

REMOVAL OF SULPHUR FROM NAPHTHA, CATALYSTS SLECTION AND ITS POISIONS

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ABSTRACT

Sulphur is treated as an impurity which has huge impact on the production cost of ammonia. It is a poisoning element for steam naphtha reforming catalyst; it should be removed from raw naphtha having maximum 1500 wt ppm sulphur. Sulphur removed from naphtha is done by two sections: one is pre-desulphurisation followed by final desulphurisation. In the pre-desulphurization process, the organic sulphur compounds are removed from the naphtha by catalytic conversion to hydrogen sulphide, which is then separated from the naphtha by distillation. The hydrogenation and stripping process is included as a primary processing step in the NFCL plant, Kakinada, to remove the bulk of the maximum 1500 wt ppm sulphur in the naphtha feed up to 2-10 ppm sulphur. The pre-desulphurisation process does not yield sufficiently low sulphur concentration in the feed to prevent poisoning of the steam naphtha reforming catalyst; thus, a final desulphurization must also be performed. The sulphur content in the outlet of final desulphurized gas is 0.1 ppm by volume; it is achieved by two beds of ZnO absorption. And here I am presenting the brief operation of pre-desulphurisation, final desulphurisation. In the present project work, to study the various catalysts to remove sulphur from naphtha and catalysts handling, best performance, operating conditions & poisoning of catalysts are studied.

CHAPTER 1

INTRODUCTION:

Urea is a widely used industrial product especially adopted as a fertilizer, although it is also used in the pharmaceutical field and that of polymeric materials. There is consequently still a high demand for processes for the production of urea with an increased productivity in combination with lower energy consumption and investment and maintenance costs, in which improvements in the yields and/or unit energy consumption, can provide great economical advantages. **M/S NAGARJUNA FERTILISERS AND CHEMICALS LIMITED** is South India's first Natural Gas based fertilizer plant situated in Kakinada, Andhra Pradesh. M/s Nagarjuna Fertilizers and Chemicals Limited, Kakinada is the flag ship company of the Nagarjuna Group Founded by Mr. K.V.K.Raju. It is the first gas based Fertilizer Plant in South India. It covers 1130 acres, of which two third is occupied by Green Belt. The main product of the company is Urea.

The mission of the company is to “Serving Society through Industry” and its mission is to become leader in core sectors of the industry. It has adopted a policy of quality management system ISO 9002, Environment Management System (ISO 14001) and OHSAS (ISO 18001) series of standards.

The technology for the fertilizers plant is provided by M/s Haldor Topsoe for Ammonia production and M/s Snamprogetti for Urea production

Ammonia-2 has facility to operate the NG ,Naphtha and mixed.In the present project work, removal of sulphur from naphtha i.e. desulphurization is carried out in two stages. In the first stage - the predesulphurization section - the sulphur content is reduced to less than 10 ppm from 1500 ppm.In PDS hydrogenation/stripping process is included as a primary processing step. The sweet naphtha from the desulphurization section will contain appreciable amounts of sulphur-bearing compounds. These should be completely removed before the steam reforming. This is done in the second stage i.e. final desulphurization section in which a further catalytic hydrogenation of the residual organic sulphur compounds takes place followed by absorption of the hydrogen sulphide on zinc oxide. NG being used as feed is mixed with sweet naphtha prior to final desulphurisation section for removal of sulphur. The consumption of zinc oxide is limited since the major part of the sulphur in The raw naphtha already has been removed in the predesulphurisation section.

This paper highlights about selction of sulphure removal catalysts based on new problems, catalysts and its best performance ,operating conditions ,how the poisoning of catalysts happens, how to early identification of poisoning,what are the remedial actions are studied.

PROPERTIES OF NAPHTHA

3.1. NAPHTHA SPECIFICATIONS AND ITS IMPORTANCE

Steam reforming of Naphtha is a sensitive process and is suitable only for certain specification of naphtha. The naphtha should be straight run naphtha obtained by straight distillation of virgin crudes. Use of cracked naphtha is seldom attempted as desulphurisation of cracked naphtha is difficult. The crude processed by various refineries are different and the import naphtha also is of wide variations.

TYPICAL SPECIFICATION OF NAPHTHA

Specific Gravity	: 0.68 - 0.72
Distillation 10%	: 45 - 85 deg. C
Distillation 50%	: 60 -110 deg.C
Final Boiling Point (FBP)	: 180 deg.C (max.)

PONA ANALYSIS

Paraffins	: 58% Min.
Olefins	: 1% Max.
Naphthenes	: 15% Max.
Aromatic	: 12% Max.
Sulphur	: 0.06% Max.
C.H.Ratio	: 5.3 - 5.6
Reid Vapour Pressure	: 0.8 Kg/cm ² (max.)
Residue on evaporation	: 2 mg/100 ml (max.)

Composite sample of Naphtha collected
from Ship MVS SWARAJ at Vizag

NFCL HPCL

Specific Gravity at 28 °C	0.7011	-
at 15 °C	0.7120	0.7165
C/H Ratio	5.5279	-
Net Calorific Value Kcal/Kg.	10465	-
Sulphur as `S` w/w ppm	70	180
Non Volatile Matter (mg/100 ml)	1.0	1.0
Bromine No.	0.44	-
Aromatics v/v %	8.34	7.5
Naphthenes v/v %	26.02	33.2
Paraffins v/v %	65.64	58.8

Olefins	v/v %	0.2	0.5
Initial Boiling Point	(°C)	46	40
10 ml		62	62
20 ml		70	71
30 ml		76	77
40 ml		84	84
50 ml		90	90
60 ml		96	97
70 ml		103	103
80 ml		110	110
90 ml		120	119
95 ml		131	125
Final Boiling Point	(°C)	142	142
Recovery	(%)	98.5	98.5
Residue	(ml)	1.0	1.0
Total Chlorides	ppm	<0.1	-
Inorganic Chlorides	ppm	0.02	-
Iron as Fe *		0.07	
Nickel as Ni	ppm	0.01	
Vanadium as V	ppm	<0.02	
Sodium as Na	ppm	<0.1	
Potassium as K	ppm	<0.1	
Lead as Pb *	ppm	<0.02	

3.2 BOILING POINT RANGE:

The final boiling point is indicative of the presence of high molecular weight hydrocarbons in the naphtha. Although the amount of high boiling hydrocarbon is small in comparison to the bulk, they tend to lay down carbon resulting in lowering of the activity of the reforming catalyst. Further, higher molecular weight hydrocarbons contain sulphur compounds which are difficult to remove.

3.3 TOTAL SULPHUR CONTENT:

Normally naphtha contains sulphur as received and is desulphurised at the ammonia plant, before reforming, bringing down the sulphur content to less than 0.1 ppm.

The specification for raw naphtha includes a maximum limit of 1500 ppm of sulphur of which not more than 100 ppm is 'unreactive sulphur' that is sulphur compounds other than sulphur, Hydrogen sulphide, mercaptans, Disulphides and Thioethers. Sulphur lowers the activity of the Nickel based reforming catalyst.

3.4 OLEFINS:

Olefin content in straight run naphtha is normally very low. To ensure that the product is straight run naphtha a nominal value of 1% is specified.

However, presence of olefins beyond limit is not desirable because of the tendency to thermal cracking and laying down carbon in vapouriser and over catalyst bed.

Also Olefins form gum if dissolved oxygen is present.

3.5 NAPHTHENES:

The naphthenes are more susceptible to dehydrogenation and deposition of carbon over the catalyst bed. However, naphthenes have been successfully reformed if present within the limit specified.

3.6 AROMATICS:

Aromatics are normally difficult to reform. Aromatic content in the naphtha is one of the factors deciding the catalyst loading and higher aromatic content than design results in reduction of throughput.

Further, operation of the plant with high aromatic naphtha will lead to higher hydrocarbon slip and continuous operation under these conditions could lead to progressive carbon lay down on the catalyst as high aromatic feedstocks are prone to deposit carbon under even slightly adverse conditions leading to severe pressure drop and loss of catalyst activity.

Higher aromatic content further implies higher amount of thiophenic sulphur which is difficult to be converted in the desulphuriser unit.

3.7 CARBON / HYDROGEN RATIO

The Carbon / Hydrogen ratio normally increases with rise in FBP. As C/H ratio increases,

H₂ yield per tonne of naphtha comes down and specific consumption of feedstock increases.

As higher C/H ratio is indicative of higher boiling hydrocarbons, severe operating conditions

are required in reformer.

3.8 REID VAPOUR PRESSURE

RVP provides a guide to the amount of extremely slight fractions present in the naphtha either as dissolved gases or as low boiling hydrocarbons.

Naphtha with high RVP leads to increased storage losses and risk in storage, increased NPSH requirement of pumps and losses in stripper section of hydrodesulphurisation.

3.9 RESIDUE ON EVAPORATION (ROE)

ROE is monitored to ensure that the naphtha is not contaminated with high boiling hydrocarbons which will deposit carbon over reforming catalyst.

ROE is limited to 2mg/100 ml.

3.10 INORGANICS

3.10.1 LEAD

There is a possibility of contamination of naphtha by lead particularly during storage and transportation in multi product installation and tankers, tank wagons etc, which handle petrol containing the anti-knocking agent called Tetra Ethyl Lead. Normally lead concentration upto 75 PPB is tolerated in the naphtha.

With presence of lead in Naphtha, there is an increased tendency for carbon formation in the vapouriser and desulphuriser catalyst. Further, lead can also cause fluxing of the corrosion resistant oxide film on the outer tube wall when naphtha is used as fuel.

3.10.2 CHLORIDES, BROMIDES

They are usually associated with lead. Chloride may also be found in feed stocks transported by sea. These can deactivate the reforming catalyst and LT shift catalyst by sintering. Chloride may also cause stress corrosion cracking.

Sulphur is treated as an impurity which has huge impact on the production cost of ammonia. It is a poisoning element for steam naphtha reforming catalyst it should be removed from raw naphtha having maximum 1500 wt ppm sulphur. Sulphur removed from naphtha is done by two sections one is pre-desulphurisation and followed by Final desulphurisation. In the pre-desulphurization process, the organic sulphur compounds are removed from the naphtha by catalytic conversion to hydrogen sulphide which is then separated from the naphtha by distillation. The hydrogenation/stripping process is included as a primary processing step in the NFCL plant,kakinada to remove the bulk of the maximum 1500 wt ppm sulphur in the naphtha feed up to 2-10 ppm sulphur. The predesulphurisation process does not yield sufficiently low sulphur

concentration in the feed to prevent poisoning of the steam naphtha reforming catalyst, thus a final desulphurization must also be performed. The sulphur content in the outlet of final desulphurized gas is 0.1 ppm by volume it is achieved by two beds of ZnO Absorption.

STORAGE TANKS

4.1 Floating roof tank:

An **external floating roof tank** is a storage tank commonly used to store large quantities of petroleum products such as crude oil, Naphtha etc. It comprises an open-topped cylindrical steel shell equipped with a roof that floats on the surface of the stored liquid. The roof rises and falls with the liquid level in the tank. As opposed to a fixed roof tank there is no vapor space in the floating roof tank (except for very low liquid level situations). In principle, this eliminates breathing losses and greatly reduces the evaporative loss of the stored liquid. There is a rim seal system between the tank shell and roof to reduce rim evaporation.

