ALKYLATION IN PETROLEUM REFINING

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DESCRIPTION

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-

- **Hydrofluoric Acid (HF) Alkylation:** 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.
- **Sulfuric Acid (H_2SO_4) Alkylation:** 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

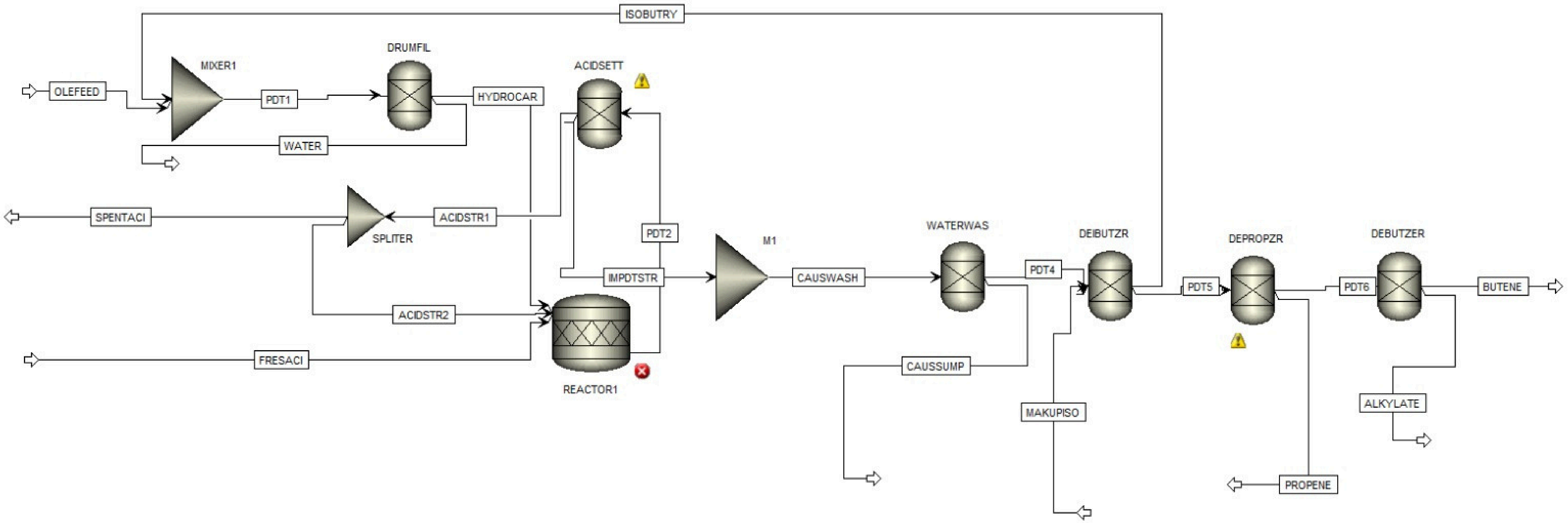
OBJECTIVES

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.

FLOWSHEET

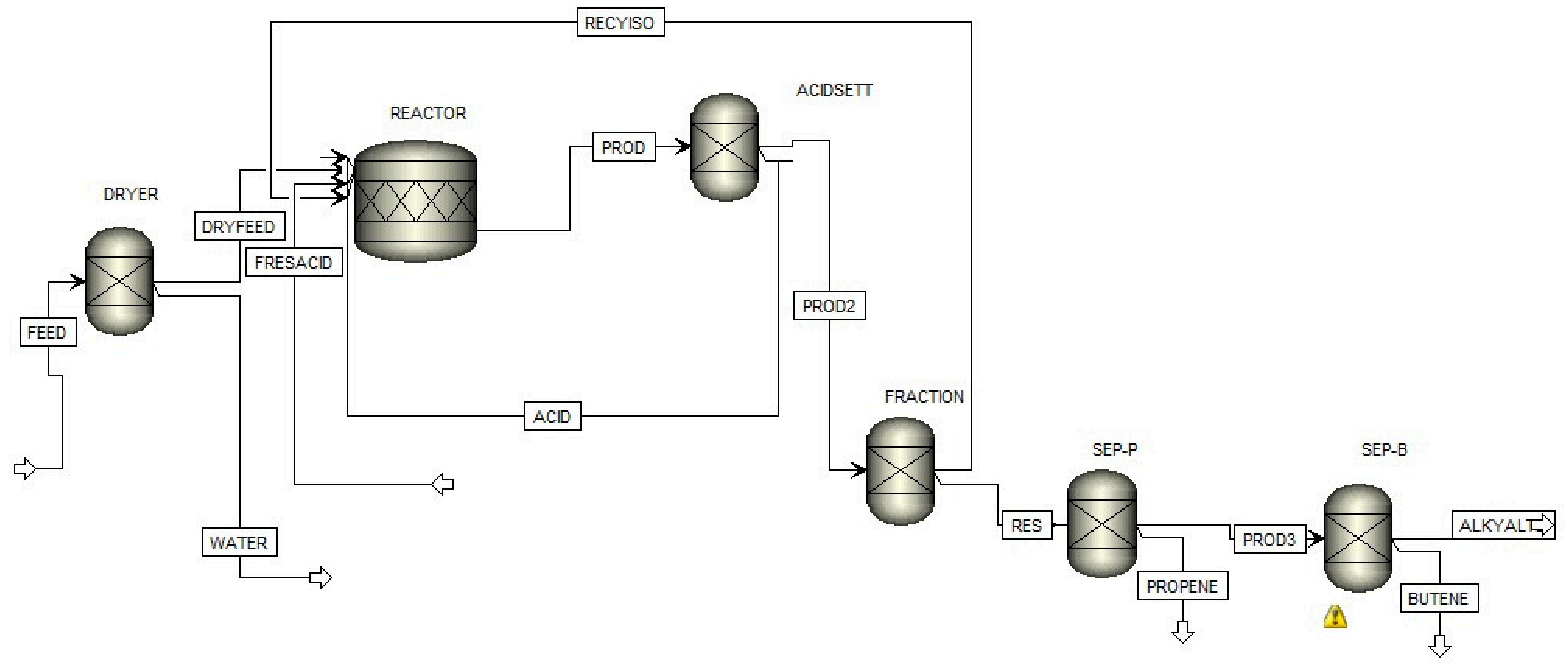
H_2SO_4 ALKYLATION PROCESS - STRATCO



Using H2SO4

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.

