Study on Optimization of natural gas desulfurization process by MDEA method

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Abstract

The desulfurization process of high sulfur natural gas in a natural gas purification plant was simulated and optimized by HYSYS software. The optimization model of H_2S and CO_2 content in the purified gas was established by regarding the concentration of hydrogen sulfide and the hydrogen sulfide loading of MDEA rich liquid as decision variables. The optimization results show that, under the premise of ensuring the quality of the purified gas products, there exists a optimal combination of the MDEA cycle and the MDEA concentration.

Keywords

Natural gas desulfurization, high sulfur natural gas, alkanolamine solution, parameter optimization.

1. Introduction

Sulfurous natural gas accounts for 31.7% of China's total natural gas production [1]. The exploitation and treatment technology of sour natural gas is relatively difficult. So far, chemical solvents (mainly alcamines) are the most frequently used methods for gas desulfurization [2]. In low pressure operation, it is more suitable than physical solvent or mixed solvent. The reason is that at this point, the removal process of H_2S and other acids is mainly controlled by chemical processes, but less dependent on the partial pressure of the components. Moreover, chemical solvents have little solubility in hydrocarbons and do not cause large hydrocarbon losses. The technology of alkanolamine method is mature, and the solvent source is convenient and highly adaptable. For large and medium-sized decarbonization units or when the degree of purification is highly required, it is usually preferred to use alkanolamine method to remove carbon dioxide. In recent years, the proportion of MDEA methord used in gas desulfurization unit increases continuously in foreign countries. According to the United States "hydrocarbon processing" for the world gas processing process statistics, the majority of commercially available solvents are mainly using MDEA solution or MDEA as the main formula.

2. Desulfurization technology

2.1 Physical properties and purification requirements of raw gas

The optimization of desulfurization unit in a gas purification plant of Changqing Oil Field Branch of PetroChina was carried out. The treatment capacity of the purified plant is $16.88\times10^4 Nm^3/d$, the feed temperature of the absorber is 36.5℃ and the operation pressure is 4.5 Mpa. The content of CO2 in feed gas is close to that of commercial gas. The content of hydrogen sulfide is high, and the ratio of carbon to sulfur is about 7.7>6. After purification, the gas should meet the current national standard "natural gas"(GB17820-2012), that is the content of H2S is less than 20mg/m3(20℃,101.325kPa).

2.2 Deacidification process.

The design process can be divided into two parts: high pressure absorption of amine liquid and low pressure regeneration. The simulation process is shown in Fig. 1. Feed gas enters the bottom of the absorption tower, countercurrent contacting with amine liquid. Then acid gas reacts with the amine liquid, resulting in the formation of amine salt. Product gas without acid gas flows out from the top of the tower for further processing. The rich amine liquid flows out from the bottom of the absorption tower. After throttling down to 400kPa, it enters the flash tank, so that alkane and other impurities which entrained in rich liquid flash out. After heated by the heat exchanger, it enters the regeneration tower to contact with the counterflow steam so as to suck out H_2S in the rich liquid. Lean liquid from the bottom of regenerator exchange heat with cold rich liquid. After pressurization and further cooling, it is injected into the top of the absorption tower by a circulation pump. The sour gas rich in H_2S flowing from the top of the tower can be sent to the sulfur plant as feed gas.

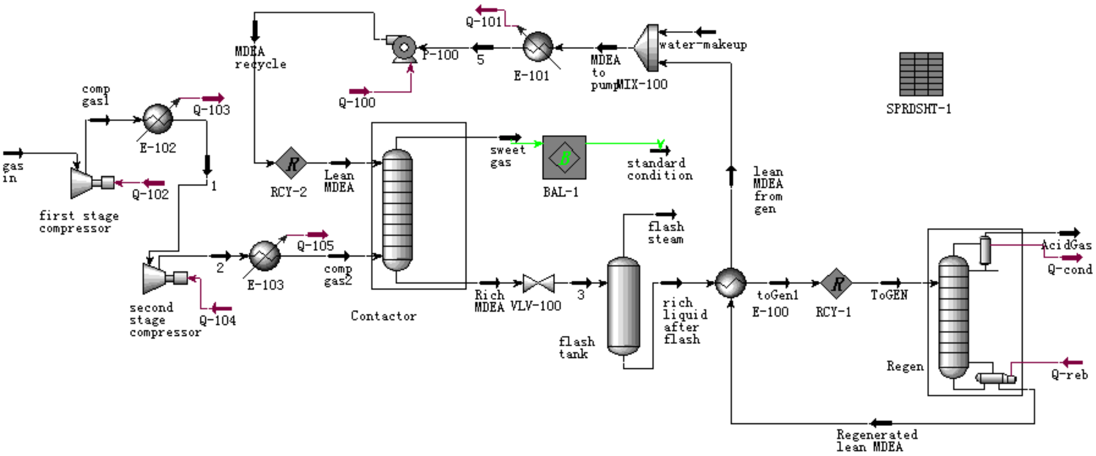

Fig. 1 Process of DE acidification by MDEA

3. Simulation of desulfurization process

Cycle volume is preliminary designed by using empirical formula and internal formula of HYSYS. After simulating the technological process, the concentration and cycle volume of MDEA lean liquid are optimized on the basis of theoretical calculation. The MDEA process conditions used in the preliminary design are shown in Table 1. The properties of each MDEA solution after simulation are shown in Table 2.

