

DESULFURIZATION PROCESSES AND SULFUR RECOVERY

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1 | Introduction

Scheduling is a decision-making process that plays an important role in most manufacturing and service industries. Scheduling problems arise in almost any type of industrial production facilities where given tasks need to be processed using specified resources. In a chemical process, production must be planned such that equipment, material and utilities are available at the manufacturing facility when they are needed to realize the production tasks. Production scheduling comprises the activity of planning in detail the production of a product or products in a given production facility. It boils down to the following main decisions (Harjunkoski et al., 2014):

- What production tasks to execute?
- Where to process the production tasks?
- In which sequence to produce?
- When to execute the production tasks?

For batch processes, short-term scheduling deals with the allocation of a set of limited resources over time to manufacture one or more products following a batch recipe (Méndez et al., 2006). There has been significant development of optimization approaches to scheduling over the last two decades. The first mathematical programming approach to the scheduling of multi-purpose, multi-product batch plants was proposed by Kondili et al. (1993). This approach introduces the state task network (STN) representation where the process is described as a bipartite graph consisting of states and tasks.

2 | Conventional Desulfurization Processes

Hydrotreating (or hydrodesulfurization) and Mercaptan Oxidation (MEROX) are the main processes used to remove sulfur from refinery streams.

2.1 Hydrodesulfurization

Hydrodesulfurization is the most commonly used method in the petroleum industry to reduce the sulfur content of crude oil. In most cases HDS is performed by co-feeding oil and H_2 to a fixed-bed reactor packed with an appropriate HDS catalyst. The standard HDS catalysts are $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$, but there are many more types available.

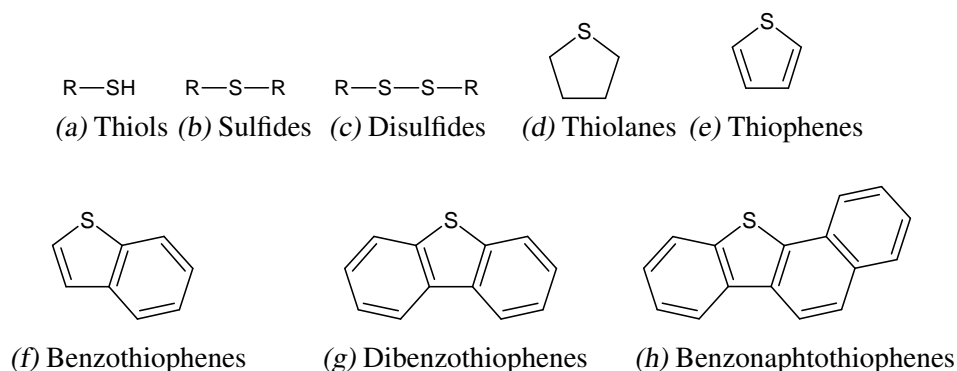


Fig. 2.1: Important classes of sulfur-containing compounds in crude oil (R =alkyl)

The most difficult sulfur compounds to eliminate by hydrogen treatment belong to the alkyl dibenzothiophene (DBT) family. 4,6-dimethyldibenzothiophene (4,6-DMDBT) is often considered to be the representative molecule of refractory compounds because it is the most abundant. However, other kinds of substituted DBT such as 4,6-diethyldibenzothiophene (4,6-DEDBT) or 4,6-diisopropyldibenzothiophene (4,6-DiPrDBT) contribute together at least to an equivalent part of the S remaining content (Breyse et al., 2003). Indeed, many lab-scale studies on novel HDS catalysts utilize solutions of compounds like DBT and 4,6-DMDBT as feed constituents to simulate sulfur containing fuels (Gupta et al., 2016; Fraile et al., 2016; Souza et al., 2015; Silva-Rodrigo et al., 2015; Wang et al., 2009). Fig. 2.2 shows typical reactions that occur during hydrotreating of sulfur-containing feeds.

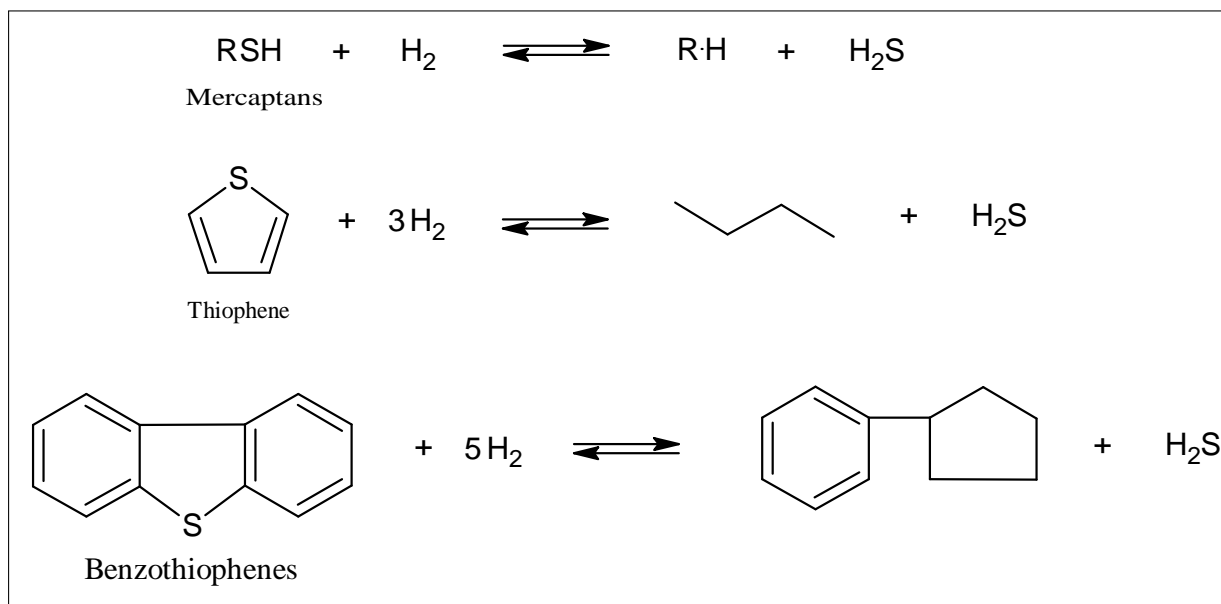


Fig. 2.2: Typical hydrodesulfurization reactions (Moulijn et al., 2001)

2.2 Selection of catalysts and reactors for hydrotreatment

The performance of hydroprocessing units is influenced by the selection of the catalysts and the type of reactor to suit a particular feed. Catalysts ranging widely in chemical composition and physical properties are available commercially. Several types of reactors are proven commercially as well. The catalysts and reactors selected for light feeds differ significantly from those selected for heavy feeds. Fixed-bed reactors have been traditionally used for light feeds.

The selection of catalysts must take into account the properties of the feed to be hydroprocessed. The values in Table 2.1 illustrate the differences in the properties of various crudes. These differences influence refining schemes in the refinery. Yields of the distillate fractions to be refined, as well as the residues to be upgraded, determine the amount of available feeds and/or the hydroprocessing capacity requirements.

The values in Table 2.1 indicate a significant difference in the content of heteroatoms among the chosen crudes. This suggests that a universal catalyst or a catalytic system suitable for hydroprocessing of feeds derived from various sources does not exist.

The selection of catalysts is application dependent. NiMo-catalysts are more hydrogenating, whereas CoMo-catalysts are better at hydrogenolysis (?). Hence, CoMo catalysts are preferred for the HDS of unsaturated hydrocarbon streams, whereas NiMo catalysts are preferred for fractions requiring extreme hydrogenation. High asphaltene and high metal content feeds

Table 2.1: Different residue compositions and physical properties (?)