HF ALKYLATION - UOP



Using HF

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.

DISCUSSION

ORIGINAL FLOWSHEET - H2SO4 ALKYLATION

STRATCO

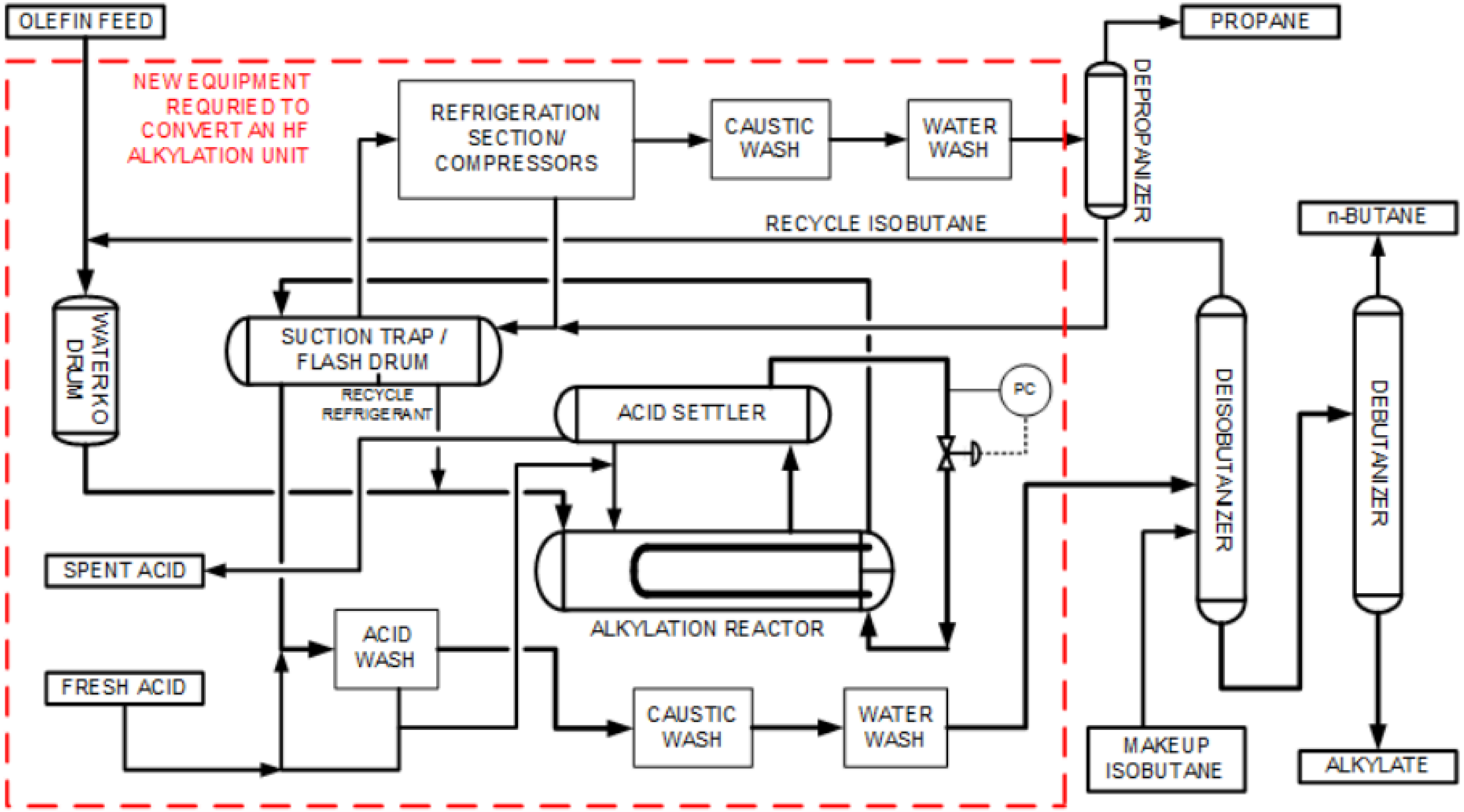
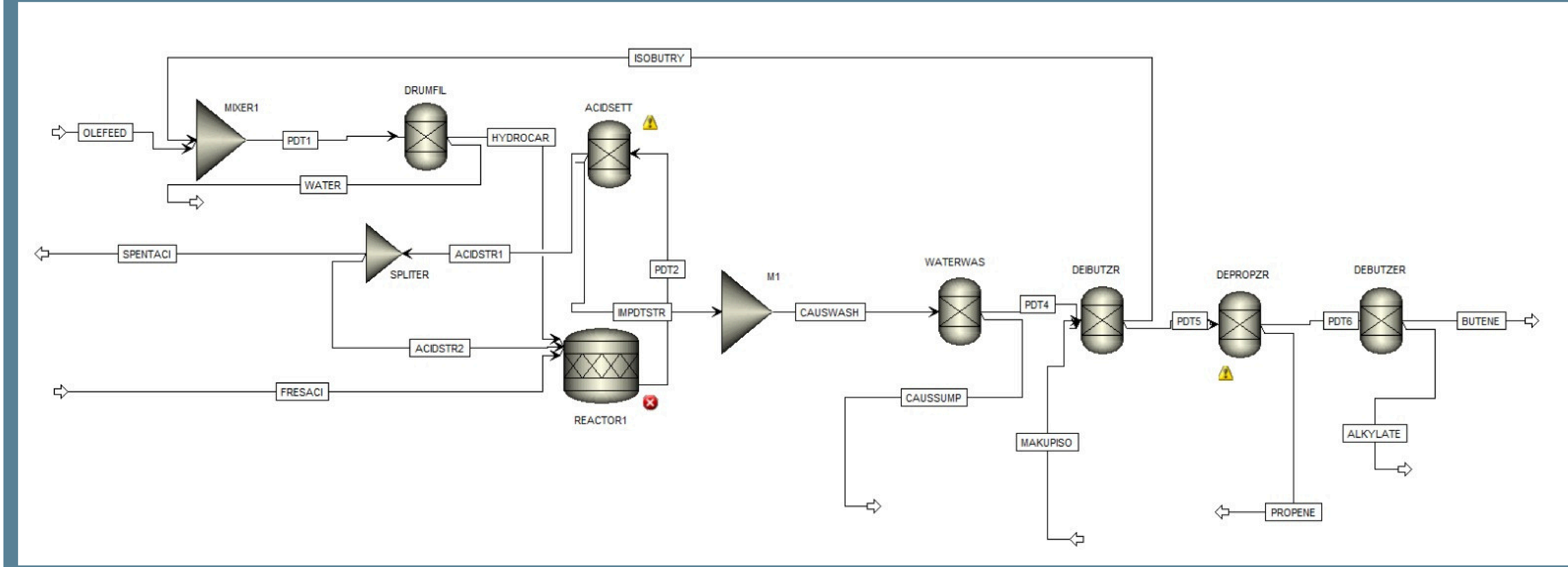


