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Control of Claus Unit Tail Gas in an Oil Refinery

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Abstract— **Due to high pollution of the Claus sulfur recovery units in oil refineries, more treatment of tail gas of sulfur recovery unit is needed. Sulfur recovery unit of a refinery in Iran had selected as a target unit and detailed condition of it had surveyed. According to different treating processes, environmental limitation and tail gas treating processes, amine- based hydrogenation process was selected as an optimum process for efficient removal of sulfuric components of tail gas. Finally, proposed process was simulated in HYSYS software and different specifications of the process were achieved.**

Keywords- Sulfur Recovery Unit, Tail Gas Treating Unit, Amine- Based Process, Sulfur Dioxide, Hydrogen Sulfide

I. Introduction

Through refining process in refineries, sulfur must be removed from petroleum hydrocarbons. In refineries, this process is carried out by hydrogenation and conversion of sulfuric compound to hydrogen sulfide. Then hydrogen sulfide flows to sulfur recovery unit, where salable sulfur produced. One of the most important sulfur recovery units is Claus unit. More than half of the refineries in the world use Claus unit, especially for units more than ۱۰ to ۱۵ tones per day sulfur production [۱, ۲]. Equation (۱), Claus unit main reaction is an equilibrium reaction, so we never have ۱۰۰٪ conversion and some unreacted sulfuric compounds exit from the system [۳].

$$۲H_۲S_{(g)} + SO_{۲(g)} \longrightarrow ۳/nS_{n(g)} + ۲H_۲O_{(g)} \quad (۱)$$

Claus unit efficiency differs according to reactor stages and feed compositions [۴]. Summery of Claus units processes are in Table I.

TABLE I. CLASS UNIT EFFICIENCY ACCORDING TO REACTOR STAGES [۴]

Reactor stages	Overall Efficiency	Efficiency	
۱	۹۰٪	*Rich Gas*	*Lean Gas*
۲	۹۴٪ ~ ۹۷٪	۹۵٪	۹۳٪
۳	۹۴٪ ~ ۹۷٪	۹۷٪	۹۶٪

On the other hand, environmental standards of sulfur recovery units are more limited and it would be restricted day to day. For example, U.S environmental protection Agency legislates efficiency of ۹۹,۸٪ for Claus unit with capacity of more than ۲۰ tones per day or ۲۵۰ ppm for exit H۲S concentration from Claus unit [۵]. According to another standard, efficiency of Claus units with capacity of more than ۱۰ tones per day should be ۹۹,۸٪ from ۱۹۹۳ [۶]. In Iran, Standards are not up to date and there is only one standard for sulfur recovery units. It is only for exhaust sulfur dioxide without capacity consideration, which is ۸۰۰ or ۱۰۰۰ ppm due to unit situation [۷], while Claus units exhaust pollutants of Iranian refineries is much higher and almost thousands of ppm. Tail gas composition is very different due to different types of Claus unit.

By considering environmental limitations and Claus unit disability for removal of sulfuric components from tail gas, it cleared that tail gas must be treated by additional process.

II. Literature Survey

Several processes were introduced for treatment of Claus unit tail gas and most of these processes could be classified as following.

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A. Dry bed process

Clauspol process or liquid sulfur production unit is one of the sulfur recovery processes. In this process, Claus reaction has done in a counter current packed reactor with a medium like organic solvent like polyethylene glycol and sodium salicilate as a catalyst and alkaline/earth alkaline organic acid salts as another catalyst. Liquid sulfur produced in this process. Some sulfur dioxide and hydrogen sulfide remain in this process. Therefore, this is a disadvantage [۸]. Another disadvantage of this process is side reactions in the reactor that produces unwanted products like alkaline sulfates and tiosulfates. They decrease efficiency of catalyst and also quality of produced sulfur. Efficiency of this process is about ۹۹,۹٪ [۹-۱۱].

B. Cold Bed Absorption

Cold bed absorption processes is another process for tail gas treatment. Claus reaction is used in this process too. Claus reaction is an exothermic reaction, so temperature is decreased below sulfur dew point (۱۳۲ ~۱۴۹ °C) in the reaction and sulfur in the gas phase is condensed and transferred the equilibrium the production of more sulfur. Liquefied sulfur deposed on the catalyst. Catalyst was generates periodically and sulfur is removed [۱۲]. So, two reactors are needed simultaneously; one for reaction and another one for regeneration. Alumina was used as a catalyst, due to big porosity and more capacity for liquefied sulfur adsorption [۱۳]. Overall efficiency of this process is about ۹۸,۵٪ [۱۴].

