<u>CHE251 PROJECT REPORT</u>
<u>ALKYLATION IN PETROLEUM REFINING</u>

<u>AUTHORS</u>

Group 8-

- Anshika Agarwal (230160)
- Tanvi Manhas (231084)
- Palak Agarwal (230726)
- Vibhanshu (231143)
- Yash Garg (231185)
- Kanishk Dhariwal (230525)
- Pravir Mishra (230787)
- Aman Singh (200105)

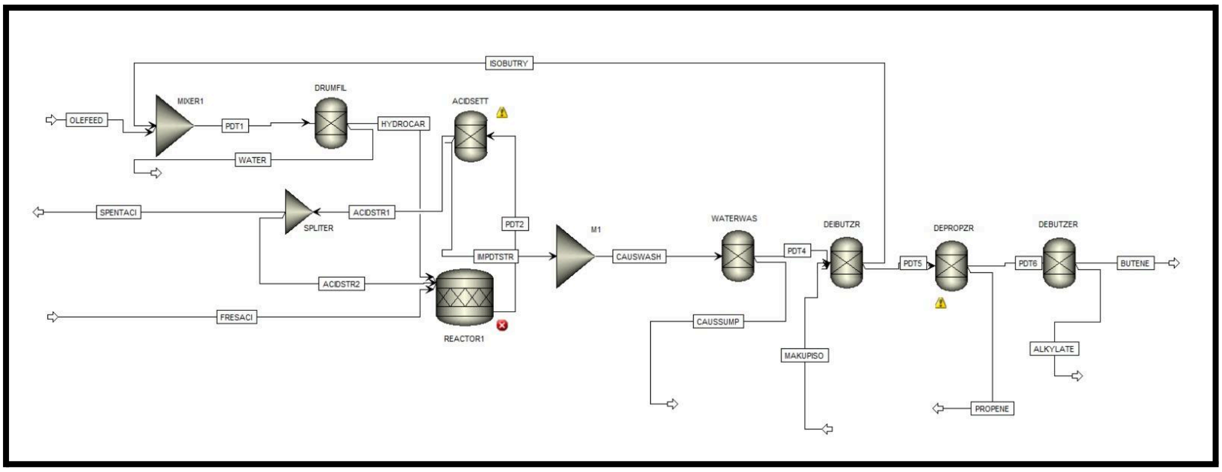
<u>DESCRIPTION</u>

Alkylation is a crucial process in the petroleum refining industry, particularly for producing high-octane gasoline. The process involves the reaction of light olefins, such as propylene (C3) and butylene (C4), with isobutane in the presence of a strong acid catalyst to form alkylate. Alkylate is a high-quality blending component for gasoline due to its high octane number, low vapour pressure, and lack of sulphur and aromatics, making it ideal for producing cleaner-burning fuels. There are two most widely used alkylation processes-

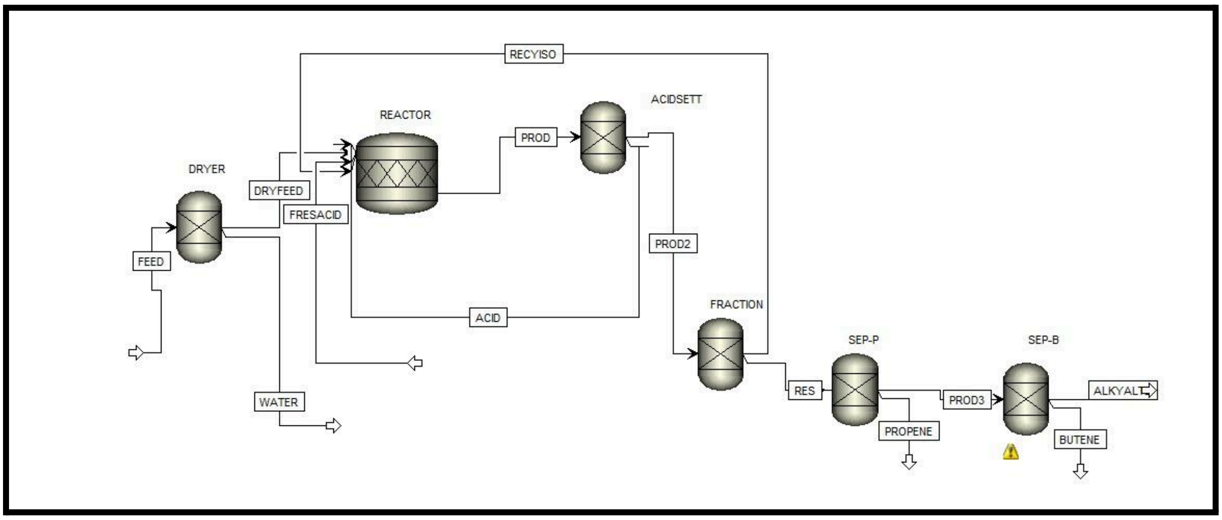
- **<u>Hydrofluoric Acid (HF) Alkylation:</u>** In this method, hydrofluoric acid is used as a catalyst. The HF alkylation process is known for its efficiency in producing high-quality alkylate. However, HF is highly toxic and poses significant risks in case of leaks or spills, requiring stringent safety measures.
- **<u>Sulfuric Acid (H_2SO_4) Alkylation:</u>** This process uses sulfuric acid as a catalyst. While safer than HF, sulfuric acid alkylation requires larger volumes of acid and more frequent regeneration or replacement due to its lower catalytic activity.

