Operational Influence on the Efficiency of Pressure Swing Adsorption Process

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Understanding the operational influence on the efficiency of the pressure swing adsorption process can help improve operational efficiency and reduce production costs. In this study, a single-bed pressure swing adsorption device was used to investigate the impact of various process parameters on the separation efficiency of carbon monoxide and nitrogen using a commercial cuprous-modified adsorbent. The gas mixture was fed into the device at an appropriate flow rate. All the steps of the pressure swing adsorption processes were executed by the programming scripts to control the actions of the valves on the device. The results indicated that increasing pressure and temperature could improve the gas yield and the carbon monoxide concentration in the product gas. However, at higher temperatures, some carbon monoxide was consumed in reducing the copper ions in the adsorbent. Reasonably increasing the feed flow rate did not affect the quality but helped save time in the adsorption step. The saturation level of the adsorption bed affects the product gas quality, and allowing a small amount of carbon monoxide to break through the adsorption bed could ensure product gas quality. Before gas production, releasing the pressure in the column to near atmospheric pressure removed residual feed gas in the voids of the adsorption bed, ensuring product gas quality. Using part of the product gas to purge the adsorption bed before gas production could further discharge residual gases, improving product gas quality but reducing the recovery rate. Overall, using a copper-modified adsorbent can effectively separate carbon monoxide and nitrogen, yielding product gas with carbon monoxide purity exceeding 99%.

Keywords: Pressure swing adsorption, Cuprous-modified adsorbent, Operational influence

1. INTRODUCTION

By-product gases in the steel industry, such as blast furnace gas (BFG) and Linz-Donawitz converter gas (LDG), contain a large amount of carbon monoxide (CO). In addition to being used as fuel, CO is also one of the basic raw materials for synthetic chemicals. Therefore, capturing CO through a gas separation process and utilizing synthetic chemicals can reduce carbon emissions caused by metallurgy procedures, also it has economic benefits with selling chemicals. The by-product gas contains CO and nitrogen (N_2), both have similar physical and chemical properties, such as boiling points of -191.5°C and -195.8°C respectively, and molecular weights of 28 g/mol, they are difficult to separate. The COSORB process developed by the American company Tenneco using cuprous ion (Cu^+)-based solvent to absorb CO, has not been widely used by the market due to problems such as solvent corrosion and environmental pollution. A newer and widely used commercial process is the pressure swing adsorption (PSA) process. The adsorbents modified with various copper salts have strong adsorption capacity for CO but do not adsorb N_2. Gases can effectively separate through the adsorbent's selective adsorption.

PSA is a technique used to separate gas from a gas mixture through adsorbents by changing pressure. Usually, gas molecules adsorb to absorbent under higher pressure in a column and release under lower pressure or in a vacuum. Enhanced pressure can help more gas molecules enter the pores of adsorbents, thereby increasing the product yield. Take the separation procedure of CO and N_2 as an example, the gas mixture continuously feeds into an adsorption column filled with adsorbents. In the column, strongly adsorbed gases CO will adsorb onto the adsorbent under higher pressure until the concentration of CO at the outlet of the column rises. In other words, the adsorption bed gets “saturated.” Then, stop feeding, release the pressure of the column, and enter the gas production step. CO would desorption from adsorbents under low pressure or in a vacuum; meanwhile, the adsorbents would regenerate. After that, the adsorbents are ready for the next cycle. A column only performs a single step at a time. Therefore, to continuously produce gas, an industrial-scale PSA process will have multiple adsorption columns, allowing multiple columns to perform different steps at a time.

In a PSA process, environmental variables including pressure, temperature, flow rate, etc., may affect the quality and cost of the gas product. For example, higher operating pressure can increase the adsorption capacity, thereby increasing the yield, but it will cause higher energy consumption of the gas compression system. Gas adsorption is an exothermic reaction. Increasing the temperature is detrimental to adsorption. However, when a weak chemical bond forms between the adsorbent and the gas, such as the CO-Cu$^+$ σ-π bond, it needs enough driving force for gas desorption. An appropriately increasing temperature might benefit it. Appropriately increasing the flow rate can shorten the time for the column to reach adsorption saturation and make the operation more flexible. However, too high a flow rate might cause adsorbent floating, or adsorbed gas breakthroughs too quickly to reduce the recovery rate. In addition, several advanced operating steps, such as depressurizing and vacuum production, or purging residual gas in the column through high-quality product gas, are also often discussed for their impact on product gas quality. In this study, the influence of process parameters on the separation of carbon monoxide and nitrogen by PSA will be discussed for enhanced operation efficiency and reduced production costs.

