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Optimization of Shale Gas Sweetening Process Coupling with Claus Process Based on Energy Synthesis

Weida Li[a], Linlin Liu[a], Lei Zhang[a], Qingwei Meng[b], Jian Du[a,*]

[a]Institute of Process Systems Engineering, School of Chemical Engineering, Dalian University of Technology, 116024 Dalian, China
[b]State Key Laboratory of Fine Chemicals, School of Pharmaceutical Science and Technology, Dalian University of Technology, 116024 Dalian, China
dujian@dlut.edu.cn

As a sort of emerging unconventional energy, shale gas has extensive market outlook by virtue of its enormous reserves, and concerns for shale gas exploitation and processing have been raised nowadays. Raw shale gas must be processed to achieve certain specifications before it can be transmitted in pipelines or utilized by consumers. Sweetening is a gas conditioning process to decrease the concentration of acid gases such as hydrogen sulfide and carbon dioxide which are not preferred in sales gas in consideration of heating value specification and corrosion prevention. However, the after-treatment of acid gases is not discussed in many research of sweetening process.

In this paper, a flowsheet of shale gas sweetening process is established using Aspen Plus v8.6. Dissolution of light gases and weak electrolyte, absorption of acid gases and reactions in electrolyte solution are considered simultaneously in process modelling. Diethanolamine (DEA) solution is employed as the solvent to separate acid gases from raw shale gas. The optimal feed stage of rich solvent regeneration and reflux ratio of regenerator are analysed to optimize the sweetening flowsheet. A three-stage Claus process is simulated coupling with shale gas sweetening process to convert hydrogen sulfide in acid gas to element sulphur for pollution reduction. A principle is proposed to determine the operating temperature of each Claus reactor which is a decisive parameter on sulfur recovery efficiency and performance of Claus process. Ultimately, the sulfur recovery efficiency of the three-stage Claus process proposed in this paper is 97.35 %. The effectivity of the principle is confirmed by the results reported in literatures. Energy synthesis is then adopted to integrate sweetening process with Claus process in both mass and energy flow. The coupled process provides with more streams than a single sweetening or Claus process, promoting the reasonability of energy utilization. Streams are extracted and matched for heat exchanger network (HEN) synthesis to reduce the energy consumption and total annual cost of the whole process.

1. Introduction

According to the data released by the US Energy Information Administration, global natural gas resources increase by 46.8 % due to the emergence of shale gas (Energy Information Administration, 2013). Although the compositions of shale gas vary from formations, methane, natural gas liquids and acid gases exist in almost all raw shale gases (Bullin and Krouskop, 2009). However, in shale gas processing, acid gases (CO_2 and H_2S, etc.) will cause problems such as degrading heat value of shale gas and corroding equipment (De Guido et al., 2017). These contaminants must be removed to meet certain specifications (Cho et al., 2015). In general terms, alkanolamine is always preferred as absorbent due to its superior characteristics in sweetening (Law et al., 2017).

Although concerns for the research on natural gas sweetening by simulation software have been raised nowadays, there is still much room for improvements in simulation and optimization (Sayed et al., 2017). A more rigorous model is needed to simulate sweetening process more accurately (Gutierrez et al., 2017). In addition, there are very few studies focusing on the treatment of acid gases which are separated from raw shale gas. Energy synthesis for energy saving is another issue that should be noted.

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In this paper, shale gas sweetening process coupling with Claus process is established by the software Aspen Plus v8.6. Firstly, a more rigorous model of shale gas sweetening process is established where aqueous solution of DEA (diethanolamine) is employed as the absorbent. Details of process modelling and parameter optimization are discussed. With a view to the disposal of acid gases separated from shale gas, a three-stage catalytic Claus process is simulated to convert the air pollutant H_2S into sulfur where the effect of operating conditions on sulfur recovery efficiency is analysed. A principle is proposed to determine the operating temperature in each catalytic reactor which dominates the sulfur recovery efficiency of Claus process. After sequential process simulation, the coupling of sweetening process and Claus process is realized by energy integration of process streams where Aspen Energy Analyzer is employed in HEN synthesis for the whole process.

