Adsorption 11: 625–630, 2005

Improved Purge Step in Pressure Swing Adsorption for CO Purification

HIDEKI MIYAJIMA*
Mitsubishi Kakoki Kaisha, Ltd, 2-1, Ohkawa-cho, kawasaki-ku, Kanagawa, Japan
miyajima@kakoki.co.jp

AKIO KODAMA
Department of Human & Mechanical Systems Engineering, Kanazawa University, Kanazawa, Japan

MOTONOBU GOTO AND TSUTOMU HIROSE
Department of Applied Chemistry and Biochemistry, Kumamoto University, Kumamoto, Japan

Abstract. Supported Cu^+ on activated carbon carrier was used to enhance the CO selectivity and thus to produce high concentration CO gas in a single stage CO-PSA which simulated a commercial 4-beds system operating in six steps (equalization, blow down, purge, desorption, repressurization and adsorption). Since the adsorbent adsorbed CO by chemisorption very strongly, we decided that a system should be high-pressure adsorption (500 kPa) and vacuum-desorption (9 kPa). In the conventional cycle operation, the total amount of purge gas has great influence on CO recovery because this system uses a part of product CO as purge gas. We focus our discussion on the effect of purge step and propose a new CO-PSA system using the Variable Purge gas Concentration Method (VPCM for short). The VPCM method was found to be able to reduce the product CO amount consumed for purge and thus to improve CO yield without any product purity reduction.

Keywords: adsorption, pressure swing adsorption, carbon monoxide, purification

1. Introduction

High purity CO gas ($<$99 vol%) is widely used for raw material of polyurethane and polycarbonate for resin, and acetic acid and ketone for chemical substances. In industrial CO production methods, CO gas is separated from synthesis gas, coke oven gas, blast furnace gas, etc which consist of CO, H_2, CH_4, CO_2, N_2, O_2, H_2O. There are three kinds of typical separation way: (1) Pressure Swing Adsorption (PSA), (2) Cryogenic process and (3) Membrane. These technologies are decided by gas manufacturing cost, product amount, and industrial purpose. The cryogenic process is suitable generally for a large-scale plant. But its needs very large energy for refrigeration and the operating cost becomes higher than other methods for small plant. The most important difference between the cryogenic process and PSA or membrane system is that non-cryogenic gases can be generated continuously at the point of use. A membrane separation process is very simple and can achieve the lowest operating cost. But the drawback is a difficulty in producing high concentration CO gas. Dutta and Patil (1995) discussed the status of technological developments for the separation and purification of CO from industrial gas streams with adsorptive and membrane processes.

A PSA process is an obviously alternative way to produce high purity CO gas. The first commercial plant for CO separation was developed by Kawasaki Steel Corporation and Osaka Oxygen Industries Ltd, Japan

---

*To whom correspondence should be addressed.

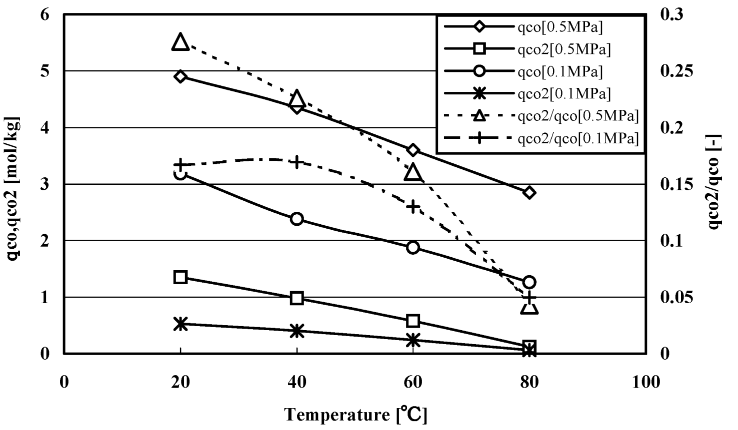

Figure 1. Adsorption isobars and CO/CO_2 selectivity on CO adsorbent with various CO and CO_2 partial pressures.