Figure 3: Simple flowsheet for Stratco Sulfuric Acid Alkylation technology

FLOWSHEET IN ASPEN

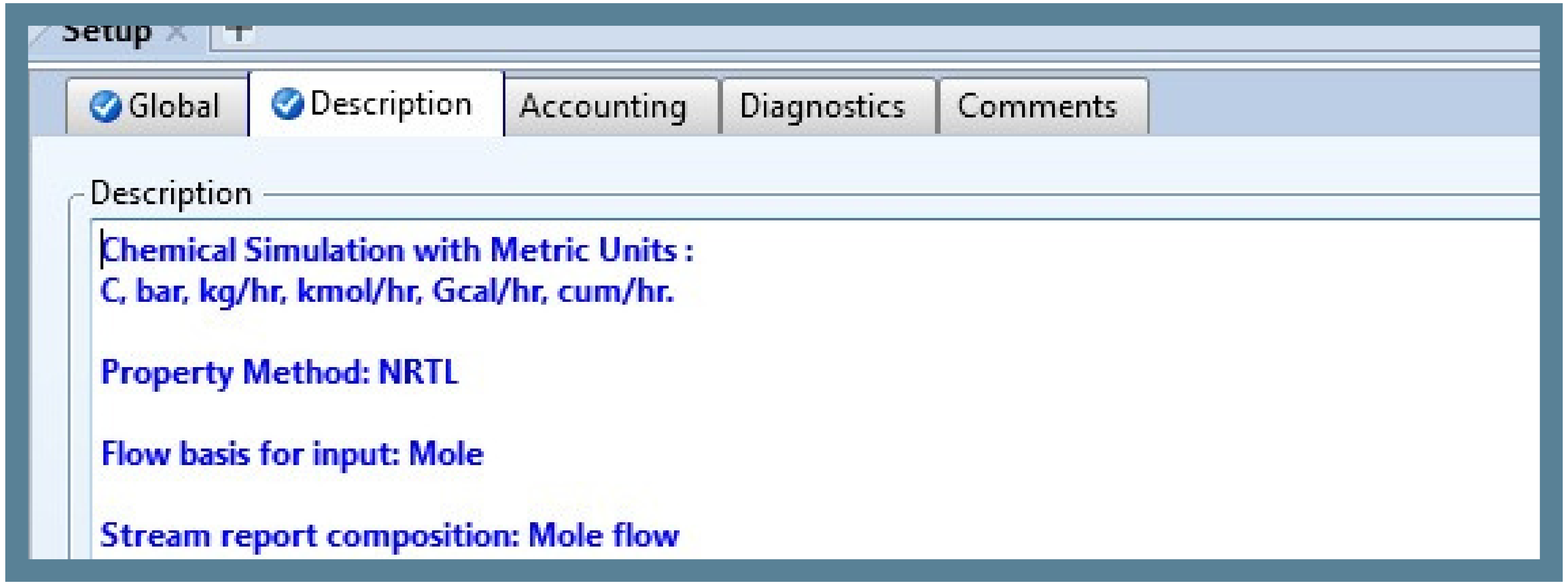
H_2SO_4 ALKYLATION PROCESS - STRATCO



CHALLENGES FACED AND ITS CORRECTIONS

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.

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.

