

# Superior gas sweetening

Tofik K. Khanmamedov, TKK Company, USA, analyses a new family of processes developed specifically to improve the efficiency of amine gas sweetening and tail gas treating.

The sour gas of natural gas, refinery fuel gas, petrochemical industry and synthesis gas of purification plants contains substantial amounts of acid gases such as CO<sub>2</sub>, H<sub>2</sub>S, COS and RSH. The bulk removal of these gases is more conventionally handled by absorption into different chemical solvents.

The alkanolamines have been widely used since 1930 when the amine unit configuration, based on phenylhydrazine as an absorbent, was developed and patented in the USA. Improvements of this process basically included new alkanolamines and plant design development.

This fundamental discovery was later improved by using alkanolamines as solvents. Besides the alkanolamine process, selexol, hot carbonate and other processes have traditionally been used for treating these sour gases and tail gases of sulfur plants.

This article is devoted to the newly developed and patented HIGHSULF™ concept of absorption/desorption gas sweetening processes based on amine or any other selective solvents. Results of computer runs comparing this new process and conventional processes for amine gas sweetening and tail gas treating are discussed.

## Amine gas sweetening process

H<sub>2</sub>S concentration in the feed gas of the Claus sulfur recovery units has an important influence on the complicated chemical reactions that are involved in the hydrogen sulfide oxidation processes in the thermal reactor at high temperature and in the catalytic reactors at the moderate temperatures. The efficiency of hydrogen sulfide oxidation reaction and sulfur recovery increases at higher hydrogen sulfide concentrations in the feed of sulfur recovery unit (Figures 1 and 2). The higher hydrogen sulfide concentration combined with lower hydrocarbon and CO<sub>2</sub> concentration in the sulfur plant feed, generate tail gas with less mass flow.

There are known correlations between H<sub>2</sub>S concentration, hydrocarbon and CO<sub>2</sub> content in the feed and the initial investment cost of the sulfur plant and tail gas treating unit. In fact, the combustible contaminants mentioned above affect both the installed and operating costs. Any diluents such as N<sub>2</sub> or CO<sub>2</sub>, increase the plant cost because most of the sulfur recovery equip-

ment is sized on the basis of mass flow. Thus the major equipment and process piping increases in size, causing the overall investment to increase.

In the case of gas processing plants, there can be high concentrations of hydrocarbons in the feed gas. These hydrocarbons generate COS and CS<sub>2</sub> in the thermal stage of the Claus unit and an undesirable mass of CO<sub>2</sub>.

The flow diagram of a typical amine gas sweetening process is shown in Figure 3. Feed gas absorbed in the absorber generates rich amine, which is sent to the regenerator column to regenerate lean amine. All acid gas obtained in the top of the regeneration column is used as a feed of Claus sulfur recovery unit.

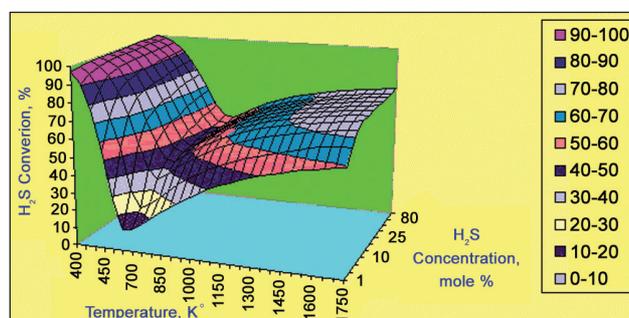


Figure 1. Equilibrium conversion of hydrogen sulfide to sulfur in Claus reaction.

