Research Project

ChE-597 Chemical Process Safety

Inherently Safer Design
Via.
Chemical Substitution

Aditya Godse
Omkar Khatke

(Group C)

PURDUE CHEMICAL ENGINEERING

Executive Summary

Process safety is an important aspect of all industries and processing plants. It focuses on dealing with the various hazards that might be present in a given process, equipment or material. A vital part of process safety would then be trying to eliminate these hazards and prevent their occurrence in the first place. This method of trying to remove or minimize hazards by making fundamental changes in the process design is called Inherently Safer Design (ISD). According to the Center for Chemical Process Safety (CCPS), ISD, also known as Inherently Safer Technology (IST), permanently eliminates or reduces hazards to avoid or reduce the consequences of incidents [1]. This way, safety is inherent and built into the process and not added on as additional layers.

ISD is not just limited to the manufacturing process but is to be considered in all stages of a process lifecycle including transportation, storage etc. ISD strategies can be divided into four different categories – substitution, minimization, moderation and simplification [7]. While it is true that complete elimination of a hazardous chemical or process is difficult and not always feasible, the first and most effective category to be considered when thinking about ISD is substitution. Specifically, when it comes to chemical synthesis, using alternate chemistry that uses less hazardous materials and chemical reactions offers the greatest potential for improving inherent safety [8]. This motivates us to look into chemical substitutions where a highly dangerous material is replaced by a milder one if the process allows it. One such substitution of interest is hydrogen fluoride (HF) by sulphuric acid (H2SO4) in the alkylation units in petroleum refineries where the acid is used as a catalyst.

Hydrofluoric acid is a strong acid, and its hazards are well known. It has a relatively high vapor pressure and can form dense vapor clouds of concentrated Hydrofluoric acid [9]. This along with its extremely toxic nature has encouraged researchers to look at alternatives for Hydrofluoric acid. A successful substitution for it has been Sulfuric acid. Although, Sulfuric acid greatly reduces the potential for an acid vapor cloud formation, it is still an unsafe chemical and introduces risks of its own into the process [8]. Thus, the objective of our report is to do an economic and technical comparison between the two chemicals and to analyse if the overall hazard level has been mitigated by the substitution.

In this report we have considered various situations such as economic differences between those two novel technologies, Transportation and storage risks, health and safety hazards associated with both the chemicals. All these attributes can be considered while choosing between Hydrofluoric acid and sulfuric acid as a catalyst for alkylation in oil refineries.

Table of content

Tables and Figures

Introduction

In today's world process safety is an important part of an industry or a plant. Engineers are always looking at ways they can reduce or avoid hazards in a process. One way to achieve this is by using Inherent safer design. According to the Centre for Chemical Process Safety (CCPS), ISD, also known as Inherently Safer Technology (IST), permanently eliminates or reduces hazards to avoid or reduce the consequences of incidents [1]. This principle behind ISD is to avoid or reduce the risk of a hazard by making changes to the process instead of adding additional layers of protection. There are four main strategies to ISD, minimize, substitute, moderate and simplify

- **Minimize** is to reduce the number or the size of equipment.
- **Substitute** is to replace a hazardous material with a less hazardous alternative.
- **Moderate** is to operate, transport, store chemicals at a moderate state where they would not be hazardous.
- **Simplify** is to design the equipment layout with less complexity and making it easier to understand.

This report would be focusing on the principle of substitution. This report would study the substitution of Hydrofluoric acid with Sulfuric acid in alkylation process in petroleum refineries where the acid is used as a catalyst. When Hydrofluoric acid comes into contact with water vapours in the atmosphere it forms an acid cloud. These significantly increases the risk of this acid cloud formation spreading off site and is a hazard. Currently to tackle this problem the industry is substituting Hydrofluoric acid with Sulfuric acid. Sulfuric acid eliminates the risk of an acid cloud formation, but it has its own set of hazards. Using large quantities of sulfuric acid increase the risk of acid spills while storage and transportation. But these risks are significantly lower than that of Hydrofluoric acid.

There are a lot of factors that needs to be considered when changing a novel technology from hydrofluoric acid to sulfuric acid. This paper would be discussing the changes in operating costs, storage, transportation, health, and safety hazards.

Analysis

Economic

While comparing the economics of both the processes this paper would look at their operational costs, chemical costs, maintenance costs. Along with that this paper will also look at the investments that would be required to change the alkylation process form using Hydrofluoric acid as a catalyst to use sulfuric acid.