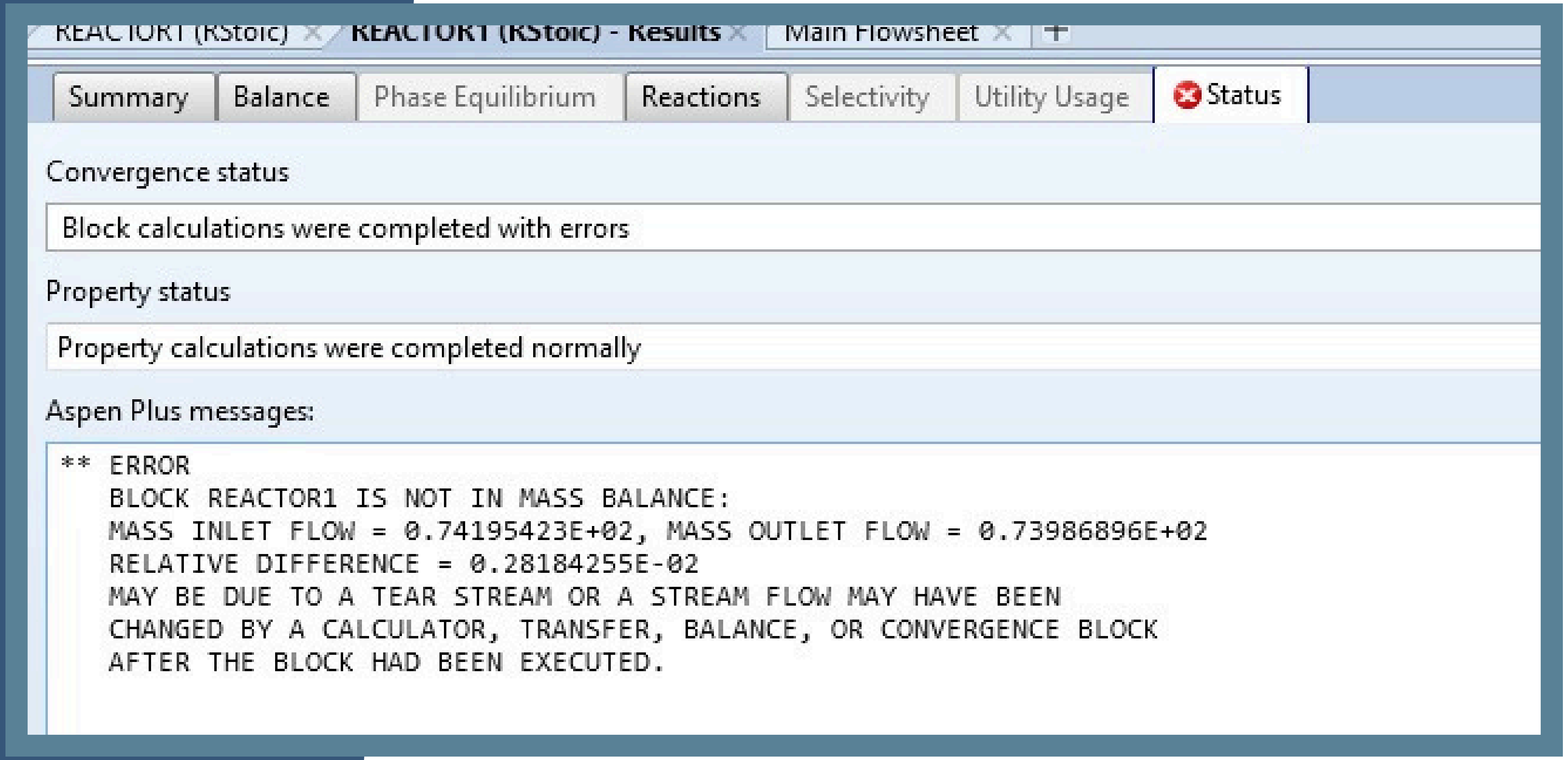


Property Method error:

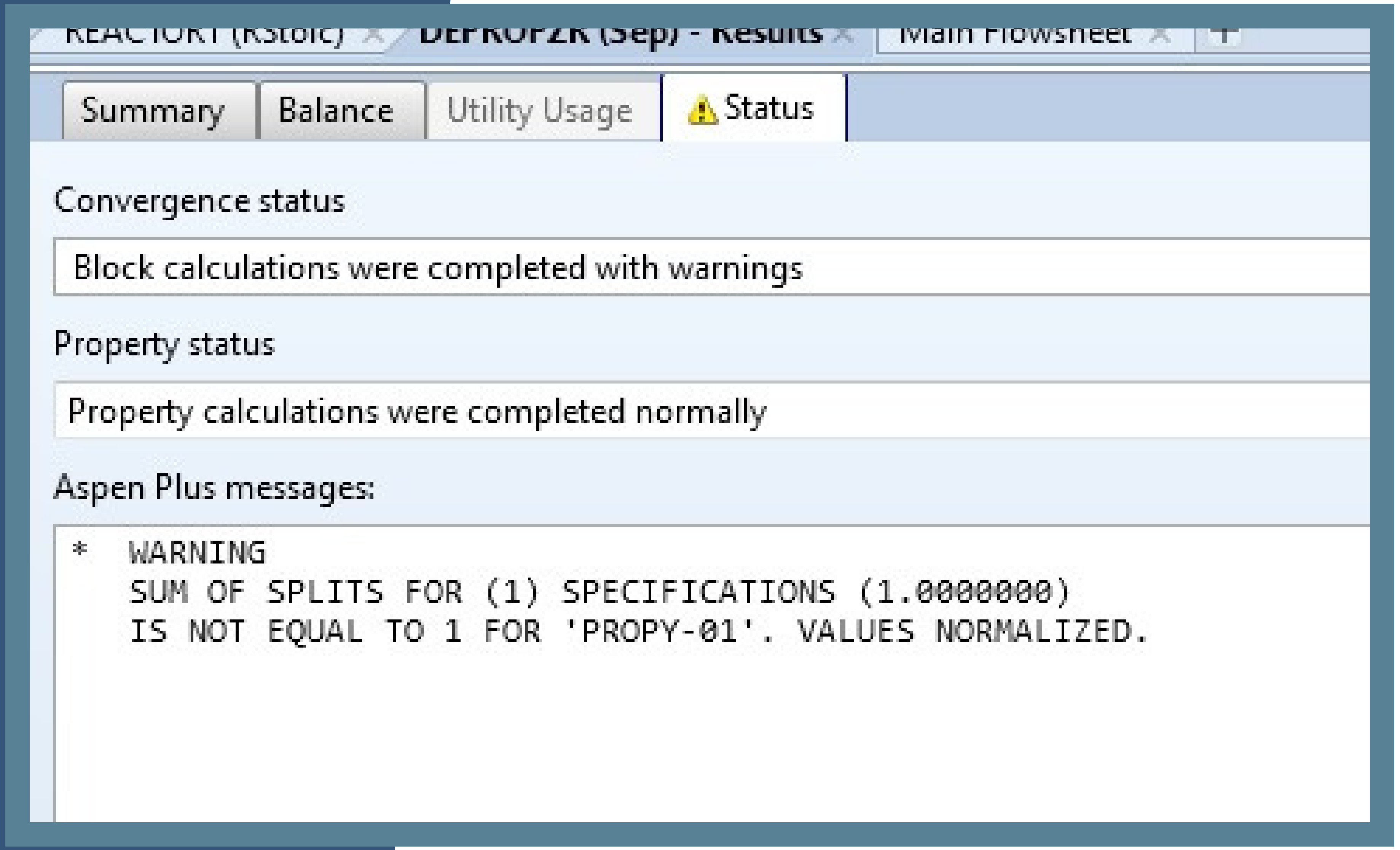
For simulating a flowsheet with the primary reaction having organic, non polar components, we used the NRTL Property Package. However, further in the flowsheet, there is an acid neutralisation reaction occurring. The NRTL package does not possess appropriate data for this reaction, which is ionic. For 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} : 178.018 kg/hr, C_7H_{16} : 10.9549 kg/hr
Butene - 7.22 kg/hr
Propane - 0.3995 kg/hr