Table 1. Acid gas composition of regular and HIGHSULF™ amine units		
Gas plant acid gas components	Acid gas composition, mole %	
	Regular amine unit, MDEA	HIGHSULF™ amine unit, MDEA
H <sub>2</sub> S	33.10	46.20
CO <sub>2</sub>	57.30	47.10
H <sub>2</sub> O	8.53	6.40
Hydrocarbons	1.07	0.3
Gasifier plant		
Acid gas components	Acid gas composition, mole %	
	regular amine unit, MDEA	HIGHSULF™ amine unit, MDEA
H <sub>2</sub> S	11.68	24.78
CO <sub>2</sub>	79.11	68.42
CO	1.76	0.23
H <sub>2</sub> O	6.40	6.38
COS	0.05	-
H <sub>2</sub>	0.996	0.19
CH <sub>4</sub>	0.004	-

	Absorber feed	Absorber offgas	Acid gas to SRU
N <sub>2</sub>	225.873	225.864	0.009
H <sub>2</sub> S	4.332	0.016	4.316
H <sub>2</sub>	20.046	20.045	0.001
CO <sub>2</sub>	59.446	52.842	6.610
H <sub>2</sub> O	38.280	12.101	0.751
CH <sub>4</sub>	0.177	0.177	
Total mole/h	348.154	311.045	11.687
Total kg/h	4455.9	4043.5	204.01

	Absorber feed	Absorber off gas	Acid gas to SRU
N <sub>2</sub>	225.873	225.848	0.025
H <sub>2</sub> S	4.332	0.015	4.317
H <sub>2</sub>	20.046	20.043	0.003
CO <sub>2</sub>	59.446	44.894	14.552
H <sub>2</sub> O	38.280	11.681	1.306
CH <sub>4</sub>	0.177	0.177	
Total mole/h	348.154	302.658	20.203
Total kg/h	4455.9	3881.1	368.3

The patented concept uses the same equipment shown in Figure 3. The feed gas stream of the absorber is enriched by the hydrogen sulfide of the acid gas. Therefore, the gas enriched with H<sub>2</sub>S is fed to the absorber with higher partial pressure of H<sub>2</sub>S than in raw gas inlet stream. A physical solvent, at relatively high pressure, may be used for processing natural gas to remove CO<sub>2</sub>, H<sub>2</sub>S, COS and CS<sub>2</sub>. A chemical solvent would be used for the process of removing (absorbing) H<sub>2</sub>S and CO<sub>2</sub> from feed streams in gas processing plants or refineries operating at relatively low pressures. Residual, unabsorbed gas, with minimal target contaminate content, is discharged from the absorber overhead and target contaminate enriched solvent stream is discharged from the absorber bottom, before passing through a lean/rich solvent heat exchanger to enter the regenerator as a heated rich solvent stream. In the regenerator, the heated rich solvent stream gives up the absorbed acid gases, which are discharged through the regenerator overhead condenser as the target contaminate rich overhead gas stream. Contaminate lean solvent stream is returned to the absorber at a reduced temperature after passing through heat exchanger and cooler. A portion of the regenerator overhead gas stream is passed through a cooler and recycled to the absorber, while the remaining target contaminate rich gas stream is passed to the next process step. A compressor, controlled by process input signal, is required in applications having an inlet pressure higher than the discharge pressure at regenerator overhead cooler. Otherwise, the respective flowrates of streams to the sulfur plant and in the recycle line are governed by fixed or variable flow restrictions, which according to the designer's choice, may be implemented by selective line sizing, flow restrictions or control valves. The possible increased capital cost of a typical gas sweetening unit is more than offset by the reduced

size, cost and efficiency of the downstream sulfur recovery unit. The HIGHSULF™ process increases the concentration of H<sub>2</sub>S and reduces hydrocarbons in the acid gas.

For a typical natural gas processing plants with low H<sub>2</sub>S concentration in the natural gas, HIGHSULF™ yields acid gas with higher H<sub>2</sub>S concentrations than can be achieved using conventional amine treatments.

Table 1 compares acid gas compositions using conventional amine treatment and the patented process. As can be seen from these computer simulation results, the H<sub>2</sub>S concentration in acid gas is 39% greater than in conventional amine treatments. Hydrocarbon content in acid gas reduced by 72%.

In other applications, as in the case of gasifier Table 1, H<sub>2</sub>S enrichment is greater than 100% and hydrocarbons and hydrogen content is significantly reduced. In the case of natural gas plants with a high CO<sub>2</sub>/H<sub>2</sub>S ratio in the feed gas, H<sub>2</sub>S enrichment is greater than 54%.