Operational costs

Sulfuric acid alkylation unit uses refrigeration, steam, and a lot of sulfuric acid for the alkylation process. Most of the cost for sulfuric acid alkylation unit is divided amongst power, steam and acid costs [2]. Whereas the operational costs for Hydrofluoric acid is due to high pressure steam and energy requirements for it reboiler. In this paper the operational costs for utility, chemical costs and maintenance costs are analysed.

1) **Utility costs –** In this case the utility cost is mostly dependent on the fuel costs and power costs. To get the required product from HF alkylation, the fuel ratio is varied according to the raw material quality. Due to which the utility costs associated with hydrofluoric acid alkylation is due to its fuel costs. Whereas Sulfuric acid alkylation process uses refrigeration which requires a lot of energy and due to this most utility cost associated with sulfuric acid alkylation is associated with its power costs. Since HF alkylation unit doesn't use refrigeration its power costs and consumption are negligible. Both the processes are steam intensive and there isn't a large enough difference in costs associated with steam. Ultimately the utility costs of sulfuric acid alkylation are much higher than that of HF alkylation. But this ratio can vary according to the plants geographical location and the difference can be lower in some parts of the world.
2) **Chemical costs-** The unit cost of hydrofluoric acid is much higher than sulfuric acid. Even though that's the case the overall acid costs for HF alkylation unit are much less than that of sulfuric acid unit. Sulfuric acid Alkylation is an acid intensive process and uses a lot of sulfuric acid whereas HF alkylation doesn't require a lot of hydrofluoric acid. This difference in the usage of acid makes the chemical costs for Sulfuric acid alkylation unit a lot larger than HF alkylation unit. To reduce the acid costs in sulfuric acid alkylation the plant has an option to add an acid regeneration unit inside the plant. This will reduce the unnecessary transportation of sulfuric acid off-site for regeneration which in turn will reduce the acid costs.
3) **Maintenance-** Compared to Hydrofluoric acid alkylation unit, Sulfuric acid alkylation units have a lot less equipment. Sulfuric acid alkylation unit mainly uses larger reactors which are much easier to maintain that HF alkylation units which uses a lot of complex equipment such as acid regeneration columns, feed driers etc. Another reason for increased maintenance costs for Hydrofluoric acid alkylation units is the down time requirements for performing the maintenance. Due to its highly toxic and corrosive nature all the equipment must be neutralized and the workers performing the maintenance work must wear proper PPE kits. Whereas for Sulfuric acid the equipment doesn't require any neutralization and the workers can complete maintenance with

normal PPE kits. The overall maintenance time required for HF alkylation unit is much more than Sulfuric acid units.

From then above points we can conclude that the operational costs for sulphuric acid alkylation is much higher than HF alkylation units. The major factors that contribute to the costs being high is the chemical costs and power costs associated with Sulfuric acid. Even though economically Hydrofluoric acid is better than sulfuric acid, the safety benefits of sulfuric acid certainly outweigh the economic benefits. As a result of the above factors nearly 90% of new units licenced since 1990, use sulfuric acid as a catalyst instead of Hydrofluoric acid [2].

Investment required to change to Sulfuric acid Alkylation

A report done by Norton Engineering on Alkylation technology study estimates the cost of replacing an existing Hydrofluoric acid alkylation unit with a new sulfuric acid alkylation unit. The fractionation system used in Hydrofluoric acid alkylation can be reused for sulfuric acid alkylation. Equipment that were used for acid regeneration would be removed. Moreover, a metallurgy of the equipment would have to be checked to see if it can be used with sulfuric acid [3]. The plot space required for the new alkylation unit would be the same unless plant wants to opt for onsite acid regeneration for sulfuric acid. In case, a new regeneration unit is required additional plot space adjacent to the current plot would be required. The setup time for the new plant would take around 6 months as it would take time to take down current HF unit and if new plot area is being used for regeneration, then the setup time can take around 60 days [3].