The roof has support legs hanging down into the liquid. At low liquid levels the roof eventually lands and a vapor space forms between the liquid surface and the roof, similar to a fixed roof tank. The support legs are usually retractable to increase the working volume of the tank.

4.2 Advantages:

External roof tanks are usually installed for environmental or economical reasons to limit product loss and reduce the emission of volatile organic compounds (VOC), an air pollutant.

Normally (roof not landed), there is little vapor space, and consequently a much smaller risk of rim space fire.

4.3 Disadvantages:

Rain water and snow can accumulate on the roof; eventually the roof may sink.

Water on the roof is usually drained from a flexible hose or other special drain line system that runs from a drain-ump on the roof, through the stored liquid to a drain valve on the shell at the base of the tank. A hose often develops leaks and drains both water and product, Other drain lines do not leak. Also pumps are used to drain the roof water through outside the tank, not through the product.

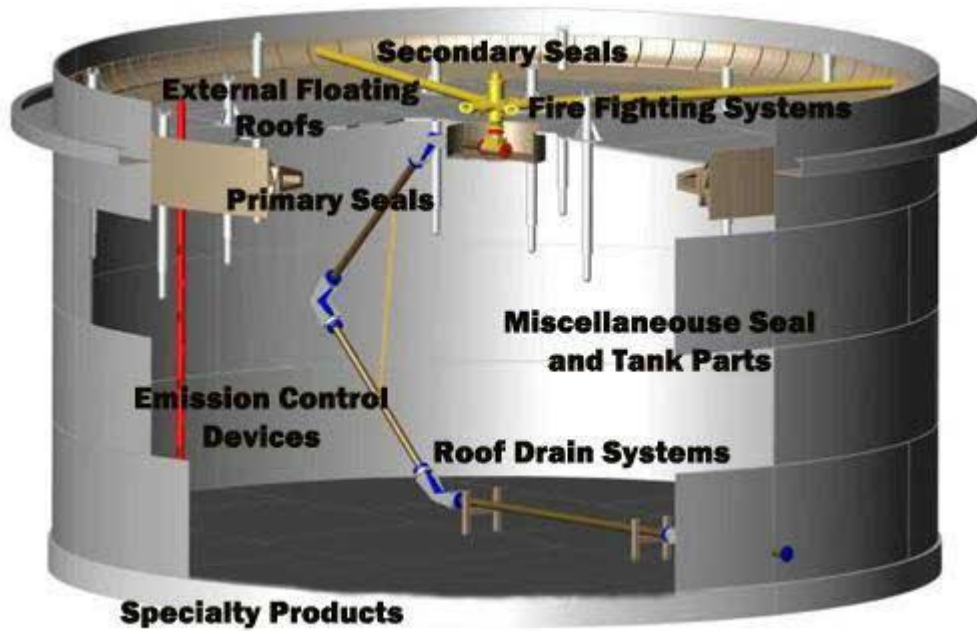


Fig.1: Floating roof storage tank

Raw naphtha used as feed & fuel in Ammonia plant-II are received from M/s Hindustan Petroleum Corporation Limited.

Naphtha from M/s.HPCL terminals is transferred to NFCL tanks through pipe lines.

4.4 Tank farm details:

(a) Naphtha tank farm consists of the following tanks:

Raw Naphtha Tank	dia (mts)	height (mts)	Calibrated volume (KL)
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# 1	22	12	3450
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# 2	22	12	3450
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Sweet Naphtha Tank

# 1	30	11	7050
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(b) Transfer Pumps

Two nos. raw naphtha centrifugal transfer pumps (one motor driven and one turbine driven) each of 60 m³/hr capacity for transferring raw naphtha to the pre-desulphurisation section.

Similarly, two nos. sweet naphtha centrifugal transfer pumps (one motor driven and one turbine driven) each of 45 m³/hr capacity for transferring sweet naphtha to the final desulphurisation section.

One tanker unloading pump is provided for unloading road trucks.

4.5 Features Of the Naphtha Tanks:

1. All the Naphtha Tanks at our site are Floating Roof Type to minimise the evaporation loss and to eliminate explosive mixture formation inside the tanks.
2. Adjustable supporting legs are provided which are normally kept at 2 mts. height. They rest the roof at 2 mts height facilitating maintenance inside the tank.
3. Neoprene Seals are provided to seal the gap between roof and tank. It also prevents the direct contact between the roof and tank eliminating the possibility of spark production due to friction. Weather plates (Zinc) are used to protect the seals.
4. Two numbers of breather vents are provided for each tank which open at 2.25 mts. height and avoid vacuum formation inside the tank.
5. One number Rim Vent is provided for each tank to release the vapour naphtha formed between the Pantoon and the Neoprene seal.
6. To drain the rain water from the roof, a roof centre drain with swivel joints, emergency drain plug, and a siphon drain are provided. An NRV at the top of roof drain to avoid naphtha reaching the roof through the drain pipe in case of drain pipe leak.
7. Tank drain is provided to drain the water collected at the bottom.
8. Each tank is provided with a Level Indicator.
9. Wind Girders are provided for giving stiffness to overcome the wind velocity.
10. Level measurements are done through dip leg which is provided with holes to eliminate the capillary effect.
11. The floating roof is electrically earthed to avoid static electricity.
12. Naphtha Tanks are earthed to avoid static electricity accumulation.
13. Naphtha tanks are painted light brown to reflect away radiational heat thereby minimising evaporation loss.

4.6 Safety features :

1. All naphtha line flanges are provided with "C" clamps to eliminate static electricity accumulation in pipes.
2. Dyke Walls are provided around the tanks to avoid spreading of Naphtha in case of damage/leakage in the tanks. They have the capacity to hold the largest capacity tank. To hold up the small leakages Bund Walls/Fire Walls are provided.
3. Fire monitors and fire hydrants are provided inside the tank farm.
4. A dedicated foam pourer system and Medium Velocity Water Curtains are installed for the Naphtha tanks.
5. A separate "Fire Alarm" push button is provided near the phone which initiates an alarm in the main control room as well as in Fire station.
6. Electrical fittings inside the tank farm are flame and explosion proof.
7. Floor in and around the storage yard dyke wall is covered with concrete slabs to avoid vegetation which is a potential source of fire.

SULPHUR REMOVAL FROM NAPHTHA**5.1 EQUIPMENTS DETAILS:**

EC-601	Raw Naphtha Deaerator	EK-601A/B	Hydrogen recycle compressor
EC-602	Naphtha stripper	EP-600A/B	Raw Naphtha transfer pumps
EE-213A	Off gas preheater	EP-601A/B	Raw Naphtha pump
EE-601 A/B/C/D	Feed effluent exchanger	EP-602A/B	Stripper reflux pump
EE-602	Effluent cooler	EP-603A/B	Hot Naphtha pumps
EE-603	Stripper feed preheater	EP-604	Anti corrosion solution pump

EE-604	Naphtha stripper over head condenser	EP-6000A/B	Sweet Naphtha transfer pumps
EE-605	Stripper re boiler	ER-601	Hydrogenator
EE-606	Sweet Naphtha cooler	ET-604	Anti corrosion solution tank
RNT-I/II	Raw Naphtha Storage Tanks	EV-601	Raw Naphtha surge drum
SNT	Sweet Naphtha Storage Tank	EV-602	Effluent separator
ER-201	Hydrogenator	EV-603	Naphtha stripper over head separator
ER-202A/B	H2S Absorbers		

5.2 DESULPHURIZATION:

The first unit process in a petroleum refinery is the crude oil distillation unit. The overhead liquid distillate from that unit is called *virgin* or *straight-run* naphtha and that distillate is the largest source of naphtha in most petroleum refineries. The naphtha is a mixture of many different hydrocarbon compounds. It has an initial boiling point (IBP) of about 35 °C and a final boiling point (FBP) of about 200 °C, and it contains paraffins, naphthenes (cyclic paraffins) and aromatic hydrocarbons ranging from those containing 4 carbon atoms to those containing about 10 or 11 carbon atoms.

Since the sulphur content of the raw naphtha is high, the desulphurization is carried out in two stages. In the first stage - the predesulphurization section - the sulphur content is reduced to less than 10 ppm.

5.3 PREDESULPHURIZATION:

In the pre-desulphurisation process, the organic sulphur compounds are removed from the naphtha by catalytic conversion to hydrogen sulphide which is then separated from the naphtha by distillation. The hydrogenation/stripping process is included as a primary processing step in the NFCL plant to remove the bulk of the maximum 1500 wt ppm sulphur in the naphtha feed. The predesulphurisation process does not yield sufficiently low sulphur concentration in the feed to prevent poisoning of the steam naphtha reforming catalyst, thus a final desulphurisation must also be performed.

THE PROCESS

In the pre-desulphurisation section the various process steps are as follows:

- a) Oxygen removal from the raw naphtha in the deaerator, EC-601, by stripping with natural gas in order to avoid gum formation which would result in increased coking of the feed heating system and of the hydrogenation catalyst.
- b) Hydrogen from the purge gas recovery unit EL-501 or Recycle gas is added as hydrogenating gas and the mixture is heated and evaporated in feed/effluent exchanger, EE 601 A/D.
- c) After further heating in the direct fired naphtha superheater, EF-601, the mixture is sent to the hydrogenator, ER-601, where hydrogenation of sulphur compounds takes place.
- d) The reaction mixture is cooled in EE-601 A/D and the hydrogenating gas is separated from the naphtha in the effluent separator, EV-602. The major-part of the gas is recycled by means of the recycle compressor, EK-601 A/B.
- e) The liquid naphtha from EV-602 is reheated in the stripper feed pre-heater, EE- 603 and the hydrogen sulphide is removed by stripping in the naphtha stripper, EC 602. The predesulphurised naphtha is cooled in EE-603 and is sent to the final desulphurization section by the hot process naphtha pump, EP-603 A/B.

The temperature of the hydrogenation reactor is controlled by the direct fired heater and the pressure in the reactor is controlled by pressure let-down of the spent hydrogenating gas from the effluent separator.

The stripping of dissolved H₂S, H₂O and hydrogenating gas is performed in a distillation column with 20 trays operating at a pressure of 10 kg/cm²g and at temperatures between 201 deg. C and 129 deg. C in the bottom and between 129 deg. C and 84 deg. C in the top, depending on feedstock.

The column feed stream is preheated by feed/effluent heating in EE-603 and the stripper reboiler, EE 605, is heated by condensing HS steam, saturated and depressurised to 25.5 kg/cm²g.

The operating pressure of the stripper is high in order to minimize naphtha loss in the offgas from the overhead drum.