As mentioned above, combustible contaminants in the Claus feed greatly increase the initial cost of the unit, since oxygen has to be supplied for burning these components. For instance, a mole of methane requires three times as much oxygen as does a mole of hydrogen sulfide in feed, and a mole of propane in the Claus unit feed requires seven times as much as does a mole of hydrogen sulfide. Since oxygen is usually supplied as air, the diluent effect of nitrogen amplifies the effect of the extra oxygen requirement. Both the air blower and its driver size increases, as well as the other Claus unit equipment, because the combustion products such as CO, CO<sub>2</sub> and H<sub>2</sub>O add to the plant cost. Obviously if new equipment is required, the initial installed cost rises. The presence of the combustible contaminants in the Claus unit feed definitely reduces the overall sulfur recovery.

The main advantages of HIGHSULF™ concept for amine gas sweetening units are:

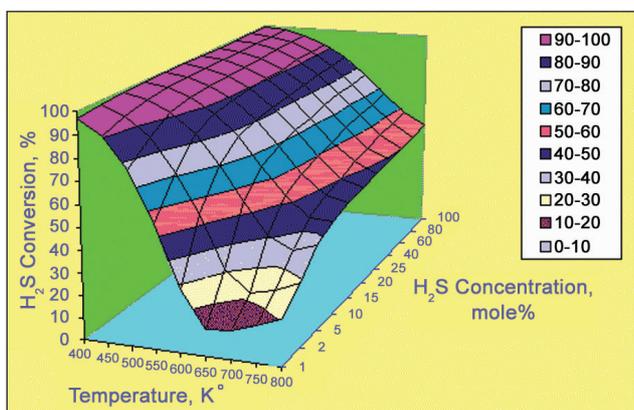


Figure 2. Equilibrium conversion of hydrogen sulfide to sulfur vs. temperature vs. concentration.

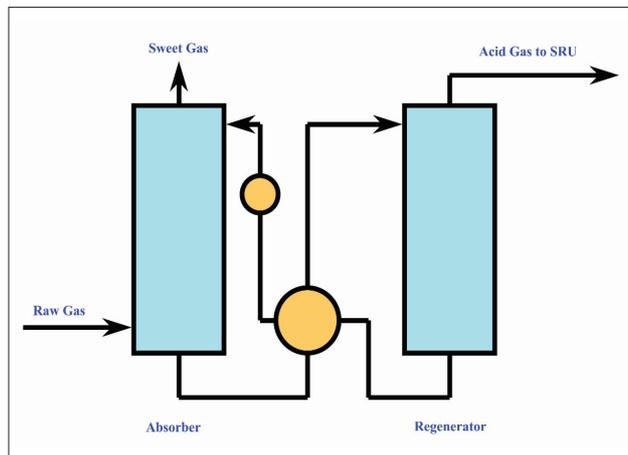


Figure 3. Amine gas sweetening process.

- The process helps to increase the concentration of H<sub>2</sub>S in acid gas.
- The process reduces level of hydrocarbons in acid gas.
- The process has significant advantages in plants with high CO<sub>2</sub>/H<sub>2</sub>S ratios.
- The process provides a means to produce sweetened gas that meets specific requirements for international gas transportation systems.
- The process provides flexibility in the utilisation of parallel sulfur plants to maintain production and product levels.
- The process has greater ability to remove H<sub>2</sub>S/COS/CS<sub>2</sub>/RSH components from natural gas.

Parameter	Conventional	HIGHSULF™
H <sub>2</sub> S in feed gas, vol%	1.24	1.24
CO <sub>2</sub> in feed gas, vol%	17.0	17.0
Total S in treated gas, ppmv	<100	<100
Lean solvent temperature, °C	38	38
Steam rate, kg/m <sup>3</sup> MDEA solution	107.85	107.85
CO <sub>2</sub> rejection in absorber, %	75.5	88.9
H <sub>2</sub> S concentration in recycle stream to SRU, vol%	21.4	36.6
Mass flow of recycle stream to SRU, kg/h	368.29	204.0
Fresh acid gas received on SRU, kg/h	2948	3052
Relative change of fresh acid gas mass flow received on SRU, %	100	103.5

## Tail gas treating process

A process flow diagram of a conventional tail gas treatment processes (TGTU) is shown in Figure 4. A TGTU includes heater, hydrogenation/hydrolysis reactor with Co-Mo or another appropriate catalyst, boiler, quench tower and selective amine absorber and regenerator.