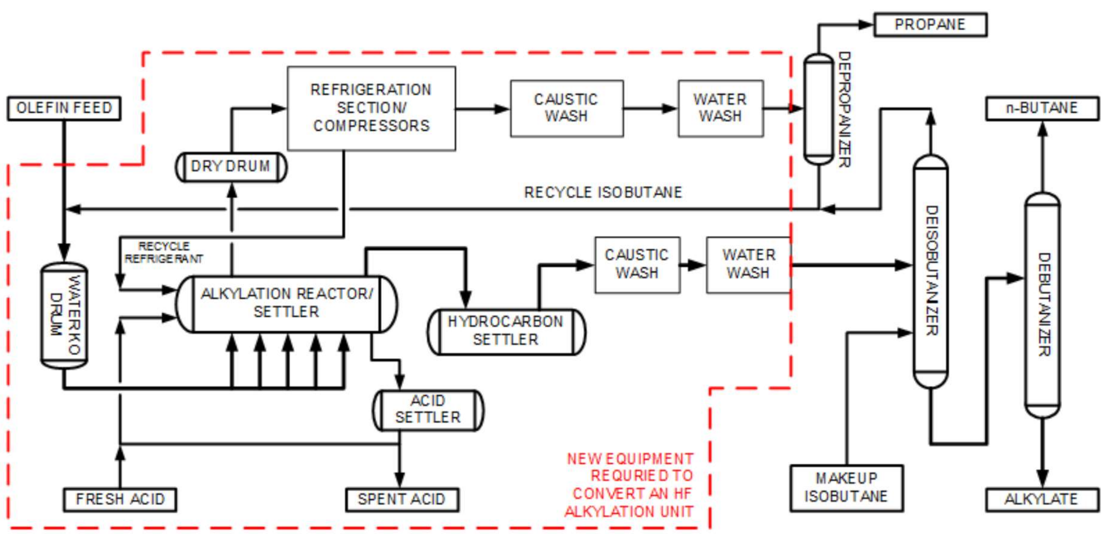

Figure 1. Simple flowsheet for ExxonMobil Sulfuric Acid Alkylation technology
Note: from Norton Engineering "Alkylation Technology Study FINAL REPORT" by S. Zhang, L. Wilkinson, L. Ogunde, R. Todd, C. Steves, S. Haydel

Figure 1. shows all the new equipment that is required to convert an HF alkylation unit into a sulfuric acid alkylation unit.

To generate a cost estimate Norton engineering considered a 25000 BPD alkylation for equipment sizing. They have also assumed a standard labour productivity rate of $85 per hour. This cost estimation only include the total installation costs and does not include the operating costs. The study also considers the cost to install a spent sulfuric acid regeneration plant. The total estimated cost to install a new sulfuric acid alkylation unit and replace the old Hydrofluoric acid unit is around 100 to 120 million USD. The cost to install an onsite sulfuric acid regeneration plant is additional 45 million USD [3].

Transportation

In this report transportation refers to the acid that is being brought into the plant for alkylation. For Hydrofluoric acid the acid is transported via trucks to the plant. Since hydrofluoric acid alkylation is not an acid intensive process, for a 15 KLPD plant, around 2 trucks of acid are enough for a month [3]. Whereas sulfuric acid alkylation which is an acid intensive process would require around 15 truck of fresh acid each day. For a 25 KLPD plant a sulfuric acid alkylation unit would require around 900 – 1500 trucks of fresh acid each month [3].

Transportation risks

Due to an increased number of fresh acid deliveries, Sulfuric acid alkylation unit carries a larger risk of off-site spills. According to a study done by Subodh R. Medhekar, Willard C. Gekler and Dennis C. Bley on “Frequency Estimates for Transport-Related Hydrofluoric and Sulfuric Acid Release Scenarios” they estimated that a large HF release due to an incident while transportation via a truck or railway can occur once in 13,400 to 40,800 years. Whereas a large sulfuric acid spill due to an incident while transportation via a truck or railway can occur once every 128 to 312 years [4]. The consequences of these release should also be taken into consideration while choosing between both acids. Even though the frequency of release is larger for sulfuric acid, the consequence of release is much smaller than that of Hydrofluoric acid. Just like in the case of operational costs, the safety concerns and repercussions of hydrofluoric acid release outweighs the frequency of accidents.

Storage

Storage is an important safety concern while handling sulfuric acid of hydrofluoric acid and hence storage conditions for both must be properly studied.

1. **Sulfuric acid-** Sulfuric acid is stored in tanks which are restricted to go beyond 100F. Necessary measure are taken to ensure that the tank is kept away from any heat source as heat can affect the quality of the acid. Tank should be strong structurally to withstand the weight load of Sulfuric acid. Sulfuric acid being a corrosive material the tank should have a protective lining and regular maintenance to avoid any leaks. Sulfuric acid storage tanks should also be easily accessible to road or railway lines for a smooth transfer of the acid. Containment wall should also be provided as a safety measure to contain any potential leak. Tank should be equipped in inerting system to get rid of light hydrocarbons that can cause fire inside the spent acid tank.

2. **Hydrofluoric Acid-** Hydrofluoric acid is stored in tanks specifically designed to store hydrofluoric acid. Small quantities of hydrofluoric acid is stored in tightly closed container because it reacts with metal, water, glass, and acids these substances should be kept away from the HF storage area. The storage area should have a proper ventilation and should be cool as well as dry place. In some instances, HF is stored in polyethylene tubs.

