Experiments of Removing Trace Hydrogen Sulfide from Natural Gas with Two Column Pressure Swing Operation

Li Zhou, Limei Zhong, Wei Su, Yan Sun, Yaping Zhou
High Pressure Adsorption Laboratory, School of Chemical Engineering and Technology
Tianjin University, Tianjin 300072, China

Removal of hydrogen sulfide from gas mixtures is an important industrial operation since a lot of organic and inorganic sulfuric compounds is usually contained in the fossil fuels (coal, petroleum, natural gas) and, hence, in the processing products of them. Hydrogen sulfide is the major contamination of natural gas, especially after preliminary sweetening treatment. The content of H_2S in the natural gas for feeding the CNG (compressed natural gas) vehicles must be less than 6 mg/m^3. However, the practical content is quite often higher than 100 mg/m^3 in some places. Apparently, removal of the trace H_2S contamination is a very important and compulsive task of a NGV fuel station. To protect environment and save petroleum, the number of natural gas vehicles (NGV) will continue to grow. Therefore, the purification task of natural gas becomes more important. Conventional methods of removing H_2S from a gas mixture [1-4] are not suitable for the specified purification due to the minor content of hydrogen sulfide, for which adsorption is the most efficient technique,[2-7] but the adsorbent saturated with H_2S cannot be regenerated at ambient temperatures.[8] Therefore, instead of PSA (pressure swing adsorption), TSA (thermal swing adsorption) must be adopted. However, TSA is not preferable because heating and heat exchanging facilities must be included in the purification process, which leads to increase in the fuel cost and quite often is unacceptable due to the limitation on the space by a CNG fuel station.

Instead of conventional solid adsorbents, a new kind of sorbents with a liquid film was applied for the removal of trace H_2S in present study. Porous solids coated with a layer of liquid are usually used in chromatography.[9] The liquid layer functions as the separation agent and is named as the stationary phase, and the solid grains are named as the carrier. However, such packing material has never been applied for PSA process previously. Chromatography operates usually in a batch manner, therefore, is not preferable for large-scale production. PSA is a continuously operated process and, hence, is preferred. The liquid layer outside the solid grains affords the sorbent better selectivity and may allow the sorbent regenerated easily. It has been experimentally shown [10,11] that such sorbent can be regenerated at the ambient temperature, and the dual modes of absorption and adsorption of H_2S by the solvent and the adsorbent provide a higher sorption capacity than the solvent or adsorbent alone. The performance of pressure swing operation relying on such kind of sorbent is experimentally studied in present work. Operational condition of the dual column process is firstly determined, and the multi-cycle operation under the condition is performed at the ambient temperature.

2. Experimental

2.1 The sorbent

The solvent selected to coat the adsorbent must satisfy some requirements. First, it possesses the selective solubility of H_2S. Second, the solubility of H_2S is sensitive to the bulk gas pressure. Third, it possesses high boiling point and is chemically stable. NMP (N-Methyl-2-Pyrrolidone) and TEA (tri-ethanolamine) meet the condition. NMP is widely used as a solvent of removing H_2S in the absorption technology. The normal boiling point of NMP is 202^{o}C. The solubility of H_2S in NMP is rather sensitive to its partial pressure. TEA has even higher normal boiling point (360 ^{o}C) and stronger basic property; therefore, is more stable and shows larger H_2S capacity and is used in the process tests.

The adsorbent used is mesoporous silica gel of particle size 0.28-0.45 mm provided by Qingdao Ocean Chemicals, China. Specifications of the product provided by the supplier include: bulk density 420 g/L; BET surface area 335 m^2/g; pore volume 0.85 ml/g; average pore size 8-10 nm. The physically adsorbed water in the silica gel has been removed before experiments with heating at 120^{o}C. The solvent quantity in sorbent is expressed in loading ratio (LR), which is the percentage weight ratio of solvent to the adsorbent.

