vent header, and at the worst case, during decommissioning with the vent line blocked inside. Another consequence would be potential overpressure of the slop drum, leading to flange leaks, loss of containment, and personnel injury.

Comparison of HF & H_2SO_4

In the U.S. HF has been identified as a hazardous air pollutant whereas sulfuric acid has not been identified as such. Sulfuric Acid at concentrations above 85 wt.% Sulfuric Acid is a corrosive and hazardous material and can cause serious burns to exposed tissue. On the other hand, HF Acid is extremely corrosive, especially in solutions with water. Human contact with this acid can lead to severe burns of the skin or lungs (if inhaled), and death can result from significant exposure if not immediately and adequately treated.

Sulfuric Acid has higher boiling point (626°F) and lower volatility than HF and is less likely to form an aerosol at atmospheric conditions. While, HF Acid has a relatively low boiling point (67 °F) and readily becomes a vapor with high vapor density when released to the atmosphere.

HF is a toxic and volatile gas at ambient conditions. On the other hand, sulfuric acid exits as a toxic liquid at ambient conditions. Therefore, it is much easier to contain the hazards associated with the spilling of sulfuric acid. During a test conducted in the Nevada desert in 1986, it was found that when HF is released, lethal concentrations of HF aerosol were present up to 8 km (5 miles) of the release point. In 1991, Quest Consultants conducted a similar test for sulfuric acid release. The test provided favorable conditions for the formation of aerosols. However, the released acid didn't remain airborne, and aerosol were not formed. Therefore, it was concluded that the sulfuric acid aerosol formation in the alkylation unit is highly unlikely.

There are significant differences in the costs of HF and sulfuric alkylation processes as well. The operating costs of HF alkylation units are primarily associated with the high-pressure steam, or the fuel required for isostripper reboiler. In the sulfuric acid units, the operating costs are evenly split between steam, electric and catalysts cost. The utility costs for sulfuric acid alkylation units are lower than HF units. The capital cost for HF alkylation units is marginally lower than that for sulfuric acid units. However, an additional cost of $2 - $5 million is added based on the complexity and effectiveness of the HF release mitigation systems (Randolph Todd, 2017). This makes the overall cost of HF units higher than that of sulfuric acid units.

Lastly, the catalyst costs for HF units are lower. While the cost of procuring HF is higher, it is used in smaller amounts. Additionally, the chemical is regenerated on-site. Contrastingly, sulfuric acid is used in larger amounts and therefore costs more to the refiners despite being cheaper than HF. Refiners either regenerate sulfuric acid on-site or they send it to an external regenerator. In the United States, most refiners send it to an external regenerator due to easy access to nearby regeneration facilities than can regenerate sulfuric acid at a reasonable cost (Randolph Todd, 2017).

Conversion

In 2010, McDermott released a report titled 'Safer with Sulfur' which explored the possibility of converting HF alkylation units to sulfuric acid alkylation units. This report was released considering the increased public scrutiny after 3 HF release incidents in the United States in 2009. The report discussed the challenges associated with the conversion and the opportunities to reduce costs. The cost of conversion remains subjective as it depends on the size of the plant. Additionally, the cost of building a new unit versus the cost of modifying an existing one also differs vastly. In 2016, Norton Engineering conducted a study to estimate the cost of converting an alkylation unit. The cost of converting a 25,000 BPD plant was estimated to be approximately $120 million. Reusing equipment from the HF alkylation unit is an effective method to reduce costs. The report released by McDermott states that reusing equipment could reduce the cost of conversion by up to 20%. The schematic of a converted alkylation unit is shown in Figure 3 below.