Crude oil	Gravity (°API)	S (wt.%)
Alaska, north slope	14.9	1.8
Arabian, safaniya	13	4.3
Canada, Athabasca	5.8	5.4
Canada, Cold Lake	6.8	5
California, Hondo	7.5	5.8
Iranian	–	2.6
Kuwait, Export	15	4.1
Mexico, Maya	7.9	4.7
North Sea, Ekofisk	20.9	0.4
Venezuela, Bachaquero	9.4	3

are processed using moving-bed or fluidized bed reactors. Multi-reactor systems consisting of moving-bed and/or ebullated bed reactors in series with fixed-bed reactors can be used to process difficult feeds. For heavy, viscous feeds, the physical properties, shape and size of the catalyst particles become crucial parameters.

Although different types of reactor designs are marketed, they all work on the same principle— all processes use the reaction of hydrogen with the hydrocarbon feedstock to produce H_2S and a desulfurized hydrocarbon product. The reaction temperature is typically on the order of 290–450°C with a hydrogen gas pressure on the order of 250 and 3000 psi – the low temperature minimizes cracking reactions (Speight, 2013). In some designs, the feedstock is heated and then mixed with the hydrogen rather than the option of passing moderately heated hydrogen into the reactor. The gas mixture is then led over the catalyst bed. The reactor effluent is then cooled, and the oil feed and gas mixture are then separated in a stripper column. Part of the stripped gas may be recycled to the reactor.

2.2.1 Downflow Fixed-Bed (Trickle bed) reactor

Fixed bed reactors are typically used in the HDS of distillates. The feed stock enters at the top of the reactor and the product leaves at the bottom. The catalyst remains in a stationary position with hydrogen and petroleum feedstock passing in a down flow direction through the catalyst bed. The HDS reaction is exothermic and the temperature rises from the inlet to the outlet of each catalyst bed. The reaction mixture can be quenched with cold recycled gas at intermediate points in the reactor system. This is achieved by dividing the catalyst charge

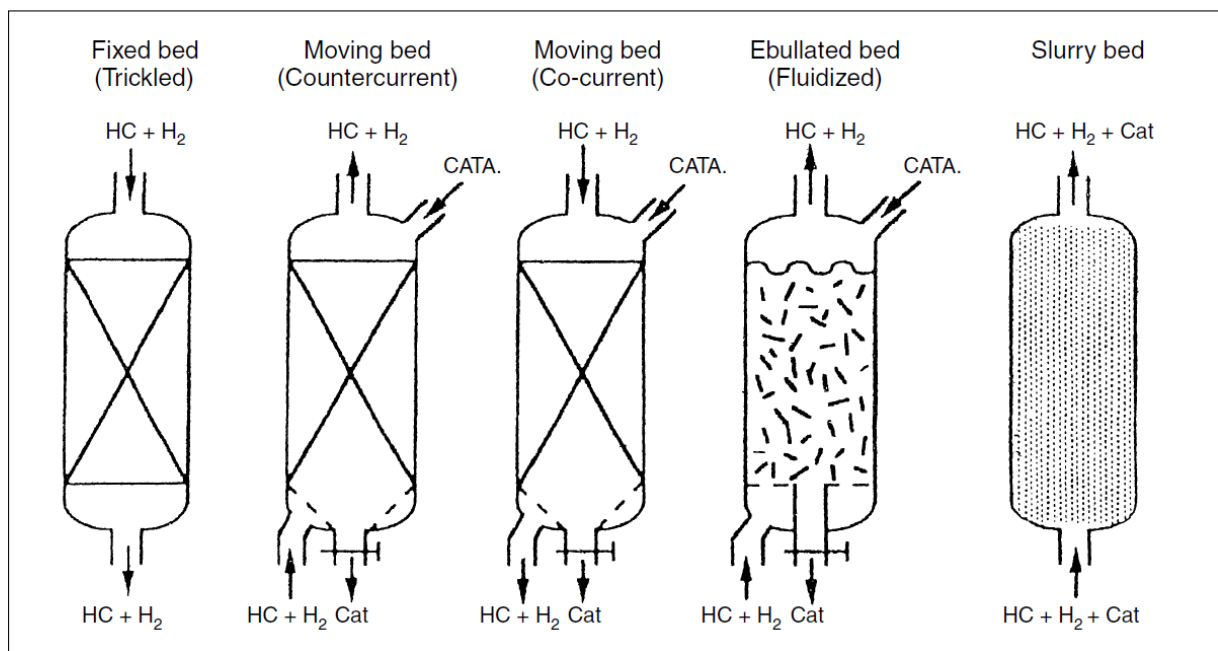


Fig. 2.3: Simplified features of catalytic reactors for upgrading heavy feeds (Furimsky, 2007)

into a series of catalyst beds and the effluent from each catalyst bed is quenched to the inlet temperature of the next catalyst bed.

The extent of desulfurization is controlled by raising the inlet temperature to each catalyst bed to maintain constant catalyst activity over the course of the process. Fixed-bed reactors are mathematically modeled as plug-flow reactors. The first catalyst bed is poisoned with vanadium and nickel at the inlet to the bed and is a cheaper catalyst (Guard bed). As the catalyst is poisoned in front of the bed, the temperature exotherm moves down the bed and the activity of the entire catalyst charge declines thus requiring a rise in the reactor temperature over the course of the process sequence.

Although fixed-bed HDS units are generally used for distillate HDS, they may also be used for heavy feedstock HDS with special precautions in processing. Heavy feedstock must undergo two-stage electrostatic desalting so that salt deposits do not plug the inlet to the first catalyst bed and the heavy feedstock must be low in vanadium and nickel content to avoid plugging the beds with metal deposits. Hence heavy feedstock HDS reactors require the use of a guard bed. Some of the commercial processes employing fixed bed reactors include:

- Unibon process
- HYVAHL process

- Atmospheric residue desulfurization (ARDS) process

2.2.2 Moving bed reactors

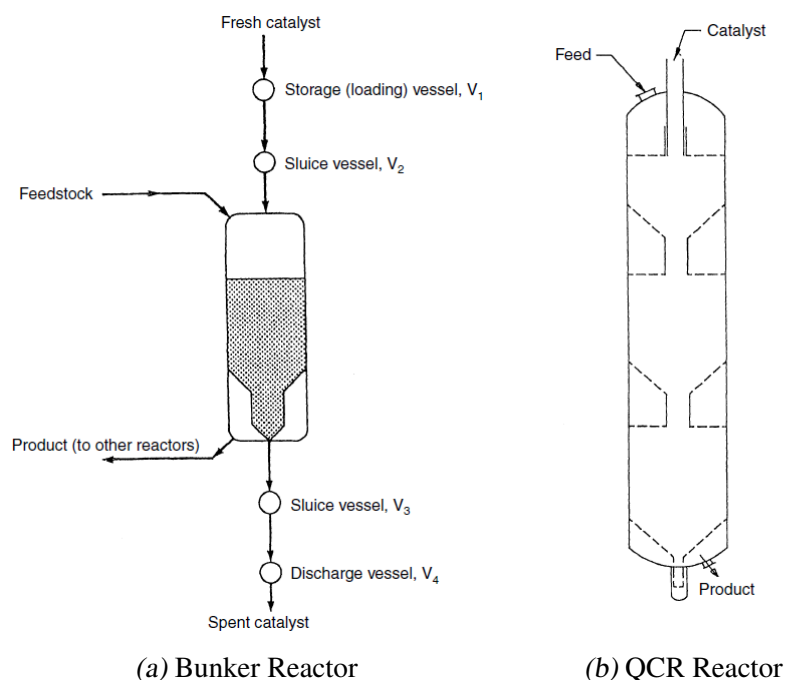


Fig. 2.4: Schematics of moving bed reactors used for hydroprocessing (Furimsky, 2007)

Expanded or moving bed reactors are used for very heavy, high metals and/or dirty feedstocks having extraneous fine solid material. They operate in such a way that the catalyst is in an expanded state so that the extraneous solids pass through the catalyst bed without plugging. They are isothermal, which conveniently handles the high exothermicity associated with high hydrogen consumption. Since the catalyst is in an expanded state of motion, it is possible to withdraw and add catalyst during operation.

