Open Journal of Chemical Engineering (OJCE)

DOI: *http://doi.org/10.7508/ojce.01.2021.05.07*

ISSN: 2377-6250 (Print)
ISSN: 2377-8318 (Online)
CODEN : OJCEB4

ARTICLE

SEPARATION AND PURIFICATION OF CO IN CARBONYL SYNTHESIS INDUSTRY

Joern Fischer*

University Institute of Chemical Technology, North Maharashtra University, Jalgaon- 425001, India
****Correspondence Author E-mail: Fischer@hotmail.com***

ARTICLE DETAILS

Article History:

Received 19 April 2021
Accepted 14 July 2021
Available online 25 July 2021

ABSTRACT

The main methods for the separation and purification of carbon monoxide in the carbonyl synthesis industry include co adsorption, membrane separation, low-temperature separation and pressure swing adsorption. The characteristics of several separation methods are analyzed, and the application of PSA in our company is mainly introduced.

KEYWORDS

CO separation; COSORB; membrane separation; cryogenic separation; pressure swing adsorption

1. COSORB

Oxo-synthesis is a type of reaction in which carbonyl and other groups are introduced into the molecule of organic compounds to become oxygen-containing compounds, which can also be called carbonylation. It is the most efficient way to produce a wide range of fine chemicals such as alcohols, aldehydes, acids, esters, and amides by reacting synthesis gas (CO and H2) with organic compounds such as alkenes, alkynes, alcohols, or halo hydrocarbon. Because many reactions in oxo are atom economic reactions, which achieve full utilization of resources and are environmentally friendly, some traditional catalytic oxidation processes are gradually being replaced by oxo technology, and the oxo industry has become the most active chemical frontier [1]. High-purity CO is a key raw material for the oxo industry, and its demand increases with the continuous growth of the oxo industry. The separation and purification of CO from CO-containing gas mixtures have always been an important research object in the oxo industry.

CO is widely present in water gas, semi-water gas, coke oven gas, synthesis gas, blast furnace gas, natural gas reforming gas, synthetic ammonia purge gas, and other industrial waste gases. At present, the technologies for separating and purifying CO from mixed gas mainly include COSORB, membrane separation, cryogenic separation, and pressure swing adsorption.

In the early 1970s, Tenneco Chemical Company of the United States successfully developed the technology for separating and purifying CO by bimetallic complexes, referred to as the COSORB.

The method uses copper aluminum tetrachloride-toluene complex as the absorbent. According to Tenneco, the recovery rate and purity of CO can reach more than 99%. This technology was used to separate CO in the first toluene diisocyanate (TDI) plant introduced in China in the 1980s. The main features of this method are:

(1) The recovery rate of CO is high and the purity of the product gas CO is high, which can reach more than 99%;

(2) The absorption capacity of the absorbent is large, the gas-liquid ratio is large, and the operating circulation volume of the absorbent is small;

(3) The absorption and separation of CO can be carried out at normal temperature and pressure, and the operating pressure range is wide;

(4) The impurity components in the raw gas, such as CO_2, N_2, H_2, and CH_4, have little effect on the absorption and separation, and do not need pretreatment.

Although the COSORB method has the above characteristics, it also has fatal disadvantages. The cuprous aluminum tetrachloride-toluene solution is sensitive to the harmful components in H_2O, NH_3, and H_2S in the feed gas. They can degrade the active components in the complex solution. They can degrade and inactivate the active components in the complex solution, and produce harmful HCl gas and copper salt precipitation, causing serious corrosion of equipment and pipelines. Therefore, the process requires a complex pretreatment system. The CO gas desorbed by heating contains toluene vapor and Cl^-, and a post-treatment process is also added. In short, the COSORB method has a large investment in equipment, high operating costs, and problems of corrosion and environmental pollution, and has been eliminated.

2. MEMBRANE SEPARATION

Membrane separation CO technology is a gas separation technology that was commercialized in the 1970s. It was first used for H_2 recovery from synthetic ammonia relaxation gas. In recent years, it has been used for gas separation in the coal chemical industry. The membrane separation device is composed of a semi-permeable membrane in a steel vessel. This technology requires an application under high syngas pressure. Each gas component enters the membrane device. Its characteristic of permeability is a function of solubility and permeability. The relative permeation of gases from fast to slow is as follows: H_2O, H_2, He, H_2S, CO_2, O_2, Ar, CO, CH_4, and N_2. The fast permeating gas molecules permeate from the high-pressure side to the low-pressure side through the fiber wall. Due to the separation driving force formed by the different partial pressures of the components in the gas on the high-pressure side and the low-pressure side, the non-permeable gas will obtain CO products. The above relative permeability clearly shows that only low-purity CO products can be produced. Usually, high-purity CO products can be obtained through the combination of multi-stage gas separation membranes and cyclic compression permeation, and the purity can reach 98%.