2.2 The testing process

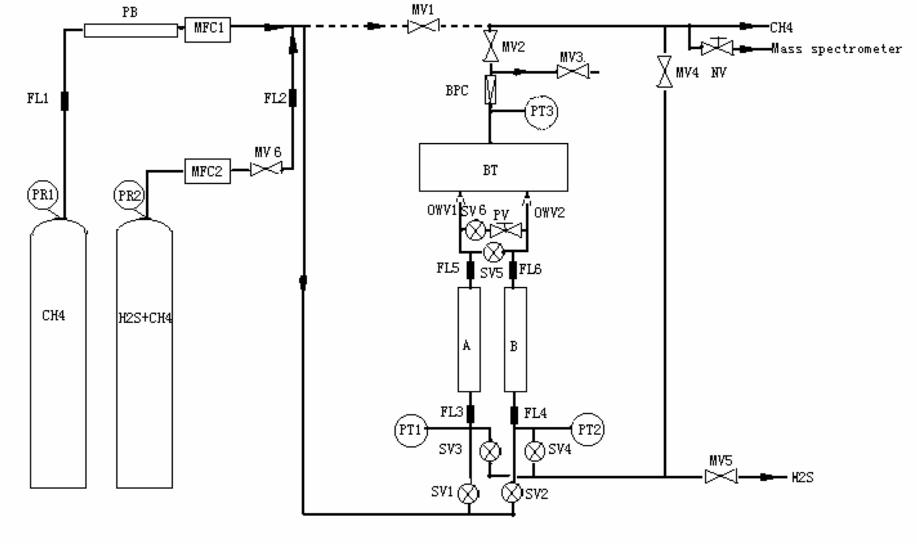

Fig. 1 The experimental process with two PSS columns

The experimental process shown in Fig. 1 consists of two columns, which are made of stainless steel of inner diameter 10 mm and length 250 mm. In each column, 11 g silica gel with loading ratio 26% TEA is packed in a section of length 230 mm. There are two passages for the feeding stream in the test process: one is for pure methane (the purity is above 99.9%), and the other is for the mixture of methane and H_2S with H_2S concentration 1340 *ppm*. The content of H_2S at the entrance of the column is maintained at 170 *ppm* through the flowrate adjustment between the two passages. Volume of the buffer tank for pure methane is 0.05 liter, and the feeding rate is kept at 400 cm^3/min. The consecutive steps included in an operational cycle are: Re-pressurization (RP) with the feeding stream to reach the adsorption pressure; Adsorption (A); Pressure equalization (PE) with the other column; Blowing down to the atmospheric pressure (BD); Purging the sorbent bed with the purified gas (PG), and RP again. A computer program controls the action of the solenoid valves and the mass-flow controllers via the LabCards. Composition of the gas stream is in-situ analyzed with a mass spectrograph. The process tests are performed at 290 K, and the effect of room temperature on the operation was later discussed.

2.3 Determination of the operation pressure

Operation pressure is the highest pressure of a pressure swing operation, at which H_2S was taken up by sorbent. Higher operation pressure results in higher productivity, but leads to smaller separation coefficient and higher energy cost. Therefore, an appropriate sorption pressure has to be determined for the given separation task and the chosen sorbent. Therefore, breakthrough curves are collected for different pressures. The feed stream containing 170 *ppm* H_2S is fed to a single column at a constant rate. The result is shown in Fig. 2, where C_0 and C are the concentration of H_2S in the feed and exit streams, respectively. It is shown that higher pressure leads to longer breakthrough time, i.e., larger capacity for H_2S. However, the breakthrough time increases slowly when pressure becomes higher than 0.43 MPa and, hence, 0.43 MPa was selected as the operation pressure.