Tail gas, typically at 150 °C enters the feed heater where it is raised to reactor temperature (approximately 260 °C). The heater may be of the indirect gas-gas type, hot oil or direct heater. Two types of direct heaters are possible. The inline burner for fuel gas combustion operates stoichiometrically, during which the tail gas temperature is elevated to downstream catalytic hydrogenation reactor inlet temperature. The other mode of inline burner operation combusts the fuel gas sub-stoichiometrically to simultaneously heat the tail gas and supply CO and H<sub>2</sub> for the reduction of all sulfur species of the tail gas.

The hot gas mixture is then discharged to the hydrogenation/hydrolysis reactor, where in the presence of Co-Mo or another appropriate catalyst, sulfur dioxide and sulfur are hydrogenated to hydrogen sulfide while carbonyl sulfide and carbon disulfide are hydrolysed to hydrogen sulfide and carbon dioxide.

The effluent gas stream from the reactor then passes through the boiler, generating waste low pressure steam and continues as partially cooled gas stream to the quench column. In the quench column, a sour water stream condenses out for further treatment in the sour water stripper and the hydrogen sulfide bearing gas stream is cooled for selective amine absorption.

The absorber is fed by the combined streams of

quench tower overhead gas stream and hydrogen sulfide enriched gas. A partial pressure of hydrogen sulfide in this combined stream is increased over that in quench tower overhead stream. In the absorber, MDEA or another H<sub>2</sub>S selective solvent absorbs hydrogen sulfide. The efficiency of this selective absorption is promoted by the elevated partial pressure of H<sub>2</sub>S in the absorber.

As was explained in the previous case, contrary to conventional TGTU, the absorber of HIGHSULF™ TGTU is fed by the combined streams of the quench tower overhead gas stream and hydrogen sulfide enriched gas. A partial pressure of hydrogen sulfide in this combined stream is increased over that in quench tower overhead stream. In the absorber, hydrogen sulfide is absorbed by MDEA or another H<sub>2</sub>S selective solvent. The efficiency of this selective absorption is promoted by the elevated partial pressure of H<sub>2</sub>S in the absorber.

The flow scheme of a TGTU in Figure 4 is intended to be general and a process flow diagram for a particular licensee may differ, as required for the individual plant design requirements.

Material balances of amine sections of HIGHSULF™ and conventional TGTU of a small refinery are given in Table 2 and Table 3. Similar absorber feeds and all other parameters in computer runs for 47.5 w. % of MDEA were used in both cases, making it easy to see most of the advantages of the patented TGTU process.

As can be seen from Table 2, the CO<sub>2</sub> rejection in HIGHSULF™ TGTU is 88.9%, which is much higher than the 75.5% achieved in the regular TGTU case illustrated in Table 3. The absorber overhead H<sub>2</sub>S concentrations are well below 100 ppmv. The H<sub>2</sub>S in overhead can be adjusted to any desirable level. In some cases, higher than the normal using temperature of the overhead of quench tower is successfully compensated for by