2. Simulation and optimization of sweetening process

2.1 Process description

The schematic diagram of sweetening process is shown in Figure 1. Shale gas flows into the absorber in which H_2S and CO_2 are eliminated by 30 wt % DEA solution and leaves from the top while rich DEA solution flows from the bottom with high content of acidic components. After contacting with shale gas, the rich solution is depressurized, preheated and regenerated. Subsequently, the acid gases from the regenerator are introduced to Claus process in order to recover sulfur, while DEA solution is recycled to the absorber.

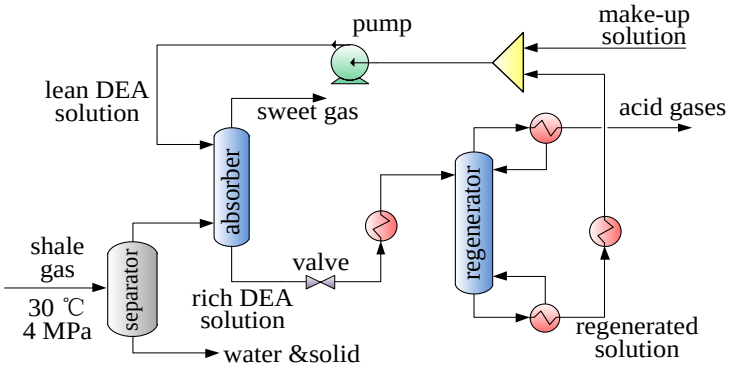

Figure 1: Schematic diagram of sweetening process

The data of the shale gas studied in this paper is extracted from literature (He and You, 2014) and tabulated in Table 1. The flow rate of raw shale gas is 5,000,000 Nm^3/d, while the temperature and pressure of the gas source are 30 °C and 4 MPa. It is demanded that volume fraction of H_2S and CO_2 in purified shale gas which is also called sweet gas should not exceed the limit of 4 ppm and 100 ppm (1 ppm=1×10^{-6}).

Table 1: Composition of raw shale gas

Components	Concentration/% (volume)
CH_4	84.58
C_2H_6	6.51
C_3H_8	1.90
n-C_4H_{10}	0.74
i-C_4H_{10}	0.55
n-C_5H_{12}	0.13
i-C_5H_{12}	0.17
N_2	2.75
H_2S	0.82
CO_2	1.64
H_2O	0.21

2.2 Process modelling

Light gases such as alkane, N_2, H_2S and CO_2 are defined as Henry components to describe the vapor-liquid equilibrium of the system. Relevant parameters of binary interaction (Henry's constants) are derived from Aspen Database. Reactions in sweetening process are considered for a more rigorous model. Equilibrium and kinetic

reactions are obtained from data package 'kedea'. Ultimately, ELECNRTL is selected as the property method to handle electrolyte system and calculate the conversion of ions in liquid phase.
The sweetening process is simulated by Aspen Plus v8.6 as the base case in this work. The volume fractions of H_2S and CO_2 in sweet gas are 3.97 ppm and 95.5 ppm. The flow rate of DEA solution is 6,347.9 kmol/h which flows through the absorber (20 trays) and the regenerator (28 trays). In addition, the reflux ratio of regenerator is set to be 1.57 and the rich solution enters the 8th stage of regenerator. The heat load of the reboiler is 11,781 kW.

2.3 Optimization of feed stage for absorbent regeneration

Ions in rich solution convert to molecular DEA and acid gases in the regenerator. Profiles of Radfrac module is utilized to obtain the generating rates of the species in liquid phase, as shown in Figure 2(a). It is seen that there are almost no acid gases generated above the 8th stage. One possible reason is that the vapor pressure of DEA is extremely low so it could hardly volatilize to the upper stages of the column. Trays above the feed stage might have little effect on regenerating.