Several moving bed catalyst reactors have reached a commercial scale. Among these, bunker reactor and Quick Catalyst Replacement (QCR) reactor are shown in Fig. 2.4a and 2.4b respectively. Compared with fixed bed reactors, the problems associated with pressure drops are not present in moving bed reactors. This allows the use of catalyst particles varying widely in size and shape. Moreover, inorganic solids present in heavy feeds move through the reactor together with the catalyst and exit at the bottom of the reactor with the spent catalyst. Therefore, processes employing moving bed reactors do not require a guard chamber.

Table 2.2: Yields and properties of products from different reactors

	Fixed/moving	Ebullated	Slurry
Naphtha			
Yield/feed, wt%	1–5	5–15	10–15
Density, kg/L	0.71–0.74	0.71–0.72	0.72
sulfur, wt%	<0.01	0.01–0.2	0.06
Nitrogen, ppm	<20	50–100	200
Gas oil			
Yield/feed, wt%	10–25	20–30	40–45
Density, kg/L	0.850–0.875	0.840–0.860	0.866
sulfur, wt%	<0.1	0.1–0.5	0.7
Nitrogen, ppm	300–1200	>500	~ 1800
Vacuum gas oil			
Yield/feed, wt%	20–35	25–35	20–25
Density, kg/L	0.925–0.935	0.925–0.970	1.01
sulfur, wt%	0.25–0.50	0.5–2.0	2.2
Nitrogen, ppm	1500–2500	1600–4000	4300
Vacuum residue			
Yield/feed, wt%	30–60	15–35	10–20
Density, kg/L	0.990–1.030	1.035–1.100	1.16
sulfur, wt%	0.7–1.5	1–3	2.7
Nitrogen, ppm	3000–4000	>3300	11
Asphaltenes (heptane)	5–10	>20	26

The feasibility of a process employing moving bed reactors compared with fixed bed reactors is affected by the capital cost of reactor systems, although this may be offset by the lower relative catalyst consumption. For example, additional high-pressure vessels upstream and downstream of bunker or QCR reactors are required which add to the capital cost. Also, the configurations of moving bed reactors are more complex than that of the fixed bed reactors. Therefore, design of fixed bed reactors is much more simple. In addition, different yield and quality of products are obtained from different reactors.

2.2.3 Ebullated bed Reactors

Ebullated bed reactors are designed to handle the most problematic feeds such as VRs and heavy crudes containing high contents of metals, asphaltenes, sediments as well as dispersed clay and minerals. The most important feature of such reactors is their capability to periodically withdraw and add catalyst to the reactor without interrupting operation (Furimsky, 1998). The bed design ensures ample free space between particles allowing entrained solids to pass through the bed without accumulation, plugging, or increased pressure drop. This allows utilization of

catalyst particles smaller than 1 mm in diameter, resulting in a significant increase in reaction rate due to reduced diffusion limitations.

2.3 Mercaptans Removal

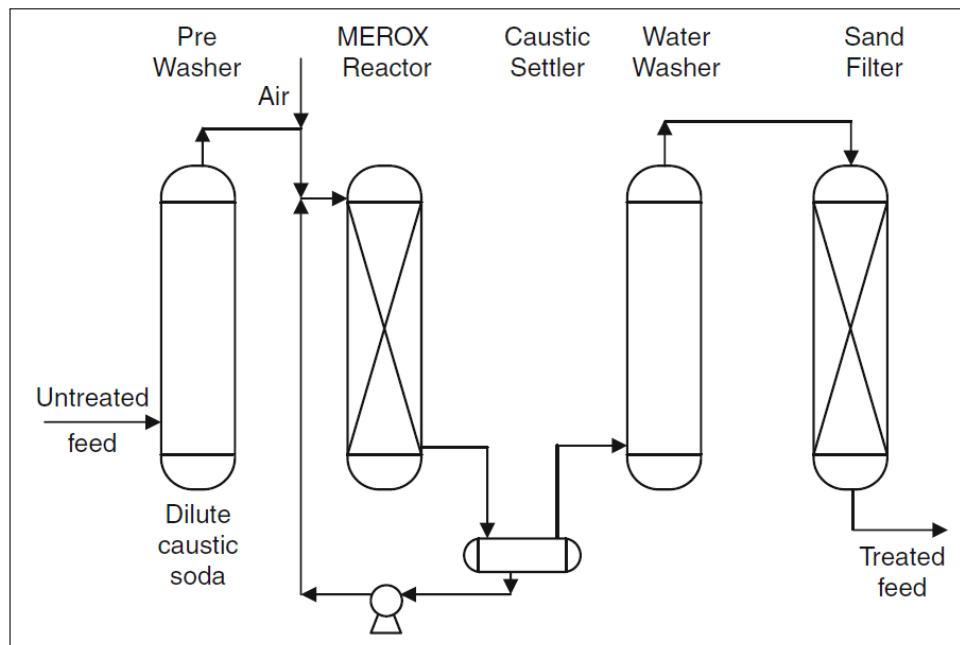
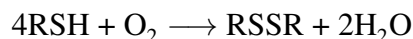
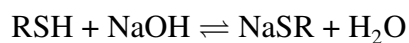


Fig. 2.5: Typical MEROX flowsheet (Fahim et al., 2010)

The predominant sulfur compounds in refinery products that usually have an unpleasant smell are mercaptans. They are corrosive and disturb fuel stability due to gum formation. The principle of mercaptans removal is oxidation (MEROX). MEROX sweetening involves the catalytic oxidation of mercaptans to disulfides in the presence of oxygen and alkalinity. Air provides the oxygen, while caustic soda provides the alkalinity. Oxygen reacts with mercaptans through the following reaction:



Removal of mercaptans by extraction starts with dissolving them in caustic soda based on the following reaction:



The equilibrium occurs between the RSH organic phase and the RSH that dissolves in the aqueous phase.

The rich caustic soda containing the extracted mercaptans in the form of mercaptides is regenerated as shown in the following reaction:

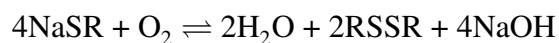


Fig. 2.5 shows the typical flowsheet of a MEROX plant. The MEROX unit consists of a fixed-bed reactor followed by a caustic settler. Air, the source of oxygen, is injected into the feedstock upstream of the reactor. The operating pressure is chosen to assure that the air required for sweetening is completely dissolved at the operating temperature. The sweetened stream exits the reactor and flows to the caustic settler. The caustic soda settler contains a reservoir of caustic soda for use in keeping the MEROX catalyst alkaline. The solvent product leaving the water wash flows to a sand filter containing a simple bed of coarse sand that is used to remove free water and a portion of the dissolved water from the product. The regenerated caustic soda is recycled to the MEROX reactor.

3 | Novel desulfurization processes

Hydrodesulfurization in combination with carbon rejection technologies, such as coking and fluid catalytic cracking (FCC) are the main technologies industrially employed for the desulfurization of crude. Although these technologies are quite capable of desulfurizing heavy oil, their carbon footprints are substantial since all of these technologies, including the production of hydrogen that is needed for HDS, involve high-temperature processing. The refining cost increases as heavier and sulfur-rich oils are being processed. Hence, alternative desulfurization pathways are of interest. In this chapter, a few non-conventional desulfurization techniques have been described.