RESULTS

H_2SO_4 (STRATCO)

Feed Stream:

Isobutane : 800 kg/hr

Olefin :100kg (95kg/hr Butene + 5kg/hr Propene)

Acid : 900kg/hr

Outlet streams :

Main product : Alkylate : C8H18 (2,2,4-trimethylpentane) =178.018 kg/hr

Side product : C7H16 (2,3-dimethylpentane) = 10.9549 kg/hr

: Butene - 7.562 kg/hr

: Propene - 0.3995 kg/hr

Spent acid : 13.47 kg/hr H2SO4, 2.19 kg/hr H2O

Caustic Impurities : NA2SO4 - 1144.64 kg/hr

: NaOH - 65.3757 kg/hr

: H2SO4 - 78.1677 kg/hr

: H2O - 307.158 kg/hr

Yield of C8H18 as calculated - 92.04%

RESULTS FROM ASPEN SIMULATION

Main Flowsheet × Results Summary - Streams (All) × +

Material | Heat | Load | Work | Power | Vol.% Curves | Wt. % Curves | Petroleum | Polymers | Solids

	Units	ALKYLATE	BUTENE	PROPENE
Molar Entropy	cal/mol-K	-213.977	-80.0144	-38.0216
Mass Entropy	cal/gm-K	-1.88839	-1.42609	-0.903541
Molar Density	mol/cc	0.00621978	0.0110368	0.000219275
Mass Density	kg/cum	704.772	619.246	9.22725
Enthalpy Flow	Gcal/hr	-0.10394	-0.00101367	4.36162e-05
Average MW		113.311	56.1075	42.0806
+ Mole Flows	**kmol/hr**	**1.66773**	**0.128682**	**0.00949368**
+ Mole Fractions				
− Mass Flows	**kg/hr**	**188.973**	**7.22**	**0.3995**
ISOBUTAN	kg/hr	0	0	0
PROPY-01	kg/hr	0	0	0.3995
2-BUT-01	kg/hr	0	7.22	0
SULFU-01	kg/hr	0	0	0
WATER	kg/hr	0	0	0
2:2:4-02	kg/hr	178.018	0	0
2:3-D-01	kg/hr	10.9549	0	0
SODIU-01	kg/hr	0	0	0
SODIU-02	kg/hr	0	0	0
+ Mass Fractions				
Volume Flow	cum/hr	0.268133	0.0116593	0.0432957
+ Vapor Phase				
+ Liquid Phase				
<add properties>				

Material | Heat | Load | Work | Power | Vol.% Curves | Wt. % Curves | Petroleum | Polymers | Solids

	Units	ACIDSTR1	ACIDSTR2	ALKYLATE	BUTENE	CAUSSUMP	CAUSWASH	FRESACI	HYDROCAR	IMPDTSTR	ISOBUTRY	MAKUPISO	OLEFEED	PDT1	PDT2	PDT4
Temperature	C	9.45333	9.45333	9.33732	9.33732	9.45334	9.45334	7.22222	8.1803	9.45333	9.33732	7.22222	7.22222	8.18034	7.22222	9.45
Pressure	bar	5.1501	5.1501	5.1501	5.1501	5.1501	5.1501	5.1501	5.1501	5.1501	5.1501	5.1501	5.1501	5.1501	5.1501	5.1
Molar Vapor Fract...		0	0	0	0	0	0	0	0	0	0	0	0	0	0	
Molar Liquid Frac...		1	1	1	1	1	1	1	1	1	1	1	1	1	1	
Molar Solid Fracti...		0	0	0	0	0	0	0	0	0	0	0	0	0	0	
Mass Vapor Fracti...		0	0	0	0	0	0	0	0	0	0	0	0	0	0	
Mass Liquid Fract...		1	1	1	1	1	1	1	1	1	1	1	1	1	1	
Mass Solid Fraction		0	0	0	0	0	0	0	0	0	0	0	0	0	0	
Molar Enthalpy	kc...	-39.9259	-39.9259	-62.3243	-7.87739	-178.24	-97.1792	-177.716	-35.5778	-97.1792	-37.3861	-37.4625	-35.1527	-36.1453	-40.2325	-40.0
Mass Enthalpy	kc...	-663.898	-663.898	-550.027	-140.398	-1970.65	-1289.68	-1973.02	-614.906	-1289.68	-643.22	-644.533	-623.126	-632.205	-668.091	-619.
Molar Entropy	cal...	-112.971	-112.971	-213.977	-80.0144	-74.9534	-101.156	-74.729	-108.064	-101.156	-110.651	-110.911	-103.78	-106.732	-113.173	-12
Mass Entropy	cal...	-1.87852	-1.87852	-1.88839	-1.42609	-0.828697	-1.34246	-0.829646	-1.86771	-1.34246	-1.90372	-1.9082	-1.83963	-1.86682	-1.87932	-1.88
Molar Density	m...	0.00975539	0.00975539	0.00621978	0.0110368	0.0194823	0.0122756	0.019544	0.0099346	0.0122756	0.00981513	0.00985859	0.0103426	0.0101027	0.0098101	0.00921
Mass Density	kg...	586.675	586.675	704.772	619.246	1762.12	924.978	1760.39	574.806	924.978	570.489	573.015	583.463	577.606	590.764	596.
Enthalpy Flow	Gc...	-175.646	-175.636	-0.10394	-0.00101367	-1.74469	-2.30163	-1.77572	-1.01521	-2.30163	-0.482415	-0.0304787	-0.567044	-1.04946	-177.948	-0.556
Average MW		60.1386	60.1386	113.311	56.1075	90.4473	75.3511	90.0733	57.859	75.3511	58.1234	58.1234	56.4135	57.1734	60.22	64.7
+ Mole Flows	**k...**	**4399.31**	**4399.05**	**1.66773**	**0.128682**	**9.78847**	**23.6844**	**9.99186**	**28.5349**	**23.6844**	**12.9036**	**0.813579**	**16.1309**	**29.0345**	**4422.99**	**13.8**
+ Mole Fractions																
+ Mass Flows	**k...**	**264568**	**264553**	**188.973**	**7.22**	**885.34**	**1784.64**	**900**	**1651**	**1784.64**	**750**	**47.288**	**910**	**1660**	**266353**	**899.**
+ Mass Fractions																
Volume Flow	cu...	450.962	450.935	0.268133	0.0116593	0.502429	1.92939	0.51125	2.87227	1.92939	1.31466	0.0825249	1.55965	2.87393	450.861	1.50
+ Vapor Phase																
+ Liquid Phase																