Health hazards

Hydrofluoric and sulfuric acids are both hazardous substances and are a cause of concern for people who come in contact with both these acids.

Hydrofluoric acid

There are multiple health hazards associated with hydrofluoric acid and they vary depending on the type of exposure and its concentration. Hydrofluoric acid is corrosive and damages human tissues, if it comes in contact with an eye it may lead to blindness or permanent eye damage. When Hydrofluoric acid comes into contact with human skin it may cause burning sensation and may permanently damage the tissue. In an acid vapor cloud release a lot of people would be inhaling hydrofluoric acid vapours, Inhalation of these vapor can damage the lungs and lead to more serious lung diseases. When a person is chronically exposed to Hydrofluoric acid, it may lead to fluorosis.

Sulfuric acid

There are also multiple health hazards associated with Sulfuric acid. Most of these are short term. Skin can become irritated and burning sensation may occur when skin comes into contact with sulfuric acid, if an eye comes into contact with sulfuric acid it can cause blindness, If someone inhales sulfuric acid vapours it can cause irritation to the throat and the nose. When exposed to large amounts of sulfuric acid it can cause severe lung diseases. Long term exposure to sulfuric acid can lead chronic health problems. Sulfuric acid is also a human carcinogen, making it a cancer risk.

Even though both acids are extremely hazardous, sulfuric acid can be preferred over hydrofluoric acid since it is comparatively less dangerous to human health.

Safety

Hydrofluoric acid is a highly regulated substance and while handling Hydrofluoric acid multiple guideline form organization such as RMP, OSHA PSM, DOT, Maritime transportation security act, Chemical facility anti-terrorism standards, and LEPC should be followed. Along with government regulations API Recommended practice 751, which is considered as global standards for HF safety and operations should also be followed [6].

There are also multiple risk mitigative measures that should be taken in a Hydrofluoric acid alkylation unit such as [6]:

- Protection for workers in the form of Personal protective equipment in case of a release
- Regular inspection and maintenance
- Use of acid detection paints to identify small releases.
- Rapid acid transfer system and remotely activated block valves to stop the flow of the acid into a compromised system and move the acid to a secture location.
- Water mitigation systems to control and stop the spread of acid vapor clouds.
- Ambient air sensors to identify a leak
- Double sealed pumps to reduce the potential of a leak through the pumps.

Figure 2. Hazardous material warning labels for Hydrofluoric acid transportation
Note: Image courtesy of NIOSH, CDC

Since Sulfuric acid doesn't carry a risk of an acid cloud formation and stays in liquid phase in case of a release, it doesn't require mitigative measures as stringent as hydrofluoric acid. Typically, Sulfuric acid unit are covered by containment walls to stop the spread of the acid in case of a leak.

Main safety concerns with sulfuric acids are related to its transportation. Due to a large volume of acid being brought into and out of the facility daily it increases the risk of off-site spills. To reduce the risk of an off-site spill, many plants consider using inhouse acid regeneration plants. It is a standard for most of the plants outside the US, using large amounts of Sulfuric acid to have an on-site acid regeneration plant. Since, most of the acid manufacturers are located close to the refineries, most US plant prefer to send the spent acid back to the manufacturer.

Figure 3. Hazardous materials warning label for Sulfuric acid transportation
Note: Image courtesy of NIOSH, CDC

Hydrofluoric acid- A risk too great

In 2013 in the US 25 out of 50 oil refineries used Hydrofluoric acid as a catalyst [5]. It is estimated that these refineries store 212,000 pounds of hydrofluoric acid [5]. 26 million people stay within the range of three to twenty-five miles of these refineries and in most of these vulnerable zones it would be impossible to evacuate quickly in case of a major release.

In 2013 a report from United steel workers released a report "A Risk Too Great Hydrofluoric Acid in U.S. Refineries" in which they studied 23 refineries which used Hydrofluoric acid as a catalyst. The found out that in a five-year period the refineries had 293 OSHA's PSM violations. Over 17 refineries had at least one Hydrofluoric acid related incident or a near miss in last three years of the report, which totalled to 131 Hydrofluoric acid related incidents or near misses. Over 15 sites reported that the lacked the PPE kits for on site workers who might need them in case of a release [5]. This survey also highlighted inadequacies in the safety systems to respond and to mitigate a release in case of emergencies for operation of hydrofluoric acid alkylation, including storage and transport. The on site and off site first responders didn't have enough training, preparation, and drills to fight a release scenario. This survey also concluded that the only way to completely eliminate the risk of Hydrofluoric acid release was to replace it with a safer alternative [5].