Table 1. MDEA process parameters

Property	Numerical value
Gas treatment capacity under standard condition (Nm^3/d)	16.88 ×104
Feed temperature of MDEA (℃)	35.6
Feed pressure of MDEA (MPa)	4.5
Concentration of MDEA (%)	45
Cycle volume of MDEA (m^3/h)	8

Table 2. Calculation results of MDEA solution properties

Parameter	Rich MDEA liquid	Regenerated lean liquid	Lean MDEA liquid
Temperature (℃)	49.59	123.5	36.62
Pressure (kPa)	4500	220	4500
Load of H_2S (%)	0.0562	0.0078	0.0022
Load of CO_2 (%)	0.1975	0.0191	0.006

For MDEA solutions, the maximum CO_2 load is 0.3, and the maximum H_2S load is 0.2. The calculation results show that the load under the cycle volume meets the requirements. While, in order to pursue the best economic effect, the optimization calculation is carried out on the basis of the theoretical calculation value.

The concentration range of lean MDEA liquid is 35%~50%, and the range of lean liquid cycle volume is 4~14m^3/h. The optimized standard is hydrogen sulfide concentration of sweet gas and hydrogen sulfide load of MDEA rich liquid. Where, the acid load is expressed by Q_S, and the hydrogen sulfide concentration is expressed in C_S. The units of both are mg/m^3. The optimization results are shown in Table 3 and table 4.

Table 3. The optimized calculation result of MDEA solution (a)

Mass concentration of MDEA		37%		40%		43%	
		Q_S	C_S	Q_S	C_S	Q_S	C_S
Cycle volume of MDEA (m^3/h)	4	0.104	842.9	0.099	658.8	0.094	518.4
	6	0.807	31.9	0.075	29.59	0.069	25.8
	8	0.063	24.7	0.058	22.3	0.054	19.3
	10	0.052	22.1	0.048	21.1	0.045	18.6
	12	0.045	21.2	0.042	20.4	0.039	17.9
	14	0.040	20.6	0.037	19.9	0.034	17.5

Table 4. The optimized calculation result of MDEA solution (b)

Mass concentration of MDEA		45%		47%		49%	
		Q_S	C_S	Q_S	C_S	Q_S	C_S
Cycle volume of MDEA (m^3/h)	4	0.090	446.8	0.087	387.1	0.084	341.3
	6	0.066	23.8	0.063	21.5	0.061	20.4
	8	0.052	18.1	0.049	16.3	0.047	15.4
	10	0.043	17.2	0.041	15.4	0.039	14.6
	12	0.037	16.6	0.035	14.8	0.034	14.1
	14	0.033	16.2	0.031	14.4	0.030	13.7

As can be seen from the table, there are two sets of optimal data in ensuring that the gas purification standards are met. That is the combination of 40% MDEA solution with a cycle amount of $14m^3/h$ and the combination of 43% MDEA solution with a cycle amount of $8m^3/h$. The pure MDEA dosages of the two schemes are $5.6m^3/h$ and $3.44m^3/h$ respectively.

By contrast, the final choice of 43% MDEA solution and the cycle amount of $8m^3/h$ is the best MDEA deacidification program. The final MDEA process conditions are shown in table 5.

Table 5. MDEA process parameters

Property	Numerical value
Feed temperature of MDEA (℃)	36.5
Feed pressure of MDEA (MPa)	4.5
Concentration of MDEA (%)	43
Cycle volume of MDEA (m^3/h)	8

The comparison of the gas properties of the gas before and after purification is as shown in Table 6. Here under standard condition, The CO_2 molar ratio of sweet gas is 2.2%, and the content of H_2S was $19.3mg/m^3$,which meet the requirements of national standards "natural gas" (GB17820-2012).

Table 6. Calculation results of MDEA solution properties

Parameter	Feed gas	Sweet gas	Sour gas
Temperature (℃)	25	37.26	50.03
Pressure (kPa)	350	4300	190
Mole fraction of H_2S (%)	0.45	1.3×10-5	20.1
Mole fraction of CO_2 (%)	3.84	2.2	73.2
Hydrocarbon dew point(℃)	-3.43	18.27	-70.85

4. Conclusion

1) With the increase of MDEA cycle volume and concentration, the hydrogen sulfide load and hydrogen sulfide concentration decreased in different degrees. The desulfurization effect becomes better, but the cost increases.

2) When the MDEA circulation increases to a certain extent, the concentration of lean MDEA liquid has less influence on the desulfurization effect. So there is a optimal combination of the MDEA cycle volume and the MDEA concentration.

References

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