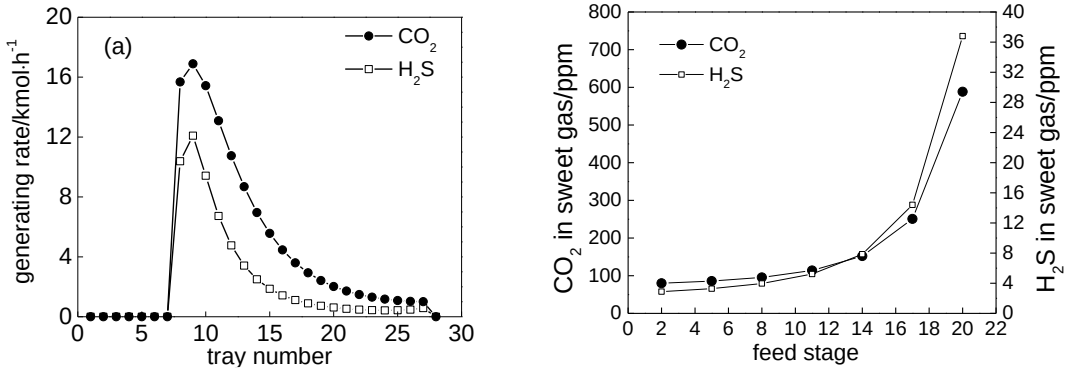

Figure 2: (a) Profiles of acid gases generation on each tray; (b) Effect of feed stage for absorbent regeneration on shale gas purification

Sensitivity analysis is then conducted and displayed in Figure 2(b). Moving down of feed stage creates a negative impact on shale gas purification. In conclusion, the second stage of regenerator is determined as the optimal feed stage for absorbent regeneration.

2.4 Optimization of reflux ratio

The increase of reflux ratio improves the regenerating performance of regenerator and enhances purifying effect of sweetening process, while the energy consumption of the column enlarges. In this work, sensitivity analysis is implemented to acquire optimal reflux ratio of the regenerator and minimize the heat load of reboiler with the constraint of H_2S purifying specification, as shown in Figure 3. Heat load reaches its minimum of 10,455 kW when reflux ratio is 1.02, 11.26 % less than that of the base case.

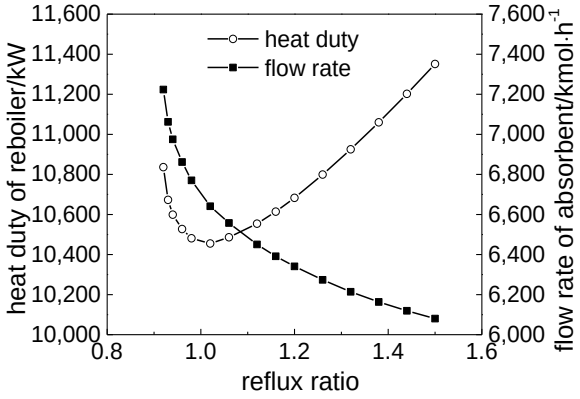

Figure 3: Optimization of reflux ratio

3. Simulation of Claus process

3.1 Process modeling

The schematic diagram of Claus process is shown in Figure 4. Acid gases and air are introduced to the furnace modelled with a RStoic module. Subsequently, stream flows to the condenser for the separation of liquid sulfur and then to a series of catalytic Claus units modelled with RGibbs modules (Bai, 2013). The stage of catalytic reactor influences the sulfur recovery efficiency of Claus process (Nabgan et al., 2016). Specifically, the sulfur recovery efficiency is 90 % - 96 % for two reactors and 95 % - 98 % for three reactors. The pressure drop of each unit is referenced from the data proposed by Bai (2013).

Table 2: Pressure drop of equipments (Bai, 2013)

Equipments	Pressure drop/kPa
Furnace	2
Condenser(1st)	3
Reactor(1st)	4
Condenser(2nd)	3
Reactor(2nd)	4
Condenser(3rd)	3
Reactor(3rd)	4
Condenser(4th)	3

Temperature is a crucial parameter in Claus process. A principle is proposed to determine the operating temperature of each Claus reactor: When the temperature increases, the equilibrium partial pressure of sulfur in reactor will decrease, while the saturated vapor pressure of sulfur will raise. Once the saturated vapor pressure exceeds the equilibrium partial pressure, the surface of catalyst will be covered with liquid sulphur and reactions in Claus unit will be terminated, which is not allowed in practical application. In this work, the point of temperature at which the equilibrium partial pressure of sulfur equals to the saturated vapor pressure of sulfur is adopted for maximum sulfur recovery. The simulation results are shown in Figure 5.

