Process Intensification Opportunities in Sulfur Recovery Units

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Abstract

Process Intensification (PI) is an engineering approach to improve processing efficiency and reducing equipment costs and size simultaneously. The processes involved with high energy consumption and relatively low efficiencies could be subjected as the first priority of process intensification. Sulfur Recovery Unit (SRU) in petroleum and natural gas refineries is a side-treatment unit to avoid flaring rich-acid gas and recovery of sulfur compounds as the elemental form. High energy consumption, and large equipment consideration, makes the SRU process feasible for intensification. In this paper applicability and technical feasibility of process intensification is discussed for each operation unit of SRU separately. The works done and similar experiences show that the intensified SRU could have an improved functionality with lower energy consumptions and higher efficiencies.

Keywords: Process Intensification (PI), Sulfur Recovery Unit, Rotating Packed Bed.

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1. Introduction

1.1. Process Intensification (PI)

Today, we are witnessing important new developments that go beyond traditional chemical engineering. Many engineers and researchers are working on novel equipments and techniques that potentially could transform our concept of chemical processing plants and lead to compact, safe, energy-efficient, and environment-friendly sustainable processes. These developments share a common focus on "Process Intensification" approach. Process intensification consists of the development of new apparatuses and methods that are expected to bring dramatic improvements in manufacturing and processing, substantially decreasing equipment size/production capacity ratio, energy consumption, and ultimately resulting in cheaper, sustainable technologies. In a shorter form, PI could be considered as any chemical engineering development that leads to a substantially smaller, cleaner, and more energy-efficient technology [1].

Many researchers and engineers have focused their works on process intensifications and implementing PI methods in industrial plants. B.G. Rong et al have developed a methodology of conceptual process synthesis for PI which results various partial solutions for process and equipment intensification. Also, this methodology is practiced for a peracetic acid production process as an example [11]. A similar work is done by K. Huang et al. to develop a systematic procedure for process intensification in reactive distillation columns [12]. In this procedure, internal mass integration and internal energy integration between the reaction operation and the separation operation involved are emphasized. Several other methodologies for process intensification implementation are presented by other researcher [13~16]. Also utilizing rotating packed beds in industrial distillation, reaction, absorption and extraction processes are investigated in many researches. Many of these works are concentrated on CO_2 capture methods [17~21]. Ch.H. Yu et al. have investigated the applicability of rotating packed beds (RPB) for carbon capture purposes with mixed alkanoamines and low regeneration energy features [17]. X. Li et al. have reviewed continuous distillation process using rotating packed beds which shows a suitable mass transfer performance [22]. All the results obtained show a feasible potential of using process intensification methods and equipments implementation in the industrial processes.

1.2. Sulfur Recovery Process

Sulfur Recovery Unit is a mandatory process in petroleum and natural gas refineries which converts the sulfur compounds in acid gas into elemental sulfur. Conventional SRU plants whole the world utilize Claus Process or its modified versions. The main process includes a thermal stage –which converts sulfur compounds to reach a 2:1 ration between H2S and SO2- via a special reaction furnace, and a catalytic stage for converting sulfur compounds to elemental sulfur. In order to maintain sulfur as liquid, and also providing proper temperatures in catalytic beds, Claus process has a high temperature nature. Since environmental regulations have been more restricted in recent years, further treatments are required to meet the allowable criteria and standards. Therefore, usually the Claus process is accompanied with other units for cleaning-up the tail gas exiting the Claus section. Also, since Claus process is suitable for a specific range of H2S concentration of acid gas stream; in case of lean acid gas feed streams, it is necessary to provide acid-gas enrichment facilities. There are some commercial processes developed for Tail-Gas Treatment (TGT), and also Acid Gas Enrichment (AGE), which mainly use absorption operations via selective amine solutions [23, 24]. Figure 1 represents a simplified schematic block flow diagram for a typical sulfur recovery unit.