ORIGINAL FLOWSHEET - HF ALKLYLATION

UOP

3.4.1 Simple Flowsheet for Modified HF Alkylation Technology

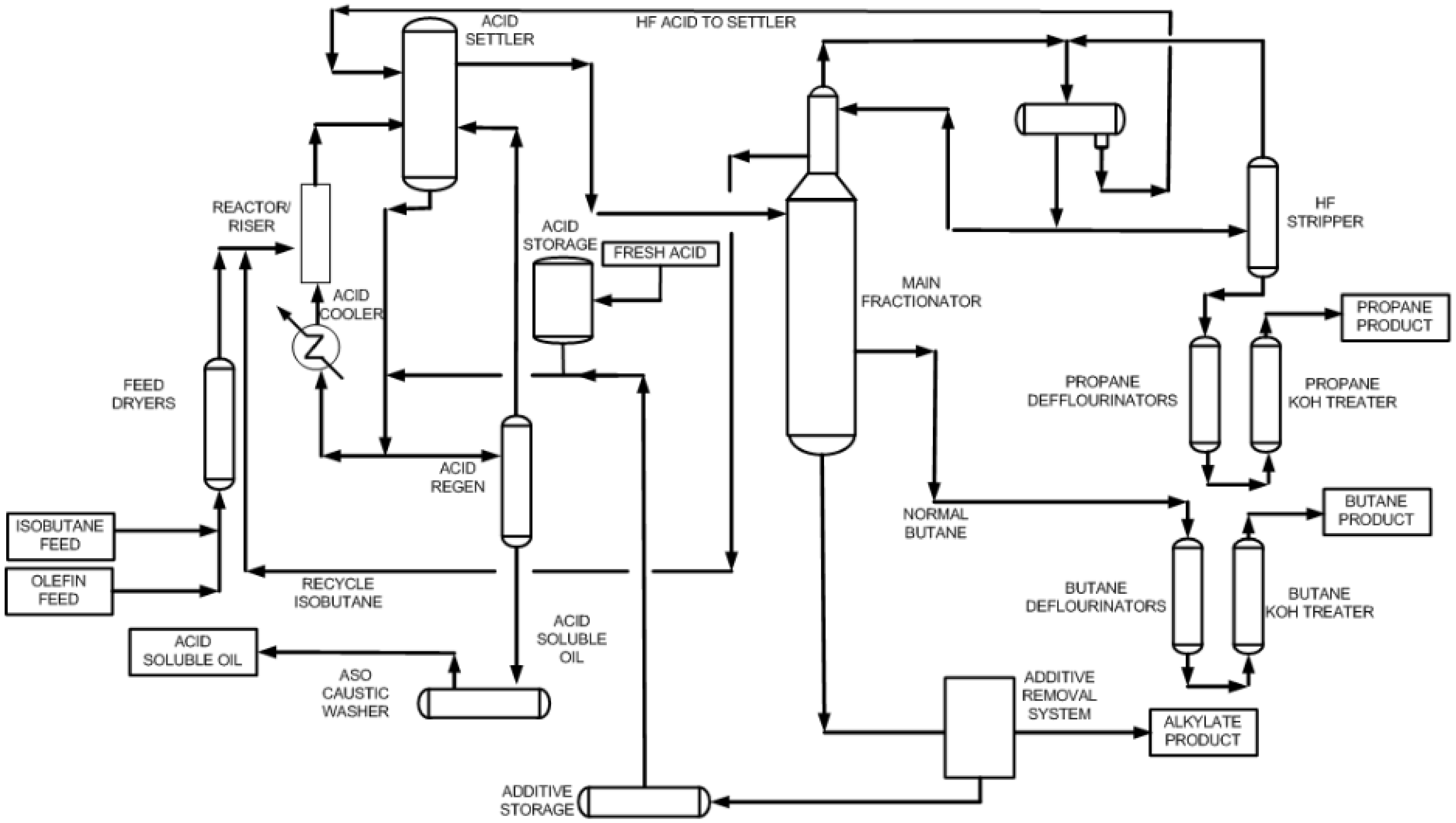
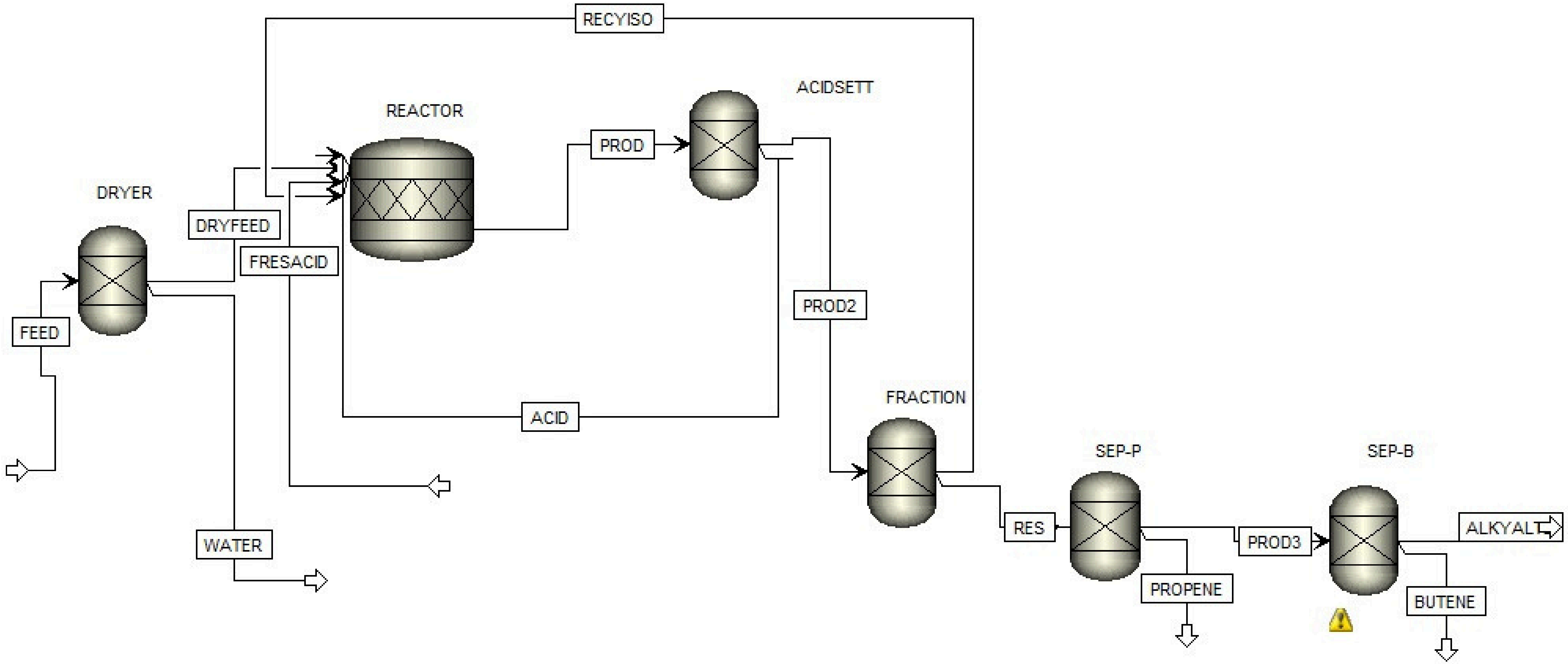