3.1 Extraction by ionic liquids

HDS is limited due to the low conversion rates of the higher aromatics. The low sulfur limits can only be met by extreme operating conditions in terms of pressure and residence time (Hansmeier et al., 2011). Hence, the process becomes uneconomic and energy inefficient. Further, in order to fulfill gasoline sulfur limits, deep desulfurization of all streams contributing to the gasoline-pool has to be carried out. Although in comparison to sulfur components in diesel fuel, HDS of thiophene is reached more easily; the bottleneck of this process is the decrease in octane number due to simultaneous hydrogenation of the olefins present in the stream. In the case of diesel fuels, due to the severe HDS conditions that are necessary to produce ultra-low sulfur diesel, the cetane number is affected as well.

Liquid-liquid extraction is a technique which has been proposed for deep desulfurization because of its simplicity and mild operating conditions. Extraction desulfurization with Ionic Liquids (ILs) as extraction solvents has the potential for alternative and future complementary technology for deep desulfurization. An ionic liquid is a non-volatile organic liquid salt, which potentially can extract sulfur and also organic nitrogen compounds in fuels by virtue of its polarity. Ito and van Veen (2006) concluded that their application for desulfurization is limited due to the co-extraction of aromatic hydrocarbons. However, due to stricter environmental regulations, the aromatic hydrocarbon content (along with sulfur content) also needs to be

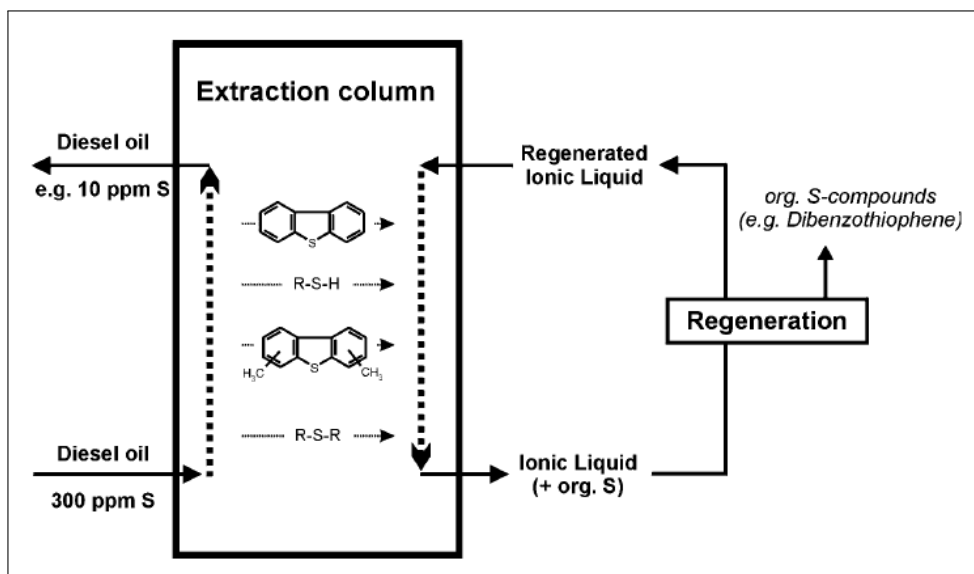


Fig. 3.1: Concept of deep desulfurization of refinery streams by extraction with ILs (Eßer et al., 2004)

reduced. Therefore, the co-extraction of aromatics may be an advantage since this allows for removal of both types of compounds in a single step.

ILs have excellent extraction properties for organic S- and N-compounds and are – if chosen carefully – insoluble in oils. The basic concept of such an extraction process is illustrated in Fig. 3.1. Hansmeier et al. (2011) have characterized the capacity and suitability of several IL solvents for thiophene and dibenzothiophene. For both sulfur aromatics, pyridinium-based ionic liquids [3-mebupy]N(CN)₂ and [4-mebupy]N(CN)₂, [4-mebupy]SCN are suitable candidates since the capacity, as well as the selectivity, are higher than those of sulfolane.¹ In case of the investigated imidazolium-based ionic liquids, only [BMIM]C(CN)₃ fulfils the criteria and is superior to sulfolane. [BMIM]N(CN)₂ only has a higher selectivity, while the selectivity of [BMIM]SCN is comparable to that of sulfolane.

Extractive desulfurization becomes increasingly difficult and unselective as the heaviness of the oil increases. Solvent loss and recovery are important detractors when desulfurizing heavy oil. The sulfur compounds are high boiling and the heavy oil is viscous. It is unlikely that a solvent can be found that will be sulfur-selective based purely on a physical extraction. It is anticipated that any breakthrough in extractive desulfurization of heavy oil will, out of necessity, be in reactive extractive desulfurization, i.e. a solvent that chemically reacts with

¹ Sulfolane is the commercial extraction solvent with the highest aromatic capacity, mostly used for aromatics extraction from different petroleum fractions. Hence results of ionic liquids are compared to sulfolane.

sulfur in sulfur-containing compounds to produce a separate phase (?). Even so, this does not eliminate the problems associated with solvent recovery, which must still be addressed.

3.2 Biodesulfurization

Biodesulfurization is a non-invasive approach that can specifically remove sulfur from refractory hydrocarbons under mild conditions and it can be potentially used in industrial desulfurization. Intensive research has been conducted in microbiology and molecular biology of the competent strains to increase their desulfurization activity; however, even the highest activity obtained is still insufficient to fulfill the industrial requirements.

Sulfur forms 0.5–1% of bacterial cell dry weight. Microorganisms require sulfur for their growth and biological activities. Sulfur generally occurs in the structure of some enzyme co-factors (such as Coenzyme A, thiamine and biotin), amino acids and proteins (cysteine, methionine, and disulfur bonds). Microorganisms, depending on their enzymes and metabolic pathways, may have the ability to provide their required sulfur from different sources. Some microorganisms can consume the sulfur in thiophenic compounds such as DBT and reduce the sulfur content in fuel. Desulfurization by microorganisms is potentially advantageous. Firstly, it is carried out in mild temperature and pressure conditions; therefore, it is considered as an energy-saving process (an advantage over HDS). Secondly, in biological activities, biocatalysts (enzymes) are involved; therefore, the desulfurization would be highly selective (an advantage over ILs).

Soleimani et al. (2007) have described three main types of biodesulfurization:

- Destructive biodesulfurization
- Anaerobic biodesulfurization
- Specific oxidative desulfurization

Aerobic BDS was proposed as an alternative to hydrodesulfurization of crude oil. It was reported that BDS by *Pantoea agglomerans* D23W3 resulted in 61% sulfur removal from a light crude oil that originally contained 0.4% sulfur and 63% sulfur removal from a heavy crude oil that originally contained 1.9% sulfur. It was found that integrated methods performed better

than just BDS. By combining ODS with BDS it was possible to achieve 91% sulfur removal from heavy oil (Agarwal and Sharma, 2010).

The main reasons that BDS is not commercially employed for crude oil desulfurization are the low activity, the logistics of sanitary handling, shipment, storage and use of microorganisms within the refinery environment.

3.3 Olefin alkylation of thiophenic sulfur

The OATS process, first developed by British Petroleum, can be seen as a good alternative for the conventional desulfurization because of the comparative advantages of mild reaction conditions, no need for other reactants and minimal loss of octane number. Typically, this process consists of two steps: first, thiophene and its derivatives are alkylated with the olefins in gasoline over some acidic catalysts; second, the alkylated sulfur-containing compounds are separated from gasoline by distillation. The alkylation technique is based on the concept that, when the boiling temperature of organosulfur compounds is shifted to a higher value, they can be removed from light fractions by distillation and concentrated in the heavy boiling part of the refinery streams.

