Journal of Engineering and Applied Sciences 13 (8): 2152-2155, 2018
ISSN: 1816-949X

An Overview of Cryogenic Separation Techniques for Natural Gas with High CO_2 Content

[1]Bhajan Lal, [1]Azmi Mohd [1]Shariff, [1]Hilmi Mukhtar, [2]Qazi Nasir and [1]Ali Qasim
[1]Department of Chemical Engineering, Universiti Teknologi PETRONAS,
Bandar Seri Iskandar, 32610 Perak, Malaysia
[2]Department of Petrochemical Engineering, College of Engineering and Architecture,
University of Nizwa, Dahiyah, Ad Dakhiliyah Region, Sultanate of Oman

Abstract: In the wake of an unprecedented growth of the market demand for natural gases, exploration and utilization are necessary for high impurity wells worldwide. Therefore, it has become vital to conduct research work on the development of optimized and automated processes for removal of natural gas impurities mainly CO_2. Conventionally, CO_2 from natural gas streams are absorbed by amine solutions or other appropriate chemical solutions but cryogenic separation technology is suitable for use if the CO_2 content of the natural gas is high. In cryogenic separation, the process principle involves the separation based on the difference in volatility and desublimation. The cryogenic separation process is classified into conventional, non-conventional and hybrid techniques. Conventional process involves Liquid-Vapor (L-V) based separation. The non-conventional method includes Solid-Vapor (S-V) based separation while hybrid technique utilizes both conventional and non-conventional methods. Cryogenic research including both L-V and solid-vapor S-V based separation has recently shown several advantages and to enhance the separation performance and energy reduction, a novel concept of cryogenic hybrid (L-V and S-V) process is also discussed.

Key words: Natural gas, conventional cryogenic separation, non-conventional cryogenic technique, hybrid method, novel, streams

INTRODUCTION

The ever-growing energy demand has led to the reevaluation of the development potential of economically unviable, contaminated natural gas reserves at diverse regions of the earth. With increasing energy demand, development of reserves with high CO_2 contents up to 80% has become imperative, requiring new research efforts (Speight, 2007). Malaysia alone constitutes more than 13 Tscf of undeveloped natural gas because of the high CO_2 concentration. In some gas fields, the concentration of CO_2 exceeds 70%. Therefore, an optimum separation of CO_2 is necessary as it reduces the energy content of the gas and affects the selling price of the natural gas. While substantial literature exists for the removal of hydrocarbons and sulfur-containing gases at atmospheric pressures, a considerable amount of research work needs to be focused on the removal of CO_2 especially at the high pipeline pressures up to 60-80 bar (Garg *et al*., 2017).

Various separation methods have been used for the CO_2 removal which includes chemical absorption, adsorption and membrane separation (Garg *et al*., 2017; Partoon *et al*., 2016). The use of chemical based technologies is difficult and expensive especially in off-shore applications with a high concentration of CO_2 in natural gas. Cryogenic purification of natural gas has recently gained significant momentum in the global scenario because of several advantages of this clean and safe technology without the use of any chemical additives. The cryogenic separation technology has been known for several decades. However, this technology was not extensively studied due to the common perception of high expected cooling duty. Cryogenic separation involves no chemical reactions and CO_2 can be captured at high pressure as well as atmospheric pressure. The product carbon dioxide is very pure and can be piped as a liquid. Cryogenic separation process based is the difference in volatility and desublimation of gases. This process can be divided into three types, conventional, non-conventional and hybrid. Conventional methods employ liquid-vapor based distillation while in non-conventional methods, CO_2 can be desublimated onto the surface of the packing inside packed bed. The

Corresponding Author: Bhajan Lal, Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610 Perak, Malaysia

hybrid cryogenic technique utilizes conventional cryogenic distillation networks in conjunction with de-sublimation based packed bed separators. Some of the advantages of the hybrid process are reduced energy requirement and equipment size (Maqsood *et al*., 2014a-d).

Given the high complexity, study and understanding of thermodynamic phase behavior are a challenging and an industrially important task especially to design a more economical route for the production, transportation and refining projects. Knowledge of accurate thermodynamic behavior is an essential requirement for the development of chemical processes. Failure of process design can often be attributed to a lack of accurate data. Phase behavior (L-V and S-V domain) is very much affected by temperature, pressure and composition of a complex hydrocarbon system. Also, with the inclusion of Heavier Hydrocarbons (HHCs) in natural gas, the phase behavior of NG is different from the binary gas mixture as L-V region shift towards higher temperatures with the increasing content of CO_2. It was also shown that for binary CO_2-CH_4 gas mixture at increasing pressure values of 20, 30, 40 and 45 bar, the phase envelope in L-V region increased with a decrease in S-V region (Ali *et al*., 2016). Currently, most of the phase behavior, L-V or S-V data available in the literature for binary and mixed natural gas component system are limited to high CO_2 at low-pressure content whereas data for the CO_2 rich mixed natural gas component system in L-V and S-V domain at high pressure are scarce in the literature.

