Reduction of Sulphur in Superior Kerosene

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Abstract-- ***Superior kerosene is one of the products produced from crude oil distillation. The sulphur present in superior kerosene makes it harmful to environment because it releases SO_x gases during combustion. Our objective is to bring down the sulphur content to ultra minimum level (10ppm) and to redesign the equipments for $80m^3$/hr feed. The sulphur is removed by hydrodesulphurisation process using Cobalt-molybdenum catalyst. This report mainly focuses on the fixed bed reactor, where the height of reactor and catalyst bed are increased.***

Keywords--- ***Superior Kerosene, Hydrodesulphurization, Cobalt-Molybdenum Catalyst, Fixed Bed Reactor, Ergun equation.***

I. INTRODUCTION

Kerosene, also known as paraffin, lamp oil, and coal oil (an obsolete term), is a combustible hydrocarbon liquid which is derived from petroleum, widely used as a fuel in industry as well as households. Its name derives from Greek (keross) meaning Wax, and was registered as a trademark by Canadian geologist and inventor Abraham Gesner in 1854 before evolving into a generalized trademark.Kerosene's are distillate fractions of crude oil in the boiling range of 150-250°C. They are treated mainly for reducing aromatic content to increase their smoke point (height of a smokeless flame) and hydro fining to reduce sulphur content and to improve odour, colour & burning qualities.

Kerosene from atmospheric distillation unit is processed, where aromatic compounds are extracted from kerosene and Linear Alkyl Benzene (LAB) is produced and sent to various industries. The kerosene without aromatic compounds is sent back to the plant, this is called as superior kerosene.

General chemical properties:

PROPERTY	SUPERIOR KEROSENE	SULPHUR	NAPHTHA	HYDROGEN	HYDROGEN SULPHIDE
Boiling point (°C)	150-275	444.6	35-200	-253	-60.33
Liquid Density (kg/m^3)	810	2070	740	42.8	993
Viscosity (Pas)	0.00164	-	0.009	8.4×10^{-6}	8.8×10^{-4}
Molecular weight (kg/kmol)	170	32	128	2	34
Melting point (°C)	-47	115	80.26	-259.2	-86
Thermal conductivity (W/m°C)	0.15	0.205	0.15	0.18	0.127

Table 1: General chemical properties

II. METHODS AND DESCRIPTION

Feed may contain appreciable quantities of sulphur, nitrogen, oxygen and metals. They are reduced to low levels by passing over the cobalt-molybdenum catalyst. Reactions for removing sulphur, nitrogen and oxygen that is present as organic compounds are characterized by the replacement of the non-hydrocarbon component with hydrogen. The non-hydrocarbon components are hydrogenated (to H_2S, NH3, H2O, etc.) and then removed by the catalyst.

Sulphur

Organic sulphur compounds normally found in petroleum include mercaptans, sulphides, disulphide, and thiophene derivatives. Because the sulphur compounds have higher boiling points than their hydrocarbon counterparts, the sulphur tends to concentrate in the higher boiling fractions. Desulphurization is accomplished by hydrogenating organic sulphur to hydrogen sulphide (H2S) and hydrocarbons. The following reactions are typical, where R1and R2 represent the hydrocarbon parts of the compounds

Mercaptan

$$R_1SH + H_2 \rightarrow R_1H + H_2S$$

Sulphide

$$R_1S\,R_2 + 2\,H_2 \rightarrow R_1H + R_2H + H_2S$$

Disulphide

$$R_1SSR_2 + 2H_2 \rightarrow R_1H + R_2H + 2H_2S$$

Thiophene

$$\text{Thiophene} + H_2 \rightarrow H_2S + \text{hydrocarbons}$$

Oxygen

Almost all crude contains some small number of organic compounds. Also, a small amount of dissolved oxygen may be present. In the desulphurizer reactor, organic oxygen compounds are converted to water and hydrocarbons. Stripping or fractionation removes the water.

Process:

The feed which is coming from the crude unit enters the charge drum. After the charge drum the feed stream is heated by exchangers in succession with stripper bottoms and reactor effluent. In heater the feed is brought up to reaction temperature. Downstream of the charge pumps a gas stream consisting of hydrogen rich gas from the HDS unit and pure hydrogen from the hydrogen production DHDS/HGU units is injected in the feed. The combined charge then enters into reactor. Several reactions take place, i.e. conversion of sulphur to hydrogen sulphide, saturation of double bonds, and practical cracking with formation of light hydrocarbons.