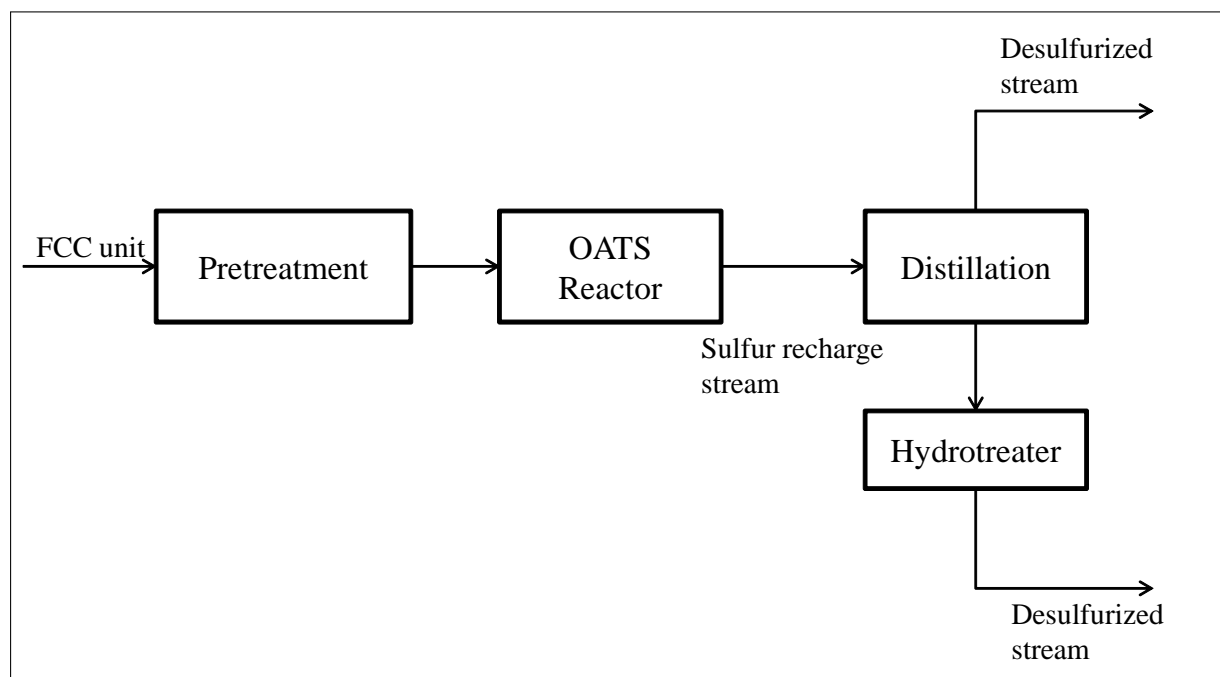


Fig. 3.2: OATS process (El-Gendy and Speight, 2015)

In conventional OATS technologies, the separations and reactions are carried out with different equipment as shown in Fig. 3.2. From a process intensification point of view, catalytic

distillation may be more effective and economical. In the process of catalytic distillation, separation and catalytic reaction occur in the same vessel, so the conversion of the reactants can be greatly enhanced.

Using equilibrium steady state simulations, Ha et al. (2014) have presented a sensitivity analysis and economic evaluation of the catalytic distillation process for alkylation desulfurization of FCC gasoline. The results indicated that the operating pressure impacts both the separation and reaction; hence increasing the operating pressure is not always beneficial to the catalytic distillation process. However, a high feed pressure is an economical option despite it having no significant effect on sulfur transfer.

A major advantage of this process is that less hydrogen is consumed since only a relatively low volume of the naphtha stream is hydrotreated. One of the disadvantages of the process is that the alkylated sulfur compounds produced require more severe hydrotreating conditions to eliminate sulfur (El-Gendy and Speight, 2015).

4 | Sulfur Recovery

The purpose of removing sulfur from acid gas streams is to reduce SO₂ emissions in order to meet environmental guidelines. In the petroleum industry, acid gas streams from HDS plants contain H₂S which are sent to sulfur recovery units, where sulfur removal is carried out along with tail gas clean up schemes.

4.1 Claus Process

The Claus process is the dominant sulfur recovery method from gaseous H₂S. The requirements to be met by Claus plants are dictated by the operating conditions of modern, flexible refineries and natural gas plants and increasingly stringent emission control norms.

Acid gas streams from hydrodesulfurization containing H₂S are sent to a Claus unit. Gases with an H₂S content of over 25% are suitable for the recovery of sulfur in the Claus process. Hydrogen sulfide produced in the hydrodesulfurization of refinery products is converted to sulfur in Claus plants (Fahim et al., 2010). The main reaction is:



The Claus plant can be divided into two stages (Fig. 4.1): thermal and catalytic. In the thermal stage, H₂S is partially oxidized at temperatures above 850°C in a combustion chamber. This causes elemental sulfur to precipitate in the downstream process gas cooler.

If excess oxygen is added, the following reaction occurs:



Air to the acid gas is controlled such that around 30% of the H₂S is converted to SO₂. The main portion of the hot gas from the combustion chamber is cooled down. This causes the sulfur formed in the reaction step to condense.

A small part of the hot gas from the combustion chamber goes to the catalytic stage. This gas contains 20–30% of the sulfur content of the feed stream. Activated alumina or titanium dioxide is used. The H₂S reacts with the SO₂ and results in gaseous, elemental sulfur. This is called the Claus reaction:

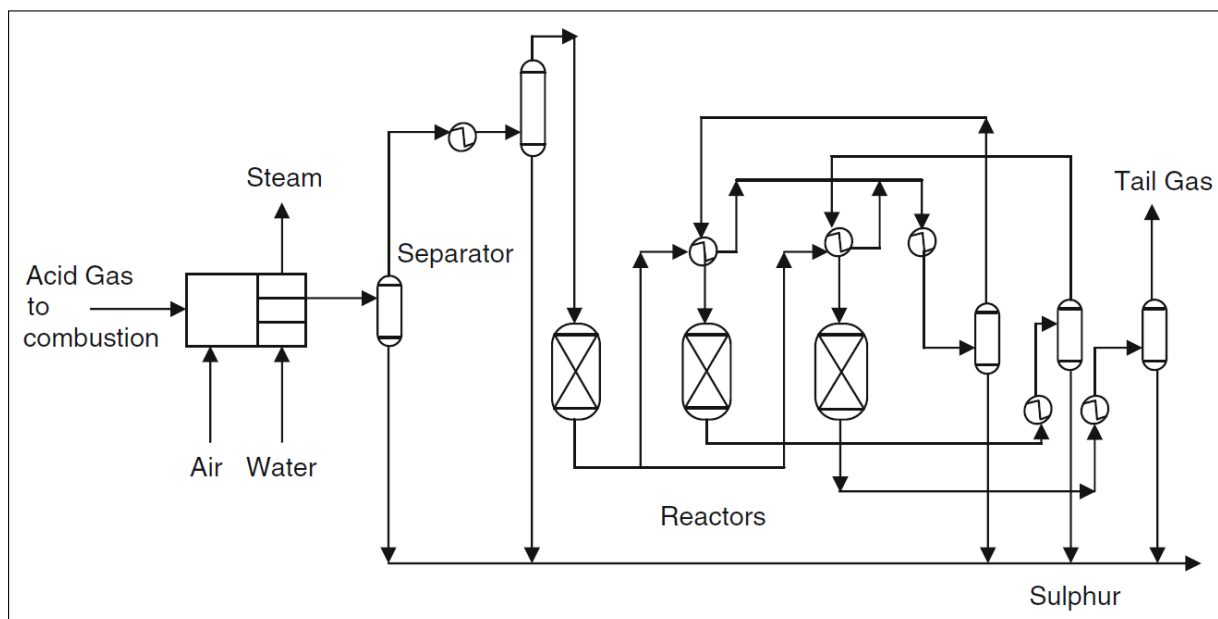
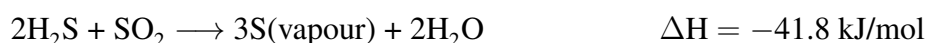
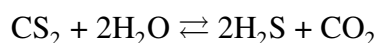
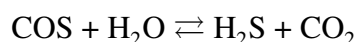


Fig. 4.1: Claus process (Fahim et al., 2010)



Heating is provided to the catalyst bed to prevent sulfur condensation which can lead to fouling. Although the catalytic conversion is maximized at lower temperatures, care is taken to ensure that the operation takes place above the dew point of sulfur. The condensation heat is used to generate steam at the shell side of the condenser. Before storage, the liquid sulfur stream is degassed to remove any dissolved gases. Over 2.6 tons of steam can be generated per ton of sulfur yield.