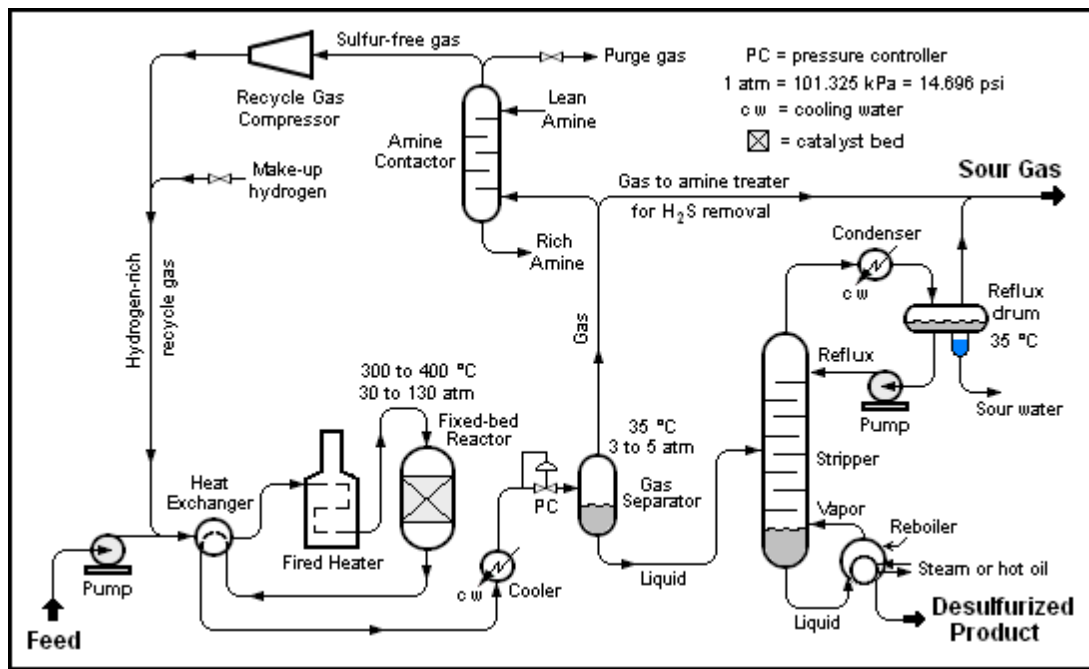
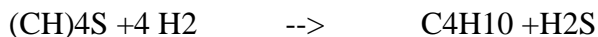
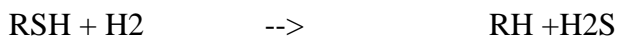


Fig.2:Sulphur removal by stripping

5.3.1 THE CATALYST:

The hydrogenator ER -601 is loaded with 15.5m³ TK-550 **cobalt molybdenum** catalyst.

It catalyses the following reactions:



(Thiophene)



etc.

Where R is a radical of hydrocarbon.

Besides the above-mentioned hydrogenation of sulphur compounds, the catalyst also hydrogenates olefines to saturated hydrocarbons and organic nitrogen compounds are to some extent converted to ammonia and saturated hydrocarbons.

CO and CO₂ shall be avoided in the hydrogenation gas during normal operation. If present, the following reactions will take place:



and in case of abnormally high content of CO, Boudouard reaction



can take place, and in this way carbon in the form of soot can deposit on the catalyst.

The catalyst has little activity for methanation at normal and high sulphur levels.

The Boudouard reaction and also the methanation reaction do not take place on the catalyst surface as the catalyst is in the sulphidized state, but Boudouard carbon may still be formed at high temperature in the feed heating system and deposit in the inlet layer of the catalyst.

The recommended operating temperature for the catalyst is about 380 deg. C. At temperatures below 330 deg. C, a poor hydrogenation will be the result and at temperatures above 400 deg. C, the tendency for polymerization and Boudouard coking on the catalyst is increased.

Hydrogen should always be present in the feed, however, operation for a few minutes without hydrogen in the feed does not harm the catalyst. Prolonged operation without hydrogen will result in coking of the catalyst to an extent where regeneration will be required.

The catalyst is delivered in the oxidized state and the most active state of the catalyst is obtained when it is sulphided.

In the sulphided state, the catalyst is pyrophoric, and it must not be exposed to air at temperatures above 70 deg. C.

The catalyst may not be exposed to hydrogen only, as the reduction which then takes place, will cause a loss in activity of the catalyst.

Notes:

While priming, the naphtha from pump discharge PI should be collected in steel buckets. Spillage on the floor should be avoided. Use of plastic containers should be avoided to avoid generation of static electricity

Use of plastic containers should be avoided to avoid generation of static electricity

5.4 FINAL DESULPHURIZATION:

The catalysts employed for the steam reforming process are extremely sensitive to sulphur compounds since these will cause deactivation or poisoning". Concentrations higher than 0.1ppm deactivate the reforming catalyst and must be avoided. The continuous leakage of sulphur to the reformer from all sources (feedstock, recycle, steam) should therefore be less than 0.1 ppm by weight relative to the hydrocarbon feed. Better operational flexibility and tolerance against upsets are obtained, however, if a smaller sulphur leakage can be achieved

The sweet naphtha from the desulphurization section will contain appreciable amounts of sulphur-bearing compounds. These should be completely removed before the steam reforming. This is done in the final desulphurization section in which a further catalytic hydrogenation of the residual organic sulphur compounds takes place followed by absorption of the hydrogen sulphide on zinc oxide. NG being used as feed is mixed with sweet naphtha prior to final desulphurisation section for removal of sulphur.

The consumption of zinc oxide is limited since the major part of the sulphur in The raw naphtha already has been removed in the predesulphurisation section.

The final desulphurization section consists of the following steps:

1. Addition of hydrogenation gas in the form of synthesis gas from the synthesis gas compressor, EK 431.
2. Heating of the feed in two steps:

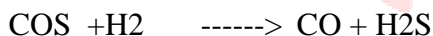
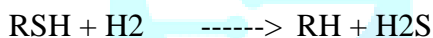
To 220°C in the steam heated feedstock preheater, EE 221, and further to 380°C in the fired feedstock superheater EF 203.

3. Hydrogenation of residual sulphur compounds in the hydrogenerator, ER 201.
4. Absorption of H₂S in the absorbers, ER 202 A/B

The H₂S absorption takes place in two ZnO containing vessels operating in series with the second vessel acting as safeguard. When the ZnO in the first vessel is spent, a break through of H₂S from the first vessel is observed. The operation will then continue with the second vessel in service, while the first vessel is being reloaded with fresh catalyst.

5.4.1 HYDROGENATION:

The catalyst in the first reactor of the final desulphurization system, ER-201 is a **cobalt-molybdenum type catalyst**. It catalyses the following reactions (similar to hydrogenation in the predesulphurisation section)



where R is a radical of hydrocarbon

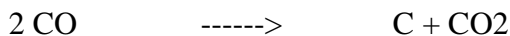
As for the predesulphurisation section the catalyst also hydrogenates olefines into saturated hydrocarbons and organic nitrogen compounds are to some extent converted to ammonia and saturated hydrocarbons.

Again CO and CO₂ shall be avoided in the hydrogenation gas during normal operation. If present, the following reactions may take place :





In the case of abnormally high content of CO₂ Boudouard reaction :



can take place, meaning that carbon in the form of soot will deposit on the catalyst. CO and CO₂ will in higher concentrations temporarily deactivate the catalysts.

No significant methanation reaction will take place because the sulphur level can be maintained at a sufficiently high level for suppressing this reaction.

The recommended operating temperature for the hydrogenation catalyst is about 380 deg.C. With fresh catalyst, lower operating temperatures may well be sufficient, whereas towards the end of the catalyst life, the temperature should be increased to the above level. At temperature above 400 deg.C, the tendency for polymerization and coking on the catalyst is increased, thus decreasing the activity.

If the catalyst gets into contact with hydrocarbons, which have not been mixed with hydrogen for more than a few minutes, the result will be poor conversion of organic sulphur compounds, giving an increased sulphur slip to the reformer. If the situation is allowed to persist, polymer formation will take place in the catalyst.

The catalyst is oxidized as delivered and obtains its maximum activity when sulphided. This maximum activity may be obtained from the very start by presulphiding of the catalyst. However, since a sufficient degree of sulphiding will be obtained during normal operation and since the catalyst volume is adequate to ensure the required efficiency of the reactor during startup, presulphiding will not be necessary.

5.4.2.SULPHUR ABSORPTION:

The catalyst in the second reactor of the desulphurization section ER-202 A/B is ZnO catalyst. Zinc oxide reacts with H₂S according to the following equation :



During normal operation, the sulphur content of the feedstock in contact with the zinc oxide catalyst is reduced according to the equilibrium constant :

$$\text{H}_2\text{S} \quad \text{-----} \quad = 2.5 \times 10^{-6} \text{ at } 380 \text{ deg.C}$$