FIGURE (FLOWSHEET)

Sulphuric acid (H_2SO_4) alkylation process- STRATCO



Hydrofluoric acid (HF) alkylation-UOP



* Refer to appendix for detail of labelled terms

OBJECTIVES

In alkylation, inorganic acid acts as the catalyst that promotes reaction between isobutane and olefins. Two common catalysts used in the alkylation process are hydrofluoric acid (HF) and sulfuric acid (H_2SO_4).

1. While observing the process of alkylation, we will compare various elements of the HF (UOP) process with the H_2SO_4 (Stratco) process. We will focus on factors such as resultant yield, space requirements, capital costs, quantity, toxicity and corrosivity of the two acids.
2. We will study the overall environmental and sustainability impact of the Alkylation process, as well as compare these for HF and H_2SO_4.

METHODOLOGY

METHODS	STRATCO(Sulphuric acid)	HF(UOP)
Reaction temperature	40F - 50F	80F - 100F
Reaction pressure	60 psig	~100 - 200 psig
Reaction phase	Acid-continuous emulsion	Acid-continuous emulsion
isobutane/olefin ratio	8:1 or greater	12:1 to 14:1
Acid/hydrocarbon ratio	1:1	1:1
Acid consumption rate	0.4 to 0.6 lb/gal	0.001 to 0.002 lb/gal alkylate
Alkylate Yield	1.78 bbl/bbl olefin	1.77 bbl alkylate/bbl olefin (C3/C4 mix)

The **alkylation process in petroleum refining using hydrofluoric acid (HF)** involves combining light olefins, such as propylene and butylene, with isobutane to produce high-octane gasoline components, primarily alkylate. The process begins with the feedstock entering a reactor where it is mixed with HF as the catalyst. The olefins and isobutane undergo alkylation reactions to form heavier, branched hydrocarbons. The mixture is then separated in a series of fractionation steps. First, the alkylate product is separated from the unreacted hydrocarbons and HF. The unreacted isobutane is recycled back to the reactor, while HF is recovered and also recycled. The final product, a high-octane alkylate, is then sent for blending into gasoline. This process is highly controlled to ensure the safe handling and recovery of HF, which is highly corrosive and toxic.

In the **alkylation process using sulfuric acid (H_2SO_4)** in petroleum refining, light olefins (like propylene and butylene) are mixed with isobutane in the presence of sulfuric acid, which acts as a catalyst. The mixture undergoes a reaction to form high-octane alkylate, a valuable gasoline component. The reaction mixture is then separated, with the denser sulfuric acid being recycled or regenerated, and the hydrocarbon stream containing the alkylate is sent for fractionation. Unreacted isobutane is recycled back into the process, while the final alkylate product is collected for use in gasoline blending. The process is carefully controlled to maximise alkylate yield and ensure efficient catalyst usage.

REACTIONS INVOLVED

C_4H_{10} (isobutane) + C_4H_8 (butylene) $\xrightarrow{Acid}$ C_8H_{18} (2,2,4 trimethyl-pentane) + Heat

C_4H_{10} (Isobutane) + C_3H_6 (Propylene) ----(acid)--➔ C_7H_{16} (2,3-Dimethylpentane) + Heat