If the acid gas feed contains COS and/or CS₂ they are hydrolyzed in the catalytic reactor:



The first converter typically operates at about 350°C in order to hydrolyze COS and CS₂. The second and subsequent converters usually operate just above the dew point of sulfur vapor. The Claus reaction is exothermic at converter temperatures, and the reaction equilibrium is favored by lower temperatures. However, COS and CS₂ are hydrolyzed more completely at higher temperatures. The first catalytic converter is therefore frequently operated at temperatures high enough to promote the hydrolysis of COS and CS₂; the second and third converters are operated at temperatures only high enough to obtain acceptable reaction rates and to avoid the deposition

of liquid sulfur.

The tail gas from the Claus process still containing combustible components and sulfur compounds (H_2S , H_2 and CO) is either burned in an incineration unit or further desulfurized in a downstream tail gas clean-up unit (TGCU). A typical Claus process with two catalytic stages yields 97% of the sulfur in the input stream.

4.2 Catalysts & reactors for the Claus process

Typically, a Sulfur Recovery Unit (SRU) is composed of a burner, a thermal reactor (TR), a waste heat boiler (WHB) (Fig. 4.2) and a train of sulfur condensers and catalytic Claus reactors.

4.2.1 Thermal reactor and waste heat boiler

The acid gas, which consists of H_2S , H_2O , CO_2 , CO , NH_3 and hydrocarbons, is mixed with air and oxidized at high temperature by means of the burner and TR, which provides for the necessary residence time.

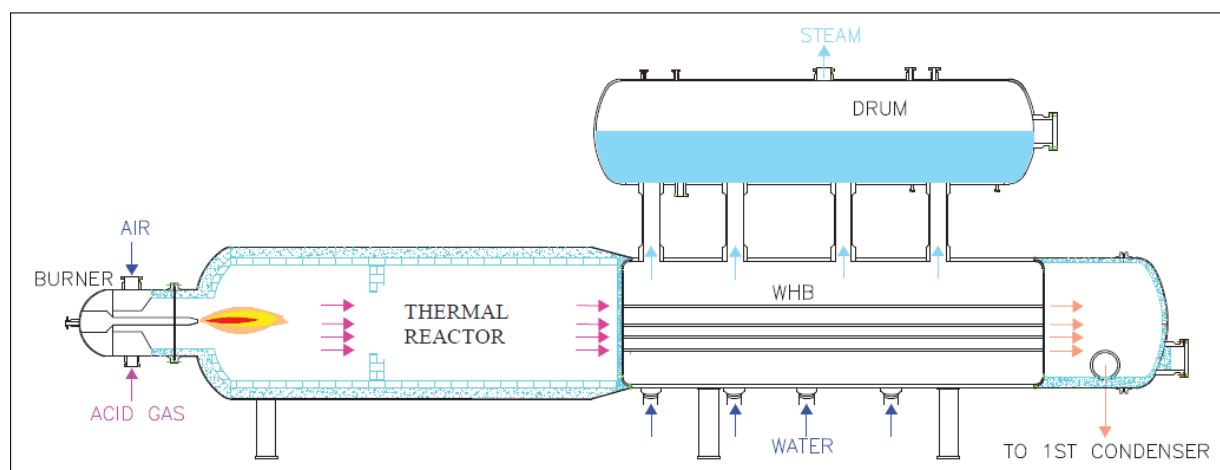


Fig. 4.2: Layout of a typical SRU Waste heat boiler (Manenti et al., 2012)

The TR is an axial-symmetric chamber internally lined by refractory to prevent overheating of vessel walls. The WHB is used for cooling the hot gas leaving the TR to an operating temperature suitable for sulfur condensation and catalytic oxidation. This boiler, directly connected to the TR, is of shell-and-tube type, with gas flowing on tube-side, and with boiling water on shell side. Either a kettle type boiler or a boiler-and-drum arrangement is used. A moderate slope towards outlet of tubes may be provided for draining possible liquid sulfur. Boiling water performs a rapid and effective removal of heat. Depending on acid gas composition, temperature of combusted gases in the TR is in a range of 1100 to 1400°C. At the boiler outlet the tem-

perature is around 300°C. However, the cooling is not rapid enough to prevent recombination reactions such as $\text{H}_2 + 0.5\text{H}_2\text{S} \rightleftharpoons \text{H}_2\text{S}$. Such reactions are exothermic, therefore, they have an impact on boiler heat transfer surface, number and operating temperature of tubes.

Manenti et al. (2012) have presented a model for the design of TR and WHB taking into account recombination reactions. The computational model was described for a monodimensional geometry and stationary conditions, and constituted of energy and chemical species conservation equations. The study showed that the TR and WHB can be considered a single plug flow reactor. The thermal reactor represents an adiabatic portion, whereas the boiler a non-adiabatic one.

4.2.2 Catalytic converter

The unreacted acid gas from the TR has an $\text{H}_2\text{S}:\text{SO}_2$ molar ratio of 2:1 (ZareNezhad and Hosseinpour, 2008). H_2S and SO_2 react further over an alumina catalyst in one or more subsequent catalytic converters according to the Claus reaction described in Section 4.1. Catalytic converters are usually designed for a flow at operating conditions of 28–56 m³/h of process gas per cubic feet of catalyst bed (GHSV = 1000–2000 h⁻¹). Because of the pressure drop, this results in a bed depth of 1–1.5 meters. The catalyst is activated alumina and/or titania which is installed on the top of a 3–6 in thick layer of more dense support material.

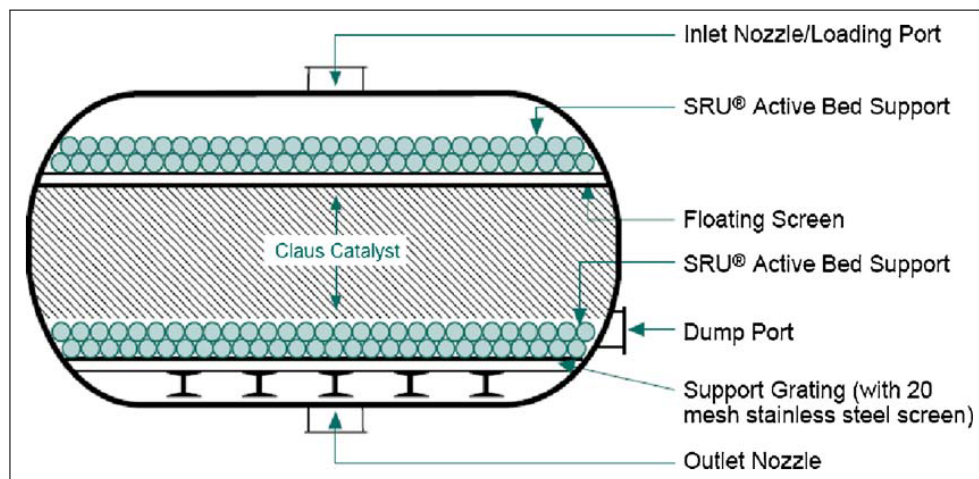


Fig. 4.3: Configuration of a Claus catalytic converter (ZareNezhad, 2009)

The first converter must handle the hydrolysis of COS and CS₂ which if not hydrolyzed will result in lower conversion efficiencies. A fuel gas fired reheater is used to run the first converter at a temperature sufficiently high to accomplish 90–95% hydrolysis of COS and CS₂.