2.4 Determination of purging ratio

How much product stream used to purge the sorbent bed is an important operation condition since larger amount is favorable for improving the product purity; however, it decreases the product recovery. The quantity of purging gas is quantified by the purging ratio defined as:[12]

$$\frac{P}{F}=\frac{Methane\cdot quantity\cdot in\cdot purging\cdot stream}{Methane\cdot quantity\cdot in\cdot feed\cdot stream}=\frac{Q_{PG}y_P}{Q_F y_F}$$

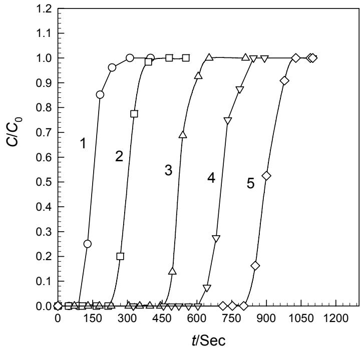

Fig. 2 Effect of pressure on breakthrough times. 1: 0.1 MPa; 2: 0.22 MPa; 3: 0.43 MPa; 5: 0.63 MPa; 5: 0.83 MPa. T=290.5 K; Feeding rate=400 cm^3/min; C_0=170 *ppm*.

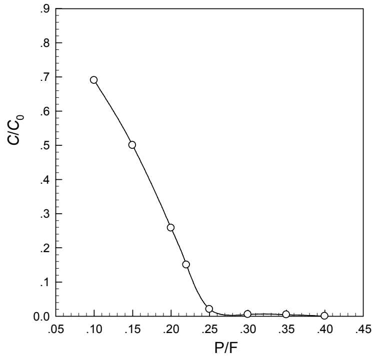

Fig. 3 Effect of P/F on product purity. p=0.43 MPa; t_A=t_{PG}=350 Sec.

where Q is the flow rate, and y is the molar fraction of methane. The subscript “PG”, “P” and “F” denote the streams of purging, product and feed, respectively. The effect of P/F on the performance is shown in Figs. 3 and 4. It seems 0.25 is the critical value of purging ratio when the H_2S concentration in the exhaust gas reaches the maximal value and the content of H_2S in the product stream is less than 6 *ppm*. To guarantee the purity of the purified stream, P/F=0.30 was selected in the process experiments and the content of H_2S in the product stream drops to below 1 *ppm*.

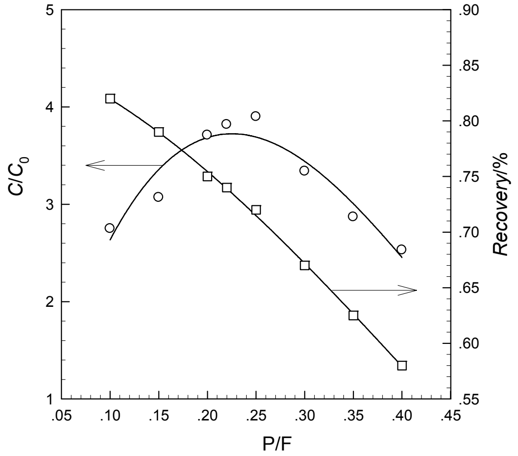

Fig. 4 Effect of P/F on methane recovery and H_2S concentration in the exhaust gas. p=0.43 MPa; t_A=t_{PG}=350 Sec.

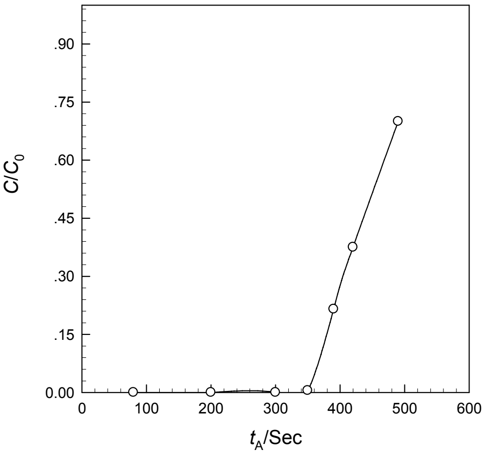

Fig. 5 Effect of adsorption time on the product purity. P/F=0.3, t_{PE}=2 sec, t_A=t_{PG}

2.5 Time allocation in an operation cycle

2.5.1 *Adsorption time*

The time allocated for the adsorption step must be shorter than the breakthrough time for a chosen adsorption pressure; therefore, the adsorption time, t_A, should be less than 420 sec, the breakthrough time for pressure 0.43 MPa. The length of the adsorption time affects the location of the front edge of the concentration profile in the sorbent bed and, therefore, affects the product purity as shown in Fig. 5. On the other hand, longer adsorption time leads to higher product recovery. However, there is an optimal adsorption time (350 Sec) that allows the H_2S concentration in the exhausted stream to reach the maximum due to the maximal use of the sorbent bed, as shown in Fig. 6. Therefore, the adsorption time was selected as 350 Sec.