The reactor effluent is cooled in stripper re-boiler and feed-effluent exchanger and flows into the 1st separator, where vapours separate. After partial condensation in the 1st separator vapours collect in the 2nd separator. Non-condensable off the 2nd separator is put to the sulphur plant. In Stripper the feed is stripped of hydrogen sulphide and light hydrocarbons, which go overhead. Light product out of the top of the tower pass into stripper overhead condenser and collect in accumulator. Liquid drops into the top of the tower as top reflux, the rest going to the crude unit. Stripper bottoms are cooled in feed-stripper bottoms exchanger, and finally routed to storage.

Feed Specifications:

Composition (by volume):

Superior kerosene : 94%

Sulphur : 1%

Naphtha : 5%

COMPONENT	VOLUMETRIC FLOW RATE (m^3/hr)	MASS FLOW RATE (kg/hr)	MOLE FRACTION
Superior kerosene	65.8	53298	0.928
Sulphur	0.70	1449	0.025
Naphtha	3.5	2590	0.045
Hydrogen	2.54	108.67	0.002
Total	72.54	57445.57	1

Table 2: Feed specifications

Reactor Specifications:

- Reactor Diameter = 1,800-mm
- Reactor height = 8,050 mm
- Reactor temperature = 280°C
- Reactor pressure = 10 KSC
- Catalyst used = cobalt-molybdenum
- Catalyst bed height = 7400 mm
- Catalyst weight = 13,000 Kg
- Catalyst support material = alumina balls
- Catalyst support diameter = ¾ inch and ¼ inch
- The top and bottom of the bed is filled with 3 inch deep layer of ¾ inch alumina balls and between ¾ balls and catalyst balls there are ¼ inch alumina balls

Process Flow Diagram:

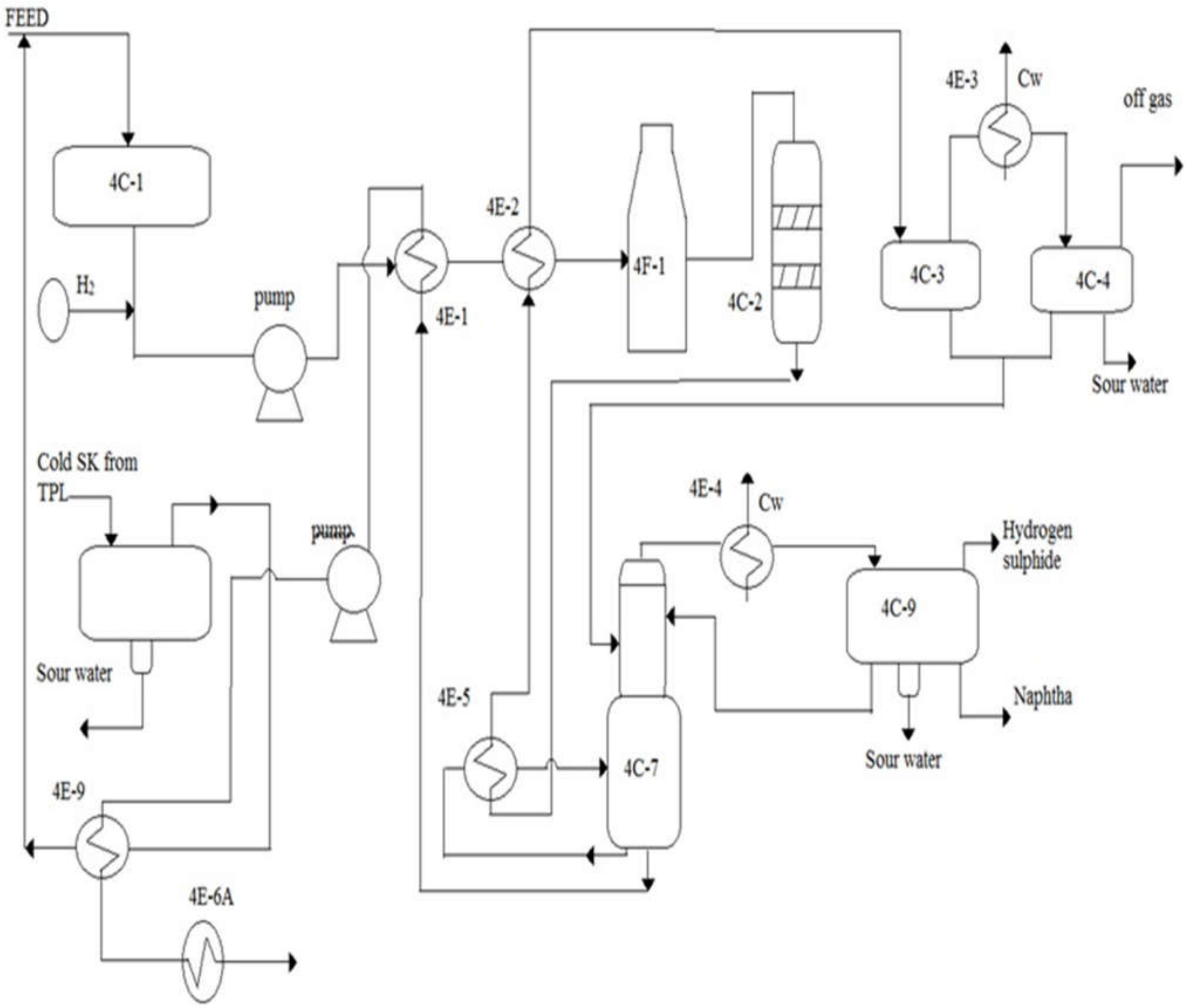

Fig 1: Process flow diagram

Equipment Nomenclature:

- 4C-1 Charge Drum
- 4C-2 Reactor
- 4C-3 Hot Separator

- 4C-4 Cold Separator
- 4C-5 Corrosion Inhibitor Tank
- 4C-6 Stripper
- 4C-7 Stripper Overhead Accumulator
- 4C-8 Dewatering Drum
- 4F-1 Kerosene Hydrotreater Heater
- 4E-1 Feed Preheat Exchanger
- 4E-2 FEED Preheat Exchanger
- 4E-3 H.P. Separator vapor Condenser
- 4E-4 Stripper Overhead Condenser
- 4E-5 Stripper Reboiler
- 4E-6 Product Cooler
- 4E-6A Product Cooler
- 4E-8 Stripper feed Exchanger

III. RESULTS AND DISCUSSIONS:

Assumptions:

- The components such as water, oxygen and nitrogen present in the feed is negligible.
- The feed is forced to stay as liquid in high temperatures by applying high pressure.
- Cracking of kerosene does not occur in the process.
- The sulphur is mainly due to presence of mercaptans.

Material Balance for Reactor:
Basis:

- 70 m^3 of feed

Stoichiometric balance:

1 mole S = 1 mole H_2S

$$\frac{1449}{32} = \frac{x}{34}$$

Amount of H_2S produced, x = 1539.56 kg/hr

Amount of H_2 reacted $= \frac{1539.56 \times 2}{34}$

= 90.56 kg/hr

Amount of H_2 unreacted = 18.16 kg/hr

Overall material balance:

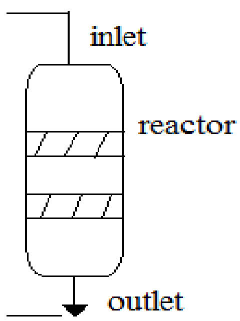

Fig 2: Reactor material balance

COMPONENT	INPUT (kg/hr)	OUTPUT (kg/hr)
Superior Kerosene	53298	53298
Hydrogen	108.67	18.16
Sulphur	1449	0.73

Naphtha	2590	2590
Hydrogen sulphide	-	1538.79
Total	57445.57	57445.57

Table 3: Reactor material balance

Material Balance for Separator:

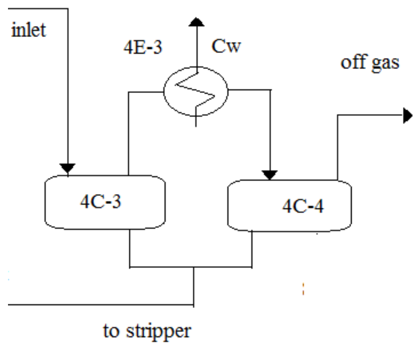

Fig 3: Separator material balance

Overall material balance:

COMPONENT	INPUT (kg/hr)	TO STRIPPER (kg/hr)	OFF GAS (kg/hr)
Superior kerosene	53298	53298	-
Naphtha	2590	2590	-
Sulphur	0.73	0.73	-
Hydrogen	18.16	-	18.16
Hydrogen sulphide	1538.79	384.697	1154.09
Total	57445.57	57445.57	