H2O

5.5 DCS-GRAPHS:

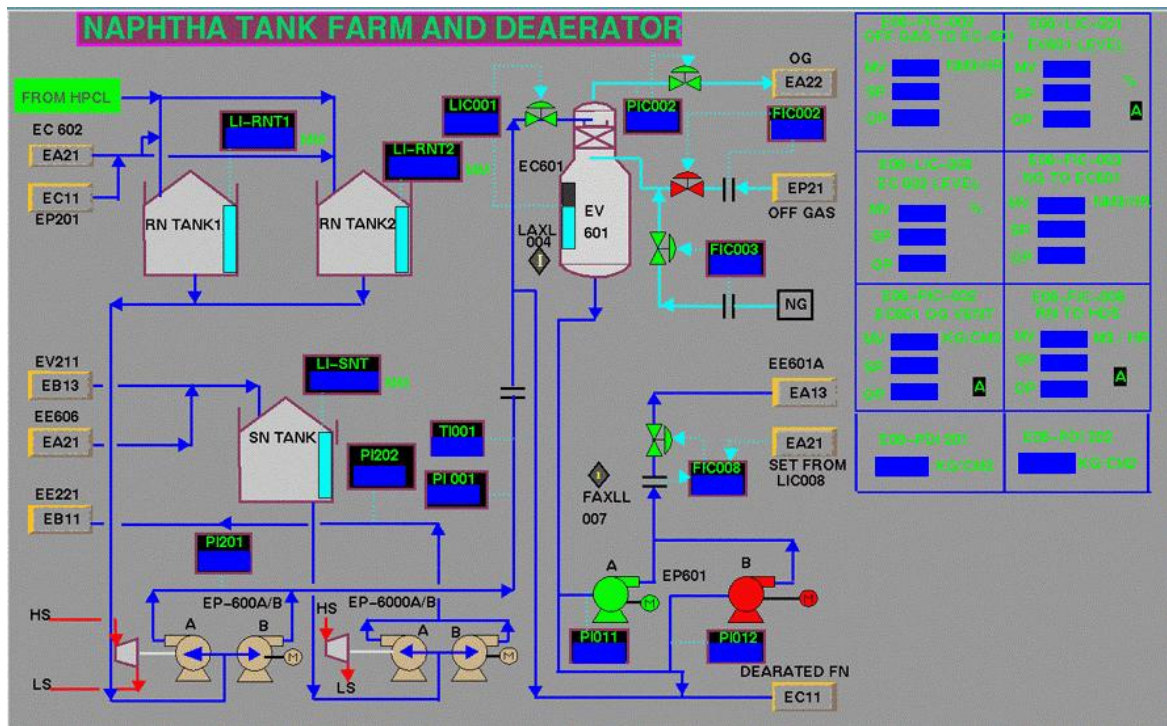


Fig.3. Naptha tank farm & Dearator

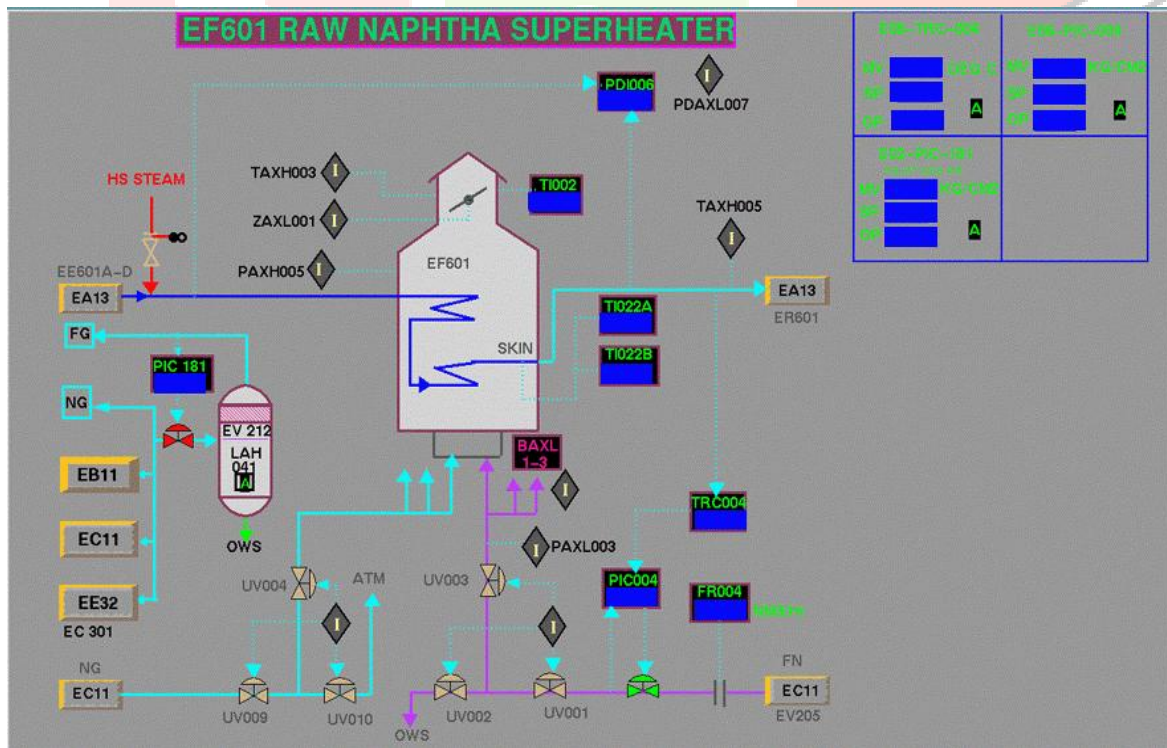


Fig.4. Naptha super heater

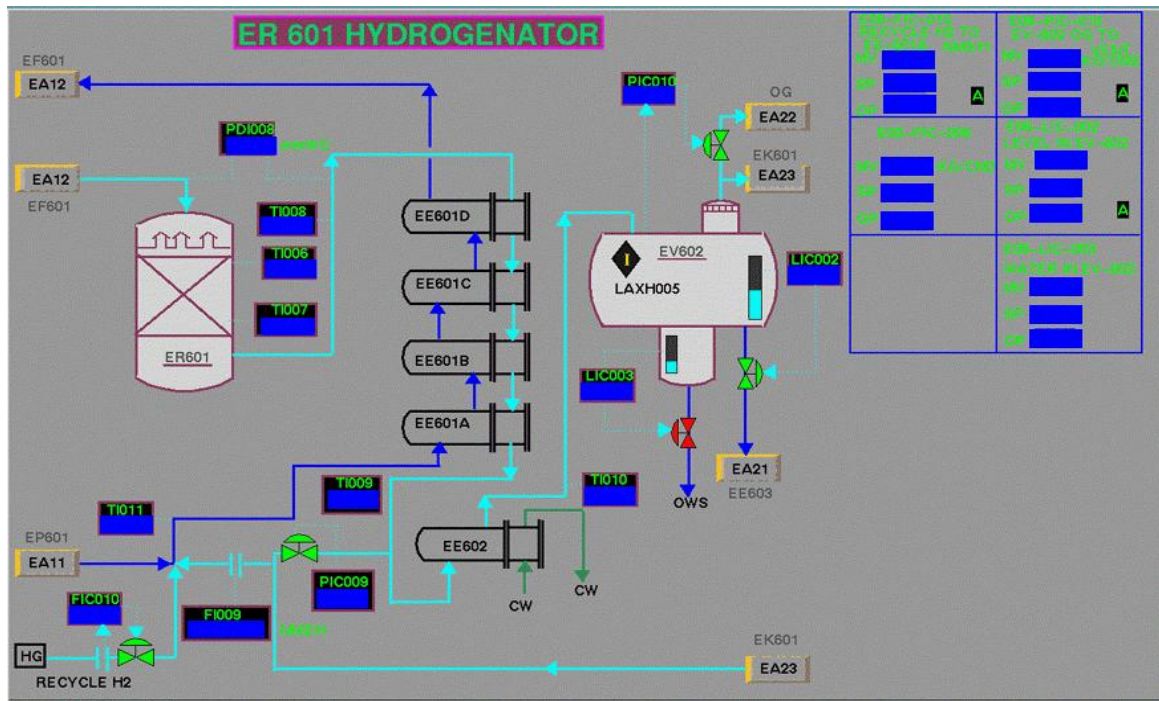


Fig.5. Hydrogenator

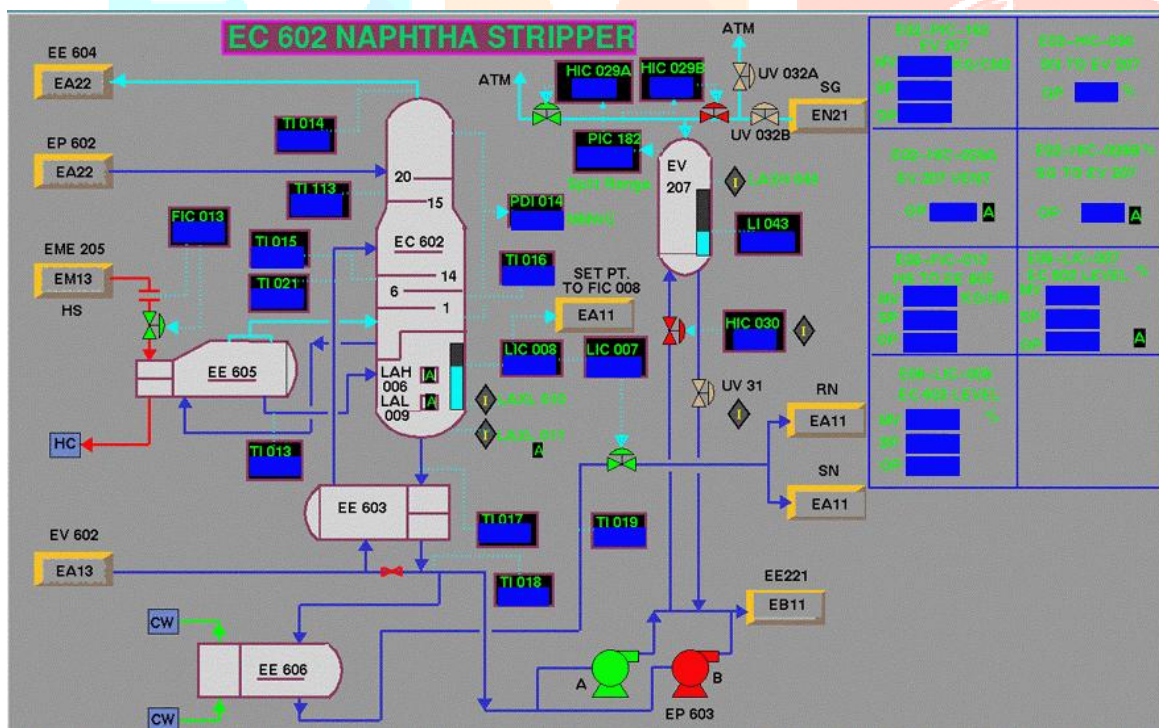


Fig:6 Naptha stripper

5.4 Equipment Details:**Naphtha stripper:**

Fluid	Design Operating conditions			Mechanical Design			
	Pressure	Temp.	Flow	Item	Material	Pressure	Temp.
	Kg/Cm ² g	°C	Kgs/hr			Kg/Cm ²	°C
Naphtha + gas	10.8	129/198	Liq=24105 Gas=147	Shell	SA 516 Gr.60	15	250
No of trays	20			Internals	AISI 304		

ER-601/201 Hydrogenator:

Fluid	Design Operating conditions			Mechanical Design			
	Pressure	Temperature	Flow	Item	Material	Pressure	Temp.
	Kg/Cm ² g	Inlet/Outlet °C	Kg/hr			Kg/Cm ² g	°C
Naphtha / Hydrogen	29	380	27049	Shell	SA387 GrII Cl - 2	39	430
Catalyst volume	15.8 m3 Topsoe TK-550			Internal	AISI-321		

CATALYSTS & ITS PERFORMANCE

6.1 H₂S Absorber ; Deatails:

Parameters	UOM	ER-202 A	ER-202 B
Catalyst	Type	KATALCOJM32-4	HTZ-3 /C7DD
Dimension	mm	2.8 - 5.0 mm Spherical granules	4mm cylinder / 3 / 16" x 1/8" tablets
Volume	m ³	10.65	3 / 7.65
Bed diameter	mm	2200	2200
Bed height	mm	2800	800 / 2000
bulk density	kg/l	1.2	1.2
Catalyst weight	Kg	12509.22	12780
Max S absorption (from Catalyst Brochure)	Kg S / 100 Kg catalyst	28.33	23.91
Max. Sulphur absorption capacity	Kg Sulphur	3544.279	3055.698

6.2 Topsoe Sulphur Absorption Catalysts HTZ:

Zinc oxide absorbent

The diverse feedstocks in use today have made variations in gas composition and concentration commonplace, and technologies that protect downstream catalysts from poisoning are increasingly important.

The HTZ-3 is a high-density zinc oxide absorbent for feedstocks with high sulfur concentrations. Proven at numerous facilities around the world, it will give your plant a cost-effective, reliable means of protecting downstream catalysts from sulfur.

Advantages

High sulfur capacity

Unmatched zinc oxide purity

Cost-effective, reliable performance

Technical specs

Size: 4 mm

Shape: Extrudate

ZnO: >99 wt%

Typical temperature range: 300–400°C

Exceptional sulfur capacity

The HTZ-3 delivers exceptional sulfur absorption thanks to its high density and a carefully designed pore structure that maximizes access to the interior of the extrudates. Optimal utilization of the extrudate mass also extends the absorbent's lifetime.