(Sakuraya et al., 1983). This process has 2-stages; (1) CO_2 removal section (by activated carbon or silica gel); (2) CO recovery section (by sodium-type mordenite). To produce high purity CO gas by a single-stage PSA process, the adsorbent must have high selectivity of CO adsorption. Hirai et al. (1983) has developed the CO-selective adsorbent characterized by Cu-supported carrier. Zhu et al. (1991) reported a PSA process with activated carbon supported copper as adsorbent for separating CO from CO-CO_2-N_2 mixture. Kasuya et al. (1991) described a commercial PSA process of a single stage for recovering high purity CO with activated alumina career, which has an appropriate pore size distribution, and used an impregnated carbon and copper compound ($CuCl_2$, CuCl) as the active chemisorption species. In these PSA processes, a purge step invariably is needed to sweep the residue gas of lower purity before the desorption step and thus to produce high concentration CO gas since this step influences the process performance such as product CO purity, recovery yield, etc. In the present paper, we will propose a new concept of the purge step, i.e. Variable Purge gas Concentration Method (VPCM for short), and examine the performance in stead of the conventional purge step with a higher constant CO concentration.

2. Adsorbent

An adsorbent used in this study was manufactured by impregnating activated carbon with cuprous chloride as Metal-Complex Adsorbent. Since this adsorbent strongly adsorbs CO with reversible chemical reaction on π-π interactions, the PSA operation must be determined to pressurize the adsorption and vacuumize the desorption. A point to notice is the fact that a little CO_2 is adsorbed simultaneously. Figure 1 shows adsorption isobars to determine CO/CO_2 selectivity in the CO adsorbent. In this figure, the q_{CO_2}/q_{CO} ratio becomes smaller as operating temperature rises. This phenomenon stems from the fact that the temperature dependence of amount adsorbed of CO_2 (physical adsorption) is much larger than that of CO (chemisorption).

The CO-PSA performance is largely affected by the temperature control due to CO chemisorption mechanism. The higher operating temperature leads to higher selectivity of CO/CO_2 although the amount adsorbed for CO decreases inversely. In this study, the desirable operation temperature was determined at 50°C to generate higher purification and higher recovery yield.

3. Conventional CO-PSA Operation and Principle of the Proposed VPCM

Figure 2 shows a typical configuration of a 4-beds CO-PSA process and additional equipment for a Variable Purge gas Concentration Method (VPCM for short) proposed. Solid lines refer to the conventional CO-PSA operation and extended equipments for installing VPCM (a circulating pump, a surge tank, control valves and piping) are indicated by broken lines. This diagram to show both flow sheet and process operating sequence is called "PSA configuration". Diagne et al. (1995) proposed a systematic way of construction of the configuration in which a pressure history is plotted against the time axis scaled outwards in a parallelogram and adsorption columns rotate in a counterclockwise permutation. The cycle operation consists of 6 steps

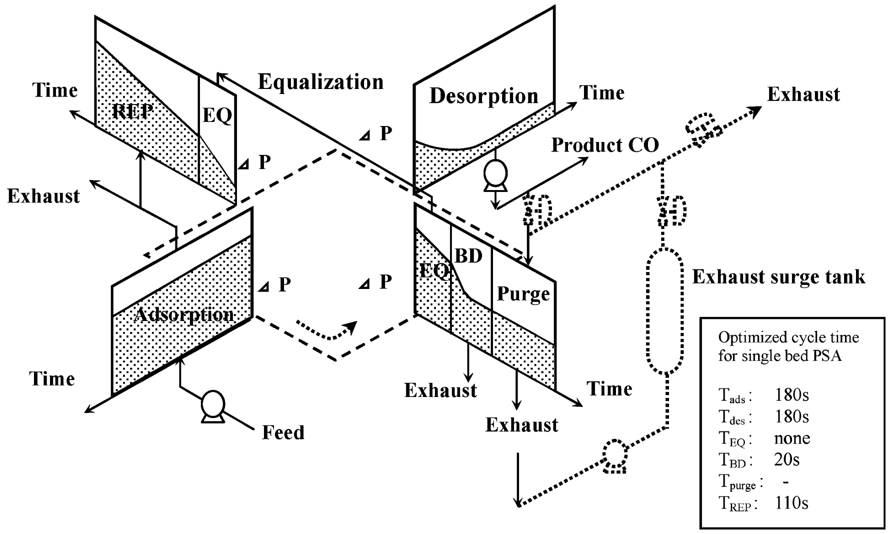

Figure 2. A configuration of the conventional 4 beds CO-PSA and the CO-PSA with VPCM (with broken line).