COMPONENTS USED

STRATCO

Components

Selection | Petroleum | Nonconventional | Enterprise Database | Comments

Select components

Component ID	Type	Component name	Alias	CAS number
ISOBUTAN	Conventional	ISOBUTANE	C4H10-2	75-28-5
PROPY-01	Conventional	PROPYLENE	C3H6-2	115-07-1
2-BUT-01	Conventional	2-BUTENE	C4H8	107-01-7
SULFU-01	Conventional	SULFURIC-ACID	H2SO4	7664-93-9
WATER	Conventional	WATER	H2O	7732-18-5
2:2:4-02	Conventional	2,2,4-TRIMETHYLPENTANE	C8H18-13	540-84-1
2:3-D-01	Conventional	2,3-DIMETHYLPENTANE	C7H16-5	565-59-3
SODIU-01	Conventional	SODIUM-HYDROXIDE	NAOH	1310-73-2
SODIU-02	Conventional	SODIUM-SULFATE	NA2SO4	7757-82-6

Find | Elec Wizard | SFE Assistant | User Defined | Reorder | Review

UOP

Select components

Component ID	Type	Component name	Alias	CAS number
HF	Conventional	HYDROGEN-FLUORIDE	HF	7664-39-3
PROPY-01	Conventional	PROPYLENE	C3H6-2	115-07-1
HYDRO-01	Conventional	HYDROGEN-SULFIDE	H2S	7783-06-4
POTAS-01	Conventional	POTASSIUM-HYDROXIDE	KOH	1310-58-3
WATER	Conventional	WATER	H2O	7732-18-5
ISOBU-01	Conventional	ISOBUTANE	C4H10-2	75-28-5
2-BUT-01	Conventional	2-BUTENE	C4H8	107-01-7
2:2:4-01	Conventional	2,2,4-TRIMETHYLPENTANE	C8H18-13	540-84-1
2:3-D-01	Conventional	2,3-DIMETHYLPENTANE	C7H16-5	565-59-3
POTAS-02	Conventional	POTASSIUM-SULFATE	K2SO4	

ASPEN FILE LINK

CHE 251 PROJECT

<u>RESULTS</u>

STRACTCO (H_2SO_4)

<u>Feed Stream:</u>

- Isobutane : 800 kg/hr
- Olefin :100kg (95 kg/hr Butene + 5 kg/hr Propene)
- Acid : 900 kg/hr

<u>Outlet streams :</u>

- **Main product :**
  Alkylate : C_8H_{18} (2,2,4-trimethylpentane) = 178.018 kg/hr
- **Side product :**
  C_7H_{16} (2,3-dimethylpentane) = 10.9549 kg/hr
- Butene - 7.562 kg/hr
- Propene - 0.3995 kg/hr
- **Spent acid :**
  13.47 kg/hr H_2SO_4, 2.19 kg/hr H_2O
- **Caustic Impurities :**
  NA_2SO_4 - 1144.64 kg/hr
  NaOH - 65.3757 kg/hr
  H_2SO_4 - 78.1677 kg/hr
  H_2O - 307.158 kg/hr

Yield of C_8H_{18} as calculated - 92.04%

UOP(HF)

<u>Feed Stream-</u>

- Isobutane-1200kg
- Olefin-100kg (95kgButene + 5kg Propene)
- Acid-1300kg

<u>Outlet Streams:</u>

- **Main product :**
  Alkylate : C_8H_{18} (2,2,4-trimethylpentane) = 177.032 kg/hr
- **Side product :**
  C_7H_{16} (2,3-dimethylpentane) = 10.89 kg/hr
- Butene - 8.056 kg/hr
- Propene - 0.4255kg/hr

DISCUSSION

STRATCO

Yield - The yield of alkylate in petroleum refining is generally high, ranging from 85-95 %, therefore the calculated yield (92.04 %) fits with the expected.

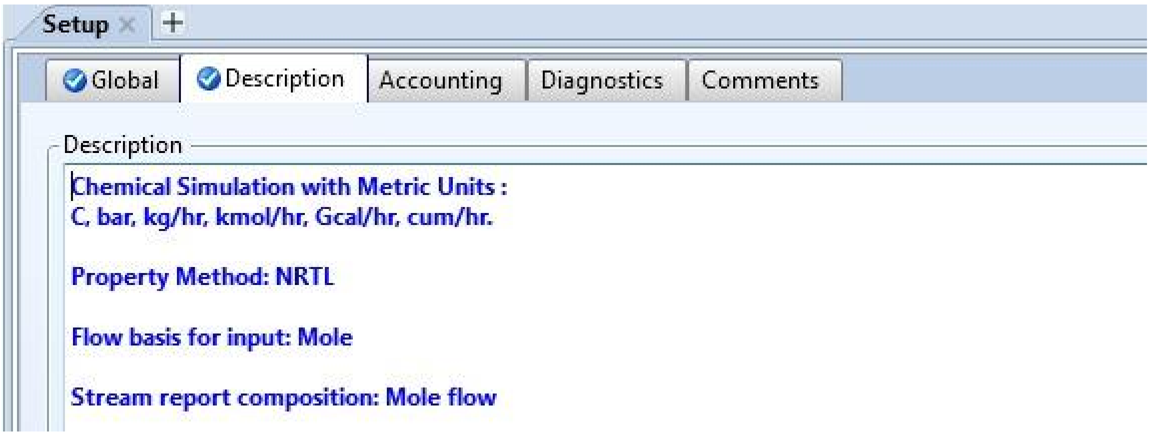
Challenges and changes:

Our primary source of the process flow was Norton Engineering Consultants' Alkylation Technology Study by South Coast Air Quality Management District (SCAQMD) Alkylation Technology Study FINAL REPORT South Coast Air Quality Management District (SCAQMD)

When we began simulating the flowsheet in Aspen, we faced some challenges in replicating the process flow in aspen. In order to avoid compromising on the accuracy of the results (as the primary product of the process is C8H18), we have taken some measures to simplify the process flow in aspen in the following areas:

1. Removing the acid wash block :
   The acid wash unit is supposed to remove spent acid (diluted or impure acid which can no longer be used as catalyst). In the process flow we already have a spent acid stream being removed at an earlier stage, rendering the acid wash unit without use.
2. Merging propane and butane treatment streams :
   The process of treatment of propane and butane side product streams and removal of impurities after the caustic wash is almost entirely similar. Therefore, in order to simplify the flowsheet, we merged the treatment streams to go through the same flow. This change has no impact on the formation of the final product (alkylate), whose reaction has already occurred earlier.
3. Property Method error:
   For simulating a flowsheet with the primary reaction having organic, non polar components, we used the NRTL Property Package. However, further in the flowsheet, there is an acid neutralisation reaction occurring. The NRTL package does not possess appropriate data for this reaction, which is ionic. For ionic reactions, the ELECNRTL package is commonly used, but ELECNRTL does not contain appropriate data for the alkylation reaction. There is no package with intersecting data. Therefore, we are giving priority to the main reaction, alkylation, and not simulating the neutralisation process in

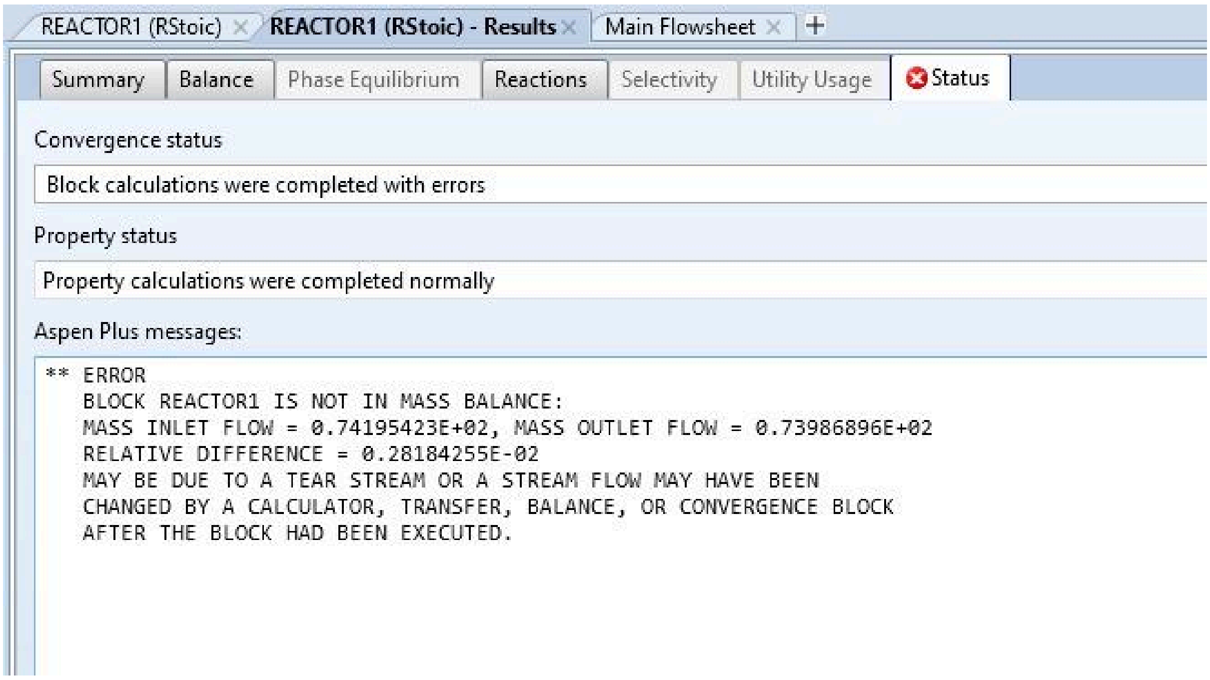
the main flowsheet. We have its data present through a separate simulation with the ELECNRTL package.