Table 4: Separator material balance

Material Balance for Stripper:

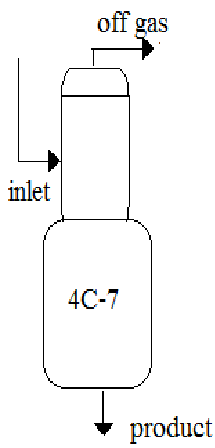

Fig4: Stripper material balance

Overall material balance:

COMPONENTS	INPUT (kg/hr)	PRODUCT (kg/hr)	OFF GAS (kg/hr)
Superior kerosene	53298	53298	-
Naphtha	2590	-	2590
Sulphur	0.73	0.73	-
Hydrogen sulphide	384.697	-	384.697
Total	56273.427	56273.427	

Table 5: stripper material balance

Energy Balance:
Specific Heat Data:

TEMP (˚C) / COMPONENT	SK	S	NAPHTHA	H_2	H_2S
200	2.235	0.91	1.007	13.53	1.292
210	2.255	0.92	1.035	13.63	1.3
220	2.275	0.93	1.062	13.81	1.3104
230	2.296	0.9407	1.09	13.86	1.3197
240	2.316	0.951	1.118	13.92	1.3289
250	2.335	0.961	1.146	13.98	1.3382
260	2.356	0.9714	1.173	14.05	1.347
270	2.376	0.9816	1.201	14.13	1.3566
280	2.397	0.992	1.229	14.19	1.3659
290	2.417	1.002	1.257	14.22	1.375
300	2.437	1.0124	1.284	14.27	1.384
310	2.457	1.023	1.312	14.31	1.394
320	2.478	1.033	1.34	14.33	1.4028
330	2.498	1.0431	1.368	14.35	1.4121
340	2.518	1.533	1.395	14.38	1.4213
350	2.54	1.0636	1.423	14.42	1.4306
360	2.558	1.0739	1.451	14.43	1.44
370	2.58	1.084	1.479	14.437	1.449
380	2.599	1.0943	1.506	14.448	1.458
390	2.619	1.1045	1.434	14.459	1.4675
400	2.642	1.1147	1.562	14.47	1.4767
410	2.66	1.125	1.59	14.48	1.486

Table 6: specific heat data(W/m˚C)

Energy Balance for Heat Exchanger I:

Hot fluid = stripper bottom

T_{hi}= 299°C, T_{ho}= 256°C

Cold fluid = feed

T_{ci}= 205°C, T_{co}= 244°C

Heat lost by hot fluid= $m_h C_{ph} \Delta T_h$

=5631.064MJ/hr

Heat gained by cold fluid = $m_c C_{pc} \Delta T_c$

=5630.067 MJ/hr

Energy Balance for Heat Exchanger II:

Hot fluid = reactor effluent from reboiler
T_{hi}= 304°C, T_{ho}= 275°C
Cold fluid= partially heated feed
T_{ci}= 244°C, T_{co}= 272°C

Heat lost by hot fluid= $m_h C_{ph} \Delta T_h$
= 4847.83 MJ/hr
Heat gained by cold fluid = $m_c C_{pc} \Delta T_c$
= 4846.94 MJ/hr

Energy Balance for Furnace:

Feed = kerosene
Fuel = heavy oil or LPG
T_{in}= 272°C, T_{out}=343°C
Calorific value of heavy oil= 43MJ/kg
Heat gained by feed = $mC_p\Delta T$
= 12293 MJ/hr
Amount of fuel required
= heat gained/calorific value
= 285.88 kg/hr

Energy Balance for Reactor:

Inlet:
T_{in}=343°C
Heat at inlet stream = $\Sigma m_i C_{pi} T_{in}$
= 48764.5 MJ/hr

Reaction:
The predominant reaction is assumed to be
R-SH + H_2 → R-H + H_2S (exothermic)

Heat produced due to H_2S formation,
ΔH= -3252 KJ/Kg
Heat produced by reaction= - $\Delta H \times m_{H2S}$
= 5004145.8 KJ/hr

Outlet:
T_{out}= 371°C
Heat at outlet stream = $\Sigma m_i C_{pi} T_{out}$
= 53768.745 MJ/hr
Heat at outle t= Heat at inlet + Heat produced by reaction
53768.745 = 48764.5 + 5004.1458
= 53768.646