2.5.2 *Blowdown time*

The column pressure drops down to the atmospheric in the blowdown step. The length of blowdown time may affect the extent of regeneration of the sorbent. Therefore, three different times, 0, 10 and 20 Sec are tested for blowdown and the effects are shown in Figs. 7 and 8. Although the effect exists, it is not considerable for both methane recovery and product purity; therefore, the blowdown time, t_{BD}, is set to zero in order to reduce the duration of an operation cycle. It means the purging step initiates as soon as the column pressure releases to atmospheric.

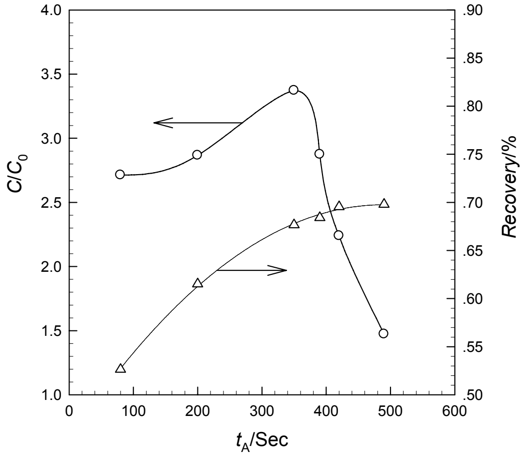

Fig. 6 Effect of adsorption time on methane recovery and H_2S concentration in the exhaust stream

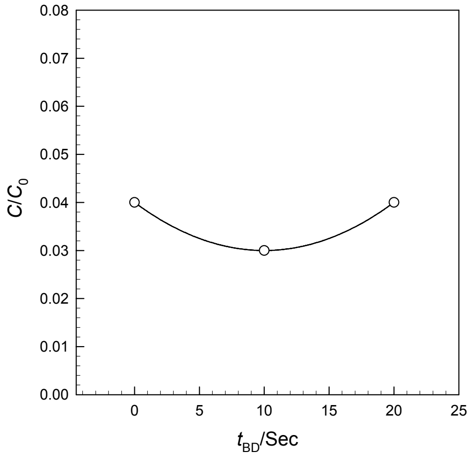

Fig. 7 Effect of blowdown time on product purity

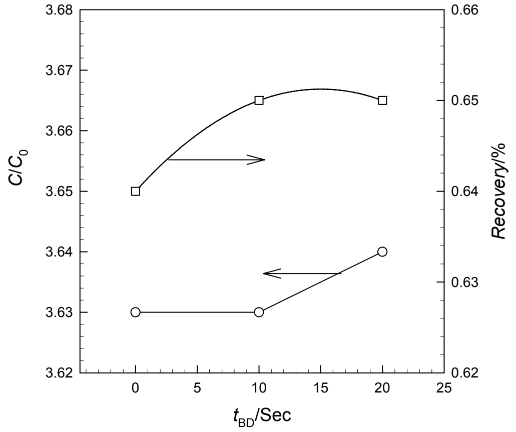

Fig. 8 Effect of blowdown time on methane recovery and H_2S concentration in the exhaust stream

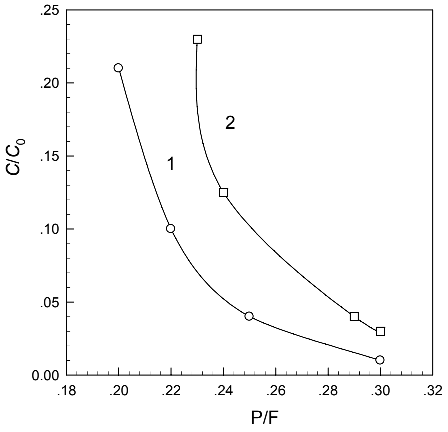

Fig. 9 Effect of purging time on product purity. 1: 350 Sec; 2: 210 Sec.