Hydrofluoric acid mitigative systems

Currently water sprays are used to stop the spread of hydrofluoric acid in case of an acid cloud formation, but this system also has a few drawbacks, Sometimes the cloud formation is at a large height and the sensors would not be able to detect a release at such heights. There might be a delay in the release reaching the sensors which might give enough time for the acid cloud to travel off site. These systems were only 25-90% effective in controlling a release in lab conditions, in real world scenarios this number might be worse [5].

Another mitigative system uses rapid transfer of acid to a safe storage tank. Although this system might be able to transport a large volume of acid, it still won't be enough to stop a large release. This system also has a few limitations including, time to detect a leak, maintenance, potential failures, etc.

Hydrofluoric acid Alkylation unit incidents

Refinery	Date	Amount of HF released	Injuries/Reason leading to a leak
CITGO Corpus Christi, Texas	5th March 2012	300 to 500 pounds	Leakage in a flange
Marathon Canton, Ohio	28th February 2011	145 pounds	Equipment failure, one worker hospitalized
CITGO Corpus Christi, Texas	19th July 2009	42,000 pounds	Explosion and a fire in alkylation unit, one worker severely injured
Sunoco (Delta), Philadelphia	11th March 2009	22 pounds	13 contract workers hospitalized
Giant Industries Refinery, New Mexico	8th April 2004	Unknown	Six employees injured and evacuation at nearby areas
Marathon Texas City, Texas	30th October 1987	Unknown	50 square block area around the refinery evacuated, 900 people needed medical treatment

Table 1. Hydrofluoric acid releases in the United States

Note: The reference for above data is taken from “A Risk Too Great Hydrofluoric Acid in U.S. Refineries” by United Steel Workers, April 2013

Alternative technologies

Many other alternative technologies are being studied to replace the Hydrofluoric acid in alkylation. Even though sulfuric acid is the most advanced process currently in use, it is still hazardous and expensive. A few of the technologies currently under development are discussed below.

Modified Hydrofluoric acid Alkylation

Modified Hydrofluoric acid alkylation unit uses an additive with Hydrofluoric acid that suppresses the volatility of hydrofluoric acid. This increases the safety of the catalyst and reduces the risk and hazards of a vapor cloud formation. Currently there are four plants in the country using this technology [3].

Ionic liquid Alkylation

Ionic liquid alkylation uses a composite ionic liquid as a homogenous catalyst for alkylation. This technology was tested in China in 2006 on an industrial scale. Currently process optimization to improve the performance of Ionic liquids as catalysts is still under development [3].

Solid onium Poly Alkylation

Solid onium Poly Alkylation also known as ALKAD is an additive with a similar goal as modified hydrofluoric acid uses amine/nitrogen containing polymer to reduce the vapor pressure of hydrofluoric acid upon release [3].

Conclusion

There is sufficient evidence to prove that hydrofluoric acid is an extremely hazardous substance and there is an urgent need to stop it use and replace it with a relatively safer chemical. Even though using sulfuric acid has its drawback, its safety benefits certainly outweigh its drawbacks.

References

1) "Final Report: Definition for Inherently Safer Technology in Production, Transportation, Storage, and Use" by Center for Chemical Process Safety, The American Institute of Chemical Engineers, July 2010
2) "H2SO4 vs. HF. A. Feed Availability and Product Requirements" by Randolph Todd, November 25, 2017
3) Norton Engineering "Alkylation Technology Study FINAL REPORT" by S. Zhang, L. Wilkinson, L. Ogunde, R. Todd, C. Steves, S. Haydel
4) Medhekar, S.R., Gekler, W.C. and Bley, D.C. (1993), Frequency estimates for transport-related hydrofluoric and sulfuric acid release scenarios. Proc. Safety Prog., 12: 166-175. https://doi.org/10.1002/prs.680120308
5) "A Risk Too Great Hydrofluoric Acid in U.S. Refineries" by United Steel Workers, April 2013
6) "Alkylation: Safety & Risk in the Production of Cleaner Fuels" by AFPM Communications https://www.afpm.org/newsroom/blog/alkylation-safety-risk-production-cleaner-fuels
7) Dennis C. Hendershot, Inherently Safer Design: The Fundamentals, Center for Chemical Process Safety, 2012
8) Guidelines for Inherently Safer Chemical Processes: A Life Cycle Approach, 3rd Edition, Center for Chemical Process Safety, 2020
9) Rudolf Diener, Mitigation of HF releases, J. Loss Prev. Process Ind., 1991, 4, 35-43