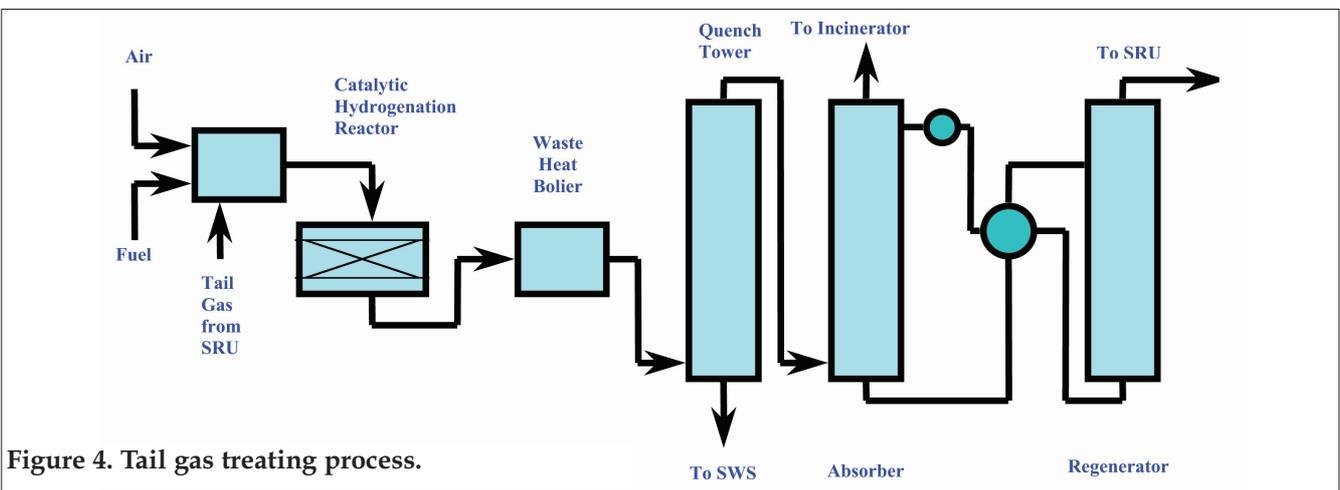


Figure 4. Tail gas treating process.

increasing the partial pressure of  $H_2S$  in the feed of absorber. This advantage of the process certainly makes it more attractive if one will consider difficulties related with quench water trim cooler operation.

The mass flow of acid gas of patented process is 1.8 times less (204.0 kg/h) than mass flow of acid gas (368.29 kg/h) in the regular process. This means that any existing regular TGTU with an absorption-regeneration section can be switched to HIGHSULF™ and this switch will increase capacity of the sulfur plant up to 3.5% and higher. Or, the patented process may lead to a significant saving from oxygen reduction in Claus units with oxygen injection in the front end.

The high pressure of the acid gas from the regenerator, compared with the pressure of the gas feeding the absorber, makes it easy to switch from an existing TGTU to the new system and it shows that it is ideal for revamps as well as for new plants.

The patented process fits perfectly in the configuration of all tail gas treating units designed with amine absorption-desorption section. It is the least complex of the known family of tail gas treating processes and it should be mentioned that it has a high turndown capability.

The summarised results of computer runs of conventional and HIGHSULF™ type TGTU for similar feed are given in Table 4.

The advantages of the new TGTU process include:

- Increased  $H_2S$  selectivity of generic MDEA and any other selective solvents in the same absorber without any capital investments, keep the same level of total sulfur in treated gas.
- Less mass flow of the recycling acid gas stream that goes back to SRU.
- Increased capacity of SRU by reducing hydraulic loading of SRU.
- May reduce duty of quench water trim cooler and lean amine water trim cooler of the existing or new TGTU.
- There is less operating cost and the need for application of expensive solvents is limited.
- Any existing TGTU can be easily and fast switched to HIGHSULF™ by enhancement of proved equipment of regular TGTU without any additional capital investment.
- The tail gas treatment process is the least complex of the known family of tail gas treating processes and has a high turndown capability.
- May reduce the circulation rate of any existing quench tower and keep the same level of  $CO_2$  rejection in absorber and overhead gas stream.

## Conclusion

The family of HIGHSULF™ processes (gas sweetening and TGTU) brings an additional and new important dimension, such as controlled partial pressure of  $H_2S$  in the feed of absorber, to gas sweetening and the control system. The concept increases  $CO_2$  rejection in the absorber of amine units and retains the required  $H_2S$  level in the absorber overhead. It also increases  $H_2S$  concentration in the acid gas, reduces hydrocarbons and controls the composition and the mass flow of acid gas of TGTU going to SRU as well as reducing capital and operating costs for the new and existing conventional TGTU related with cooling requirements.

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