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Review article

Investigation and comparison of technologies and methods of sulfur recovery and production processes

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ABSTRACT

Sulfur is found at the land's surface, in quarries, and as a natural sulfur resource. However, most of the part sulfur is obtained during the sulfur removal processes from crude oil or gas. These recovery processes are essential for the global energy resource market. Approaches to sulfur mining and recovering techniques are discussed and compared during the literature review and description analysis. Methods that are majorly used in the industry, their process flow diagrams, and principal of work are explained and compared relative to the modern methods of sulfur removal processes.

Keywords: *Sulfur, Claus process, Frasch method, catalyst, unit, heater, reaction, conversion.*

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Научный обзор

Исследование и сравнение технологий и методов процессов извлечения и производства серы

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АННОТАЦИЯ

Сера встречается на поверхности земли, в карьерах и в виде природных серных ресурсов. Однако большую часть серы получают в ходе процессов удаления серы из неочищенной сырой нефти или газа. Эти процессы извлечения необходимы для глобального рынка энергетических ресурсов. Подходы к методам добычи и извлечения серы обсуждаются и сравниваются в ходе обзора литературы и анализа характеристик. Методы, которые в основном используются в промышленности, их технологические схемы и принцип работы объясняются и сравниваются с современными методами процессов удаления серы.

Ключевые слова: *сера, процесс Клауса, метод Фреша, катализатор, установка, нагреватель, реакция, конверсия.*

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Ғылыми шолу

Күкірт алу мен өндірудің процестерінің технологиялары мен әдістерін зерттеу және салыстыру

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АННОТАЦИЯ

Күкірт жер бетінде, карьерлерде және күкірттің табиғи ресурсы ретінде кездеседі. Алайда күкірттің көп бөлігі тазартылмаған шикі мұнайдан немесе газдан күкіртті тазалау процестері арқылы алынады. Бұл қалпына келтіру процестері әлемдік энергия ресурстары нарығы үшін өте маңызды. Күкіртті өндіру және алу әдістерінің тәсілдері әдебиеттерді шолу және сипаттамаларды талдау кезінде талқыланады және салыстырылады. Негізінен өнеркәсіпте кеңінен қолданылатын әдістер, олардың технологиялық сызбалары және жұмыс принципі түсіндіріліп, күкіртті жоюдың заманауи әдістерімен салыстырылады.

Негізгі сөздер: *Күкірт, Клаус процесі, Фреш әдісі, катализатор, қондырғы, қыздырғыш, реакция, конверсия.*

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Introduction

Sulfur is an element that is widely found in the content of crude oil and raw petrochemical resources. Usually, considered an undesirable by-product in the industrial production of petroleum resources as it is able to produce sulfur dioxide and affect the catalytic reaction of the refinery processes, therefore sulfur removal is one of the crucial processes in petrochemistry [1].

Sulfur can have a ring or chain structure and can be existed as “Sx”, where x can vary from 1 up to 8, this relativity is depended on the temperature.

Figure 1 illustrates the dimensional structure of octasulfur (S8). Figure 2 shows the dependence of sulfur vapor species on the temperature.

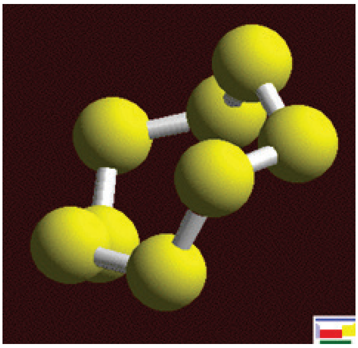

Figure 1. Octasulfur, S_8

Source: inside.mines.edu

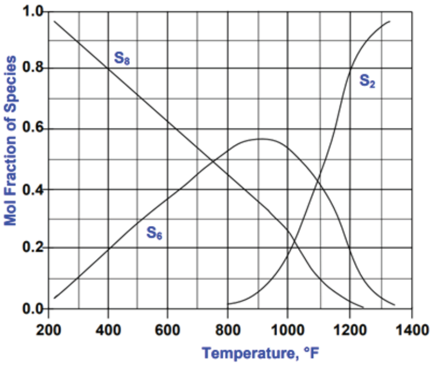

Figure 2. Sulfur mole fraction species and temperature dependence

Source: inside.mines.edu

Sulfur is obtained during the processing of crude oil; the amount of sulfur in the content of crude oil directly depends on the grade and quality. Species of sulfur remained after the processing is removed through the conversion processes during the cracking of hydrocarbon molecular bonding and formation of H_2S. There is also an approach to sulfur removal by hydrotreating, where the sulfur is replaced with hydrogen atoms in order to release H_2S. Combining processes, listed above, released and formed H_2S gas is granulated and converted into elemental solid sulfur. Then it can be sold in the global market in solid or liquid phases.