2. EXPERIMENTAL METHOD

2.1 Apparatus

Fig.1 shows a single-bed PSA device that was developed to analyze the influence of PSA process parameters such as pressure, temperature, flow rate, and operating procedures such as feeding ration, depressurized level, and gas purge impact on the separation results of CO and N_2 using a commercial copper-salt modified adsorbent. Both high-pressure CO and N_2 supplied by gas cylinders were reduced to the appropriate pressure by pressure regulators. The ratio of mixing gas was regulated by gas mass flow controllers, which were installed at the inlet of the packed column. Additionally, a gas mass flow controller at the top outlet of the packed column regulated the pressure within the column. The adsorbents were loaded in a stainless-steel column, which was wrapped with heating coils and insulation materials. The temperature was adjusted by controlling the power of the heating coils. The product gas was produced from the bottom of the column by a vacuum pump and the flow rate was adjusted by a gas mass flow controller. The concentrations of feed, vent gas, and product gas were analyzed by a gas analyzer, which uses a non-dispersive infrared (NDIR) type sensor to analyze CO and carbon dioxide (CO_2) concentration.

2.2 Activation of Adsorbent

When the fresh adsorbents were loaded into the column, an activation procedure must be performed before the experiment. After preheating the column to 100°C, the reducing gas consisting of 10% CO and 90% N_2 was introduced with a gas flow rate of 5 standard liters per minute (SLPM). The activation procedure is an exothermic reaction, so the temperature in the column must be carefully controlled to remain below 150°C. The temperature should be gradually and slowly increased until it approaches 150°C. When the adsorbent undergoes an activation reaction, an increase in the concentration of CO_2 in the vent gas at the top of the column was observed by the gas analyzer, until the concentration of CO_2 was close to zero. Meanwhile, the concentration of vent gas was close to the incoming reducing gas, then the activation procedure was completed.

2.3 Experimental Procedures

The PSA experiment would sequentially carry out steps such as pressurizing, feeding and adsorption, depressurizing, purging by the product gas, and producing

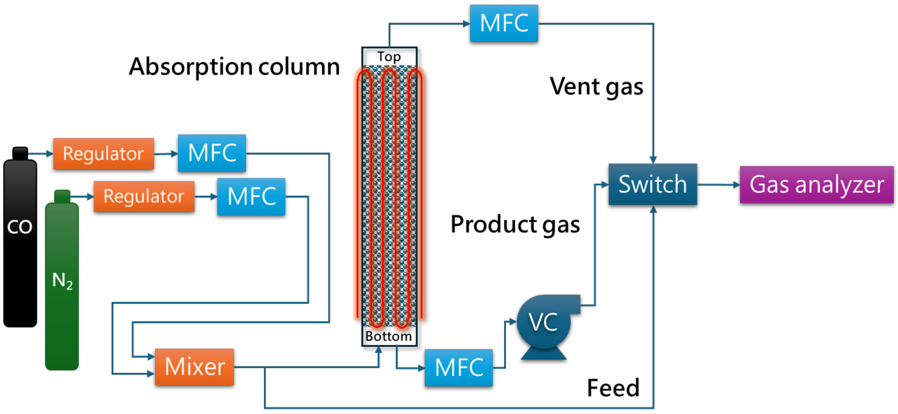

Fig.1. Schematic diagram of single-bed pressure swing adsorption device.

gas product by vacuum pump. A computer program was applied to control the pneumatic valves in each pipeline to perform those actions. For example, in the pressurizing step, the valves before the inlet of the column were opened, but the valves at the top and bottom of the outlet pipelines of the column were closed. The parameters like pressure, temperature, gas flow rate, valve state, etc., could predefine in the computer program and perform the procedures automatically.

3. RESULTS AND DISCUSSION

Fig.2. shows the effect of operating pressure on CO adsorption amount, CO production amount, and CO product quality at the condition fed with 5 SLPM 20% CO/80% N_2 mixture at 70°C. Increasing the pressure resulted in higher CO adsorption amount, CO production amount, and CO product quality. Higher pressure gave enough driving force to allow the gas molecules to enter deeper pores of the adsorbent and fill the porous space, so the adsorption amount increased. Similarly, the CO production amount increases with the increasing pressure, but not very much. It's worth noting that the CO adsorption and production amount were not equal because of the CO-Cu^+ σ-π bonds, which affect the desorption rate. It needed more time or enough drive forces such as rising temperature or lower pressure to force the CO molecules to be desorbed.