C. Amine- Based process

Shell Claus Off-Gas treating process is one of these processes. In this process, tail gas reacts with a reducing gas like hydrogen and all of sulfuric compound are converted to H_2S. Then they flow to an amine absorption stage to absorb H_2S from gas stream. Efficiency is about ۹۹,۹٪ , which is more than other tail gas treating units are. Also with minor changes in operations higher efficiency, (۹۹,۹۹+ %) could be achieved. This process named as a "best available control technology" [۱۵].

D. Redox- Based process

Beavon/stretford or lo-cat process are examples of this process, Tail gas is scrubbed with an alkaline solvent like di-sodium antra-quinon di-sulfate salt and soluble sodium vanadate in a counter current absorber. Solvent reduced and hydrogen sulfide is oxidized to sulfur. So sulfur concentrated absorber contacts with oxygen in a desorption tower and foamed sulfur is floated at the top of tower and is remove with filtration.

Stretford solvent is another medium for this process. In this solvent on aldehyde like formaldehyde added to beavon solvent. Stretford solvent increases the efficiency and decreases side products like tiosulfate salts [۱۶].

It suggested that for higher efficiencies, first all of sulfuric compounds regenerated to H_2S and then reacted with a medium [۱۷].

Another redox-based process uses iron chelated groups as a medium which reduces Fe^{3+} to Fe^{2+} and oxidizes H_2S to elemental sulfur. Name of this medium is Lo-CAT and efficiency of this unit is about ۹۹,۸۵٪ [۱۸].

E. Oxidation processes

One of elementary processes for H_2S decrease is incineration of tail gas and conversion of H_2S to SO_2. By increasing temperature to about ۶۵۰ °C all of sulfuric compound were oxidized to SO_2 in an incinerator. These processes produce poisonous gases such as SOx so oxidation process is not environmentally friendly [۱۹].

III. SELECTION OF OPTIMUM UNIT

For selecting an optimum tail gas-treating unit, the following factors must be considered:

- Unit efficiency and exit sulfur concentration and exit gases standards
- Feed characterization such as: flow rate, H_2S content, feed composition and impurities
- Operation simplicity, investment cost, operational cost and finally unit situation [۲۰].

By considering current treating units and their advantages and disadvantages and information of Iranian refineries, it seemed that amine- based process is the best process for tail gas treating in Iranian refineries.

The reasons of this suggestion are as follows:

- This process is best available control technology.
- H_2S concentration in Claus tail gas (in refineries) is very high and due to high efficiency of this process, pollutants could be removed efficiently.
- Availability of hydrogen gas (Hydrogen production unit is available in refinery).
- Due to lack of the waste disposal system, there is no tend to waste producing processes, so selected process is a proper item because it does not produce any waste.
- Since all the refineries have amine units, so operation of the amine section of the selected process is more convenient.
- All sulfuric compounds could be removed from tail gas.
- Spent amine in the process could be used in amine unit of refinery so operational cost would be decreased.
- Claus unit flow rates and compositions are fluctuating most of the times, and amine-based process is a proper choice to treat this tail gas.

IV. AMINE- BASED HYDROGENATION PROCESS SIMULATION

In continue, a refinery was selected and detailed information of claus unit and results of simulation for amine based process in HYSYS software is written. Figure I shows schematic of an amine– based hydrogenation unit and composition of tail gas in different stages of this process is in Table II.

TABLE II. CHANGE IN COMPOSITION OF TAIL GAS THROUGH DIFFERENT STAGES IN SUGGESTED PROCESS

Point	H_2S	SO_2
۱	۹,۸۷۴e-۳	۹,۲۵e-۳
۲	۱,۴۵۲۵e-۲	۴,۶۲e-۴
۳	۸e-۶	۶,۱e-۴

* Data are in mass fraction

V. CONCLUSION

Tail gas of sulfur recovery units of an oil refinery even in optimum operational conditions has many pollution and releases dangerous pollutants into the environment like hydrogen sulfide and sulfur dioxide. So another process should be used after sulfur recovery unit to treat tail gas.

In Iran, tail gas flows into an incinerator and all sulfuric compounds combusted with oxygen and change to sulfur dioxide.

Therefore, the exhaust gases releases to the environment, concentrates in sulfur dioxide and have high pollution.

Present research is carried out based on environmental purposes. This research introduces a new horizon in Iranian oil refining industry. In this research, first sulfur recovery units of Iranian refineries were studied in details. Then different tail gas treating processes were studied. Finally, among all processes, amine-based hydrogenation process selected as the best choice. the selected unit was simulated with HYSYS software. Results of simulation show exhaust clean gas is evacuated from hydrogen sulfide and sulfur dioxide and could be vented to environment safely.

