Lecture 8

Desulphurisation Processes
And Recovery of Sulphur
LECUTRE 8

DESULPHURISATION PROCESSES AND RECOVERY OF SULPHUR

The level of sulphur in the past two decades has steadily increased due to use of more and more heavier crude, use of cheaper high sulphur crude which has forced the refining industry to go for additional facilities like ultra-desulphurisation for gasoline and diesel to meet the requirement of the stringent sulphur emission standards. Requirement of sulphur content for MS and HSD is given in Table M-VI 8.1. Sulphur is one of the major impurities in heavy crude resulting higher concentration of sulphur compounds in the un-desulphurised product stream. Sulphur content in the crude varies widely depending on the origin. Table M-VI 8.2 shows sulphur content in crude oil. The variation is considerable and this impacts the processing scheme as well as the product slate [Goel et al., 2008]. Sulphur content of commonly used sweet and sour crudes. Due to increasing environmental concerns, stringent limits on sulphur levels in fuel are being implemented world over to achieve target of sulphur below 100 ppm, deep hydrodesulphurization is required which is an additional capital cost as well as an energy intensive step [Garg, 2010]. Table M-VI 8.3 given the details of reactivity of sulphur compounds present in crude oil

Table M-VI 8.1: Sulphur Requirement in Different Gasoline & Diesel in PPM

<table>
<thead>
<tr>
<th></th>
<th>BIS 2000</th>
<th>Bharat stage-II</th>
<th>Euro-III equivalent</th>
<th>Euro-IV equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS</td>
<td>1000</td>
<td>500</td>
<td>150</td>
<td>50</td>
</tr>
<tr>
<td>HSD</td>
<td>2500</td>
<td>500</td>
<td>350</td>
<td>50</td>
</tr>
</tbody>
</table>

Table M-VI 8.2: Sulphur Content in Crude Oil

<table>
<thead>
<tr>
<th>Crude Name</th>
<th>‘S’ Content, (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bombay High</td>
<td>0.17</td>
</tr>
<tr>
<td>Bonny Light</td>
<td>0.14</td>
</tr>
</tbody>
</table>
### Arab Heavy 2.87
### Arab Light 1.09
### Doba 0.016
### Ratawi 3.88
### Miri light 0.078
### Tapis Blend 0.028

<table>
<thead>
<tr>
<th>Sulphur compound</th>
<th>Relative reaction rate</th>
<th>Boiling points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiophene</td>
<td>100</td>
<td>185</td>
</tr>
<tr>
<td>Benzothiphene</td>
<td>50</td>
<td>430</td>
</tr>
<tr>
<td>Dibenzothiophene</td>
<td>30</td>
<td>590</td>
</tr>
<tr>
<td>Dimethyldibenzothiophene</td>
<td>5</td>
<td>600-620</td>
</tr>
<tr>
<td>trimethyldibenzothiophene</td>
<td></td>
<td>630-680</td>
</tr>
</tbody>
</table>

Source: Nakamura, 2004

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**SULPHUR OUTPUT**

Sulphur output from the refinery takes places as one of the following [Goel, 2008]

- Sulphur content in finished product
- Sulphur emission into atmosphere in the form of SO2
- Sulphur recovery in sulphur recovery unit

Sulphur distribution in typical refinery is given in below

- Sulphur in various products 58%
- Product sulphur 41%
- Sulphur emission 1%

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**FUTURE DEMAND IN INDIAN REFINERIES**

Use of more sour crudes

- More stringent sulphur specifications for distillate products
- More stringent specifications for SOx emission through flue gas
Leading to enhancement in sulphur recovery and capacity augmentation

Estimated sulphur recovery capacity in Indian Refineries to be more than double in near future

Environmental regulation shave been the major driving force for reducing sulphur in refinery products.

**Process Used to Remove Sulphur from Different Products**

- LPG - LPG treating unit
- Gasoline - Hydrotreating Unit
- ATF - Merox / Hydrotreating
- Diesel - Hydrotreating
- Sulfur lands up in the fuel gas as H₂S during Hydrotreating
- H₂S in fuel gas produces SOx while burning in the fired heater
- Environmental Norm for SOx : 50 ppm while burning fuel gas

**Hydro Treatment Processes**

Hydro treatment of the various streams from refinery and petrochemical industries has become integral part in order to meet the feed standards of various processes in order to avoid catalyst poisoning, improving quality of products and meet the environmental standards.

Hydroprocessing technologies consist of any one of the following processes

Pretreatment (Hydrotreatment) of naphtha and gas oil, residue for Catalytic reforming, Catalytic cracking and Hydrocracking. These processes have been discussed separately in the chapters catalytic reforming catalytic cracking and hydrocracking.