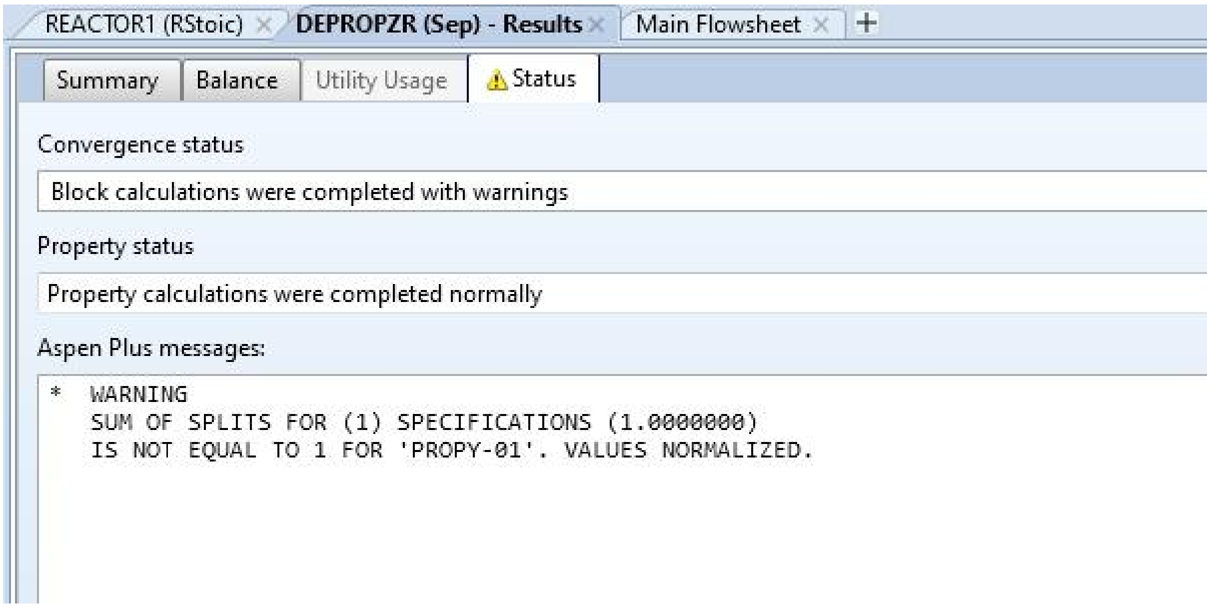
Explaining the errors shown in running the flowsheet:

We are receiving accurate results with respect to the alkylate product, as well as the leftover propene and butene. On running the flowsheet in aspen, the following warnings/errors show:

1. The reactor shows a mass imbalance of the order 10^-3. This is a slight oversight due to manual calculations for specifying some streams as the input data we had presented was for yields. The error has been resolved by aspen itself by compensating for the components required.



2. Sum of splits not equal to 1 for two separators: The error is once more due to some point differences in the split fractions, which aspen resolves by normalising the fractions.



Apart from these minor errors, we are getting accurate results for our product streams, i.e.

Alkylate - C_8H_{18} : 178.018kg/hr, C_7H_{16} : 10.9549 kg/hr
Butene -7.562 kg/hr
Propane - 0.3995 kg/hr

<u>UOP:</u>

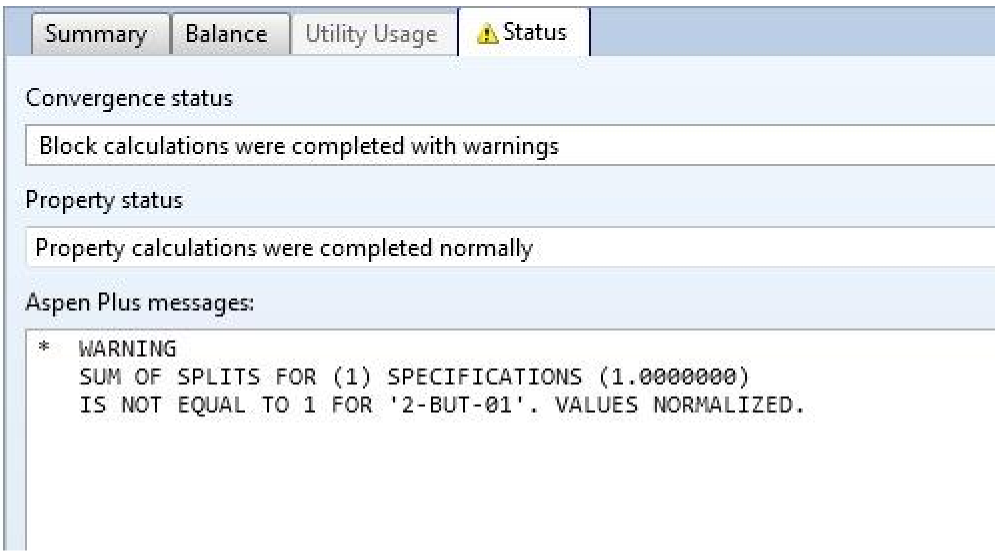
<u>Yield -</u> The yield of alkylate in petroleum refining is generally high, ranging from 90-95 %, therefore the calculated yield (91.52 %) fits with the expected.