Sulfur production processes

There are three main approaches to sulfur production:

1. Sulfur removal processes at oil and gas process plants.
2. Frasch method of sulfur production from mining wells.
3. Dug out of open quarries.

Claus process description

Claus process is widely used in the oil and gas industry in the oil refinery fields where the H_2S content is around 25%. The purpose of the Claus unit is to desulfurize the incoming amounts of sulfur from the fed stream. There are two major stages of sulfur removal, thermal and catalytic, where the catalytic stage helps in 3 steps. It is reheating of the reagent, then the catalytic reaction is performed and the final stage is cooling and condensation.

The first thermal stage is held at the temperature level of 850°C, after the reheating of the reagent catalyst is used as a surface of the reaction, where remained H_2S enters the reaction with SO_2 to form sulfur, this reaction is held at the temperature range of 200–350°C. After the catalytic reaction gas is cooled to 100–150°C and sulfur is condensed and removed from the process [2].

Figure 3 illustrates the sulfur recovery unit of the Claus process with 3-stage reactors where the catalytic reaction has occurred.

The overall equation of Claus reaction is stated as:

$$2H_2S+O_2 \rightarrow 2S+2H_2O \quad (1)$$

The catalytic stage contains a reheater, catalytic bed, and condenser.

The burning process includes the reaction of 1/3 of H_2S gas with the air as a result sulfur dioxide is formed. The equation of this reaction is stated as:

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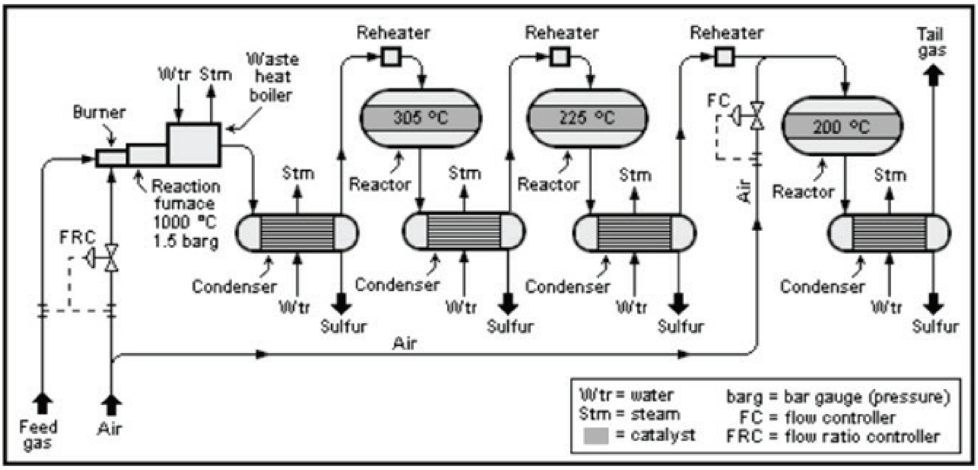

Figure 3. Claus sulfur removal unit process flow diagram

Source: valcogroup-valves.com

$$2H_2S+3O_2 \rightarrow 2SO_2+2H_2O + heat \qquad (2)$$

The operating conditions of the furnace are around 1000–1500°C and 70 kPa. Hot gas released from the bed needs to be extinct before it enters the condenser. This approach is crucial for the formation of the generation of gases at high and medium pressures. The major part of released heat can be used as a source of energy for the other utilities of the plant. Formed sulfur at liquid phase and pumped to the sales pipeline or railcars for third-party users. Through this process, almost 60–70% of fed sulfur is removed and recovered. The rest of the fluid is sent to catalytic chambers [3].

The remained amount of H_2S (2/3 part) reacts with sulfur dioxide and forms sulfur through the Claus reaction:

$$2H_2S+SO_2 \longleftrightarrow 3S+2H_2O + heat \qquad (3)$$

The operating temperature of this catalytic reaction should be held in the range of 200–300°C. The reaction is in equilibrium, therefore, it is impossible to complete the reaction and convert all H_2S to sulfur. 2 and more stages are used to maximize the recovered amount of produced sulfur. The regular capacity that can be recovered during the single stage of the catalytic reaction is one 2/3 of the fed sulfurous fluid. Considering equilibrium reaction and appropriate quantity of catalytic stages, after the Claus process 3–5% of entered sulfur cannot be removed from the stream.