Figure 2: Simple flowsheet for modified HF Alkylation technology

HF ALKYLATION - UOP



CHALLENGES FACED AND ITS CORRECTIONS IN UOP (HF)

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. The overall process could become safer, more efficient, and potentially more economical.

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. 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

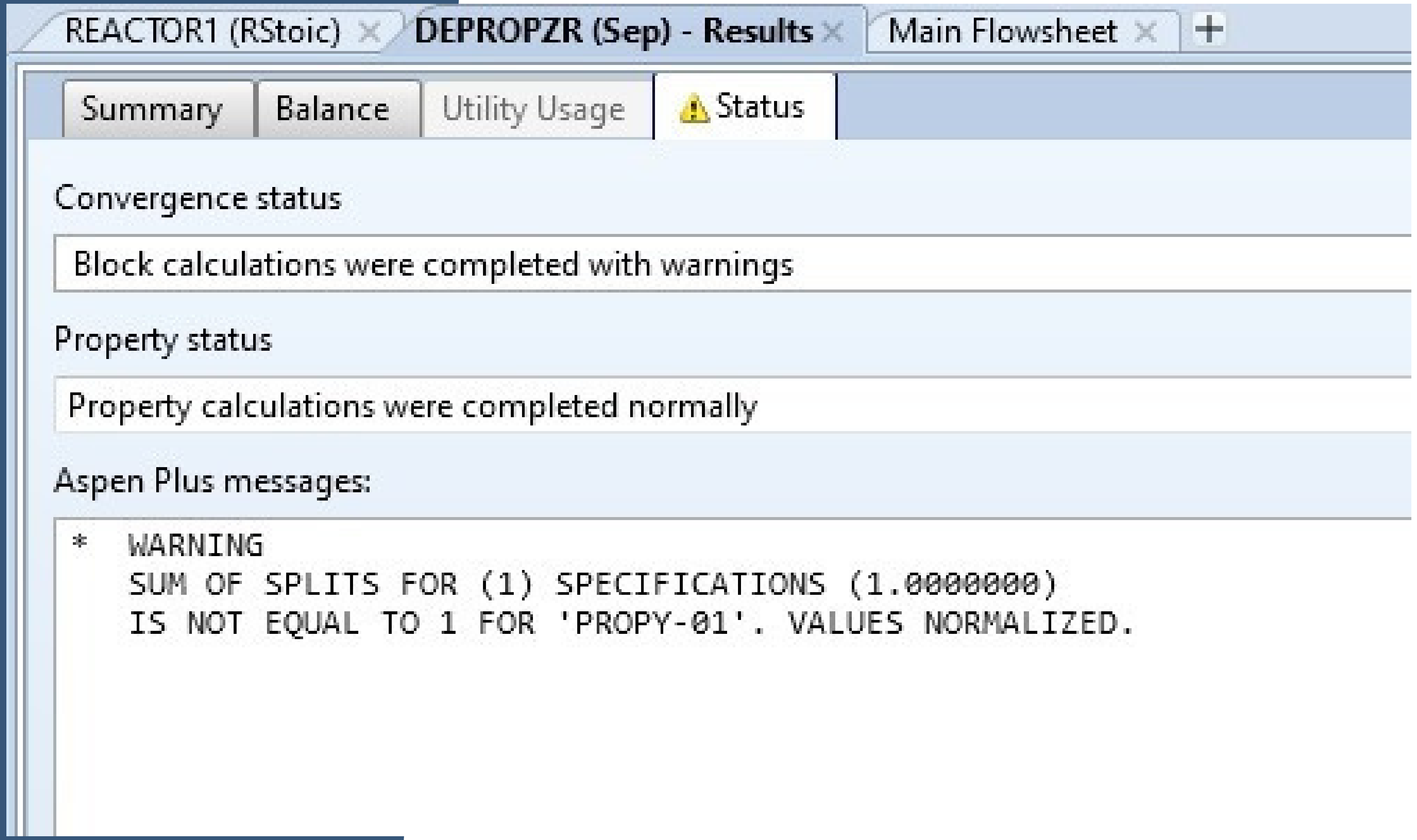
Removal of Caustic Washer :
The caustic washer is used to remove acidic impurities, specifically trace HF acid, from the hydrocarbon streams before further processing.but in this process we don’t want soluble oil as our one of our desired product so for simplification of flow sheet we can remove this segment of flow sheet

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.