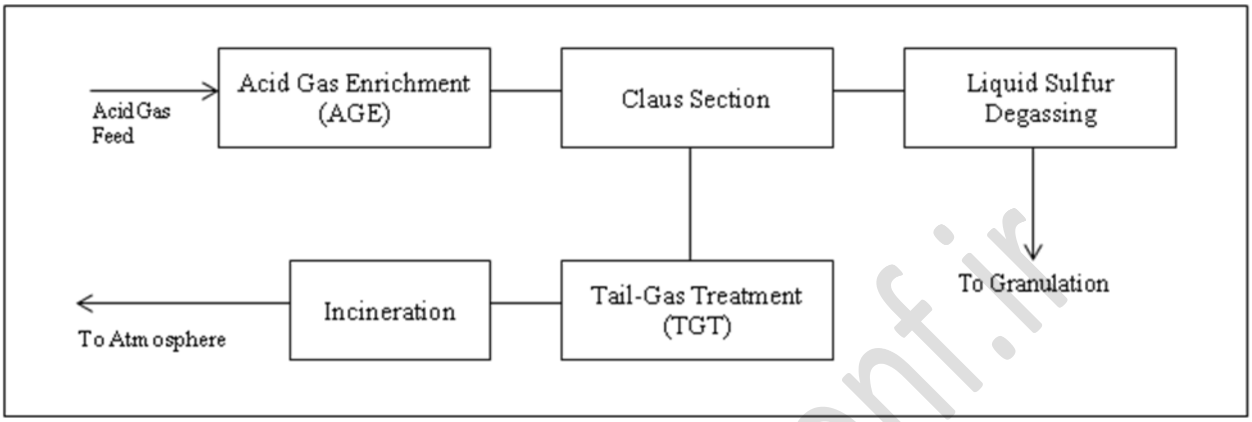

Fig. 1 – Schematic block flow diagram for a typical sulfur recovery unit

2. Process Intensification Methods

Process Intensification (PI) could be studied from two aspects, PI equipments, and PI methods. Many special apparatuses and equipments are developed for process intensification purposes which may be involved with chemical reactions or not. These equipments main include spinning disc reactors, static mixer reactors, heat exchange reactors, static mixers, compact heat exchangers, rotating packed beds, etc. Process intensification methods consist of techniques and technologies which could be considered in design of PI equipments. These methods could be categorized as multifunctional reactors, hybrid separators, alternative energy sources (e.g. using centrifugal fields, microwave, electrical fields, plasma technology, etc.) and the other methods such as supercritical fluids dynamic reaction [2,3]. All the main process components of sulfur recovery unit will be reviewed from PI point of view, and potential of intensification methods implementation will be discussed.

2.1. Claus Section

The Claus Section is the heart of a sulfur recovery unit in which all the conversion of sulfur compounds into elemental sulfur takes place. This section consists of thermal and catalytic stages. In thermal stage, due to very high temperatures and combustion process features, there is no potential for substitution with other process. However, for mixing and preheating the reaction-furnace streams, static mixers and integrated heat exchangers could be used. The important point which should be noted is that since Claus process is a low-pressure process, therefore pressure drops through the lines should be considered carefully. Also, one of the more important disadvantages of static mixers is their relative high sensitivity to clogging by solids; hence, utilizing static mixers in places which there is the possibility of sulfur fog or mist formation, requires extra studies. Since static mixers could be fabricated from non-metallic material, further corrosion issues could be eliminated the capital costs could be decreased consequently.

In the catalytic stage, in where proper mixture of H2S and SO2 passes through the alumina based catalyst beds, the liquid elemental sulfur will be achieved. Although using inline catalytic micro-reactors are preferred to the conventional catalytic beds, but because of forming liquid sulfur during the reaction, and the possibility of plugging the channels, it is not recommended. However, utilizing micro-reactors and inline catalytic reactors, higher conversion efficiencies with smaller equipments/beds could be achieved, due to the higher catalytic reaction surface area. Obviously, because of channel-structure of inline catalytic beds, plugging a channel will result a significant decline in conversion efficiency and catalyst active surface area.

Sulfur condensers at downstream of each catalytic bed condense the formed sulfur vapors to liquid. Because of high temperature of the reactors outlet, this is carried out through steam generating heat exchangers. Similarly, it seems that using multifunctional and compact heat exchangers are not suitable for this purpose.