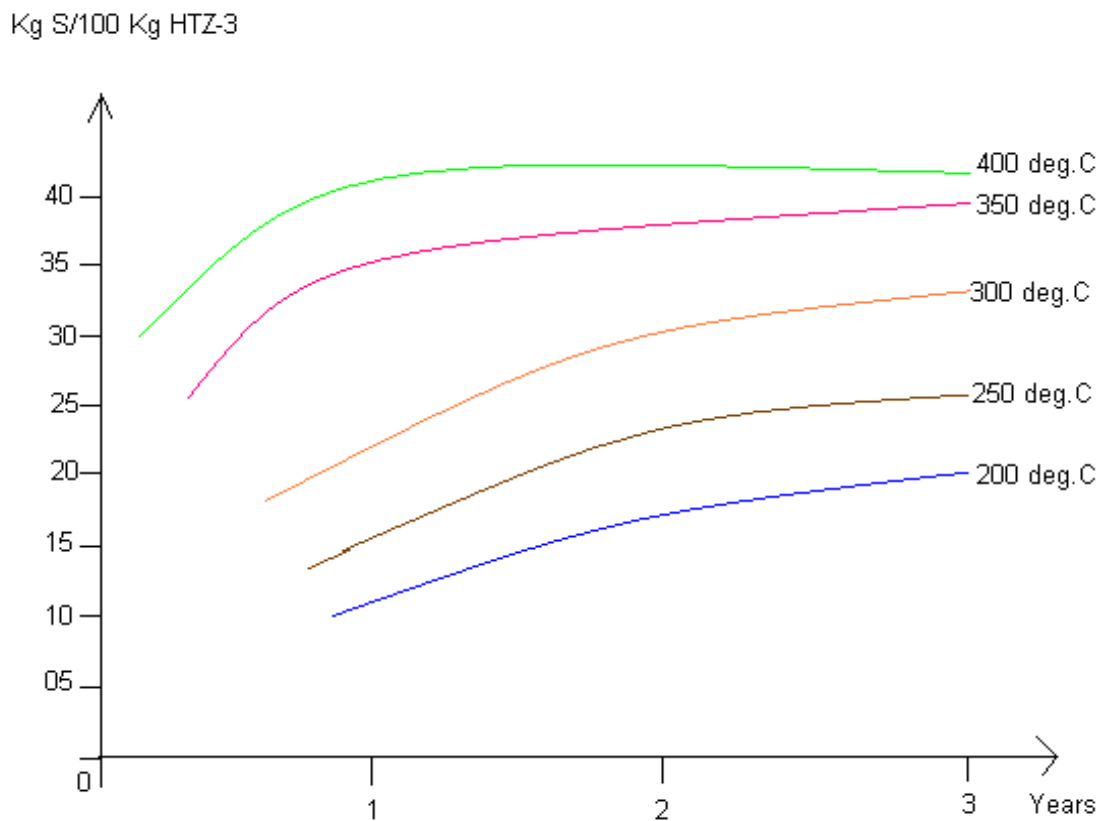


Fig:7 Zink oxide catalyst

6.2.1 Sulphur pickup-Features of HTZ-3:

HTZ-3 is Topsoe's standard sulphur absorption catalyst. HTZ-3 is characterised by its high purity (>99% of ZnO) and can absorb up to 39 KG sulphur per 100 KG catalyst. This feature has, in industrial reactors, typically extended the period between replacements by 20-40% compared with other commercial available ZnO catalysts operating at the same conditions.

Although HTZ-3 normally operates and removes H₂S, and to some extent Organic sulphur compounds, at temperatures in the range 300-400 deg.C, it can be operated at any temperature down to ambient for removal of H₂S alone. However the sulphur absorption capacity is reduced at low temperatures as shown in fig.



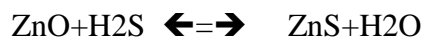
Sulphur pickup versus operating time, as a function of temperature

Fig:8 Sulphur pickup Vs Time as a function of temperature

6.2.2 EQUILIBRIUM CONSTANT:

The Sulphur Absorption Process:

In natural gas used as feed for steam reforming the sulphur conc. Must be low. Preferably below 0.05 wt. ppm. The main part of the sulphur in the gas is present as H₂S but some sulphur may be in the form of COS, RSH, CS₂, R₂S₂, R₂S reacts at ambient temperature



Where as much higher temperatures are required before the heavier sulphur compounds start reacting.

The sulphur conc. Down stream the HTZ bed is in most cases determined by the chemical equilibrium concentration for the reaction between ZnO and H₂S at the operating conditions.

The chemical equilibrium constant is equal to the ratio of the partial pressure of water vapour and hydrogen sulphide.

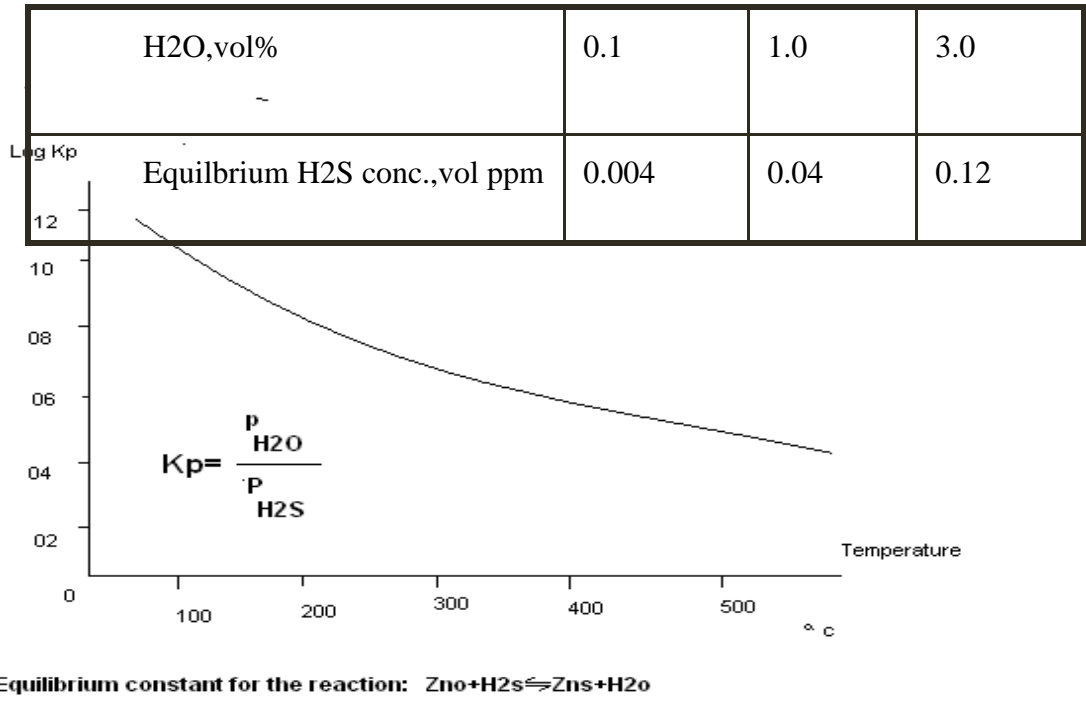


Fig: 9 Equilibrium constant for the reaction

6.2.3 Axial Sulphur profile in Zinc oxide bed:

At the inlet to Zinc oxide bed (Zone -1a) the HTZ is bulk saturated and completely converted into Zinc sulphide. Further down in the bed the HTZ has not been completely saturated and the rate of absorption in zone -1b determined by the rate of diffusion in the solid state from the surface into the interior of the material.

In Zone 2 – the main absorption front – the reaction rate is mainly determined by gas diffusion. This is much faster process which gives a sharper declining profile.

In the first part of zone 3 solid is chemisorption saturated and no chemisorption takes place there after follows the second absorption front - the chemisorption front - which extends to the end of the Zone 3 . Here the gas phase concentration has been reduced to the chemisorption equilibrium.

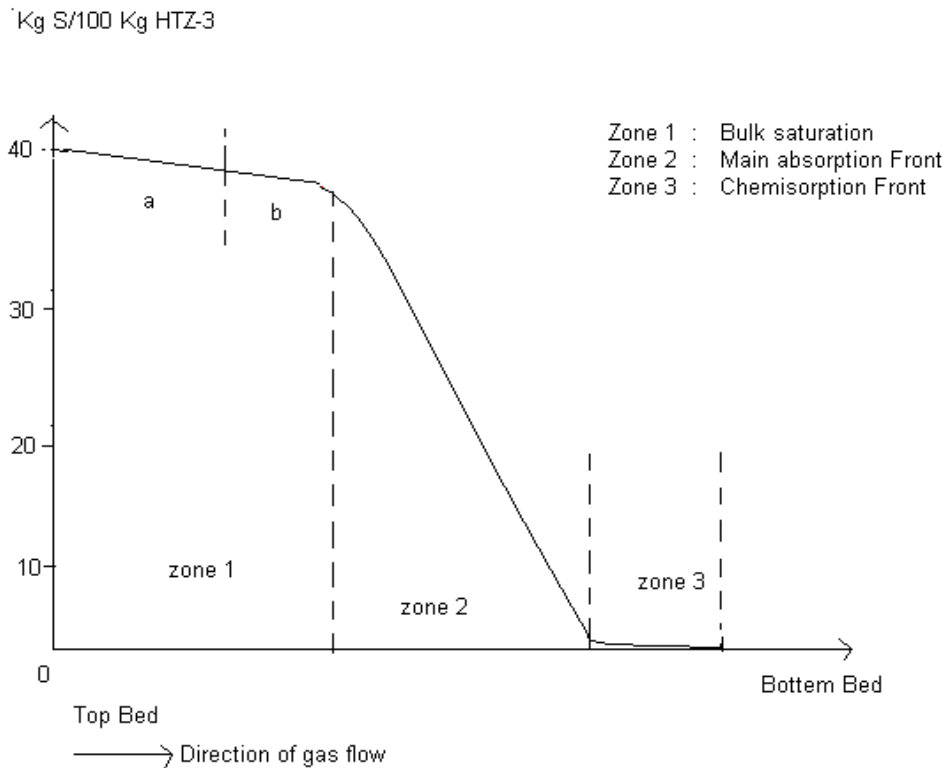


Illustration of an ideal axial sulphur profile in a zinc oxide bed, with the main absorption front in zone 2 and the chemisorption front in zone 3

Fig:10. Graph of Absorption front moves through the Zinc oxide bed

6.4 For the bed with a 2 years life time

As the time passes the absorption front moves slowly through the bed as shown in figure.

When the front reaches the outlet the sulphur conc. Downstream the the absorber starts to increase. The HTZ catalyst should be changed as soon as sulphur is detected in the exit gas.

For the bed with 70 months life time

The actual sulphur profile from an industrial HTZ – 3 bed showing in bottom figure the high sulphur pickup obtainable with HTZ- 3, even at low sulphur content in the feed gas.

The shape of the absorption front and there by the amount of ZnO left unused is influenced by the operating conditions. The length of the front also increases with increasing inlet sulphur conc., with high gas velocity and with low temperature.

Often to ZnO absorbers are operated in series in order to allow full saturation of the lead vessel prior to discharge. The two absorber could be operated in “swing operation” or with unchanged sequence, i.e., always using the downstream vessel as a cleanup guard.