Our primary source of the process flow was Norton Engineering Consultants' Alkylation Technology Study by South Coast Air Quality Management District (SCAQMD) Alkylation Technology Study FINAL REPORT South Coast Air Quality Management District (SCAQMD)

Challenges and changes:

When we began simulating the flowsheet in Aspen, we faced some challenges in replicating the process flow in Aspen. To avoid compromising on the accuracy of the results, we have taken some measures to simplify the process flow in Aspen in the following areas:

1. Removal of additive storage system and Acid storage:
   The additive storage system is likely used to store and feed specific additives into the process.Acid storage is used to maintain a reserve of fresh HF acid or regenerated acid for the process.Removing them could simplify the process flow, potentially reducing maintenance and operational complexity.and the overall process could become safer, more efficient, and potentially more economical.
2. Removal of Propane and Butane Deflourinator and KOH treater:
   In this process Propane and Butane are not the desired products. Defluorinators add to both capital and operational costs, as well as maintenance requirements. Removing them could reduce operational expenses.and as we are taking these streams there is no need for KOH treater for the neutralisation any acidic components, particularly residual HF acid, in the propane and butane streams
3. Removal of Caustic Washer :
   The caustic washer is used to remove acidic impurities, specifically trace HF acid, from the hydrocarbon streams before further processing.but in this process we don’t want soluble oil as our one of our desired product so for simplification of flow sheet we can remove this segment of flow sheet
4. Removal of HF Stripper:
   We are increasing the efficiency of Acid settler so that there is no need for multiple units for the recycle of HF and adjusting it such it efficiency is equal to the Efficiency we get from multiple units for HF recycle this will simplify the process and then we no longer be needed the HF stripper.
5. Replacement of distillation column in fractionator with separators-In fractionator instead of distillation column we have used 3 separators due to our insufficient knowledge of using and specifying the separator in aspen.However replacing it did not affect the process much and we still got our desired results



Explaining the warnings shown the running flowsheet:

We are receiving accurate results with respect to the alkylate product, as well as the leftover propene and butene. On running the flowsheet in aspen, the following warnings show:

- Sum of splits not equal to 1 for two separators: The error is once more due to some point differences in the split fractions, which aspen resolves by normalising the fractions.This was the error encountered in both the separators.

Apart from these minor errors, we are getting accurate results for our product streams, i.e.

Alkylate : C_8H_{18} = 177.032 kg/hr, C_7H_{16} = 10.89 kg/hr
Butene - 8.056 kg/hr
Propene - 0.4255kg/h

COST COMPARISON

- OPERATIONAL COSTS-In UOP(HF) process, most of the acid is effectively regenerated, requiring only minimal makeup acid which leads to-
  1)Higher transportation costs of H_2SO_4 acid in Stratco process.
  2)Stratco process require significant expenses for disposing of large quantities of spent acid. This disposal process also increases environmental impact and drives up operational costs.
  Therefore, UOP processes generally have lower operational costs compared to sulfuric acid processes.
- CAPITAL COSTS-
  1)UOP process require additional equipment—such as the HF stripper tower, HF regeneration tower, and neutralisation facilities—to recover and neutralise HF acid, unlike Stratco process.
  2)The high toxicity of HF acid demands extensive safety equipment, adding to capital costs of UOP process
  Therefore, UOP processes generally require higher capital investment compared to Stratco processes.