2.5.3 *Purging time*

Different purging time means different purging rate for a chosen purging ratio. Two purging times are tested at the condition of t_A=350 Sec and t_{PE}=2 Sec. The effects are shown in Figs. 9-11. It is seen that longer purging time is preferable for the system. However, the purging time cannot be longer than the adsorption time for the two column process; therefore, t_{PG} is set equal to 350 Sec.

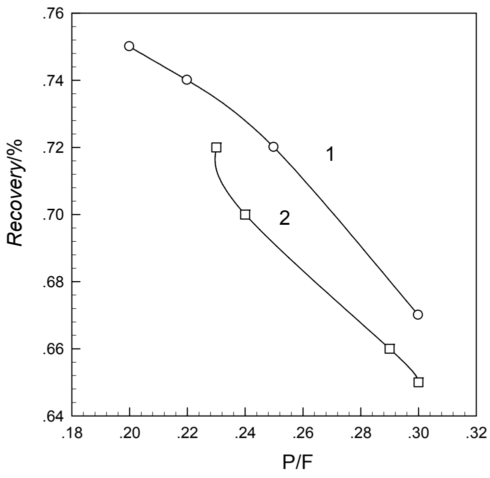

Fig. 10 Effect of purging time on product recovery. 1: 350 Sec; 2: 210 Sec.

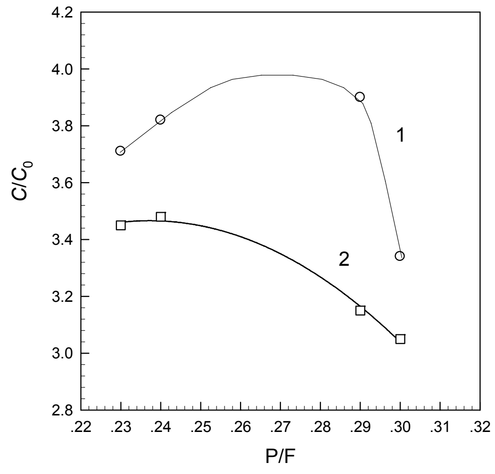

Fig. 11 Effect of purging time on the H_2S concentration in exhaust gas. 1: 350 Sec; 2: 210 Sec.

2.5.4 *Pressure equalization time*

The step of pressure equalization aims to increase the recovery of both the product and the mechanical energy. However, too long time for this step will cause desorption of H_2S, but too short time will cause disturbance of the sorbent bed; therefore, an appropriate time allocated for pressure equalization is quite important. Effect of this time is shown in Fig. 12. The shortest time of pressure equalization results the best performance; therefore, t_{PE} was set equal to 2 Sec.

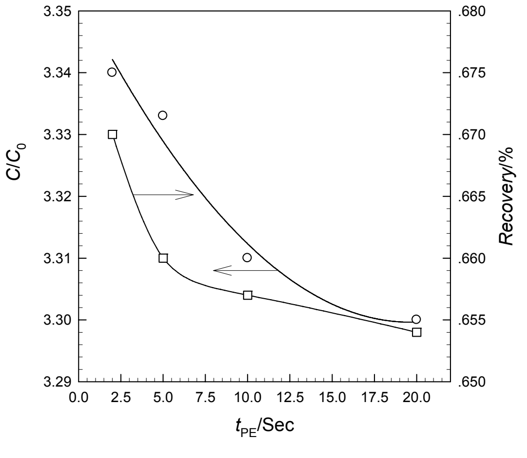

Fig. 12 Effect of t_{PE} on methane recovery and H_2S concentration in the exhaust gas. p=0.43 MPa; t_A=t_{PG}=350 Sec; P/F=0.3.