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REFERENCES

[۱] Polasek, J. C., J. A. Bullin, Effect of Sulfur Recovery Requirements on Optimization of Integrated Sweetening, Sulfur Recovery and Tail Gas Cleanup Units, Technical Paper, Bryan Research & Engineering, Inc., (۱۹۹۳).

[۲] Kurimura, H., G. T. Rochelle, K. Sepehrnoori, An Expert System to Select Acid Gas Treating Processes for Natural Gas processing Plants, Gas Separation and Purification, V, pp ۱۵۱-۱۵۸, (۱۹۹۳).

[۳] Pool, J. V., US Pat. No ۴,۳۳۱,۶۳۰, Phillips Petroleum Company, (۱۹۸۲).

[۴] European Commission, Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries, (۲۰۰۳).

[۵] Linde BOC Process plants, Sulfur Process Technology, (۲۰۰۷).

[۶] Lurgi Company, www.lurgi.com.

[۷] Kayvani, N., environmental standards and laws, department of environmental publish, (۳۸۶).

[۸] LeComte, F., Ch. Streicher, D. Benayoun, C. Barrere-Tricca, US Pat. ۶,۲۷۷,۳۵۲B۱,Institute Francais du Petrole, (۲۰۰۱).

[۹] LeComte, F., Ch. Streicher, C. Barrere-Tricca, US Pat. ۶,۲۸۰,۶۹۸B۱, Institute Francais du Petrole, (۲۰۰۱).

[۱۰] Smith, D., D. Benayoun, C. Dezael, US Pat. ۶,۴۱۳,۴۸۸B۱, Institute Francais du Petrole, (۲۰۰۲).

[۱۱] Dezael, C., F. Lecomte, US Pat. ۶,۶۲۷,۱۰۸B۱, Institute Francais du Petrole, (۲۰۰۳).

[۱۲] Kunkel, L. V., J. W. Palm, L. E. Petty, H. Grekel, US Pat. ۴,۰۳۵,۴۷۴, Standard Oil Company (Indiana), (۱۹۷۷).

[۱۳] Tsybulevski, A. M., L.V. Morgun, M. Sharp, M. Pearson, O.E. Filatova, Catalysts Macro porosity and Their Efficiency In sulfur Sub-Dew Point Claus Tail Gas Treating Processes, Applied Catalysis A: General, ۱۴۵, pp ۸۵-۹۴, (۱۹۹۶).

[۱۴] Lell, R., G. R. All-Muddarris, R. Pachaly, US Pat. ۴,۳۱۵,۹۰۴, Davy International Aktienges ellschaft Company (۱۹۸۲).

[۱۵] Taggart, G. W., Ch. L. Kimtantas, H. T. Ball, J. H. Dibble, K. F. Butwell, EU Pat. ۰,۱۴۰,۱۹۱, Ford, Bacon and Davis Inc. (۱۹۸۵).

[۱۶] Fenton, D. M., B. B. Woertz, US Pat. No ۴,۰۸۳,۹۴۵, Union Oil Company of California, (۱۹۷۸).

[۱۷] Peterman, L. G., E. US Pat. ۴,۱۵۵,۹۸۷, Atlantic Richfield Company (۱۹۷۹).

[۱۸] Portz, B. D., US Pat. No ۲۰۰۲/۰۰۹۴۳۰۸A۱, Druce Dean Portz Co., (۲۰۰۲).

[۱۹] Pool, J. V. US Pat. ۴,۲۴۱,۰۴۰, Phillips Petroleum Company (۱۹۸۰).

[۲۰] Rameshni, M., State of Art in Gas Treating, British Sulfur ۲۰۰۰, San Francisco, CA-USA, (۲۰۰۰).

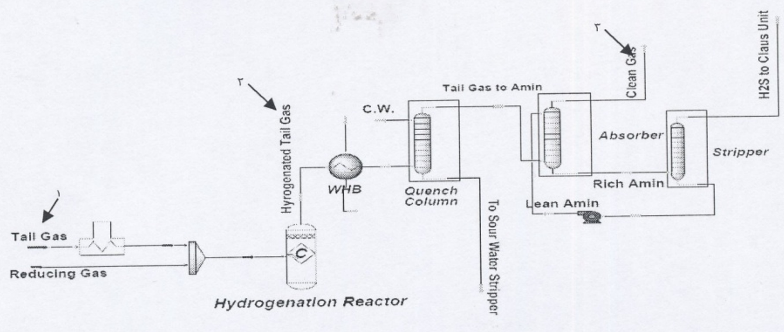

Figure ۱. Schematic flow sheet of amine- based unit