SPACE REQUIREMENT COMPARISON-

- Reactor and Separator Units:Stratco typically requires larger reactor vessels to handle the volume needed for chemical reactions and catalyst circulation.UOP process feature more compact equipment due to their emphasis on modular design, which can result in smaller reactor footprints.UOP's compact design may reduce the overall space needed for these separation units compared to Stratco.
- STORAGE FACILITIES-Stratco processes necessitate considerable space for large storage tanks for raw materials and products.UOP processes may minimize storage requirements due to more efficient processing and recovery methods, potentially leading to smaller storage needs.
- PLANT LAYOUT- Stratco often requires a more complex layout, accommodating various units and leading to a larger overall plant area.UOP tends to have a simplified and efficient layout, allowing for a more compact facility that saves space while ensuring safety and operational effectiveness.
- SAFETY SPACE-More space needed in UOP for safety measure due to high toxicity and hazard associated with HF tha H2SO4.

TOXICITY COMPARISON-

- TOXICITY-HF is extremely toxic and poses significant health risks, even at low concentrations. It can cause severe burns and damage to skin, eyes, and respiratory system.While H_2SO_4 is hazardous and can cause severe burns upon contact, its toxicity is generally lower compared to HF.
- HEALTH HAZARD- Exposure to HF vapors can lead to respiratory distress and pulmonary edema, making it particularly dangerous in poorly ventilated areas.HF can be absorbed through the skin, potentially leading to systemic toxicity and metabolic disruptions. While H2SO4 poses risk only in direct contact,not through inhalation and do not cause systemic toxicity.

UOP(HF) is significantly more toxic than Stratco(H_2SO_4), posing severe health risks with potential systemic effects, while H_2SO_4 primarily presents risks through contact and fumes.

CORROSIVITY COMPARISON

- HF is highly corrosive to most metals, glass, and many construction materials, requiring specialised materials for storage and handling.
- H_2SO_4 is also very corrosive, particularly to metals, but it can be effectively handled with more common materials like stainless steel or other corrosion-resistant alloys.

- HF can react with metal surfaces, leading to formation of a protective oxide layer which may affect equipment integrity over time.
- H_2SO_4 releases heat when mixed with water, increasing its corrosive potential during handling and requiring careful dilution practices.

Both acids are highly corrosive, but HF requires specialised materials for handling, whereas H_2SO_4 can often be managed with standard corrosion-resistant metals.

SAFETY MEASURE

- ADDITIVES and EQUIPMENT DESIGN- HF can create a hazardous vapor cloud if sprayed into the atmosphere so use additives in HF to minimize vapor cloud formation and employ equipment design changes that reduce the amount of HF present. while H_2SO_4 can produce toxic fumes when heated or mixed with water so for H_2SO_4, ensure equipment is resistant to corrosion and can safely contain the acid.
- EMERGENCY SYSTEM -Establish emergency dumping protocols for both acids, directing excess material to underground storage tanks to prevent exposure in the event of a system failure.Ensure accessibility to emergency showers, eye wash stations, and first aid kits in acid handling areas.
- SPILL CONTAINMENT: Utilize absorbent materials and neutralizing agents for both acids to manage spills effectively.
- STORAGE GUIDELINES: Store acids in compatible, corrosion-resistant containers, away from incompatible substances.
- REGULAR INSPECTION: Conduct routine checks of tanks and equipment to identify leaks and maintenance needs.
- SAFETY DATA SHEET- Maintain accessible SDS for both acids and ensure staff are familiar with safety precautions.
- PROPER DISPOSAL: Follow regulatory guidelines for the safe disposal of HF and H_2SO_4, ensuring neutralisation and environmentally responsible methods to prevent contamination.

CONCLUSION

In conclusion, both the hydrofluoric acid (HF) and sulfuric acid (H_2SO_4) alkylation processes are critical for producing high-octane gasoline components in petroleum refining, with each offering distinct advantages and challenges. The HF alkylation process provides greater efficiency and lower operational costs due to lower acid consumption and effective recycling, albeit with higher capital costs and safety requirements due to HF's high toxicity and corrosivity. Conversely, the H_2SO_4 process is generally safer and less toxic, though it requires larger quantities of acid and increased handling, which raises disposal and operational expenses.

Environmental and health concerns are paramount in both processes, with HF's acute toxicity presenting higher risks in the event of a leak, while H_2SO_4's hazards primarily involve direct contact. The choice between these processes must weigh factors such as cost, safety, yield, and environmental impact. Advanced safety protocols, emergency response systems, and equipment modifications are essential to mitigate risks associated with each process.