(Adsorption, Desorption, Equalization (EQ for short), Blow down (BD), Purge and Repressurization (REP)). In adsorption step, CO is adsorbed at high pressure and raffinate is exhausted as dilute CO gas. A concentrated CO stream is produced by vacuum desorption at the bottom of column.

The conventional cycle operation uses a part of product CO flow for purge gas with a uniform concentration as high as product CO purity (≧99 vol%). Therefore the total volume of purge gas has a great influence on CO recovery yield and then the exhaust gas in purge step contains the large amount of CO(≧85 vol% on average) in the conventional purge method.

The VPCM concept is based on a consideration that the CO concentration in the bed at the initial purge step is about 50 vol% and the initial CO concentration in purge gas is not necessary to be so high as the desired product CO gas (≧99 vol%). The CO concentration of purge gas is varied in the VPCM by mixing a part of product flow and exhaust gas in purge step at an arbitrary ratio. The VPCM functions with 2 control valves that control the product CO flow in desorption step and the recycle exhaust flow via the surge tank in purge step, as shown in Fig. 2. This method can reduce the amount of product CO gas consumed for purge and improve CO recovery yield.

4. Experimental

The experimental apparatus used was a simplified single bed PSA system to simulate the above complete VPCM cycle. The column was made of 22 mm i.d. SUS tube packed with adsorbent up to 200 mm height and the corresponding mass of CO adsorbent was 58.5 g. The apparatus was operated at 600 kPa in adsorption and 4 kPa in desorption step. The operation cycle consisted of 5 steps as shown in Fig. 2 except for EQ step. A Programmable Logic Controller (PLC) controlled the operation sequence by actuating solenoid valves and back-pressure regulators to keep pressures of product and purge lines. Feed gas was assumed as methanol decomposition gas and the composition was set at H_2:66%, CO:33%, CH_4:0.8% and CO_2:0.2% in volume. A make-up gas with 99 vol% CO was prepared as a simulated product gas and mixed with the exhaust gas to supply the purge gas circularly at an arbitrary history of CO concentration. Flow rate of feed, purge and repressurization gas were adjusted to the desired value by mass flow controllers and the purge CO concentration can be changed according to a desirable curve by the PLC for VPCM. The PSA operating temperature was controlled by hot water flowing around the adsorption bed to keep it warm at arbitrary temperature (50°C usually).

5. Results and Discussion

5.1. Optimization of Purge Cycle Time T_{purge}

An influence of purge cycle time (T_{purge}) was examined to decide the conditions for purge step in the conventional purge method where the column was purged with a constant CO concentration throughout the purge step. An optimized purge flow rate had been determined to be 100 Ncm^3/min in a preliminary experiment in advance. The desirable CO purity ($\geqq$99 vol%) can be generated when T_{purge} is longer than 120 s as shown in Fig. 3 and a productivity of CO product did not change in the whole period of purge step. The operating T_{purge} was determined at 120 s and this result was a standard against which we can evaluate the effect of VPCM.

5.2. *Effect of VPCM*

Figure 4 shows experimental results of four different patterns of time variations in purge concentration set for VPCM as well as the conventional purge pattern given by a horizontal line. Each pattern was projected as follow.

Pattern ①: It is the simplest single step control where the CO concentration in purge gas changes linearly from 90 vol% to 99 vol% until the end of purge step.

Pattern ②: The CO concentration changes linearly from 90 vol% to 99 vol% during the initial half time in purge step and after then it is kept constant at 99% as in the conventional purge method.