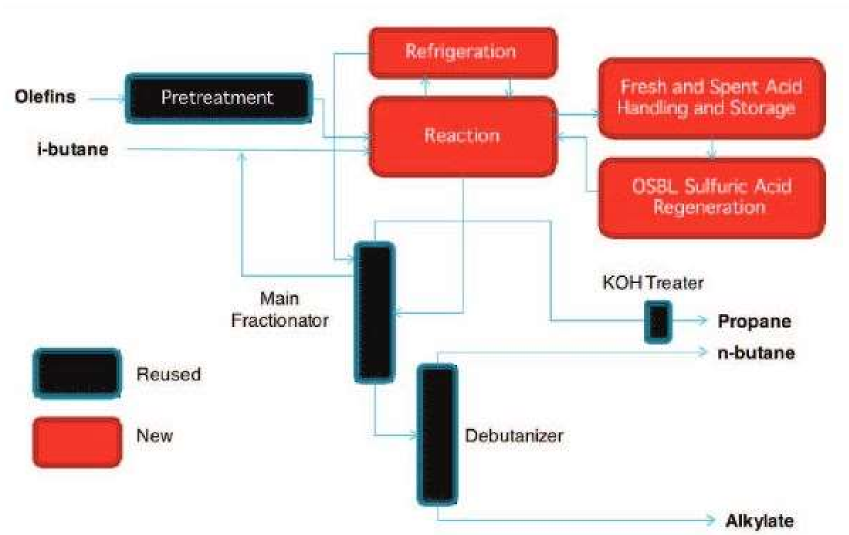

Figure 3. Converted Alkylation Unit (“Safer with Sulfur", McDermott, 2010).

The feed pretreatment section can be reused for the converted alkylation unit. Typically, HF units have lower feed impurity specifications than sulfuric acid. Therefore, when the HF feed pretreatment unit is reused for sulfuric acid, it reduces the contamination of the catalyst. Hence, the operating cost is reduced as the requirement for fresh sulfuric acid is reduced. The reaction section cannot be reused in the converted unit. This is because of the significant differences in the mixing, separation, and inventory requirements of both the processes. HF alkylation process operates at near ambient conditions, whereas sulfuric acid process operates at lower temperatures. The difference in relative activity of both the chemicals results in longer reactor residence time for sulfuric acid, which leads to greater amount of inventory. Therefore, the existing equipment may be undersized. A new reactor, new effluent coalescers, and circulation pumps are some of the most significant additions to the converted unit. Since the sulfuric acid process operates a lower temperature, a refrigeration system would have to be added adjacent to the reaction section.

The fractionation section can be reused in the converted unit with some modifications. The HF alkylation reaction is designed to run with a higher isobutane to olefin ratio (10-12:1) as compared to sulfuric acid (8:1). Therefore, the fractionation section for HF units is larger due to the significantly higher flow of isobutane into the recovery section. In a converted unit, the isobutane recycle is taken as a side stream from the main fractionator. In a HF unit, the overhead from the main fractionator is sent to a stripper to remove HF from the propane/HF mixture. However, in a converted unit sulfur dioxide is a reaction byproduct. Thus, the propane product treatment section can be reused by decommissioning the stripper and adsorbing sulfur dioxide from the product stream. Lastly, an HF alkylation unit operator regenerates the catalyst on-site whereas a sulfuric acid unit operator has a choice between regenerating on-site or using an external regenerator. In the United States, using an external regenerator is more economical due to ease of access. Therefore, the existing on-site regeneration unit cannot be reused. Instead, for external acid regeneration requires the installation of new fresh and spent acid storage tanks.

Alternate Processes

While sulfuric acid is a safer alternative to HF, it is still hazardous to the plant personnel and the neighboring communities. Therefore, in parallel to the conversion of alkylation units, studies are also being conducted to develop alternate processes. UOP is currently the most prominent company that is developing alternate processes. Some examples of alternate processes are Ionic Liquid Alkylation, Solid Onium Poly Alkylation (Alkad), Fixed Bed Alkylation, and Slurry Catalyst Alkylation. The study conducted by Norton Engineering analyzed the viability of these 4 processes. The Ionic Liquid Alkylation and Slurry Catalyst Alkylation processes are in different stages of development whereas the Solid Onium Poly Alkylation and Fixed Bed Alkylation processes have been abandoned.

The Alkad process was first introduced in 1992 at Texaco's El Dorado Refinery in Kansas. It was abandoned as it was considered commercially unviable. The Fixed Bed Alkylation process was developed by Haldor- Topsoe and was also abandoned due to commercial unviability. In 2012, UOP filed for a patent describing the general concept of a Slurry Catalyst Alkylation process. However, no tests have been conducted yet to determine the viability of this process. In this process the hydrocarbon feed is mixed with a finely distributed solid catalyst between 20 to 200 microns in size, before entering the reactor.