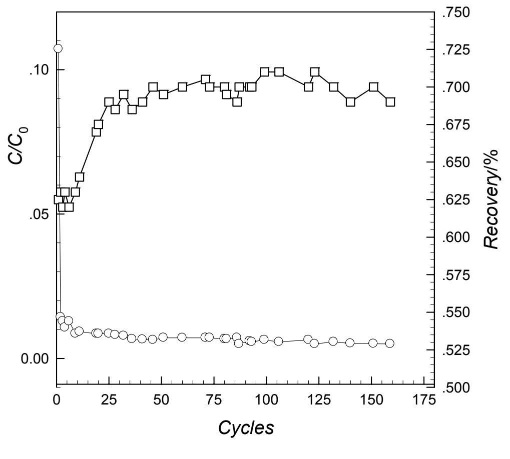

Fig. 13 Variation of product purity and recovery during continuous operation.

2.5.5 *Summary*: *of time allocation*

The period of an operation cycle lasts for 704 Seconds, in which 350 Sec is allocated for adsorption, 350 Sec for purging, and 2 Sec for pressure equalization (twice a cycle).

2.6 Test on continuous operation

To test the operability of the PSS process at ambient temperature, continuous operation is carried out for 160 cycles under the previously determined condition. Variation in the product purity and recovery are shown in Fig. 13. It is shown that the product purity drops to about 1 *ppm* after 5 cycles, and the recovery reaches stable in about 30 cycles. Since there are only two columns operating in the process, the product purity and the H_2S concentration in the exhaust gas as well as the column pressure vary remarkably with time during the period of a cycle as shown in Figs. 14 and 15. The column pressure reaches stable in 30 seconds after pressure equalization. The content of H_2S in the product and the exhaust stream varies inversely. However, both concentrations will approach constant if more columns are included in the process.

2.7 Test on the effect of environment temperature

It is known that environment temperature affects the performance of a PSA process.[13] This effect might be of special concern due to the coverage of solid adsorbent with a film of liquid solvent. For example, whether the process can or cannot operate for different places or different seasons? Therefore, variation of the sorption capacity with temperature and the regeneration performance at different temperatures are tested. Breakthrough curves, shown in Fig. 16, were collected for temperature 253 K to 313 K with single column. The sorbent

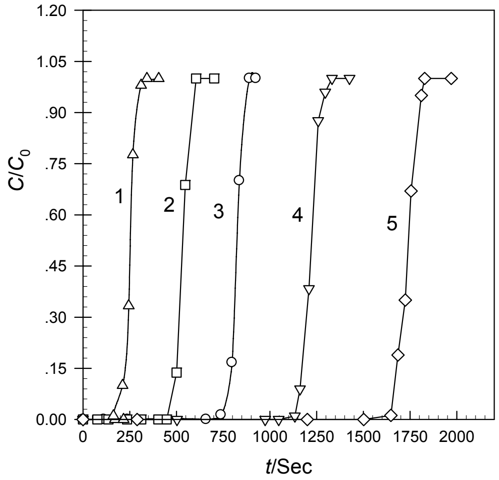

Fig. 16 Breakthrough curves collected at different bed temperature. 1: 313 K; 2: 298 K; 3: 290 K; 4: 273 K; 5: 253 K.

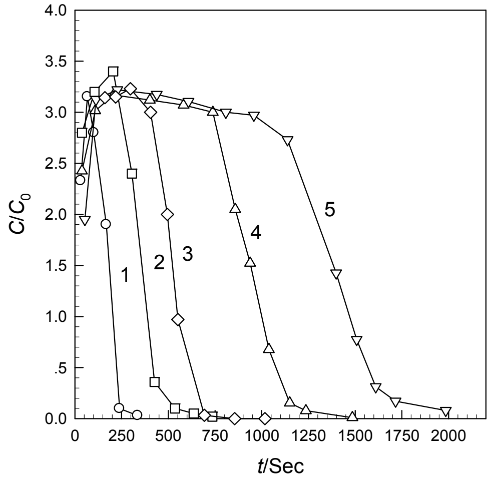

Fig. 17 Regeneration curve at different bed temperature. 1: 313 K; 2: 298 K; 3: 290 K; 4: 273 K; 5: 253 K.