Regarding CO product quality, increasing the pressure was beneficial to increasing the CO concentration of the product gas. When the operating pressure exceeded 2 kg/cm^2, the CO concentration of the product gas reached more than 95% and then increased slightly. The column was filled with bead-like adsorbents but left a lot of gaps because of the shape. The feed gas mixture remained in the voids of the packed bed. Even weakly adsorbed nitrogen can still enter the pores of the adsorbent. When producing CO products, these residual impurities dilute the CO and make it difficult to achieve 100% CO concentration in the product gas. Therefore, using a small amount of product gas to replace the residual gases in the voids is an effective procedure for improving the quality of the product gas.

Low temperature is beneficial for gas adsorption onto the adsorbent, while high temperature is unfavorable for adsorption but helpful for desorption. However, the adsorbent modified by cuprous has the characteristics of forming the CO-Cu^+ σ-π bonds. The appropriate temperature might provide enough activation energy to break the coordination bond and desorb CO. Fig.3. shows the effect of operating temperature on CO adsorption amount, CO production amount, and CO product quality at the condition fed with 5 SLPM 33% CO/67% N_2 mixture at an operating pressure of 4 kg/cm^2. The temperature was gradually increasing from 30°C to 120°C. Increasing the temperature resulted in higher CO adsorption amount, CO production amount, and CO product quality. The observation that the CO adsorption amount increases was contrary to the concept that higher temperatures are unfavorable for gas adsorption. When the temperature was raised, the CO production amount did not increase significantly. In addition, the CO product concentration was stably higher than 99% when the temperature was higher than 50°C, and no significant increase when the temperature was kept raised.

To explain the observation results, Fig.4. shows the concentration trends of CO and CO_2 while performing PSA cycles in various operating temperatures. The dashed lines point out the step switch moments of a PSA cycle, which label A: feed and adsorption; Label B: depressurizing; Label C: producing in a vacuum, and the

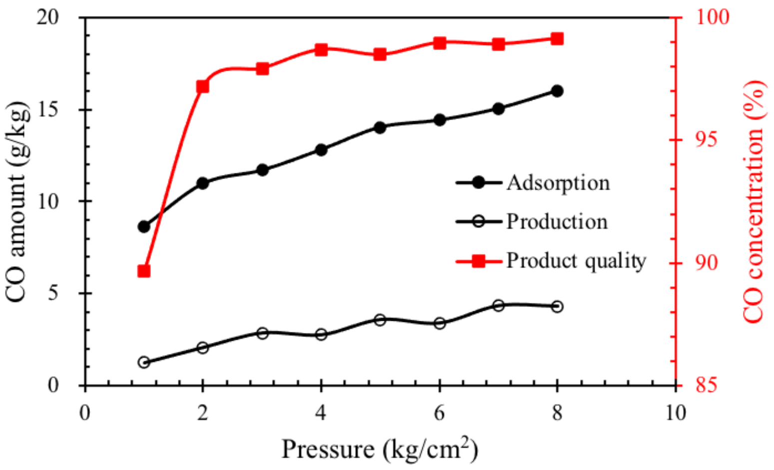

Fig.2. Pressure effect on CO adsorption, production amount, and product quality.

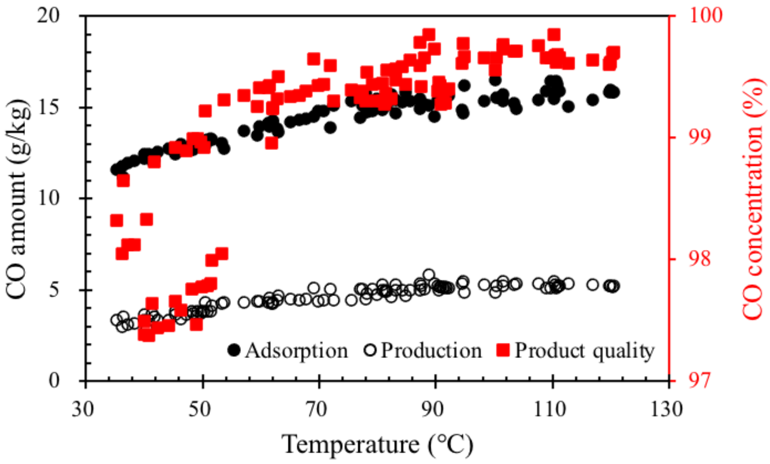

Fig.3. Temperature effect on CO adsorption, production amount, and product quality.