In the application of gas membrane separation technology, Prism from Air Products and Chemicals, Cactus membrane separator, and Prism membrane separator from Monsanto company are the most widely used. Anhui Huaihua Fine Chemical Co., Ltd. has a device that uses Prison membrane to separate and extract CO from Texaco gasifier water gas, and the design value of CO product purity is ≥96%. The CO separation process of the 20T annual output acetic acid unit of Hualu Hengsheng uses membrane separation technology. Shanghai Coking Co., Ltd. also chooses a new set of devices that use membrane separation to produce high-purity CO.

Although the membrane permeation method has the advantages of a short construction period, low investment, simple and reliable process, low energy consumption, and preparation of CO products under high pressure, etc., it requires high compression power of syngas. So, when high CO purity is required, this method is not suitable.

3. CRYOGENIC SEPARATION

The cryogenic separation method, also known as the cryogenic rectification method, utilizes the difference in the boiling point of various gas components to separate gas mixtures through cryogenic distillation. It was successfully developed by the German company Linde in 1925 and has been used in industry to prepare high-purity CO since the 1960s. Cryogenic separation technology has been adopted in China for decades. The technology has been localized since the 1990s and has become more and more mature.

The cryogenic CO separation technology is further divided into methane washing process and partial condensation. The methane washing process utilizes the relatively strong dissolving power of liquid methane to CO at low temperatures. Liquid methane is used to wash the CO in the raw gas in the washing tower, and then high purity CO is obtained by distillation in the CO/CH_4 tower. The purity of CO is greater than 99%. The purity of H2 should be greater than 98%, and the product is medium and high pressure. The partial condensation method makes use of the difference between the condensation points of CO and other gas components. At the low temperature of -165 ~ -210 ℃, one or more components of the mixture are condensed and liquefied, and the other components remain in the gaseous state, to separate CO. This method is generally used when the product CO purity is required to be greater than 99%. The H2 purity is only required to be 96% to 98%, and the product is low pressure.

Shanghai Wujing Chemical Plant has introduced a 55,000 t·a-1CO unit for the 100,000 t/year acetic acid project of British BP Company. The cryogenic separation process of the CO separation process adopts the patented technology of the German Linde Company. The key equipment cold box is provided by Linde Company. The device was commissioned in August 1996, and the CO purity was 98.9%, reaching the design target. In 2009, the Sino-British joint venture 500,000 t·a-1 Yangzi BP acetic acid project of Sinopec Yangzi Petrochemical Co., Ltd. adopted the cryogenic separation process to produce CO. The cold box of the separation unit adopts the methane scrubbing cryogenic separation technology of Air Products. Product purity can reach 99%.

The cryogenic method has the advantages of mature technology, large processing capacity, and high recovery rate. But it also has many disadvantages: (1) It consumes a lot of cold energy; (2) Because of N_2, the relative molecular weight and boiling point of CO are almost the same. When the raw material contains N_2, the power consumption is large; (3) H_2O, CO_2, and other components in the raw gas become solid at low temperature, which is easy to block the pipe and must be removed; (4) The low-temperature alloy steel and key equipment used need to be imported. In short, the cryogenic process equipment is complex. the investment is large. And the operating cost is low. The method is only economical when used in large-scale installations with high CO content and output.

4. PRESSURE SWING ADSORPTION

The application of pressure swing adsorption technology to extract CO is a technology developed by the German Linde company in 1979. The first set of industrial equipment was established in 1984. The basic principle is a separation process designed according to the principle that the adsorption capacity of different adsorbates in the mixture on the adsorbent is different, and the adsorption capacity of the same adsorbate on the adsorbent varies with the partial pressure of the adsorbate. In China, the Southwest Chemical Research and Design Institute of the Ministry of Chemical Industry built a PSA-C0 device with a production capacity of 500m3/h for the first time in Zibo, Shandong in 1992.

In 2008, Yankuang Guotai Chemical Co., Ltd. built a set of 70000Nm3·h-1 PSA purification devices for CO. After the transformation, the operation is stable, and the qualified CO gas (CO≥98.5%, H2≤0.50%, H2S+COS≤0.2 × 10-6) is sent to the acetic acid synthesis section to produce acetic acid, and H2 with a purity of ≥91% is sent to the methanol synthesis section to produce methanol. The device adopts the patented technology of PSA purification of CO by Chengdu Tianli Company. The whole set consists of 4 processes, namely PSA-CO2-I, PSA-CO2-II, PSA-CO-III, and PSA-H2S-IV. The PSA-CO2-I crude decarburization process adopts 32 adsorption towers, 5 towers for simultaneous adsorption, and 23 continuous pressure equalization. This is the 32-5-23 process flow. PSA-CO2-□fine decarburization process adopts 18 adsorption towers, 5 towers for simultaneous adsorption, and 8 continuous pressure equalization, namely 18-5-8 process flow. The PSA-CO-IIICO purification process adopts 20 adsorption towers, 5 towers for simultaneous adsorption, and 13 continuous pressure equalizations. This is the 20-5-13 process flow. The PSA-H2S-IV sulfur concentration process adopts 28 adsorption towers and a five-stage concentration process. Among them, only the PSA-H2S-IV sulfur concentration process adopts vacuum desorption. The other 3 processes use flushing desorption and eliminate the vacuum equipment. The main features of this device are as follows.