**Hydrocracking processes**

Hydrotreatment of the fuels and lubricants, Hydro treatment of naphtha, gas oil and residue for catalytic reforming, catalytic cracking and hydrocracking processes. These processes have been discussed separately in the chapters catalytic reforming catalytic cracking and hydrocracking.

Various hydrotreatment processes removes sulphur compound which must be recovered in sulphur recovery units. **Figure M-VI 8.1** illustrates the major sources of sulphur & recovery processes in refinery.
Main reaction involved in desulphurization is removal of sulphur compounds in form of H₂S. Degree of desulphurization varies from feed to feed with nearly complete removal to about 50-70 percent for heavier residual materials.

Relative desulphurization reactivity is in order of increasing difficulty is given below:

Thiophenol > ethyl mercaptan > diethyl sulphide > diphenylsulphide > 3-methyl-1-butanol > diethyl sulphide > di[ropyl sulphide] > diisomyl sulphide > thiophene

Figure M-VI 8.1: Major sources of Sulphur & Recovery Processes in Refinery

Sulphur Recovery Units Characteristics – Refineries

- Small to Medium Size Sulphur Recovery Units
- From a few tons to a few hundred tons/day
- Guwahati Refinery, IOCL : 5 TPD
- Reliance Refinery, Jamnagar : 2025 (3 x 675) TPD
- Feed composition varies, linked to Refinery operating mode and Crude feedstock
- High flexibility required, multiple trains
• Acid Gas always rich (high H₂S content)
• Ammonia (from Sour Water Stripper) always present, sometimes in relatively high quantities

Source: Tarapdar, T., Sulphur recovery technologies- Present and future development June 2011 Petrotech

SULPHUR RECOVERY UNIT

Sulphur recovery unit consist of recovery of sulphur from H₂S present in acid gas from Amine Treating/ Regeneration unit and H₂S from sour water stripper section Hydrogen sulphide content of the feed gas is converted to elemental sulphur. Typical sulphur recovery unit is shown in Figure M-VI 8.2.

Amine absorption and Regeneration: Absorption of H₂S bearing stream and regeneration of amine. H₂S rich stream from amine regeneration is sent to sulphur recovery unit.

Sour Water Stripping: Sour water is stripped off its sulphur and recycled. H₂S is sent to sulphur recovery unit.

Amine Absorption Unit: Various hydro desulphurisation processes in the refinery and hydrocracker unit generate large quantity of H₂S. H₂S bearing gases from various unit is sent to Amine treating unit which uses amine as a solvent for absorbing H₂S and subsequently releasing H₂S as H₂S Rich stream in the amine generator.

MEROX (MERCAPTAN OXIDATION UNIT)

Merox process is used in the refinery for controlling the mercaptan sulphur in gases, LPG, naphtha and other petroleum fractions. The Process is used for the chemical treatment of LPG, gasoline and distillates from FCCU, OHCU etc to remove mercaptans.

Mercaptans are either extracted from the stream or sweetened to acceptable disulphides. For treatment of light feed stocks such as LPG, no sweetening is required as mercaptans are nearly removed by extraction. However, feed containing higher molecular weight mercaptans and may require a combination of Merox extraction and sweetening using catalyst. Catalysts promote the oxidation of mercaptans to disulphide using air as the source of oxygen. Merox treatment can in general be used in following ways [Dziabis, 2003]
To improve lead susceptibility of light gasoline
To improve the response of gasoline stocks to oxidation inhibitors added to prevent gum formation during storage
To improve odor on all stocks
To reduce the mercaptans content to meet product specifications
To reduce the sulphur content of LPG and light naphtha products
To reduce sulphur content of coker FCC olefins to save acid consumption in alkylation

**Process**

\[ \text{RSH} + \text{NaOH} \rightarrow \text{RSNa} + \text{H}_2\text{O} \]

Pretreatment (Remove H₂S and Naphthenic Acids by dilute Alkali Solution)

Extraction (Remove Caustic soluble Mercaptans)

Sweetening (Oxidation of mercaptans to disulphides)

\[ 4\text{NaSR} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{RSSR} + \text{NaOH} \]

Post Treatment (Remove Caustic Haze)
(Caustic Settler, Wash Water, Sand, Clay Filters)

**Sulphur Recovery from H₂S**

Sulphur recovery now has become one of the most critical aspects of sulphur management and affects emission sulphur dioxide significantly in the refinery. There are two sulphur recovery processes are

- Claus process (used earlier)
- Supr Claus process

Conventional Claus process has only 99% sulphur recovery. In order to meet the sulphur emission standards now Claus process has been improved substantially to meet the standards. Modern claus process is shown in Figure M-VI 8.3. New processes are characterized by