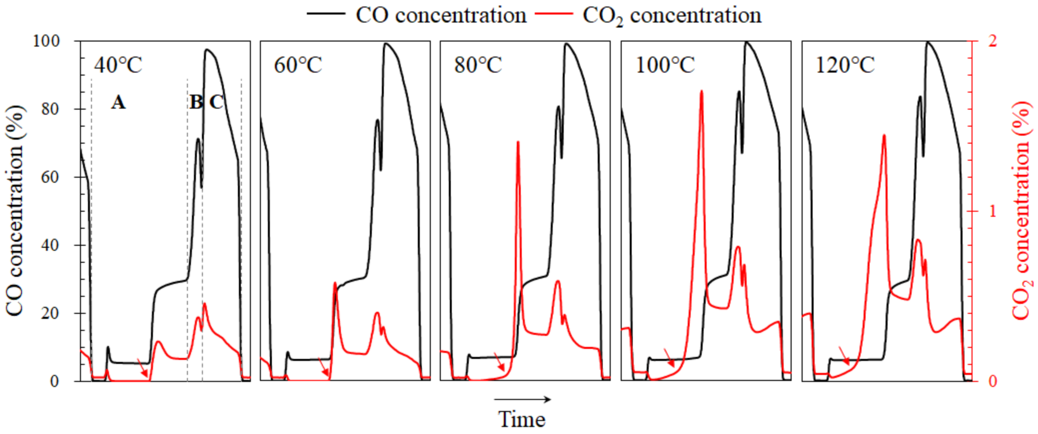

Fig.4. The concentration trends of CO and CO_2 while performing PSA cycles.

red arrows indicate the breakthrough point of CO_2. The CO_2 concentration of the vent gas at the top of the column increased as the temperature increased while breaking through the adsorption bed. Also, the breakthrough points of CO_2 were early when the temperature kept rising. The temperature programmed reduction (TPR) was applied to study the reduction reaction of adsorbent using 10% CO and 90% Helium (He), the result shown in Fig.5., indicating that the reduction reaction of the adsorbent occurred between 100°C and 350°C. It means that part of the CO in the feed during a PSA cycle at a higher temperature probably reacted with the copper salt causing the copper salt to reduce, while the CO to oxidize into CO_2.

The feed flow rate is related to the time it takes for the adsorption bed to reach saturation breakthrough. Fig.6. shows the effects of different feed flow rates on CO adsorption amount, CO production amount, and CO product quality at the condition fed with 33% CO/67% N_2 mixture at an operating temperature of 70°C and pressure of 4 kg/cm^2. The feed flow rate was gradually increasing from 5 SLPM to 15 SLPM. The results showed no significant influences on CO adsorption amount, CO production amount, and CO product quality when the flow rate got high. It means that the CO adsorption efficiency of the adsorbent was excellent and that the factory operations would be more flexible.

To maintain good product gas quality and recovery rate, the adsorption step of a PSA cycle usually continues until there is a trace breakthrough of strongly adsorbed gas in the vent gas. Otherwise, the residue gases might lower the quality if the adsorption bed has not reached saturation. But, if too much strongly adsorbed gas breaks through, the recovery rate will decrease. In the study, to discuss the effect of adsorption bed saturation on product quality, the saturated level of the adsorption bed was controlled by adjusting the time of the adsorption step by giving a very short time or even adsorption reached

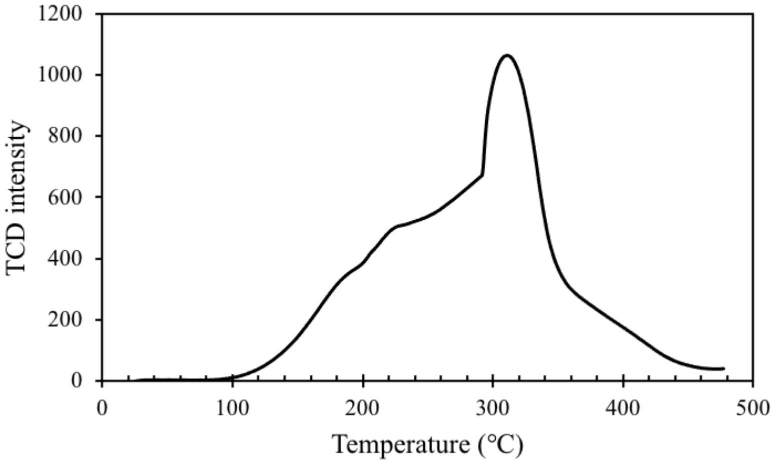

Fig.5. The CO-TPR profile of the adsorbent.