Some previous experiences proved that oxygen enrichment of the combustion air in Claus reaction furnace can cause the benefits such as greater processing capacity, lower capital costs for smaller equipments in new plants, smaller tail-gas clean-up processing equipments, smaller mist and vapor losses, and lower reheater and incinerator fuel costs. Thus, oxygen enrichment of combustion air in reaction furnace and removing nitrogen as the major heat sink, could be considered as an able and efficient process intensification method in Claus section [4, 5]. Other main advantages of using oxygen enrichment include higher flame temperature and improved flame stability, burning unwanted hydrocarbons, ammonia, etc. from upstream, higher sulfur yield, relative higher conversion and recovery efficiency, and lower energy consumption [4].

The Claus process is highly sensitive to the operational variables changes and any little deviation from the optimized conditions may cause significant reduction in recovery and conversion efficiency. Therefore, utilizing process intensification techniques is not recommended in Claus section, due to the vital risks in disrupting normal and optimized operation, and also lack of flexibility in process operating variables. However, some burner manufacturers claim to provide high intensity burners which achieve rapid combustion in very small volumes in a wide range of conditions. This intensification is based on special designs on spin vanes to create vortex recirculation zone upstream of the burner discharge. Also in this type of burners, hot flue gas is recirculated into the burner mixing zone to create a highly stable flame front [25].

2.2. Tail Gas Treatment (TGT) Section

Since the conversion efficiency of the Claus section is not 100%, the un-reacted sulfur compounds will leave it. On the other hand, carbonyl sulfide (COS) and carbon disulfide (CS_2) will be formed in reaction furnace. Thus burning and releasing tail-gas stream is not feasible environmentally and economically. Local environmental regulations restrict industries to reduce sulfur emissions to minimum possible levels. Thus, further treatments are required to clean-up the tail gas and route-back the sulfur compounds to the Claus section. The most sulfur recovery units whole the world use selective amine absorption process for tail-gas treatment. In this section, the lean amine (often MDEA) solution is contacted with tail gas in a packed-bed or tray column. The sulfur compounds are absorbed in liquid phase and regenerated in another column. The regeneration column is a packed-bed (or tray) separation column which is equipped with a reboiler at the bottom which results desorption of sulfur compounds and recycling them to the Claus section.

A very simple and efficient process intensification method is to use high-gravity fields in separation equipments. Absorption in a high-gravity field, results remarkable intensification in heat and momentum transfer, as well as mass transfer. A special absorption/extraction equipment is developed for high-efficiency mass transfer, called Rotating Packed Bed (PBR). In this equipment, rotating the packed bed generates high gravity field; gas and liquid phases contact to each other counter-currently and mass transfer takes place in a thin film of liquid on the packing surface area. Previous investigations and experiences show that H_2S and CO_2 selective absorption with amine-based absorbents has a higher efficiency and makes possible to treat large amount of gas streams with considerable lower energy consumption, very smaller equipments, and easier operation [6-10]. Figure 2 represents a scheme of rotating packed beds.

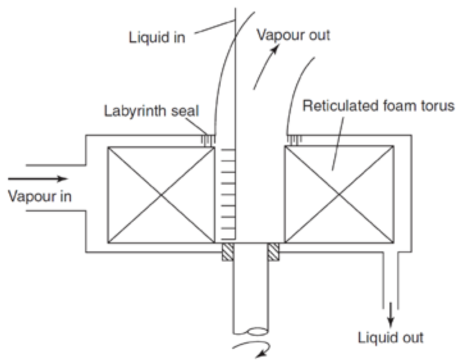

Fig.2. Scheme of a rotating packed bed [2]

According to the previous studies, the rotating packed bed has higher gas-liquid mass transfer efficiency which is evidenced by the fact that the volumetric mass transfer coefficients within an RPB are an order of magnitude higher than those to absorb CO2 with aqueous solutions of alkanoamine [6, 7 and 8]. The reaction of CO_2 with the MDEA is the control step of the selectivity of H_2S in an RPB. A viewpoint that the intensification is achieved by a larger gas-liquid effective interfacial area being produced under centrifugal field is widely accepted. The liquid flow in the RPB has been supported to be laminar film flow on the packing surface. The thinner films resulting from a large centrifugal acceleration can expand the gas-liquid contact surface area and increase the mass transfer rate [7].