This design criterion is also combined with having a TiO_2 catalyst that in the bottom half of the catalyst bed at the first converter promotes hydrolysis reactions. Fig. 4.3 shows the typical configuration of a Claus converter.

Conventional activated alumina Claus catalysts have high activity for converting H_2S and SO_2 to sulfur under most normal conditions. However, alumina has two serious limitations. The first is its limited ability to decompose COS and CS_2 , and the second is the overall activity under severe sulfating conditions for even the $\text{H}_2\text{S}/\text{SO}_2$ reaction. In these two situations, the use of titania catalyst is recognized as the better solution because of its ability to give high conversion of all the sulfur species to elemental sulfur, even under conditions when alumina is deactivated from sulfation.

4.2.3 Catalysts

Two main types of catalysts are used in conventional Claus units: activated alumina (UOP product numbers S-201 and S-2001) and titania catalysts (UOP product number S-7001). They vary in their capability to hydrolyze COS and CS_2 and to resist poisoning (sulfation). These Claus catalysts may be used alone or in combination in the beds depending upon performance requirements.

The UOP S-201 catalyst (activated alumina) delivers excellent results when H_2S is the primary compound to be removed from the feed gas. S-2001 provides exceptional conversions of $\text{H}_2\text{S}/\text{SO}_2$, COS and CS_2 due to its high macroporosity, high surface area, and thermal stability without sacrificing physical properties. S-2001 is also more effective for COS and CS_2 conversion than S-201, and is therefore preferable for use in the first reactor of a typical Claus plant.

The UOP S-7001, a titanium dioxide-based Claus catalyst, has a tailored pore structure that allows for high rates of diffusion of reactants and products. S-7001 is well suited for maximizing the conversion of COS and CS_2 in the first converter. In the second and third converters, it is very beneficial due to its resistance to sulfur poisoning and longevity in maintaining high $\text{H}_2\text{S}/\text{SO}_2$ conversion.

The general classification of Claus sulfur recovery catalysts together with the different manufacturers are given below (ZareNezhad, 2009):

1. Conventional alumina-based sulfur conversion catalyst used in natural gas plants, refineries and smelters having Claus process plants and other types of sulfur recovery plants: UOP, S-201; Axens, CR; ShanDong XunDa, A918.
2. New generation catalyst for Claus units in natural gas processing plants, oil refineries, coke plants, and sub-dewpoint tail gas units such as MCRC (Mineral and Chemical Resource Co.), CBA (Cold Bed Adsorption) or Sulfreen. It provides high conversions of $\text{H}_2\text{S}/\text{SO}_2$, COS and CS_2 due to its high macroporosity, high surface area, and thermal stability: UOP, S-2001; Axens, CR 3S; Almatiss, DD431; ShanDong XunDa, A2000.
3. Sulfation resistant sulfur recovery catalyst used in natural gas plants, refineries, and smelters having Claus process plants and other sulfur recovery plants. Also, used in first reactors for improved COS/ CS_2 conversion: UOP, S-501; Axens, CSM 31; ShanDong XunDa, A931.
4. Promoted activated alumina that is used to scavenge oxygen in Claus reactors employing alumina catalyst. It is used as a top layer in Claus catalyst beds to protect the alumina catalyst bed beneath it from being poisoned by sulfation due to oxygen breakthrough: UOP, S-601; Axens, AM; ShanDong XunDa, A958.
5. Specialty titania sulfur recovery catalyst for Claus units in natural gas processing plants, oil refineries, and coke plants. It is particularly suited for use in the first converter for the high conversion of COS and CS_2 . This extra high COS/ CS_2 conversion is especially important for Claus plants that employ tail gas treating units that may not completely convert COS and CS_2 , such as selective-oxidation units and sub-dewpoint systems: UOP, S-7001; Axens, CRS 31; ShanDong XunDa, A988.
6. Top and bottom support in Claus catalyst beds and adsorption beds. The use of activated alumina support allows for cost saving compared to the use of inert support due to the lower bulk density of the activated alumina, and the activated alumina support provides some Claus catalytic activity or adsorption capacity: UOP, CBS; Axens, DR.

There are various parameters which should be considered for final selection of a Claus

catalyst. Typical chemical and physical properties of a suitable alumina Claus catalyst are given in Table 4.1 (ZareNezhad, 2009).

Table 4.1: Chemical and physical properties of alumina Claus catalysts

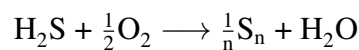
Composition	Al ₂ O ₃ >93 wt.%, Na ₂ O: 0.30.5 wt%, LOI (1000°C): 26 wt%
BET surface	>325 m ² /g
Particle size	1/81/4 in. (usually 3/16 in. 5 mm)
Mean pore size	40–90 Å
Total pore volume	>0.50 mL/g
Macroporosity (>750 Å)	>0.15 mL/g
Mechanical strength (5 mesh)	>140 N/cm
Bulk density	<641 kg/m ³
Attrition loss	<0.4 wt.%

With more stringent regulations, the concentration of residual sulfur compounds in the tail gas from a Claus plant is still unacceptable. Developments such as the SuperClaus process (Section 4.3) and the SCOT process (Section 4.4) have resulted in sulfur recoveries of nearly 100%.

4.3 SUPERCLAUS process

The SUPERCLAUS process was developed to catalytically recover elemental sulfur from H₂S containing Claus tail gases to improve overall sulfur recovery level of a sulfur recovery facility. The process was commercially demonstrated in 1988, and today more than 160 units are under license and over 140 are in operation.

The process is based on a proprietary catalyst for the selective oxidation of H₂S to elemental sulfur in the last reactor stage according to the following reaction:



The reaction is thermodynamically complete and high conversion of H₂S to elemental sulfur can be obtained (van Nisselrooy and Lagas, 1993).

In the SUPERCLAUS process (Fig. 4.4) the conventional H₂S:SO₂ = 2:1 ratio is no longer applied. Instead, the H₂S concentration in the gas leaving the second Claus reactor stage is

controlled between 0.8–1.5 vol.%. The thermal stage and the two catalytic Claus reactor stages are therefore operated with excess H_2S . The combustion air is divided into two streams. The major portion (95%) is charged to the acid gas burner in the combustion chamber, and the remaining quantity is mixed with the tail gas coming from the second Claus reactor stage. This gas mixture is passed to the selective oxidation reactor (the SUPERCLAUS reactor).