Pattern ③: It has 3 steps variation where the CO concentration linearly changes from 90 vol.% to 92 vol% during the initial half time in purge step and changes from 92 vol% to 99 vol% in the next 20 s. The rest of purge step is same as the conventional method.

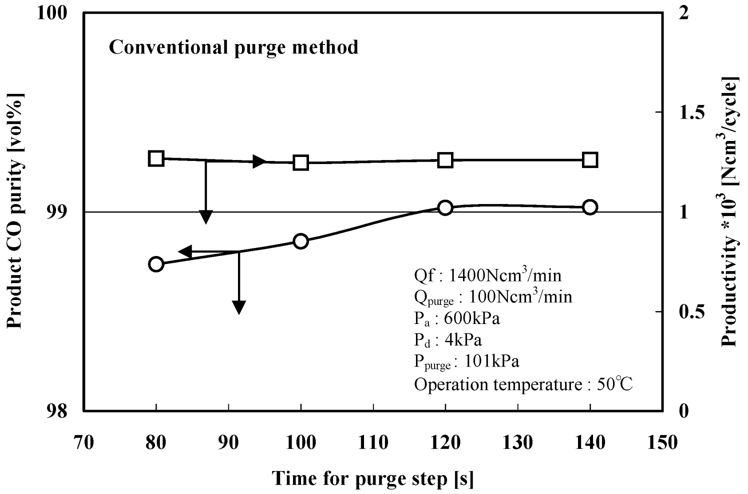

Figure 3. An influence of purge cycle time (T_{purge}) for product CO purity and productivity. (Conventional purge method).

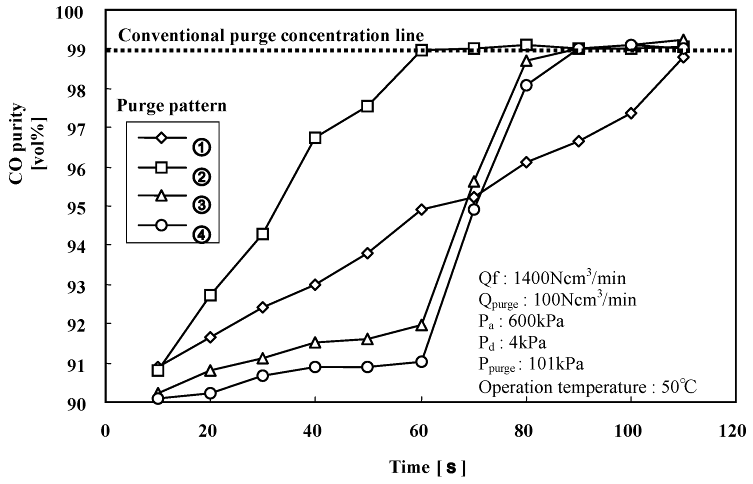

Figure 4. Experimental results of four different purge patterns with time variations in purge step.

Pattern ④: It also has 3 steps variation where the CO concentration linearly changes from 90 vol% to 91 vol% during the initial half time in purge step and changes from 91 vol% to 99 vol% in the next 20 s. The rest of purge step is same as the conventional method.

The purge effect with VPCM was examined to compare PSA performance between the conventional purge and the above four patterns of VPCM. The performance examined involves (1) product CO purity, (2) purge efficiency, (3) productivity and (4) recovery yield. The purge efficiency is defined as a ratio ($V_{\text{purge}}/V^*_{\text{purge}}$) of product CO consumed in purge step with VPCM to that in the conventional purge, V^*_{purge}. The experimental results carried out under the conditions given in Fig. 4 are summarized in Table 1. The desirable CO purity and higher efficiency of $V_{\text{purge}}/V^*_{\text{purge}}$ were satisfied in the case of purge pattern ③. The recovery yield in this case was more than 5% superior to the conventional purge pattern.