Thus both absorption and desorption processes in tail-gas treatment section could be carried out using rotating packed beds. The lean amine solution in the absorption RPB removes H_2S from the tail-gas and the absorbed sulfur compounds will be desorbed in another RPB in which the rich amine solution is heated up. Substitution of conventional large absorption/regeneration columns with rotating packed beds, will affect the economic aspect and feasibility of sulfur recovery units significantly.

2.3. Acid Gas Enrichment (AGE) Section

Since the performance of the Claus process is limited for a specific range of Acid Gas H2S concentration, a pre-treatment is required to increase H2S concentration to the acceptable level. In most sulfur recovery units this operation is carried out via amine-based absorption process. The H2S then will be desorbed in the regeneration column and routed back to the Claus section. The basis of the AGE process is quite similar to TGT section and therefore rotating packed bed absorbers could be used with higher efficiency and capacity.

2.4. Integration of Intensification Methods

Considering the mentioned solutions to implement process intensification techniques, now an intensified sulfur recovery unit could be developed with considerable low energy consumptions, smaller equipment sizes, and higher capabilities. Combination of a high-efficiency reaction-furnace with oxygen-enriched combustion air in Claus unit, followed by a system of rotating packed beds for acid gas enrichment, tail-gas treatment, and hydrogen sulfide regeneration operations could be considered as an intensified sulfur recovery process. In case of using higher concentrations of oxygen in the combustion air, the treated tail-gas may not be required to further treatments or incineration. Depending on the local environmental regulations, it might be possible to release at a safe location.

The schematic form of an intensified sulfur recovery unit could be considered as figure 3.

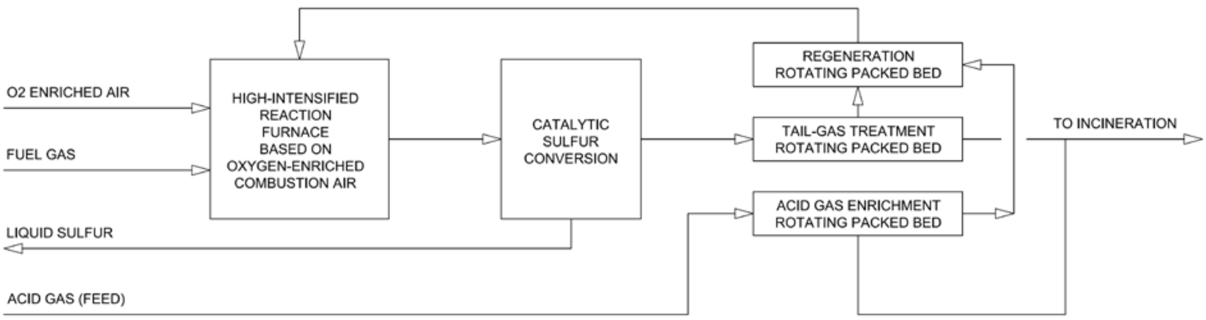

Fig.3. Scheme of Intensified Sulfur Recovery Process

3. Conclusions

Process Intensification is an engineering approach to improve processing efficiencies and reducing costs and energy consumptions simultaneously. In this paper, the major possible opportunities for process intensification in sulfur recovery unit are discussed. Operating experiences show that since the Claus process is too sensitive to the variations in operating variables, implementing process intensification may cause major concerns and issues. However, it is well-proved that oxygen enrichment of the combustion air in Claus reaction furnace has considerable beneficial effects on the operation. Tail-gas treatment and acid gas enrichment, as well as amine solution regeneration could be carried out in rotating packed beds easily which is accompanied to significant decrease in equipment capital costs, maintenance issues, energy consumption, etc. and increase in mass transfer efficiency and capability. According to the results from modeling and design of RPBs in pilot plant scale, new sulfur recovery units could be designed and developed based on intensified TGT and AGE sections.

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