and its packing is same as that mentioned in previous section. The content of H_2S in the feeding stream is 190 *ppm* and the feeding rate is. 280 Ncm^3/min. The column was purged with pure methane after being saturated, and the regeneration curves obtained at different temperature are shown in Fig. 17. The flow rate of purging stream is kept at 100 Ncm^3/min. It is shown that higher temperature yields shorter adsorption time and shorter purging time; therefore, shorter period of an operation cycle. Lower temperature yields the opposite consequence, but pressure swing operation is still feasible.

3. Conclusion

It is demonstrated that a pressure swing sorption (PSS) process operated at ambient temperature can be used to remove the trace H_2S contamination due to the use of a new kind of sorbent. Such sorbent can be regenerated by pressure reduction and back-purge with the purified gas. The critical purging ratio is 0.25. Smaller purging ratio is possible if the mass transfer kinetics could be improved. Therefore, the new technique can replace the conventional thermal swing adsorption (TSA) mode of purification, which requires high temperature regeneration. This represents a major breakthrough in the natural gas purification technology.

Acknowledgements

The financial support of the National Natural Science Foundation of China (grant number 20336020) is greatly acknowledged. The authors are very grateful to Professor Shivaji Siecar for his valuable suggestion during the preparation of the paper.

References

1. Riesenfeld，F. C.; Kohl, A. L. *Gas Purification*，4th ed，Gulf Publishing, Houston，**1985.**
2. Nedez, C.; Ray, J. A New Claus Catalyst to reduce Atmospheric Pollution, *Catalysis Today*, **1996**, 27, 49.
3. Maddox, R. N.; Burn，M. D. Physical solution is key to sweetening processes, *The Oil and Gas. J*, **1968**, 66 (2), 78-87.
4. Kaliva, A. N.; Smith, J. W. Oxidation of Low Concentration of Hydrogen Sulfide by Air On a Fixed Activated Carbon Bed, *Can. J. Chem. Eng*., **1983**, 61, 208.
5. Cheremisinoff, P. N. (ed.) *Carbon Adsorption Handbook*, Ann Arbor Science, Ann Arbor, **1978.**
6. Barrer, R. M. New Selective Sorbents: Porous Crystals as Molecular Filters, *Brit. Chem. Eng*. **1959**, 4, 267.
7. Chou, T.; Lin, T. Y.; Hwang, B. J.; Wang, C. C. Selective Removel of H_2S from Biogas by a Packed Silica Gel Adsorber Tower, *Biotech. Progr*. **1986**, 2, 203.
8. L. Zhou, P. Chen, M. Li, Y.-P. Zhou. A Study of the Removal of Minor Amounts of H_2S from Natural Gas by Activated Carbon, Adsorption Science and Technology, **20**, 969-976 (2002).
9. Heftmann, E. (ed.) *Chromatography: Fundamentals and related differential migration methods*, 5th ed. Elsevier, Amsterdam, **1992.**

10. Zhou, L.; Yu, M.; Zhou, Y. P.; Zhong, L. M. Feasibility Study on Pressure Swing Sorption for Removing H_2S from Natural Gas, *Chem. Eng. Sci*. **2004**, 59, 2401.
11. Zhou, L.; Zhong, L. M.; Yu, M.; Zhou, Y. P. Sorption and Desorption of Minor Amount of H_2S on Silica Gel Covered with a Film of TEA, *Ind. Eng. Chem. Res*. **2004**, 43, 1765.
12. Yang, R. T.; Doong, S. J. Gas Separation by Pressure Swing Adsorption: A Pore-Diffusion Model for Bulk Separation, *AIChE Journal*, **1985**, 31, 1829.
13. Ruthven, D. M.; Farooq, S.; Knaebel, K. S. *Pressure Swing Adsorption*, VCH Publishers, New York, **1994**.