The purpose of purge step is to clean up impurities that remain staying in void space and adsorbed in pores. When the average CO concentration in the bed at the initial purge step is nearly 50 vol% as mentioned above, there is a little lowering of efficiency of adsorption kinetics under the influence of the difference in the initial CO concentration in purge gas between the conventional purge method (99 vol%) and the VPCM (90 vol%). The efficiency of purge is affected by driving force in terms of CO concentration difference between purge gas and residue gas in pores or void space. So the purge pattern ③ is just suited in this adsorption system.

This recovery yield is calculated with experimental results for the single-bed CO-PSA apparatus. The commercial 4 beds CO-PSA can be realized identically by extending the equalization step and the exhaust recycle line. In this process, the recovery yield is expected to be extremely higher value (higher than 90%) with VPCM. So the VPCM will help to decrease the operating cost in the commercial plant by just a simple installation of VPCM into the conventional CO-PSA process without a large number of additional equipments.

Table 1. CO-PSA performances on various purge concentration curves.

Purge pattern	Product CO purity (vol%)	$V_{\text{purge}}/V^*_{\text{purge}}$ (−)	Productivity $* 10^3$ (Ncm^3/cycle)	Recovery yield (%)
Conventional	99.02	−(1.0)	1.259	78.0
①	98.33	0.5	1.122	83.8
②	99.08	0.75	1.211	80.1
③	**99.11**	**0.49**	**1.265**	**83.9**
④	98.47	0.45	1.269	84.9

6. Conclusions

CO-PSA processes consisting of special adsorbent such as supported Cu^+ on activated carbon carrier are efficient for CO production at the use point owing to high CO selectivity. The conventional CO-PSA includes purge step, but unfortunately it is found to be a primary factor of decreasing CO recovery yield since the CO concentration in consumed purge gas is as high as product purity. Then we developed a higher efficiency PSA process for CO separation by taking into account the VPCM (Variable Purge gas Concentration Method). The VPCM controlled CO concentration profile in purge gas to a favorable curve by mixing a part of product stream and exhaust gas from purge step. Effect of VPCM was experimented by a simplified single bed PSA. The CO recovery yield was found to become nearly 5% higher than the conventional process by the optimized purge CO concentration curve with VPCM. The commercial CO-PSA will be a 4-bed system and more efficient performance than these experimental results is expected. Nevertheless the influence of operating temperature is large with this adsorbent, and it is necessary to verify these results by a bench scale or pilot scale CO PSA process.

Nomenclature

P_a	Pressure in adsorption step (Pa)
P_d	Pressure in desorption step (Pa)
P_{purge}	Pressure in purge step (Pa)
Q_f	Feed flow rate (m^3/s)
Q_{purge}	Purge flow rate (m^3/s)
T_{ads}	Time for adsorption step (s)
T_{des}	Time for desorption step (s)
T_{EQ}	Time for equalization step (s)
T_{BD}	Time for blow down step (s)
T_{purge}	Time for purge step (s)
T_{REP}	Time for repressurization step (s)
V^*_{purge}	Volume of product CO in conventional purge step (m^3)
V_{purge}	Volume of product CO in purge step with VPCM (m^3)

References

Diagne, D.D., M. Goto, and T. Hirose, "Parametric Studies on CO_2 Separation and Recovery by Dual Reflux PSA Process Consisting of Both Rectifying and Stripping Sections," *Ind. Eng. Chem. Res.*, **34**(9), 3083–3089 (1995).

Dutta, N.N. and G.S. Patil, "Developments in CO separation," *Gas. Sep. Purif.*, **9**(4), 277–283 (1995).

Hirai, H., K. Wada, and M. Komiyama, *Chem. Lett.*, 361 (1983).

Kasuya, F. and T. Tsuji, "High Purity CO Gas Separation by Pressure Swing Adsorption," *Gas. Sep. Purif.*, **5**, 242–246 (1991).

Sakuraya, T., et al, *Kawasaki Seitetsu Giho* (1983).

Zhu, L.Q., J.I. Tu, and Y.J. Shi, "Separation of CO-CO_2-N_2 Gas Mixture for High-Purity CO by Pressure Swing Adsorption," *Gas. Sep. Purif.*, **5**, 173–177 (1991).