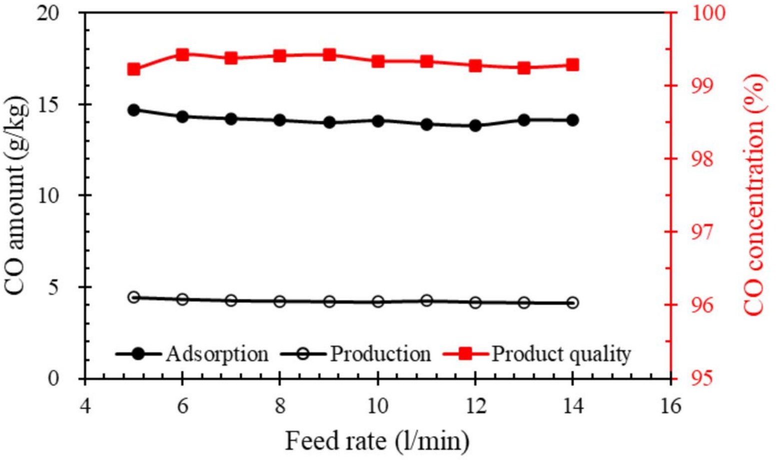

Fig.6. Feed flow rate effect on CO adsorption, production amount, and product quality.

breakthroughs till equilibrium at the condition fed with 5 SLPM 33% CO/67% N_2 mixture at an operating temperature of 70°C and pressure of 4 kg/cm^2. The results are shown in Fig.7., where 100% represents the time point when the CO in the feed gas breaks through the adsorption bed. When the adsorption time was too short, the CO concentration of the product gas was reduced significantly due to less CO adsorbed in the adsorbent, and the residue gas remained in the void of the adsorption bed, causing the dilution of the product. When the saturated level is about 60%, the CO concentration of the product gas reaches more than 95%. However, the CO production amount was gradually increased until closer to the breakthrough time.

The residual gas in the void of the adsorption bed will have a negative impact on the quality of the product gas. Therefore, in the VPSA process that pursues high product quality, before the gas production step, it will depressurize the column until atmospheric pressure. Fig.8 shows the impact of depressurizing degree on CO product quality by adjusting the time of the depressurizing step in a consistent flow rate of 5 SLPM at the condition fed with 5 SLPM 33% CO/67% N_2 mixture at an operating temperature of 70°C and pressure of 4 kg/cm^2. If the depressurizing degree was insufficient, the product did not achieve high quality due to too much residual gas. When releasing pressure, the strongly adsorbed CO was also slowly released, which would benefit the discharge of residual gas. The quality would rise, but the recovery rate of CO would fall. For this reason, the pressure would be used to pressurize another column so that the released CO could be adsorbed by another column,

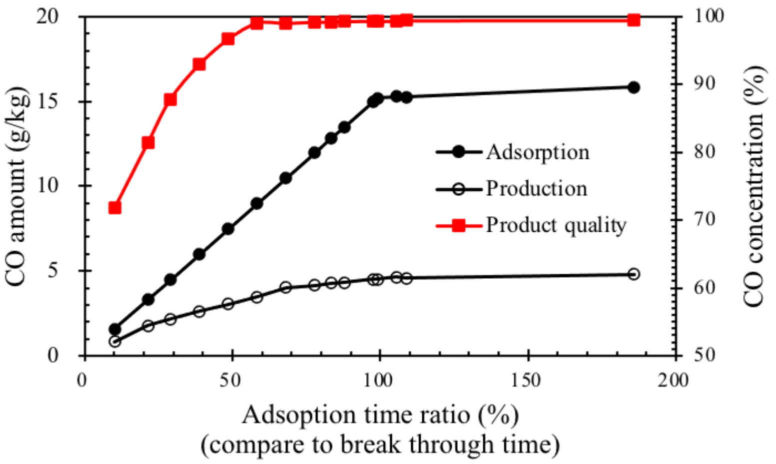

Fig.7. Saturated level of the adsorption bed effect on CO adsorption, production amount, and product quality.