The sources of steam used for reheating purposes can vary due to the different types of fuel. for the natural gases and gaseous

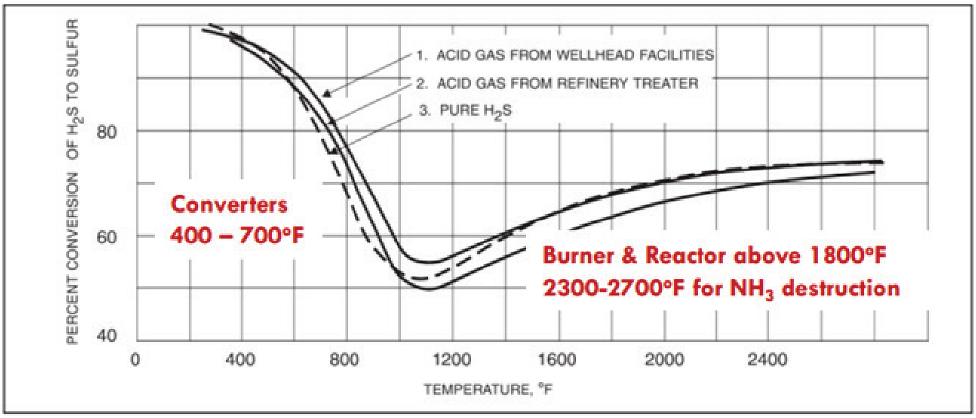

Figure 4. Equilibrium of H_2S conversion to sulfur

Source: inside.mines.edu

substances that are released during the process, steam is supplied from heat exchangers and other secondary burners. Meanwhile, for crude oil refineries, used steam pressure for steam is normally in the range of 3500–4200 kPa. Outlet streams of the Claus process are released after the final catalytic stage in the form of tail gas, which contains sulfur, H_2S, SO_2 other inert gases that do not participate in the reaction. Therefore, the tail gas clean-up unit is used in addition to the Claus unit to achieve the highest recovery percentage [3].

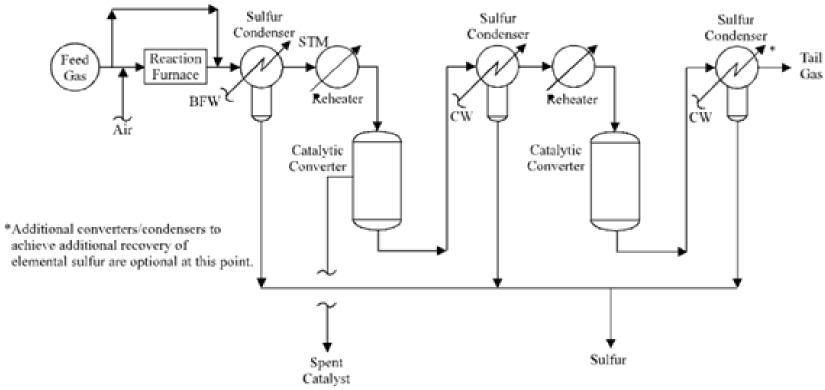

Figure 5. Claus reaction step-by step process illustration

Source: epa.gov

During the combustion reaction in the furnace, the following side reactions may occur due to the oxidation:

$$CO_2+H_2S \rightarrow COS+H_2O \quad (4)$$

$$COS+H_2S \rightarrow CS_2+H_2O \quad (5)$$

$$2COS \rightarrow CO_2+CS_2 \quad (6)$$

Sulphur recovery from the mines

The fundamental principle of this method is the usage of hot water as the initiator of the mining process for the source of native sulfur. During the process, the sulfur is melted and pushed to the surface by the force of compressed air. The Frasch process utilizes a steel tube made up of three concentric pipes that are driven underground to reach the sulfur deposit. Superheated water is pumped down under significant pressure in the outermost pipe to melt the sulfur. Air pressure from the innermost tube forces the sulfur up the third pipe to the surface where it cools and solidifies [4]. The Frasch process is not applicable in the oil industry as it is used in the sulfur mines only.

Modern and perspective sulfur removal technologies

The AECOM "CrystaSulf®" Process

The operating cost of single-use chemicals for the sulfur removal processes is higher and strongly depends on the total gas streams (amine treatment units and clause process units). During the CrystaSulf process, SO_2 is used as an oxidant by the use of the modified Claus process occurred at the liquid phase as the elemental sulfur can be completely soluble. This approach is used to avoid the formation of solids in the vessels and pipes that can cause damage to the equipment. Crystalized sulfur is solidified and separated at the equipment designed for solid handling [5].