The Ionic Liquid (IL) Alkylation process was first tested on an industrial scale in China by CUP & PetroChina in 2006. This primary reaction is the combination of an isoparaffin with an olefin to make a high-octane product in the presence of an acid catalyst contained within the ionic liquid. Since then, Chevron and UOP have indicated that they are also developing their own versions of Ionic Liquid Alkylation technology. However, no further test runs have been conducted yet. The IL catalyst was reported by CUP & PetroChina as noncorrosive. The catalyst is benign and not pyrophoric when exposed to air. However, it is moisture sensitive and can become corrosive when exposed to water. Therefore, if an HF unit is converted to an IL alkylation unit, then the existing feed dried would be reused to remove water from the feed.

Regulations

In August 2021, The American Petroleum Institute released the 5th edition of its Recommended Practice 751 titled "Safe Operation of Hydrofluoric Acid Alkylation Units". The purpose of this document is to provide guidance to refiners on the safe operations of HF alkylation units. The document specifically covers areas like hazards management, operating procedures, worker protection, materials & new construction, inspection and maintenance of HF units, transportation, inventory control, relief systems, utility systems, and mitigation options. The document also provides information related to HF audits, HF exposure limits, as well as corrosion and material considerations. While these guidelines provide helpful information for safe refinery operations, they are not enforceable. API has also been criticized for not including key stakeholders such as refinery workers and labor unions in the formulation of these guidelines.

In 2019, the U.S. Chemical Safety Board (CSB) released a letter calling on the Environmental Protection Agency (EPA) to review its existing 1993 Hydrofluoric Acid study. This letter was released after an explosion in the ExxonMobil refinery in Torrance, CA, and the Husky Energy Refinery explosion in Lake Superior, WI. The ExxonMobil refinery explosion occurred in 2015 when the electrostatic precipitator (ESP) in the FCC unit exploded during maintenance. Two workers were injured, and debris were dispersed in the neighboring communities. The Husky Energy Refinery accident occurred in 2017 resulting in an explosion followed by fire. 11 workers were injured and 36 people sought medical attention. The root cause of the incident is yet to be determined.

The CSB had requested the EPA to determine whether the existing Risk Management Plan (RMP) of these refineries was adequate to prevent catastrophic releases as well as evaluate inherently safer alkylation technologies. These incidents led to a widespread call to ban the use of HF in refineries. The community surrounding the Husky Energy refinery demanded the complete ban of HF in the state of Wisconsin.

Recommendations

Regulations

While API's Recommended Practices 751 is a useful document for promoting safe operations in refineries that use HF, it is not a legally enforceable document. The guidelines are only useful if followed. OSHA can sometimes use API's guidelines to establish a PSM standard, which is enforceable. A legally mandated safety standard should be introduced due to encourage refineries to implement the necessary changes. The safety standard should also require Process Hazard Analysis (PHA) studies to be conducted at reasonable intervals.

Secondly, a periodic review of a plant's Emergency Response Plan should be mandated. The hazardous nature of HF poses an immense risk towards the plant personnel and the neighboring population. It is important for refiners to include all stakeholders such as the operators, labor unions, neighboring populations, local authorities, and the emergency responders in the decision-making process.

Mitigation of HF release

It is important for refiners to have an updated Risk Management Plan (RMP) available. The document should be accessible to all the relevant stakeholders. The EPA should regularly check if the refineries are complying with their RMP. The refiners should continually strive to improve the integrity of the process and make the process inherently safer. While this may be expensive, it will significantly reduce the risk of immense losses in case of an accident. Improvements can be made in areas such as using noncorrosive construction material, favorable process conditions, and reducing the amount of HF stored on site.

The PHA & RMP studies should be used to design efficient HF release detection and containment systems. The present water mitigation system is only 90% efficient. Research related to designing more efficient mitigation systems should be subsidized by the industry as well as the government. Lastly, the EPA should conduct a new study to evaluate the hazards of using HF and compare it to the currently available mitigation systems. The last study was conducted in 1986.

Process Improvement

In order to ensure the operating condition is fall in the range in case of losing efficacy in the flow control valve, first recommendation is installing a flow indicator controller in the inlet line of the acid regenerator. Another recommendation is to monitor and estimate the process condition by installing a HF/water ration analyzer in the reactor and constructing a calculation in the pressure control system for the acid regenerator isobutane/acid ratio.