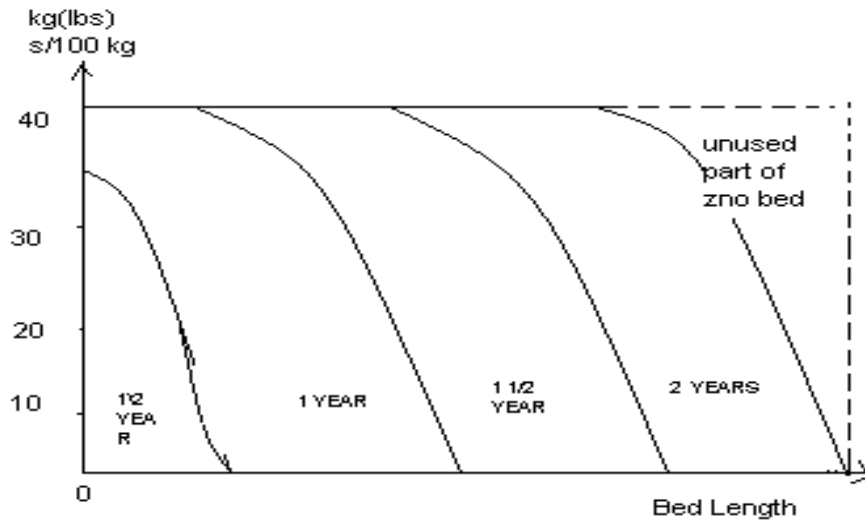
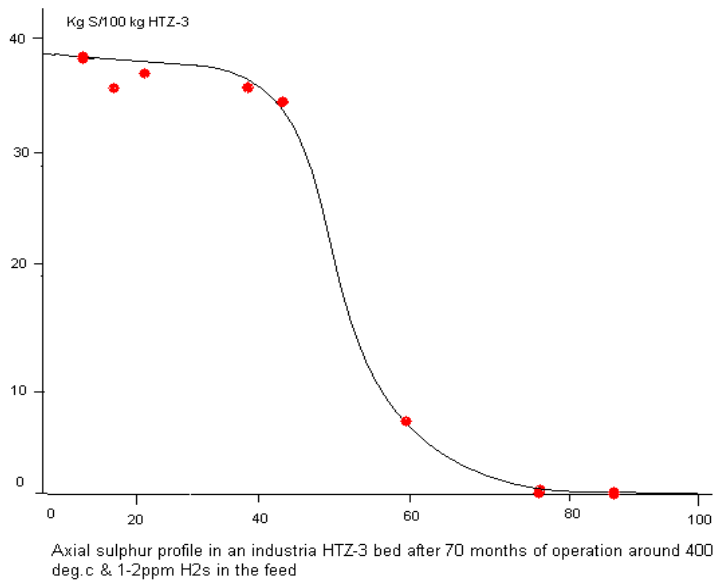


Fig:11. Graph of Absorption front moves through the Zinc oxide



bed

Fig:12. Graph of Absorption front moves through the Zinc oxide bed

CASE STUDIES

7.1CASE STUDY.1:

PREDESULPHURISATION BLOCK DIAGRAM WITH MODIFICATION

After commissioning the stripper performance was very bad due to low temperature in Stripper, so that Pre desulphurization section outlet sulphur slip was not reduced to design value. After inspection of tower found normal, but reboiler weir (liquid level plate) was missed, so that low residence time in the reboiler so that insufficient heat transfer resulted in poor stripper performance. Then a modification is planned with a team of NFCL, Kakinada as mentioned below. Later it was observed that stripper bottom temperatures lower side due to low residence time in reboiler.

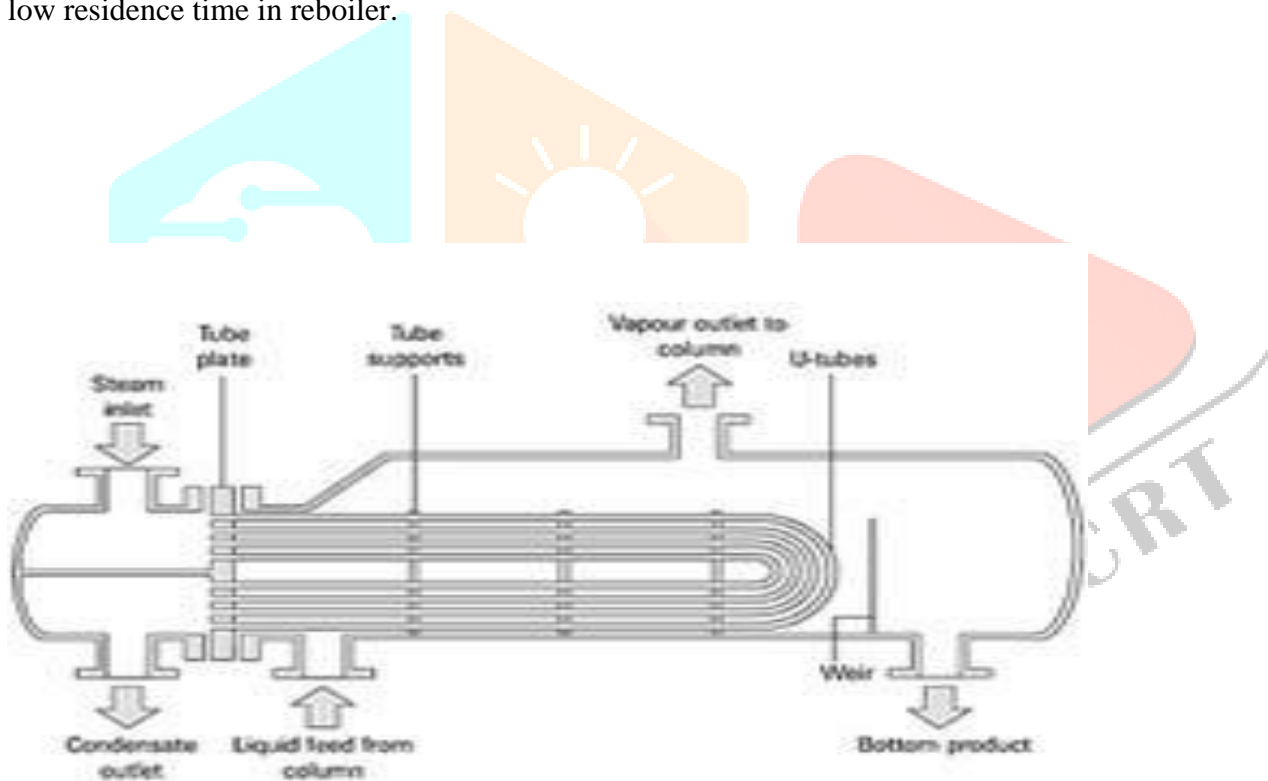


Fig:13 Reboiler

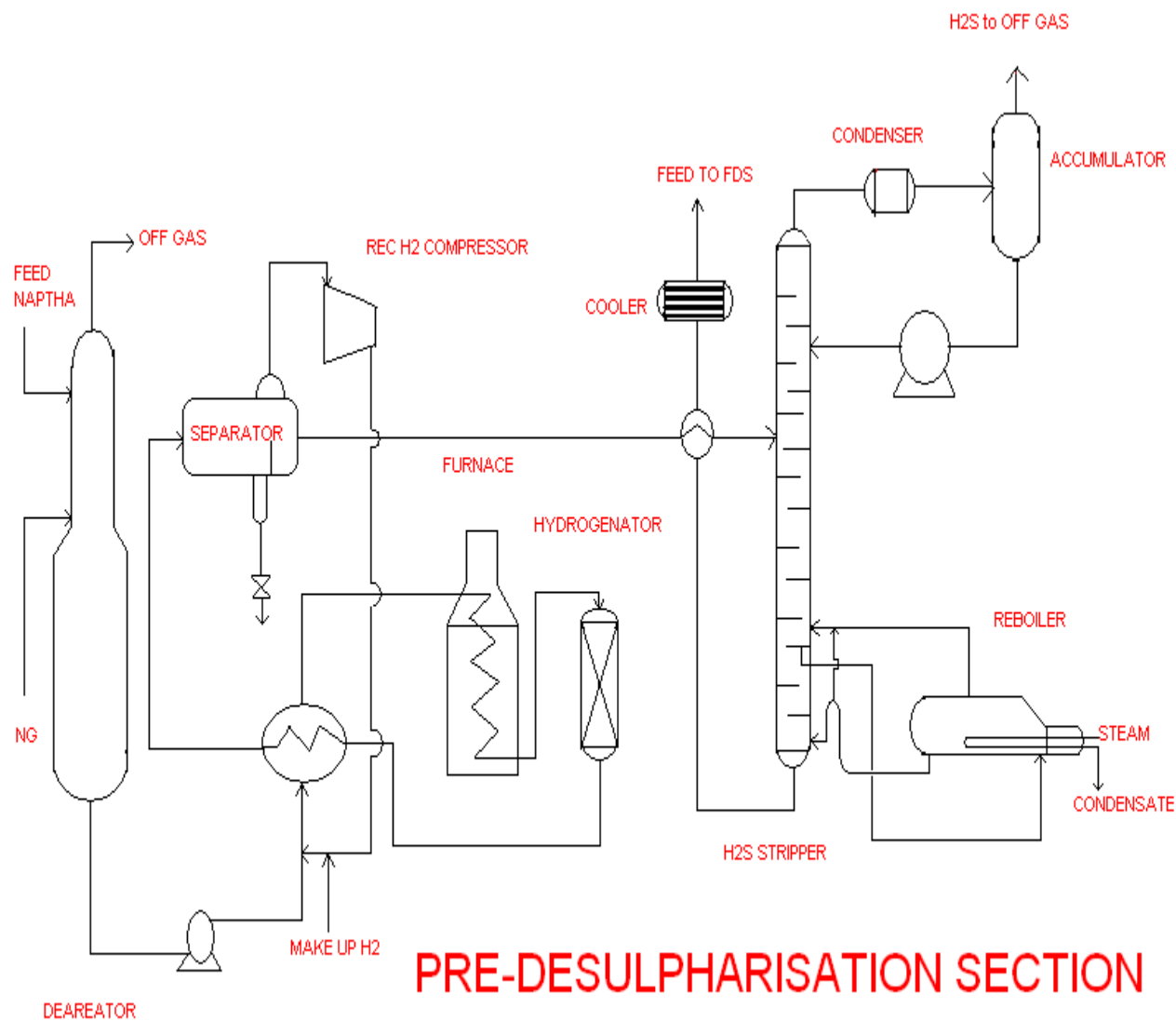


Fig.14:Predesulphurisation-with modification

Modification:

To increase the temperatures in stripper, So reboiler liq o/l line was modified with inverted “U” bend to increase residence time in the reboiler such that stripper temperatures will increase. After start up the stripper performance was found good.

7.2.CASE STUDY-2:**REPORT ON PRE-REFORMER (ER-206) CATALYST FAILURE IN
AMMONIA PLANT- 2**

In the night shift of June 30, 2004, the pre-reformer reactor (ER-206) process gas sampled at the first sample point located at 42% bed depth analyzed a C6+ of 0.73 % against the normal value of less than 40ppm. Also the Z70/Z90 plots which approximately indicate the % depth of the catalyst bed at which the reaction is complete, showed a steep increase from 26% to 54% between June 21 and July 01, 2004. We immediately contacted Haldor Topsoe, Denmark with the pertinent details. In their response HTAS suspected serious poisoning of the catalyst probably due to sulfur. We pulled out feed naphtha from the pre-reformer in the after noon of July 5, 2004 and ran on only NG feed albeit on low load. We reintroduced naphtha in the afternoon of July 27, 2004 after decontaminating the RN tank #2 and SN tank and ensuring that the NVM (Non volatile matter) values of naphtha in the tanks were at acceptable levels. What follows is a detailed account of the events that took place, study and analyses done by various agencies, sources of contamination, the cause and corrective & preventive actions taken.