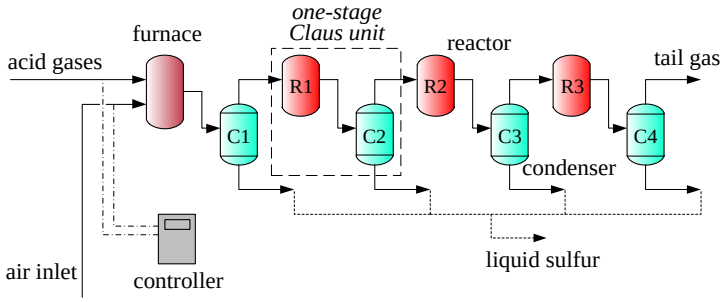

Figure 4: Schematic diagram of a three-stage catalytic Claus process

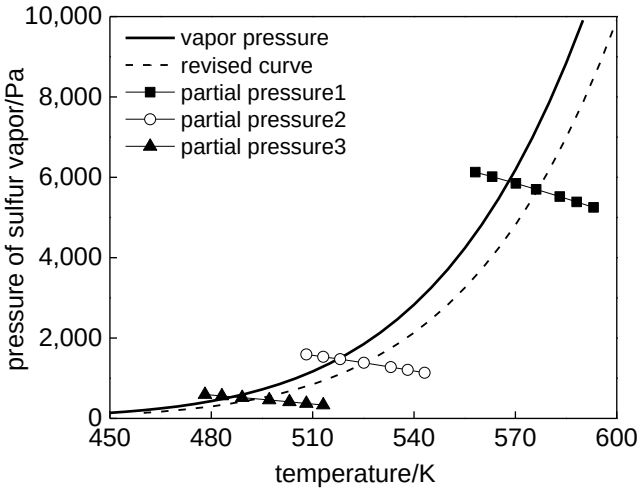

Figure 5: Determination of operating temperature in each catalytic reactor

3.2 Result of Claus process

In Figure 5, the solid line represents saturated vapor pressure of sulfur while the dash line is the revised curve when a margin of 10 °C is introduced taking account of operating security. The lines with symbols are equilibrium partial pressure curves of sulfur in three Claus reactors under various temperatures. Intersection of symbol line and dash line is determined as operating temperature in each Claus reactor.
As shown in Figure 5, when the reactor operates at a lower temperature compared with the temperature of intersection, there will be a potential condensation of sulfur. On the other hand, a higher temperature in reactor will lead to a lower equilibrium partial pressure of sulfur and reaction conversion. Based on this principle, operating conditions of the whole process are settled, as shown in Figure 6.
It could be found in Figure 6 that the sulfur recovery efficiency is 95.49 % after two reactors and the final sulfur recovery efficiency of three-stage Claus process established in this paper is 97.35 %. The results quite fit the data reported in the literature (Nabgan et al, 2016). The effectivity of the principle proposed is confirmed and the method could provide conference for the design of Claus process.

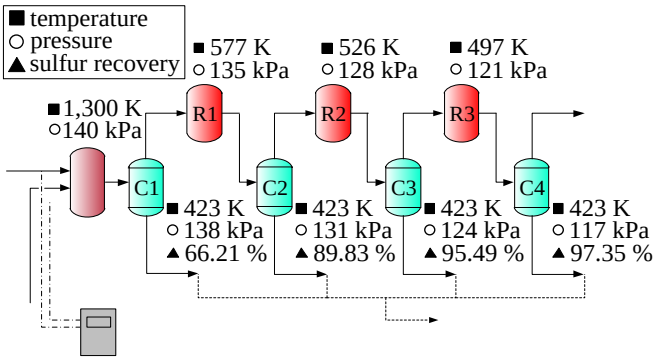

Figure 6: the operating condition in each unit

4. HEN synthesis

Aspen Energy Analyzer is employed to synthesize the HEN of the whole process, the methodology of which is finding the optimal match between process streams and utilities under specific objective (Aspen Technology, Inc., 2014). The streams participating in heat exchanging is extracted and listed in Table 3.