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 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 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

RESULTS

HF (UOP)

Feed Stream:
Isobutane : 1200kg
Olefin :100kg (95kgButene + 5kg Propene)
Acid :1300kg

Outlet Streams:
Main product :
Alkylate : C8H18 (2,2,4-trimethylpentane) = 177.032 kg/hr
Side product :
C7H16 (2,3-dimethylpentane) = 10.89 kg/hr
Butene - 8.056 kg/hr
Propene - 0.4255kg/hr

Yield of C8H18 is as calculated- 91.52%

RESULTS FROM ASPEN SIMULATION

Heat | Load | Work | Power | Vol.% Curves | Wt. % Curves | Petroleum | Polymers | Solids

	Units	ACID	ALKYALTE	BUTENE	DRYFEED	FEED	FRESACID	PROD	PROD2	PROD3	PROPENE	RECYISO	RES	WATER
lass Flows	**kg/hr**	**1299.65**	**2592.52**	**8.056**	**1301**	**1310**	**1300**	**5009.13**	**3709.48**	**2600.57**	**0.4255**	**1108.48**	**2601**	
HF	kg/hr	1299.65	1300	0	0	0	1300	2599.65	1300	1300	0	0	1300	
PROPY-01	kg/hr	0	0	0	5	5	0	0.4255	0.4255	0	0.4255	0	0.4255	
HYDRO-01	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	
POTAS-01	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	
WATER	kg/hr	0	1	0	1	10	0	1	1	1	0	0	1	
ISOBU-01	kg/hr	0	1103.61	0	1200	1200	0	2212.1	2212.1	1103.61	0	1108.48	1103.61	
2-BUT-01	kg/hr	0	0	8.056	95	95	0	8.056	8.056	8.056	0	0	8.056	
2:2:4-01	kg/hr	0	177.012	0	0	0	0	177.012	177.012	177.012	0	0	177.012	
2:3-D-01	kg/hr	0	10.893	0	0	0	0	10.893	10.893	10.893	0	0	10.893	
POTAS-02	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	

Mass Liquid Fraction														
Mass Solid Fraction		0	0	0	0	0	0	0	0	0	0	0	0	
Molar Enthalpy	cal/mol	-67139.9	-60172	-6919.94	-33966.7	-34706.3	-67139.9	-60112.4	-55760.7	-60082.9	-67139.9	-36299.7	-60084.6	-68034.
Mass Enthalpy	cal/gm	-3355.93	-1988.38	-123.334	-587.779	-609.686	-3355.93	-2038.5	-1576.93	-1982.6	-3355.93	-624.528	-1982.82	-3776.4
Molar Entropy	cal/mol-K	-5.5156	-30.757	-76.9221	-103.787	-102.172	-5.5156	-29.1651	-44.2439	-30.8097	-5.5156	-107.169	-30.8033	-38.219
Mass Entropy	cal/gm-K	-0.275693	-1.01636	-1.37098	-1.79599	-1.79485	-0.275693	-0.989032	-1.25123	-1.01665	-0.275693	-1.84381	-1.01652	-2.1215
Molar Density	mol/cc	0.0461041	0.0265549	0.0104355	0.00931431	0.00951502	0.0461041	0.0269883	0.0209327	0.0265041	0.0461041	0.00919415	0.0265071	0.05448
Mass Density	gm/cc	0.922374	0.803602	0.585508	0.538257	0.541641	0.922374	0.795844	0.740186	0.803211	0.922374	0.534395	0.803234	0.98154
Enthalpy Flow	cal/sec	-1.21153e+06	-1.43192e+06	-275.993	-212417	-221858	-1.21186e+06	-2.83642e+06	-1.62489e+06	-1.43219e+06	-396.652	-192299	-1.43259e+06	-9441.
Average MW		20.0063	30.2619	56.1075	57.7882	56.9248	20.0063	29.4885	35.3602	30.3051	20.0063	58.1234	30.3026	18.015
Mole Flows	**kmol/hr**	**64.9617**	**85.6695**	**0.143581**	**22.5132**	**23.0128**	**64.9794**	**169.867**	**104.906**	**85.8131**	**0.0212683**	**19.0712**	**85.8343**	**0.49957**
Mole Fractions														
Mass Flows	**kg/hr**	**1299.65**	**2592.52**	**8.056**	**1301**	**1310**	**1300**	**5009.13**	**3709.48**	**2600.57**	**0.4255**	**1108.48**	**2601**	
HF	kg/hr	1299.65	1299.57	0	0	0	1300	2599.65	1300	1299.57	0.4255	0	1300	
PROPY-01	kg/hr	0	0.4255	0	5	5	0	0.4255	0.4255	0.4255	0	0	0.4255	
HYDRO-01	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	
POTAS-01	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	
WATER	kg/hr	0	1	0	1	10	0	1	1	1	0	0	1	
ISOBU-01	kg/hr	0	1103.61	0	1200	1200	0	2212.1	2212.1	1103.61	0	1108.48	1103.61	
2-BUT-01	kg/hr	0	0	8.056	95	95	0	8.056	8.056	8.056	0	0	8.056	
2:2:4-01	kg/hr	0	177.012	0	0	0	0	177.012	177.012	177.012	0	0	177.012	
2:3-D-01	kg/hr	0	10.893	0	0	0	0	10.893	10.893	10.893	0	0	10.893	
POTAS-02	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	

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 process.

- **CAPITAL COSTS-**

1)UOP process require additional equipment—such as the HF stripper tower, HF regeneration tower, and neutralization 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 and 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

- HFishighly 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.
- HFcanreact with metal surfaces, leading to formation of a protective oxide layer which may affect equipment integrity over time.
- H_2SO_4releases 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.

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.

THANK YOU