1.0 Basic details of ER-206 Catalyst bed

Name of the catalyst	: RKNGR Pre-Reformer Catalyst
Catalyst form	: 4.5 mm x 4.5 mm cylinders
Name of the supplier	: HTAS, Denmark
Catalyst Volume	: 19.15 m ³
Bed Dimensions	: 3200 mm (dia) x 2400 mm (high)

2.0 History:

The first charge of Pre-Reformer catalyst supplied by HTAS had been in service since commissioning (Mar1998) and became due for change out in 2003. The plant was operated either on full NG or full naphtha mode since commissioning to July 1999. From July 1999, the plant has been being operated on mixed feed mode of varying Natural Gas & Naphtha proportions. The catalyst performance was being monitored, by plotting Z90/Z70 curve as recommended by HTAS. The catalyst became due for change towards end 2003 and Sweet Naphtha load was restricted to 5 Te/hr to extend the catalyst life till PTA 2004. During March 2004,

approximately 1.95 meters of top portion of the catalyst was unloaded under nitrogen atmosphere and 15.0 m³ of fresh catalyst was loaded leaving the old 4.15 M³ at the bottom in consultation with HTAS. This 2nd charge of catalyst has been in service since end March 2004.

After PTA 2004, Pre-reformer was being operated at a Sweet Naphtha load of ~15 Te/hr till third week of June '04 due to low NG availability and restriction on availability of Naphtha. After 24th June, Sweet Naphtha load was increased to ~19.8 Te/hr due to enhanced availability of Naphtha, shortage of NG and fouling of Fuel Naphtha Vaporizers (EE-212 A/B).

3.0 Incident

C₂₊ and C₆₊, higher hydrocarbon in the gas from 1st sample point of ER-206 is monitored by laboratory once a week and was found to be <40 ppm till June 23, 2004. On 30th June night, during scheduled sampling laboratory reported a higher slip of 0.73%, C₆ exit 1st bed of ER-206. Catalyst temperature and process gas analysis data were collected and the problem was immediately referred to HTAS on 1st July. Catalyst bed temperature profile and Z70 curve were checked by Process section on 2nd July and found that the activity got shifted to ~54% of the catalyst bed from 26% and the deterioration had commenced from 21st June 2004. HTAS are of the opinion that severe poisoning of the catalyst is taking place, most probably due to sulphur and requested us to identify the source. We also contacted M/s Johnson Matthey and M/s Sud-Chemie who indicated that the deactivation of the catalyst could be due to poisoning, coke formation, sintering or polymerization. But none of the catalyst manufacturers recommended immediate isolation of Sweet Naphtha feedstock.

4.0 Activities after the incident

4.1 As a precautionary measure the following actions were initiated on 2nd July 2004:

- * Sweet naphtha load to ER-206 was reduced from ~16 Te/hr to 8.0 Te/hr
- * Recycle Hydrogen / Naphtha ratio was increased from 0.25 to 0.35
- * Steam / Carbon ratio was increased from 3.5 to 3.7
- * Recycle hydrogen header drains near FV-11/FV-36 were checked for oil/condensate and found to be nil.
- * First Zinc oxide bed (ER-202A) by pass valve was checked for passing and found to be in closed condition

4.2 On 3.7.2004, as recommended by Sud-Chemie, operating conditions like, ER-206 inlet temperature, Steam-Carbon ratio and Recycle Hydrogen ratios were varied one after another to see the effect on catalyst performance.

ER-206 inlet temperature	S/C ratio	Recycle H ₂ /HC ratio	C ₂ + exit ER-206 1 st bed	C ₆ exit ER-206 1 st bed	C ₆ exit ER-206
500	3.5	0.25	1.56	0.64	<40
500	3.5	0.50	1.43	0.56	139
500	3.8	0.25	2.36	1.26	<40
505	3.5	0.25	2.0	1.03	<40
510	3.5	0.25	1.82	0.89	<40
510	3.5	0.5	1.55	0.72	<40
510	3.8	0.5	1.63	0.79	<40

4.3 On 4.7.2004, it was decided to keep the Pre-Reformer running with 8 Te/hr of Sweet Naphtha and 17800 NM³/hr of NG with S/C ratio of 3.8 and H₂/HC ratio of 0.7 and Pre-reformer inlet temperature of 510 °C.

4.4 Mr. Alok Verma from HTAS, New Delhi visited the plant on our request and reiterated the opinion of HTAS, Denmark on deactivation of catalyst. On 5.7.2004, Sweet Naphtha feed was totally cut off and NG flow was increased to 26000 NM³/hr to see the effect on catalyst bed with Natural Gas alone as feed.

4.5 On 6.7.2004, discussions were held with representatives from HPCL and the serious damages caused by the poor quality of naphtha was strongly represented. The following action plans were proposed to HPCL:

- * No further consignment of contaminated Naphtha will be accepted from the available stock at Rajamundry and Kakinada terminals.
- * Contaminated naphtha stock at NFCL tanks to be replaced by HPCL with fresh stock of good quality of Naphtha (NVM less than 2mg/100ml).
- * Test certificates are to be sent in advance and naphtha samples will also be analyzed by NFCL before acceptance. HPCL would commence pumping naphtha only on clearance from NFCL who would check the quality of naphtha in their own laboratory.

4.6 Mr. Mads Feddersen of HTAS, Denmark rushed to Kakinada and stayed here on 7th, 8th and 9th July. The sequence of events and possible causes of deactivation were discussed at length. According to HTAS, the catalyst deactivation could be either due to sulphur poisoning or gum formation. HTAS requested NFCL to send sample of deactivated catalyst to identify the exact cause of failure and recommended to replace ~8-10 m³ of catalyst. At the top.

4.7 Based on discussions with Mr. R.S. Nanda (D&COO) on 6th July and with Mr. S. Stalin (ED) between 8th and 10th July, the following action plans have been finalized:

- a) Monitoring of critical operating parameters and reporting of deviations to be strengthened and systematized.
- b) Quality Plan to be reviewed and enforced strictly.
- a) More vigilance and seriousness to be brought into the systems and practices.
- b) All personnel to be trained/retrained on importance, effects and analysis of plant data.
- c) Third party analysis of the naphtha to be done to reconfirm the accuracy of our own analysis.
- d) Information to be gathered from other fertilizer units about their experience with Pre-Reformer catalyst.
- e) Present stock of naphtha to be returned to HPCL and/or used as fuel till receipt of fresh consignment of good naphtha.
- f) To minimize loss of production, LSHS firing to be resorted to in auxiliary boilers thereby utilizing the NG released from auxiliary boilers in Ammonia plant-2 as feed. LSHS firing was started in the auxiliary boilers on July 11, 2004.
- g) Shutdown planning to be finalized for ER-206 catalyst changing.
- h) Action to be initiated for procurement and replacement of Pre-reformer catalyst.
- i) On receipt of fresh naphtha, Sweet Naphtha feed to be reintroduced again to Pre-reformer and the performance of the catalyst to be monitored closely. Based on the performance, schedule for replacement of catalyst should be finalized.

5.0 Analysis of possible sources for catalyst poisoning / deactivation / deterioration:

In our plant, the following are the possible sources for catalyst poisoning/deactivation:

1. Poisoning or deterioration during plant trips/upsets
2. Contamination through naphtha due to Sulphur, heavy metals, Chlorides and gum forming compounds
3. Slippage of sulphur from Final De-sulphurisation section

4. Contamination through process steam/steam from condensate stripper (GV chemicals, chlorides, silica)
5. Contamination through Recycle hydrogen
6. Contamination through NG

5.1 Poisoning or deterioration during plant trips/upset

The catalyst has been in service since end-March 2004 and there was no trip of Reformer since then.

The production interruptions since April 2004 are detailed below:

	Date	Nature of interruption	Cause of interruption
A	3.5.2004	Stoppage of EK-431 (Syn gas compressor) due to entry of seal oil into compressor	Malfunction of LT-382 (LP seal oil overhead tank level controller)
B	8.5.2004	Trip of PGRU (Purge Gas Recovery Unit)	“Pausing” of adsorber cycle during cooling step
C	10.6.2004	Stoppage of Backend	To attend EP-302A semi-lean pump in CO ₂ removal section discharge isolation bypass line weld failure
D	23.6.2004	Trip of Methanator	False activation of high temperature switch

A) On 03.05.2004, EK-431, Synthesis Gas Compressor was tripped due to LT-382 malfunction resulting in ingress of seal oil into process gas side and drop in lube oil console level. During the upset, there existed the possibility of oil entry into the reformer loop through Recycle Hydrogen line. After tripping the compressor, during restart-up, Recycle Hydrogen was lined up initially from Ammonia-1. During start up all the lines were drained and there were no signs of oil entry into the process. There was no sign of Pre-Reformer catalyst deterioration after the incident.

B) On 08.05.2004, during trip of PGRU there was no upset in reformer conditions.

C) On 10.06.2004, as the stoppage of backend was planned and executed slowly, there was no upset in reformer operating conditions.

D) During the trip of Methanator on 23.06.2004, there was a delay of 5 minutes, before recycle hydrogen from Ammonia-1 could be lined up. This could affect the performance of Final De-sulphurisation and Pre-reformer catalyst. However, as per Z90/Z70 curve, the deactivation of the catalyst started before the incident, i.e. on 21st June.

5.2 Contamination through Naphtha

Since commissioning, we have been getting Naphtha of good quality with less Sulphur. HPCL terminal due to logistic reasons gets Naphtha from Tatipaka refinery and Vizag refinery through road tankers and at times through ship in case of large quantities.

On 18.06.2004 one consignment of 17000 MT Naphtha was received from Vizag refinery through ship. According to the test certificate dated 9.6.2004 submitted by HPCL prior to the pumping, the quality parameters were within limits. However, on analyzing in NFCL laboratory major deviations, as detailed below, were noticed in the sulphur content and NVM/ROE.

Source	S', ppm	NVM, mg/100 ml	ROE, mg/100 ml
Test certificate from HPCL	50	1.4	1.2
Analysis as per NFCL Laboratory	60	1.59	
Earlier consignments as per NFCL lab	30-93	3-10	

The discrepancy was reported to HPCL on 19th June. Since we were having very low stock of naphtha, we had no option and started using the same since 04:45 hrs of 19.6.2004. Moreover, the impact of high ROE on the reformer catalyst was underestimated due to insufficient knowledge.

Since the effect of NVM/ROE on pre-reformer catalysts is not known, as a precautionary measure steam/carbon ratio was increased from 3.5 to 3.6 on 19.6.2004. No visible problems were noticed other than faster choking of Fuel Naphtha vaporizers (EE-212A/B). Compared to earlier occasions, the deposit on EE-212 bundle was loose and easy to remove.

Steam/Carbon ratio was normalized to 3.5 on 22.6.2004, as per instructions, to optimize energy.

5.3 Slippage of sulphur from Final De-sulphurisation section

ZnO beds of Final De-sulphurisation section was unloaded and reloaded as detailed below during PTA 2004:

ER-202A: 1.5 m³ of fresh Chloride guard on top followed by 1.6 m³ of old HTZ3 catalyst from ER-202A and 7.5 m³ of old HTZ3 catalyst from ER-202B.

ER-202B: 3.1 m³ of old HTZ3 from ER-202B on top followed by 5.5 m³ of fresh C7-6 catalyst from Sud-Chemie and 2.0 m³ of fresh Deep De-sulphuriser Catalyst.

Sulphur at the out let of Pre Desulphurisation and Final Desulphurisation sections was being continuously monitored. The results of Sulphur analysis were well within the limits (<0.05 ppm) eliminating the possibility of poisoning due to Sulphur from Final Desulphurisation section.

5.4 Contamination through process steam / steam from condensate stripper

Steam condensate of HS steam and steam exit of Process Condensate stripper were analyzed for 'S' and found to be free of sulphur.