In case of low pressure in the acid regenerator, replacing the manual valve at the top of the column by a safety valve and installing a bypass system to send the stream to the flare header reduces the risk of exposure to releasing HF. To prevent high pressure in the closed drain drum, relocating the pressure indicator and restrictive orifice of the inert gas (Nitrogen gas) to the slop drum vent downstream of the bypass pressure control valve is recommended. Additionally, refineries install a pressure indicator in the top of the drum in order to monitor the pressure.

Conversion

The primary obstacle to conversion of alkylation units is the high costs and the potential loss of revenue during the conversion. However, reusing equipment is a good way to reduce the cost of conversion. Research should be conducted into finding ways to reuse more equipment from the original plant. This would also reduce the shutdown time for the facility. Additionally, the concerned authorities should also formulate a plan to phase out the use of HF. This can be done using a combination of legally enforceable standards and subsidies.

Alternate Processes

Alternate alkylation processes are also an effective way to reduce the use of HF. Currently, all the processes are in the development stage and there are no pilot plants operating. Companies like UOP are actively pursuing these technologies but at a slow pace. This is caused by the uncertainty about commercial viability and high capital costs. An effective way to encourage such companies would be to offer favorable patent protection rules and gradually increase the cost of using HF and sulfuric acid by means of taxes. The taxes collected can be used to subsidize research of alternate processes and setting up of pilot plants. Pilot plants can further be promoted by requiring large refiners to operate a pilot plant in their existing facilities alongside their HF or sulfuric acid alkylation units.

Conclusion

Hydrofluoric Acid (HF) is extensively used as a catalyst in the alkylation units of refineries. However, the HF is extremely volatile and toxic. HF is a powerful acid which can cause deep severe burns and damage the eyes, skin, throat, nose, and the respiratory system. Therefore, the HF is gradually being replaced with sulfuric acid in the alkylation units. Sulfuric acid is less toxic and volatile than HF and at the ambient conditions it exists as a liquid. Thus, it is easier to contain a sulfuric acid spill. However, the operating cost of sulfuric acid alkylation unit is higher since a larger amount of sulfuric acid is consumed in the process. Currently, HF alkylation units pose a greater amount of risk to human lives than any other industrial process. As of 2013, it was estimated that there are 50 refineries in the U.S. These refineries are located close to major cities such as Houston, Philadelphia, Memphis and Salt Lake City. Thus, 26 million Americans are at risk of being exposed to HF.

The pressure on refiners to switch from HF to sulfuric acid is increasing. This is due to an increasing number of incidents in the recent past that have affected the plant personnel as well as the neighboring population. This change is also being driven by the increased involvement of regulatory agencies such as the U.S. Chemical Safety Board (CSB) and the Environmental Protection Agency (EPA) along with legislative bodies. Despite a desire to make the switch, refiners are hindered by the expensive conversion costs and long shutdown times of the plant. The process conditions for the sulfuric acid alkylation unit differ significantly from the HF unit. Thus, the installation of expensive new equipment such as a refrigeration unit are required. The cost of conversion for a 25,000 BPD plant was estimated to be $120 million. Studies are being conducted to reduce the costs by up to 20% by reusing some of the equipment.

Alternate alkylation technologies are also being developed simultaneously. Some of the prominent companies that are leading this development are PetroChina, UOP, and Chevron. Ionic Liquid Alkylation, Solid Onium Alkylation, Fixed Bed Alkylation, and Slurry Catalyst Alkylation are some examples of alternate technologies. However, commercial viability is a major hurdle for their development. Currently, the development of these technologies is stalled since there are no pilot plants operating. It is anticipated that the development of these processes will be resumed once the focus is placed on replacing sulfuric acid as well. While sulfuric acid is less volatile and toxic than HF, it is still hazardous to humans.

In the meantime, it is recommended that the refiners focus on increasing the integrity of their HF alkylation unit and continually strive to make their process inherently safer. Using noncorrosive materials, favorable process conditions, and minimized on site presence of HF. These actions have to be ensured by means of regulatory requirements. It is recommended that OSHA should legally enforce the safe operation guidelines for HF in refineries outlined in API's Recommended Practices 751. It is also recommended that the EPA regularly audit the refineries for Risk Management Plan (RMP) compliance.

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