Table 3: Information of process streams

Stream	Description	Temperature inlet/K	Temperature outlet/K	Heat load/kW
H1	Lean solvent cooling	385	307	12,582
H2	Condenser	365	303	3,485
H3	Cooling after furnace	1,300	423	4,912
H4	Reaction heat in R1	577	576	186.6
H5	Cooling after R1	576	423	757.4
H6	Reaction heat in R2	526	525	53.2
H7	Cooling after R2	525	423	458.9
H8	Reaction heat in R3	497	496	25.0
H9	Cooling after R3	496	423	318.7
C1	Rich solvent preheating	326	363	6,980
C2	Reboiler	384	385	10,455
C3	Preheating before R1	423	577	690.3
C4	Preheating before R2	423	526	446.7
C5	Preheating before R3	423	497	317.3

The target of energy synthesis in this paper is to acquire the HEN with the least total annual cost. The minimum heat transfer temperature difference is assumed to be 10 °C while the heat transfer coefficient is assumed to be 400 W/(m^2·°C). The max split number of a stream is set to be 3.
Eventually, HEN with a minimum total annual cost of 730,080 $/y is obtained by Aspen Energy Analyzer, as shown in Figure 7, assuming annual operating duration of 8,000 hours. 15 heat exchangers (9 heat exchangers for process streams, 2 heaters and 4 coolers) are contained in the HEN. In addition, consumption of hot utilities and cold utilities are 6,206.0 kW and 10,096.2 kW.

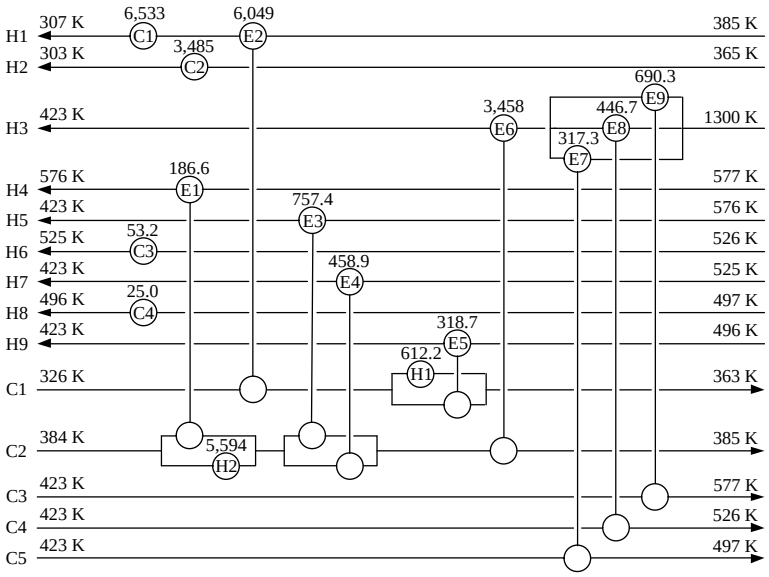

Figure 7: HEN of sweetening and Claus process

5. Conclusions

As important segments of shale gas pretreating, sweetening and Claus process are studied in this work. A more rigorous model on sweetening process is established in which dissolution, absorption and reaction are considered simultaneously. Besides, parameters of the flowsheet are optimized reducing the heat load of reboiler by 11.26 %. Then, Claus process is simulated and the operating conditions of reactors are also discussed, with the sulfur recovery efficiency of 97.35 %. A principle for determination of the operating temperature in each Claus reactor is also proposed, which could provide guidance for research and design of Claus process in the future. Eventually, the HEN of the coupled process with minimum total annual cost of 730,080 $/y is synthesized for energy saving.

Acknowledgments

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