5.5 Contamination through Recycle hydrogen

Recycle hydrogen from Synthesis gas compressor (EK-431) was analyzed for oil and sulphur. Oil was found to be <5 mg/m³ and 'S' less than 0.01 ppm.

5.6 Contamination through NG

The sulphur content in Natural gas remained to be <2 PPM all through and sulfur exit Final Desulphurisation section was <0.05 ppm.

Exact cause of deactivation of Pre-Reformer catalyst could not be established from the then available data/information.

6.0 Analysis of Naphtha quality

6.1 Analysis of Naphtha by external laboratory

As part of investigation, Naphtha samples were sent to Andhra Petrochemicals Limited, Chennai Petroleum Corporation Limited, Sri Ram Test House and HTAS.

Parameter	Unit	Andhra Petrochemicals Ltd.		Chennai Petroleum Corp.		Sri Ram Test House
		Raw Naphtha	Sweet Naphtha	Raw Naphtha	Sweet Naphtha	
Density at 15 °C	g/ml	0.730	0.7250	0.734	0.7212	Results awaited
Total Sulphur	ppm w/w	240	0.375	90	37	- do -
Non-volatile matter	mg/100 ml at 100 °C	60.1	80			- do -
Residue on evaporation	mg/100 ml at 140 °C	15.9	17	4.2	5.8	- do -
Initial Boiling point	°C	46	46	48.4	46.3	- do -
Final boiling point	°C	156	156	170.3	169.5	- do -

The analysis report from APL is matching with our laboratory reports. CPCL have reported high sulphur in the sweet naphtha sample. On enquiry, CPCL have confirmed that the sensitivity of the equipment is min 30 ppm. Hence the Sulphur analysis result for Sweet Naphtha are not reliable.

6.2 Analysis of Naphtha and investigation by HTAS

HTAS have analyzed samples of Raw Naphtha, Sweet Naphtha exit Pre-Desulphurisation section and Sweet Naphtha feed to Pre-Reformer. According to HTAS, naphtha samples were indicating the presence of heavier sulphur compounds such as Dibenzothiophenes and the deactivation of Pre-reformer catalyst could only be due to heavier sulphur compounds, which could not be removed in both the Desulfurizer sections.

HTAS have also informed that, the heavier sulphur compounds such as Dibenzothiophenes are more difficult to hydrogenate and hence will pass unconverted through normal Desulphurisation section. The Dibenzothiophenes are likely to be present in the ROE since it has higher boiling point range. More

importantly, the presence of heavier sulphur compounds cannot be detected by 'Raney Nickel method' since the method detects hydrogenated organic sulphur as H_2S . This is the analytical method being used by almost all units.

7.0 Experience of other fertilizer units

We have contacted a few fertilizer units in India as well as Refineries/ Petrochemical companies operating hydrogen units that employ pre-reforming catalyst to know their experience with Pre-Reformer catalyst.

IFFCO, Kalol informed that they too faced deactivation of the Sud-Chemie, India supplied pre-reformer catalyst due to sulfur poisoning.

IOCL-Barauni and IOCL-Panipat who are using the same HTAS pre-reformer catalyst informed that their experience is satisfactory.

Andhra Petrochemicals, Vizag who are using Johnson Matthey pre-reforming catalyst and used the same consignment of naphtha as NFCL supplied by HPCL informed that their NVM value was also high in the naphtha (but considerably lower than that reported by NFCL). But their problems were confined only to Naphtha vaporizer and did not spread upto Pre-reformer.

Similarly Asian Peroxides, Sullerpet, TN also received the naphtha from HPCL at the same time as NFCL. Their NVM values were also similar to those of APL, Vizag. Asian Peroxides do not have a pre-reformer but direct primary reformer. They blended this naphtha with good naphtha to lessen its impact. So they too did not face any problem. They also receive naphtha from IOCL.

A Korean Refinery experienced deactivation of HTAS pre-reforming catalyst in their hydrogen plant due to gum formation a decade ago. The failure was attributed to presence of high content of olefins and lower operating temperature. They invoked the performance guarantee clause on HTAS and replaced their catalyst.

8.0 Meeting with HPCL for Quality assurance of Naphtha.

A meeting was held with senior representatives from HPCL that included both technical and marketing divisions on July 22,2004 at Kakinada in which our ED also participated and impact of naphtha quality on ammonia production, critical quality parameters, quality assurance plan etc were mutually discussed and agreed upon. The discussions were minuted and return of the signed MOM copy from HPCL is awaited.

9.0 Decontamination of Naphtha tanks and Reintroduction of Sweet Naphtha feed

While the plant was operating on Natural gas feed, steps were taken to decontaminate the naphtha tanks. Major portion of naphtha with high ROE was returned to HPCL and the same was replenished with fresh stock of good naphtha. Fresh naphtha was received only in Raw Naphtha Tank-2 and the naphtha was used as fuel till the ROE dropped to normal value (less than 6 mg/100ml). Sweet Naphtha Tank was emptied to Raw Naphtha Tank-1. Pre-Desulphurisation section was started with good quality naphtha on 26th July to fill Sweet Naphtha Tank. During receipt of naphtha to RNT-2, naphtha from RNT-1 was used only as fuel.

Sweet Naphtha feed was introduced on 27th July in presence of Mr. Raman Sondhi of HTAS, New Delhi and stabilized at 8.0 Te/hr of feed rate. Even though sweet naphtha was with a ROE of <5.0-mg/100 ml, higher ROE was reported at the exit of ER-201 (CoMoX Hydrogenator) and ER-202A/B (Zinc oxide beds). ER-206 bed profile was identical to the earlier trend. With continued operation, the ROE values began dropping slowly. We contacted HTAS who opined that the high boiling point ROE in the naphtha might be chromatographing through the catalyst bed. This meant that some of the ROE hydrocarbons may have accumulated in the catalyst beds, when operating on naphtha with high ROE and getting slowly released when good quality naphtha is processed.

The operation of the Ammonia plant continued with naphtha at a constant rate of 8 MTPH as advised by HTAS till the night shift of Aug 4, 2004 when A2 and U2 plants shut down had to be taken to attend to a few jobs. During this entire period the performance of the pre-reformer catalyst remained stable. There was only a marginal shift of about 2% (i.e. from 52 % to 54 %) in the Z 70/90 plots compared to the time when naphtha was taken out on July5, 2004. This shows that deactivation rate is normal. The operating data were sent daily to HTAS and their comments and suggestions were sought.

The four sample points in the pre-reformer bed, which were connected to a common manifold, were segregated to facilitate independent sampling. This is to avoid any possibility of valve passing and thus affecting the accuracy of the analyses. The samples from each point are being drawn at regular intervals. On Aug 2, 2004 HTAS advised us to increase the feed naphtha rates to achieve desired level of Urea production.

Presently sweet naphtha stock is being built up and the ammonia plant which was restarted on July 6, is being run at low rate on only feed NG awaiting the start up of Urea plant –2 to avoid further ammonia inventory build-up which is already high in the storage.

Upon restart up of the Urea plant –2 the naphtha rate would be gradually increased to about 15 MTPH to sustain an overall complex urea production of 4100 MTPD. The performance of the pre-reformer catalyst would be continued to be monitored and the residual life assessed for timely procurement of the required fresh catalyst charge in consultation with HTAS. Also as on date the RNTK#1 is containing about 950 MTPD naphtha with a NVM of 10.5 mg/100ml. A fresh parcel of about 1350 MT of good naphtha from HPCL would be taken into this tank to bring down the NVM value to 6mg/100ml or less. With this the decontamination of RNTK#1 would also be complete.

10.0 Effect on CoMoX catalyst in the Desulfurization sections

We have contacted Sud-Chemie and John Matthey to know what effect the high ROE naphtha could have had on CoMoX catalysts in the Desulfurization sections. While the reply from Johnson Matthey is awaited, Sud-Chemie informed that if no increase in the pressure drop and also with the normal naphtha run no sulfur slips are seen, then it could be assumed that no significant damage has occurred to CoMoX beds. In our case no increase in pressure drop was seen and also the sulfur slips remained as before. Hence it appears that the CoMoX beds are not significantly affected. However, the performance of these beds will be continued to be watched.

11.0 What was missed?

1. There was a major deviation in the Naphtha quality of the consignment received on 18th June from HPCL w.r.t NVM / ROE as stated in the test certificate from HPCL and as analyzed in our laboratory. The discrepancy was reported to HPCL on 19th June. But the consignment of naphtha was not rejected by NFCL.
2. Even though the effect of NVM/ROE on Pre-reformer catalysts/process is not known, the matter was not referred to HTAS immediately. So to say, its impact was under estimated.
3. Though there was a doubt on the effect of ROE on the process/catalysts, no action was initiated to increase the frequency of analysis, monitoring of temperature profile of catalyst beds and plotting of Z90/Z70 curves.

4. On 20th June, Sweet Naphtha exit Pre-Desulphurisation and Final Desulphurisation sections were analyzed for NVM and found to be 130 mg/100ml and 140 mg/100 ml respectively. The analysis report was informed to all concerned. But no action was initiated to identify the effect on catalyst/process.
5. In spite of the fact that temperature profile of ER-206 catalyst bed varies due to frequent changes in the feed mixture, operation personnel could have still noticed the shift in the active temperature spot of the catalyst bed between June 21 and July1.
6. On 23rd June, slight increase in C6+ slip in the first bed exit gas was noticed by the laboratory. But this was not reported or highlighted to the concerned. The deviation was neglected as analytical error due to fluctuations in the plant load. No action was initiated to repeat the analysis after stabilization of the plant.
7. Even though C6+ slip was analyzed and reported to be high on 30th night, the matter was not immediately referred/highlighted to the concerned.
8. On 1st July, the operating data were collected by operations and sent to Process for plotting temperature profile and Z90/Z70 curves. The operating data was sent to HTAS. Interpretation of the operating data, plotting of temperature profiles and Z90/Z70 curves were done on 2nd July and no corrective actions were initiated till reply from HTAS was received.
9. Though HTAS suspected excessive poisoning of the catalyst, the Naphtha feed was not taken out completely. The Naphtha feed was reduced to 8 Te/hr and was totally cut off only on 5th evening on recommendation of HTAS representative.

CONCLUSION

8.1 General

1. Quality Plan for raw materials, in-process materials and final products, etc should be reviewed and enforced strictly.
2. Monitoring of critical operating parameters and reporting of deviations to be strengthened and systematized.
3. More importance / attention to be paid to deviations in process parameters and maintenance problems.

4. More vigilance and seriousness to brought into the systems and practices.
5. All personnel to be trained/retrained on importance, effects and analysis of plant data.

8.2 Specific to Pre-Reformer

1. Raw Naphtha quality should be analyzed before receipt from HPCL. Any off-spec quality naphtha should be rejected summarily.
2. Temperature profile across ER-601 and ER-201 Hydrogenator beds should be monitored closely. Increase in bed temperature across the catalyst bed is an indication of hydrogenation of olefins and higher unsaturated hydrocarbons. In case of increase in delta T, recycle hydrogen flow should be increased followed by reduction in naphtha feed.
3. Higher Hydrogen/hydrocarbon ratio to be maintained during mixed feed/full feed operations to prevent gum formation on Pre-reformer catalyst bed.
4. Catalyst bed temperature profile should be monitored for all reactors and any deviation should be analysed immediately.
5. Laboratory instruments should be made available for analysis of 'S' at ppb (parts per billion) level.

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