APPENDIX

In the STRACTCO flowsheet terms labelled are described here as follows :

- OLEFEED : (Olefin feed) It is the input feed fed to the reactor which contains olefins, acid and isobutane.Olefins (such as propylene and butylene) are fed into the system as the primary feedstock for alkylation.
- MIXER1 : This mixer takes in the input feed along with the recycle stream of isobutane.
- PD1 : It is simply the output stream of mixer 1.
- DRUMFIL : (Drum filter) It is a separator which is used to separate water and hydrocarbons.
- HYDROCAR : It is one of the output stream of DRUMFIL which contains hydrocarbon
- REACTOR1 : It is the main reactor where the reactions occur.The core unit where the actual alkylation reaction occurs. In this reactor, olefins react with isobutane in the presence of sulfuric acid as a catalyst to form high-octane alkylate. The fresh and recycled isobutane mix with the olefins to produce the desired alkylation reaction.
- ACIDSETT : (Acid settler) It is a separator which separates impure product stream from acid. After the reaction, the acid and hydrocarbon phases are separated in this vessel. The hydrocarbon stream is further processed, and the sulfuric acid is recycled back into the reactor.
- FRESACI : It is the fresh acid stream fed to the reactor for the reaction to occur.
- SPENTACI : This stream removes some excess acid from the process.
- ACIDSTR1 : (Acid stream 1) One of the output stream of Acid settler which contains acid.
- IMPDTSTR : It is the impure product stream containing products other than acid.
- WATERWAS : (Waterwash) It removes all the caustic impurities from the product and the other stream goes to deisobutanizer. It removes traces of caustic and salts
- DEIBUTZR : (Deisobutanizer) This column separates unreacted isobutane from the hydrocarbon mixture for recycling back to the reactor.
- MAKUPISO : This is the stream which adds some more isobutane to the deisobutanizer.
- DEPROPZR : (Depropanizer) This unit separates propane from the product stream. Propane is a by-product and can be further used or sold.
- DEBUTZER : (Debutanizer) This unit separates normal butane from the alkylate product. Butane can be used as a fuel or in other petrochemical processes.
- BUTENE : This stream contains unreacted butene after reaction.
- ALKYLATE :The final product of the process, alkylate, is a high-octane component used in blending gasoline.
- PROPENE : This stream contains unreacted propene after reaction.
- ISOBUTRY : This is the recycle stream. Isobutane is recycled within the process for reuse in the alkylation reaction. It reacts with olefins to form the desired alkylate

product.Fresh isobutane is periodically added to the system to replace any losses and maintain the desired concentration for the alkylation reaction.

In the UOP flowsheet terms labelled are described here as follows:

- FEED-It is the total hydrocarbon feed containing-olefin(propylene,butylene), isobutane with some amount of water
- DRYER-It is a separator which removes the water in the feed upto 90% percent.
- WATER- This stream comprises of water coming out of the dryer
- DRYFEED- Feed after removal of water that goes in reactor
- REACTOR- Stoichiometric reactor where main reaction occurs
- FRESACID- It is the fresh acid that acts as catalyst in reaction and goes in reactor
- PROD-Output stream coming out of reactor after the reaction
- ACID- Recycle acid stream going in reactor
- ACIDSETT- It is a separator which removes pure acid stream from other products which can be used for recycling.
- FRACTION- It is a separator used for removing isobutane from other products which is sent again for recycling in the reactor.
- RECYISO- Recycle isobutane stream coming out of the separator and going inside reactor.
- PROD2-Stream coming out of acid settler which contains hydrocarbon products from the reactor after removal of acid
- RES-Stream coming out of Fraction separator containing propylene, butene and main products.
- SEP-P- It is a separator used for separation of unreacted propylene from RES
- Propene- This stream contains unreacted propene after reaction(0.4255kg/hr)
- PROD3- Stream coming out of SEP-P after removal of propylene from RES containing butene and main products
- SEP-B- It is a separator used for separation of unreacted butene from PROD3
- BUTENE- This stream contains unreacted butene after reaction(8.056kg/hr)
- ALKYLATE- This is the final output stream containing our main output product isooctane(177.012 kg/hr) and side product -2,3-dimethyl pentane(C_7H_{16}-10.893 kg/hr)

REFERENCES

- Norton Engineering Consultants' Alkylation Technology Study by South Coast Air Quality Management District (SCAQMD) Alkylation Technology Study FINAL REPORT South Coast Air Quality Management District (SCAQMD)
- FUNDAMENTALS OF PETROLEUM REFINING from TOMSK Polytechnic University "https://portal.tpu.ru/SHARED/b/BELINSKAYA/UchWork/PPAYAmaster/Unit13_Alkylati on_Lecture.pdf
- Petroleum Refining Technology and Economics- James H .Gary, Glenn E Handwerk, Mark J. Kaiser