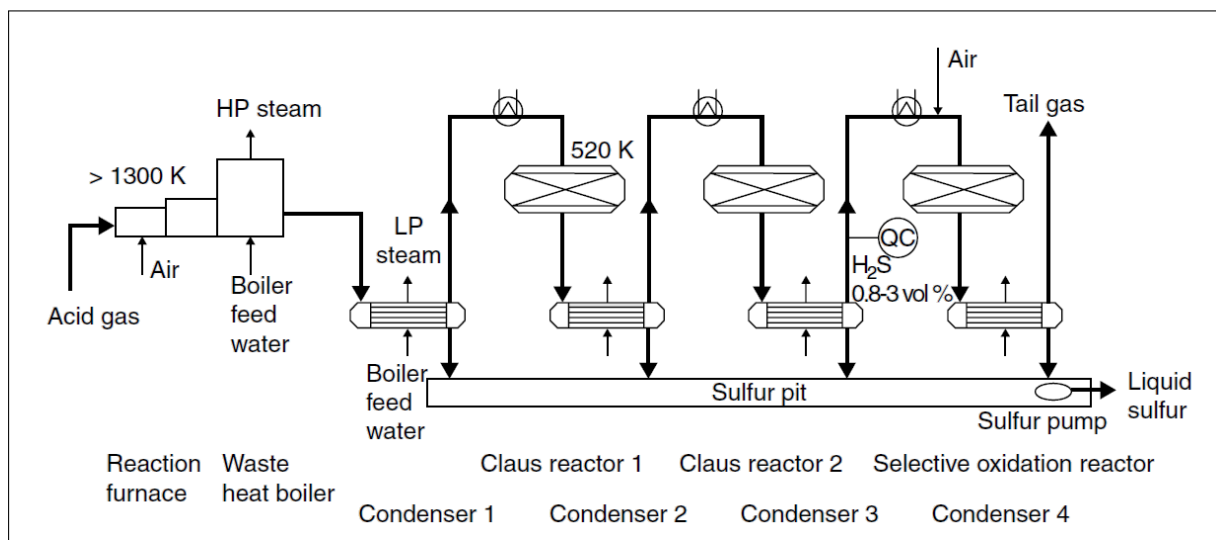


Fig. 4.4: Flow scheme of the SUPERCLAUS Process (Moulijn et al., 2001)

The Claus reaction ($2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{S}(\text{vapour}) + 2\text{H}_2\text{O}$) now takes place in the thermal stage as well as in both Claus reactor stages, but now with excess H_2S . This shifts the equilibrium in such a way that the SO_2 concentration in the gas will be depressed. The H_2S is subsequently oxidized in the SUPERCLAUS reactor to elemental sulfur according to the reaction $\text{H}_2\text{S} + \frac{1}{2}\text{O}_2 \rightarrow \frac{1}{n}\text{S}_n + \text{H}_2\text{O}$.

4.4 Shell Claus Off-gas Treating Process

In the SCOT process, all the sulfur-containing components in the Claus off-gas (SO_2 , CS_2 , COS) are converted to H_2S in the presence of hydrogen and a catalyst. The Claus tail gas is injected in a special burner, which produces reducing gas (H_2 and CO) by incomplete fuel combustion. If available, an external source of reducing gas can also be used. In the SCOT reactor, conversion into H_2S takes place by reaction with hydrogen. After cooling of the gas, H_2S can then be removed from the gas stream by absorption in an alkanolamine solution.

An appreciable amount of CO_2 is present in the gas stream to the absorber, so ceH_2S absorption should be selective. This is achieved by choosing the conditions in the absorber such

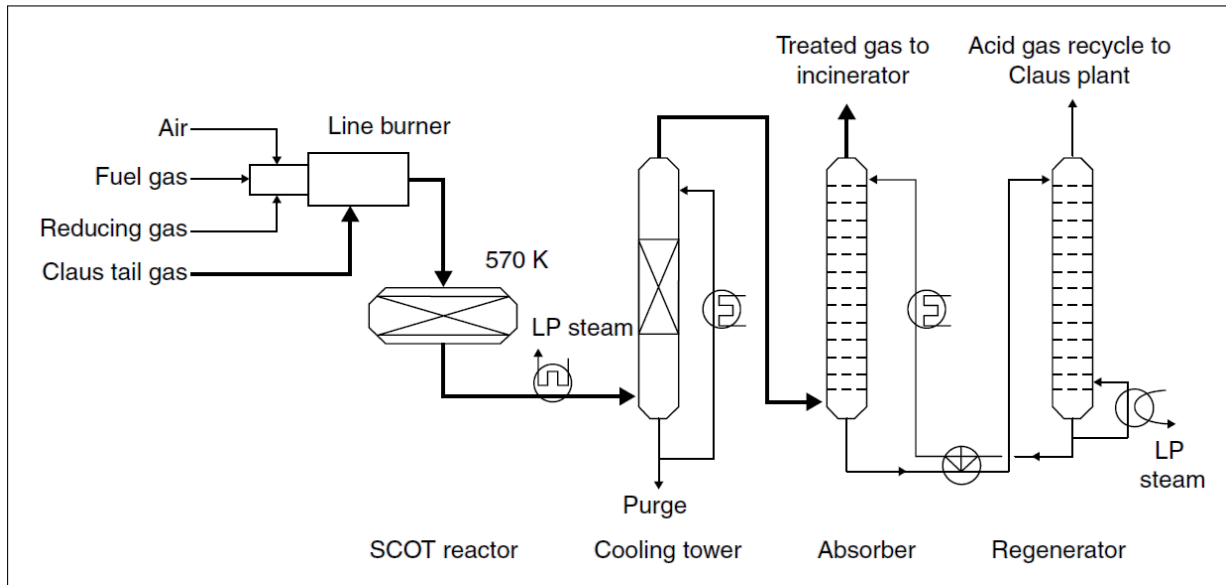


Fig. 4.5: Flow scheme of the SCOT process (Moulijn et al., 2001)

that the bonding of H_2S to the amine is strong, while reaction of carbon dioxide with the amine is minimal (Moulijn et al., 2001).

As shown in Fig 4.5, the process has three sections:

1. a reduction reactor, in which all the sulfur compounds present in the Claus tail gas are converted to H_2S
2. a cooling/quench section, where the reactor off-gas is cooled and the water is condensed
3. an absorption section, in which H_2S is selectively absorbed by an amine solution. The loaded solvent is regenerated and the acid gas released is recycled to the inlet of the Claus unit.

Selective absorption is based on the fact that the rate of absorption of H_2S in alkanolamines is substantially more rapid than that of CO_2 . Appreciable selectivity may be attainable by proper selection of the amine and by designing the absorber for short gas and amine solution contact times. In most applications, methyldiethanolamine (MDEA) is the preferred solvent.

SCOT units can be designed with a dedicated amine regenerator or with a shared amine system. The overall costs are lower if a common amine regenerator is used for the desulfurization and SCOT units (Kohl and Nielsen, 1997)

5 | Conclusions

Desulfurization by way of hydrotreating in the oil refining industry is largely seen as a mature technology. However, as the availability of crude and quality of crude decline, refiners must ensure that they have the capabilities to ensure that statutory fuel standards are met. Hydroprocessing is still the most prevalent technique for desulfurization of gasoline and diesel. In HDS based technologies, less room for breakthroughs exists. Process intensification of the current conventional processes is the most challenging option for the improvement of HDS based technologies.

Novel processes such as biodesulfurization and extraction, have to show a competitive advantage over the tried-and-true chemical methods present in the industry. Biodesulfurization may lead to successful desulfurization, but there are technical difficulties related to the refractory nature of the sulfur molecules that must be metabolized. Microorganisms with a high sulfur specificity are required, as well as ways to overcome transport limitations. The main disadvantage of extractive processes is that the involvement of an additional phase would lead to large process equipment and reduced efficiency. Although in this report only three non-conventional desulfurization processes have been discussed, the review is by no means an exhaustive one. Selective oxidation of sulfur compounds into hydrocarbons and volatile sulfur products might also be attractive for desulfurization. Autoxidation (oxidation with air as oxidant) is a viable desulfurization strategy for heavy oil. Autoxidation itself leads to little desulfurization and it must be used in combination with a sulfur removal step.

The Claus process is limited by the equilibrium relationships of the chemical reactions on which it is based. To overcome these limitations, the basic Claus process has to be supplemented with another process specifically designed to remove residual sulfur compounds from the Claus plant tail gas. The recovery efficiency of Claus plants is continuously being improved by better plant operation, better design methods, and developments of the process technology. Control of air pollution, rather than recovery of sulfur is the main driving force in the development of efficient Claus-type processes.

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