4.1 Process technology

The mature and advanced patented pressure swing adsorption technology purifies CO, with a high CO recovery rate and low operating cost. The power consumption per 1Nm3 of CO produced is 0.057kWh, and the economic benefit is significant.

4.2 Special program-controlled valve technology for PSA

Due to the particularity of the pressure swing adsorption device, a large number of program-controlled valves are required to operate frequently. The program-controlled valve is an important part of the pressure swing adsorption device to complete the process. It is also the key equipment for the device to achieve normal operation and reliable operation. Therefore, the operating indicators and requirements of the program-controlled valve are much higher than that of the general valve. In addition to having good sealing performance and fast opening and closing speed, it must also be able to operate for a long time under frequent actions. The special program control valve used in the device has the advantages of small fluid resistance and long service life of the sealing surface. The valve has good sealing performance and flexible switching. The continuous average trouble-free running time of the device is greater than 30000h. The inner and outer seals of the valve meet the sealing requirements of ANSI B16.104 after 500,000 actions.

4.3 Special adsorbent technology for PSA

Adsorbents commonly used in pressure swing adsorption devices include silica gel, alumina, activated carbon, and molecular sieves. The good adsorption performance of the adsorbent is the basic condition of the adsorption separation process. In the selection of adsorbents in the pressure swing adsorption process, the separation coefficient between the components should be considered as large as possible. This is beneficial to resolve the contradiction between adsorption and desorption. The adsorbent should have a larger adsorption capacity for impurities. At the same time, the adsorbed impurities should be easily desorbed to reach the adsorption-desorption equilibrium in a short time. In this way, the separation and purification process can be maintained. The larger the separation coefficient of the gas components, the easier the separation, the higher the purity of the obtained product gas, and the higher the recovery rate. Whether the choice of adsorbent is reasonable or not is directly related to the separation effect of PSA and the gas recovery rate. Therefore, special adsorbents with excellent performance are selected.

4.4 Special hydraulic drive system technology for PSA

The adopted pressure swing adsorption hydraulic control system has the characteristics of high operation stability, good rigidity, stable operation, safe and reliable action, and long service life. Its valve opening speed adjustment function can control the pressure equalization speed, reduce the scour of the airflow to the adsorbent, greatly prolong the service life of the adsorbent, and reduce the noise of the device.

4.5 Special control system technology for PSA

The advanced and mature control software package of this device can automatically realize the optimization of adsorption time. This ensures that the highest CO recovery rate is pursued under the condition that the product purity is qualified. The adaptive follow-up adjustment software used has the function of automatic tower cutting. When the adsorption tower fails, the software can automatically cut the tower to run and conduct maintenance without stopping. The operational reliability of the device is greatly improved. To ensure the long-term reliable and stable operation of the device, according to the operation data collected by several large-scale pressure swing adsorption industrial devices, a complete pressure curve is drawn for the adsorption towers in different working states. Combined with the program control experience, it is analyzed one by one in various working states. Due to the bad factors brought by the tower-cutting, the tower-cutting program is specially compiled. The tower-cutting program is flexible in operation. Under computer program control, various modes of operation can be combined. When any one or more adsorption towers are in a fault condition, they can be safely removed from the unit. A single segment can cut up to 5 towers for operation. After the tower is cut, the device capacity does not change much, which greatly improves the reliability of the device operation.

PSA gas separation technology has the advantages of small capital investment, low water and electricity consumption, low operating cost, good safety performance, simple operation and maintenance, quick start of gas supply, high degree of automation, no equipment corrosion, and environmental pollution. The disadvantages are: (1) Higher requirements for the feed gas. When the CH_4^+Ar in the feed gas reaches 1%, the CO purity can only reach 96%; (2) If the CO concentration of the feed gas is low, the CO recovery rate decreases accordingly; (3) The scale of the PSA unit is limited to a certain extent. If the processing gas volume is large, multiple sets of parallel operations are required.

REFERENCES

[1] Xia, C.G., Chen J. 2006. Application of oxo synthesis technology in fine chemicals. Fine Chemicals Raw Materials and Intermediates, 2006, (9): 3-5.

[2] Zhang, W.X., Geng Y. F. Carbon monoxide separation technology. Modern Chemical Industry, 2003, 23(10): 43-45.

[3] Gu, C.X. 2006. Pressure swing adsorption technology for separation of CO and its application in oxo industry. Shanxi Chemical Industry, 26(3): 49-51.

[4] Zheng, Z.N. 1992. Production technology of carbon monoxide. Nitrogen fertilizer design, 30 (6): 62-74.

[5] Li, Z.L. 2004. Gas membrane separation technology and its application. Design technology of small nitrogen fertilizer, 25 (1): 6-10.

[6] Jing, Z.H. 2006. Technical and Economic Analysis of Coal-to-CO. Oil and Gas Field Surface Engineering, 2006, 25(11):51-52.

[7] Xu, N.C. 1996. 7000Nm3·h-1CO device. Shanghai Chemical Industry, 1996, 21(6): 4-7.