- New Catalysts
- COS and CS₂ hydrolysis (increased recovery)
- Direct conversion of H₂S to Sulphur by oxidation (Super Claus Process)
- Direct conversion of H₂S to Sulphur by reduction (Pro Claus Process)
- High efficiency burners (NH3, BTEX destruction)
- Analysers based control
- Enriched air or Oxygen blown thermal reactors

**Figure M-VI 8.2: Typical Sulphur Recovery Unit**

**Figure M-VI 8.3: Modified Claus Process**

Sources: Taraphdar, 2011
SUPER CLAUS PROCESS
The SUPER CLAUS process was developed to catalytically recover elemental sulphur from H₂S containing Claus tail gas to improve the overall sulphur recovery level. The SUPERCLAUS process was commercially demonstrated in 1998, and today now more than 160 units are under license and over 140 are in operation. SUPERCLAUS process achieves high sulphur recover levels by suppressing SO₂ formation in claus stages and selectively oxidizing H₂S in presence of oxygen using proprietary catalyst [Scheel, 2011].

A typical SUPER CLAUS sulphur recovery unit consist of following sections:
- Combustion Chamber
- Claus reactor
- Super claus Reactor
- Incinerator
- Degassing Section

Function of Claus reactors:
- Claus reaction at catalytic region
  \[ 2H_2S + SO_2 \rightarrow 3/ \times S_\times + 2H_2O + 93k \] (Where \( x = 6 \) and 8 mainly)
- Hydrolysis of COS and CS₂ at temperatures above 300°C
  \[ COS + H_2O \rightarrow CO_2 + H_2S \]
  \[ CS_2 + 2H_2O \rightarrow CO_2 + 2H_2S \]

Function of Super Claus reactor
\[ H_2S + 0.5SO_2 \rightarrow 1/8S_8 + H_2O + 208kJ \]
SUPER CLAUS Process use selective oxidation catalyst minimizes side reactions & increase sulphur recovery

Claus Process Limitations:
- Thermodynamically limited conversion: \( 2H_2S + SO_2 \rightarrow 3S + H_2O \) the ‘air to clean gas’ ratio’s is maintained to produce an \( H_2S/\text{SO}_2 \) ratio of exactly 2/1 (optimum ratio) in the burner effluent gases.
- Increases H₂O content to 30 vol% decreasing H₂S and SO₂ concentrations.
Formation of non-recoverable S-compounds due to side reactions
The big difference between SUPER CLAUS catalyst and Claus Catalyst is that the reaction is not equilibrium based. Therefore, the conversion efficiency is much higher than the equilibrium limited Claus reaction. SUPER CLAUS is a non-cyclic process that has repeatedly shown simplicity in operation, high online reliability and sulphur guarantees up to 99.3 percent [Scheel, 2011]

**Super Sour Process:** Stringent environmental regulations have necessitated higher recovery of H2S from sour water stripper unit design. Super Sour process ensures minimum H2S loss. The process employs additional hot feed flash drum upstream of cold feed surge drum. The H2S rich vapours from hot feed flash drum upstream of cold feed surge drum is routed to a small amine scrubber to absorb liberated H2S. The H2S lean gas containing primarily hydrocarbons is then routed to incinerator of the sulphur recovery unit. The absorbed H2S rich amine is recovered in the amine regenerator and is fed to the sulphur unit for converting it to sulphur [Sharma and Nag 2011].

**INDE Treat and INDE Sweet Technology [Indian oil Technologies 2001]:** INDE Treat and INDE Sweet Technology is based on the Continuous Film contactor(CFC) for effective removal of undesirable compounds at lower cost. It can remove H2S from LPG, Mercaptans from LPG, naphtha, gasoline and ATF/Kero, naphthenic acid from diesel, acid gases from natural gases, fuel gases and can regenerate spent caustic if required. CFC technology which is the heart of process. Salient features of CFC are

- Non-dispersive contacting
- Enormous surface area
- High mass transfer efficiency
- Based on caustic/amine
- Efficient removal of contaminants
- No aqueous phase entrainment
- Low caustic/amine consumption
- Low cost
- Can be easily retrofitted in existing mixer settler units

**Merichem Fibre film Contactor Technology:** The process is based on Continuous Film contactor (CFC) Fibre film Contactor technology for removal of impurities from hydrocarbon
The process achieves non-dispersive phase contact without problem inherent in conventional dispersive mixing devices.

REFERENCES
1. “INDE Treat and INDE Sweet Technology” Indian Oil Tech/T/2003/2004
6. Scheel, F., “Innovative approach to sulphur recovery unit emissions Reductions” compendium 16th Refinery Technology Meet, Feb 17-19, 2011 organized by Centre of high technology and Indian oil Corporation Ltd, Kolkata India

Garg, 2010