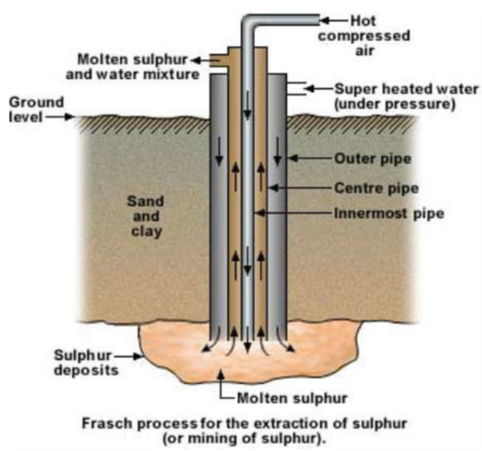

Figure 6. Illustration of Frasch process

Source: nuroil.com

Finally, the sulfur is removed from the feed stream and able to reach the specification of 4 ppm of H_2S at the operating pressure of 10 bars. Furthermore, CO_2 has no effect on the whole process of sulfur removal and pH measurement is not required. In addition, CrystaSulf is able to operate at high and low pressure gas streams and it is applicable for the sulfur recovery process of the gas streams containing 5% wt of sulfur. Production range varies from 0.2 up to 25 tons per day for the gas streams with higher concentration of sulfur Claus process is recommended. Operating temperature is between 40–80°C, used solvent does not form foams or sulfur settling with feed gas streams containing hydrocarbon groups [6].

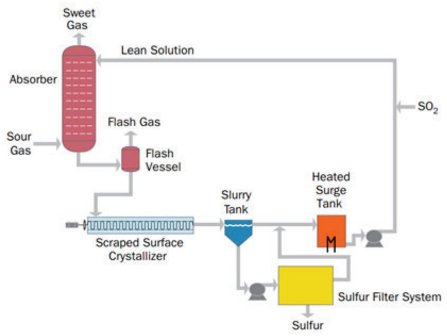

Figure 7. Process flow diagram of Crystalsulf process

Source: aecomprocesstechnologies.com

The Selectox Process

This approach is applicable for the feed gas streams with the content of hydrogen sulfur in the range between 5 molar% and 40 molar%. The conversion of sulfur can vary between 90–95%.

Selective amine is used for the hydrogen sulfur removal in the hydrogenation reactor (Exxon Flexsorb SE Plus or Union Carbide UCARSOL HS-103 represented in figure 8). Regeneration of selective amine causes the formation of reach sulfur gas. The process contains Selectox reactor and condenser. The outlet temperature of the reactor should not exceed 400°C. for the gas streams with 40 molar% of sulfur content, two staged Selectox reactor is used. This process is performed without flames and only catalytic reactions occur in the reactors. Special catalyst occupies the surface of the bed for the oxidation, where the most SO_2 is formed, it the remained space of the vessel Claus process is performed with Claus catalyst [7].

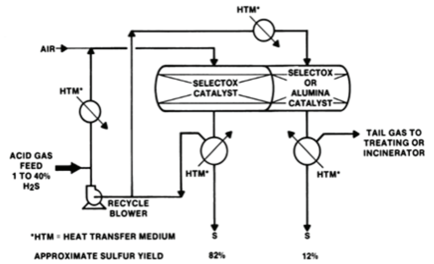

Figure 8. Process flow diagram of two-stage Selectox process

Source: chempedia.info

Conclusion

It can be seen that there are three major sulfur production approaches. They can be defined according to the depth of natural sulfur resources. Sulfur can be found at the careers or mined from the surface of the land. It can be mined using the simple Frasch method and recovered from the gas processing plants.

Mainly, the Claus process is the most widely used process in the petrochemical industry. However, through the years of exploitation and usage of Claus units, the process of sulfur removal and the types of used catalysts were modernized in order to reduce the cost and increase the efficiency of the process according to the modern specification. The latest changes to the Claus unit give the ability to increase the conversion rate nearly equal to 100%. for instance, CrystalSulf process has relatively lower treatment and maintenance costs, the solubility of sulfur is higher, avoids the formation of solid sulfur, etc. Meanwhile, Selectox process operates at lower temperatures to avoid burning and combustion, therefore it performs a catalytic reaction. However, some of these processes are applicable or the gas streams with low concentration of sulfur, therefore, Claus process is used and combined. In addition, Claus process, tail gas treatment units and SCOT processes are used for steam generation due to high heat release.

Considering the fact that sulfur removal units are mostly used to remove sulfur from crude oil or natural gas. Therefore, removal processes are crucial for the global energy resource market; as the removal expenses and technologies are directly affect the price of crude oil and gas.

ДОПОЛНИТЕЛЬНО

Источник финансирования. Автор заявляет об отсутствии внешнего финансирования при проведении исследования.

Конфликт интересов. Автор декларирует отсутствие явных и потенциальных конфликтов интересов, связанных с публикацией настоящей статьи.

ADDITIONAL INFORMATION

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