Energy Balance for Stripper:

$$Q_{in} + Q_s = Q_{out} = Q_{top} + Q_{bottom}$$

Inlet:
T_{in}= 43°C
Heat at inlet stream = $\Sigma m_i C_{pi} T_{in}$
= 5130 MJ/hr
Outlet:
$T_{stripper}$= 290°C
Heat at outlet stream,Q_o = $\Sigma m_i C_{pi} T_{stripper}$
= 38786.3 MJ/hr
Amount of steam required,m_s = Q_s/λ_s

Latent heat of steam, λ_s= 2013 KJ/kg
Q_{out}= 16719 Kg/hr

Energy Balance for Reboiler:

Hot fluid = reactor effluent
T_{hi}= 371°C, T_{ho}= 304°C
Cold fluid= stripper heavy ends
T_{ci}= 290°C, T_{co}= 361°C

Heat lost by hot fluid = $m_h C_{ph} \Delta T_h$
= 9776.09 MJ/hr
Heat gained by cold fluid= $m_c C_{pc} \Delta T_c$
= 9775.77 MJ/hr

IV. DESIGN OF FIXED BED REACTOR:

Design Parameters:

Reactor diameter= 1800mm
Reactor height= 8050mm
Catalyst bed height= 7440mm
Catalyst diameter= 1.587 mm
Catalyst weight= 15670 kg
Reactor temp= 343˚C
Reactor pressure= 26 kg/cm^2
Rate constant= 343.2 lit/mol s

$$H_2 + S \rightarrow H_2S$$

Design equation:

$$\frac{W}{\rho Vo} = \int_{CA}^{CAo} \frac{dCA}{-rA}$$

$$= \int_{CA}^{CAo} \frac{cAo\, dXA}{KCACB}$$

The reaction is in the form,

$$A + B \rightarrow C$$

Since A & B react with a 1 to 1 stoichiometry,
[A] = [Ao] – x, [B] = [B_o] – x , then

At any time t, [A] = [B] i.e. C_A=C_B
Then,

$$\frac{W}{\rho Vo} = \int_{CA}^{CAo} \frac{dXA}{kCAo(1-X)^2}$$

$$\frac{WCAok}{\rho Vo} = \int_{0}^{XA} \frac{dXA}{(1-XA)^2}$$

Substituting and integrating,
We get,

$$X_A = 0.995$$

Bed Porosity,

$$\varepsilon = \frac{V - \frac{\rho cp}{mcp}}{V}$$

$$\varepsilon = 0.31$$

Residence time,

$$\tau = \frac{V\varepsilon}{Vo}$$

τ = 291 seconds

Pressure drop in reactor:
Ergun equation:

$$\frac{dP}{dz} = \frac{-G}{\rho gcDp}\left[\frac{1-\varepsilon}{\varepsilon^3}\right]\left[\frac{150(1-\varepsilon)\mu}{Dp} + 1.75G\right]$$

Superficial velocity, $u = V_o/A$
$= 0.0255$ m/s

Mass velocity, $G = \rho u$
$= 21.38$ kg/m^{2}s

$\frac{dP}{dz} = -5486$

Integrating with limits
z=0, P=Pi &z=1, P=P$_o$.

$\Delta P_R = 4.0816$ Kg/cm^2

Design summary for FBR:

PARAMETER	VALUE	UNIT
Bed porosity	0.31	-
Coversion	0.995	-
Superficial velocity	0.0255	m/s
Mass velocity	21.38	kg/m^{2}s
Pressure drop	4.0816	Kg/cm^2

Table 7: Design summary for FBR

V. CONCLUSION

Thus the fixed bed reactor is redesigned in order to increase the capacity from 12 m^3 to 14.5 m^3. This was done by increasing the flow rate of the feed to the reactor from 63 m^3/hr to 70m^3/hr thereby resulting in the reactor height. Also the conversion is improved by increasing the height of reactor. Thus the performance of the reactor is improved.

Overall design summary:

PARAMETER	ACTUAL	PROPOSED
Feed flow rate (m^3/hr)	63	70
Reactor capacity (m^3)	12	14.5
Reactor height (mm)	6700	8050
Catalyst bed height (mm)	6400	7440
Sulphur in product (ppm)	250	13
Pressure drop in reactor (KPa)	6.5	4.082

Table 8: Overall design summary

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