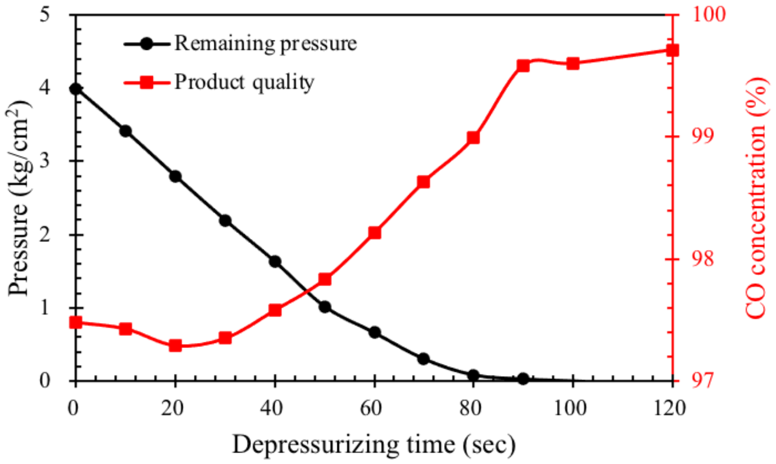

Fig.8. Depressurizing degree of the adsorption bed effect on CO product quality by adjusting the time of the depressurizing step.

the step called "pressure equalization."

In addition to using released CO from the adsorbent to discharge the residue gas during the depressurizing step, purging by the high-quality CO product is also an operating mode of PSA to further improve product quality. 99.99% CO supplied by gas cylinder was used to substitute the CO product as the purge gas to study the effect of purge on the CO product quality at the condition fed with 5 SLPM 33% CO/67% N_2 mixture at an operating temperature of 70°C and pressure of 4 kg/cm^2. The purge gas was introduced into the column after complete depressurizing. Fig.9. shows that discharging the residual gas with purging by CO product increased the product quality, and the injected purge CO product would also become part of the CO product, so the CO production amount was slightly raised. It must be known that it is an unreasonable operating condition when the amount of purge gas input in the column is higher than that of CO production because there had no more product would be produced in this situation.

4. CONCLUSIONS

In this study, a single-bed pressure swing adsorption device was used to investigate the impact of various process parameters on the separation results of carbon monoxide and nitrogen using a commercial copper-salt-modified adsorbent. The results indicated that increasing pressure and temperature could improve the gas yield and the carbon monoxide concentration in the product gas. However, at higher temperatures, some carbon monoxide was consumed in reducing the copper ions in the adsorbent. Reasonably increasing the feed flow rate did not affect the quality but helped save time in the adsorption step. The saturation level of the adsorption bed affects the product gas quality, and allowing a small amount of carbon monoxide to break through the

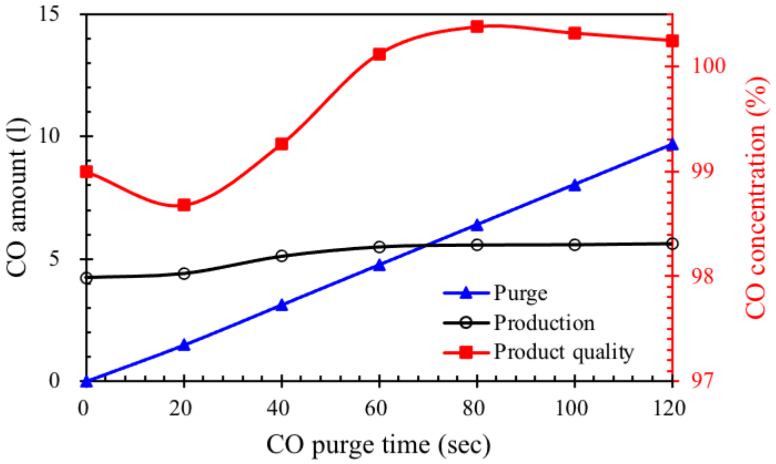

Fig.9. Effect of purge by partially CO product on CO adsorption, production amount, and product quality.

adsorption bed could ensure product gas quality. Before gas production, releasing the pressure in the column to near atmospheric pressure removed residual feed gas in the voids of the adsorption bed, ensuring product gas quality. Using part of the product gas to purge the adsorption bed before gas production could further discharge residual gases, improving product gas quality but reducing the recovery rate. Overall, using a copper-modified adsorbent can effectively separate carbon monoxide and nitrogen, yielding product gas with carbon monoxide purity exceeding 99%.

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