In the present study, the hybrid cryogenic technique is proposed for separation of CO_2 from natural gas mixture components. This hybrid process separates the heavier hydrocarbons in L-V domain while CO_2 will be captured in S-V domain.

MATERIALS AND METHODS

Cryogenic separation process classification: The cryogenic separation process is classified into conventional, non-conventional and hybrid methods. The description and details of these processes are discussed in the following sections.

Conventional cryogenic separation process (L-V): Conventional Cryogenic Technology (CCT) process is carried out at a low temperature. CCT includes simple cryogenic distillation and extractive distillation. Cryogenic distillation is carried out at low temperatures and high pressures to separate CO_2 and other components based on their different boiling point. This method directly produces liquid CO_2 or CO_2 vapour at a high pressure which reduces extra costs of compression for storage purposes. This technology is not economical and energetically viable for dilute gas streams. One of the major operating problems is the solid formation and choking of the column in distillation columns in both low and high-pressure ranges (Partoon *et al*., 2016). Solid formation during separation of CO_2 has been reported in the literature (Donnelly and Katz, 1954).

Maqsood *et al*. (2014) conducted a study with different configurations of cryogenic distillation networks to remove CO_2 from NG feed with high hydrocarbons. It was found that higher operating pressure leads to a reduction of energy requirements but operational problems in distillation columns can arise due to the thermodynamic behavior of CO_2-CH_4 system due to CO_2 solidification (Maqsood *et al*., 2014). Valencia *et al*. patented a method for separating carbon dioxide from methane using Helium as an additive which facilitated the separation process and prevented solid CO_2 formation. However, the separation of He from CH_4 at higher pressure is quite problematic as the mixture becomes azeotropic and difficult to separate. Atkinson *et al*. (1988) introduced a dual pressure distillation process intended for the removal of high concentration carbon dioxide from methane. It comprised of two distillation columns operating in different pressure to avoid carbon dioxide solidification (Atkinson *et al*., 1988). Berstad *et al*. (2012) reported a low-temperature process for CO_2 removal from natural gas before liquefaction. They simulated a three distillation column network by using pentane as an additive in ASPEN Hysys with Peng-Robinson equation of State for the separation of CO_2 from natural gas. Their resaerch included only simulation results and experimental work was not performed (Berstad *et al*., 2012).

Non-conventional cryogenic separation process (S-V): The non-conventional cryogenic technologies focus on separation of CO_2 via. solidification of CO_2 in the S-V zone. Packed bed column is used at low temperature wherein CO_2 is desublimated onto the surface of the packing (Maqsood *et al*., 2014).

Clodic *et al*. (2005) used a desublimating carbon capture system consisting of three heat exchangers. The first one condenses to water, the latter remaining water vapour and the last one de-sublimates carbon dioxide. They used a flat-plate heat exchanger for the desublimating stage. The system used by them was an inherently batch process, and the amount of CO_2 captured was small compared to the mass of the heat exchangers on which it was collected. It presented a significant practical problem. Also, the process did not handle the feed at higher pressure, so, high-pressure application is not available. Separation of CO_2 from natural gas was not considered in the process and the process involved a binary mixture of carbon dioxide and hydrogen (Clodic and Younes, 2002; Clodic and El-Hitti *et al*., 2005). Schah *et al*. worked on CO_2 capture from flue gas by de-sublimation. They modelled the process using ASPEN Plus featuring finned-plate heat exchangers (Schach *et al*., 2011). Tuinier and Annaland (2012) employed dynamically operated cryogenic packed beds to separate CO_2 from a biogas mixture consisting primarily of methane and carbon dioxide. The process was based on the dynamic operation of packed beds, operated in cooling, capture and recovery steps. The method was not employed in high-pressure applications and did not include heavier hydrocarbons in the feed stream (Tuinier and Annaland, 2012). Ali *et al*. (2014) published a research where they have explored the minimization of energy consumption for a counter current switched packed bed intended to separate CO_2 and other components of natural gas. The effect of essential process parameters as feed composition, feed flow rate on energy requirement, bed saturation and bed pressure and cycling times were investigated (Maqsood *et al*., 2014). Abul Hassan developed an experimental setup for cryogenic separation of CO_2 from natural gas with high CO_2 content. In this study, the CO_2 concentration was used up to 70%. The separation principle of CO_2 from natural gas was based on the de-sublimation principle in countercurrent cryogenic packed bed. Multiple cryogenic packed beds were used for CO_2 separation. The study dealt with the binary CO_2-CH_4 gas mixture and separation involving multi-component natural gas mixture containing up to higher hydrocarbons can further be performed (Karen, 2013).

RESULTS AND DISCUSSION

Hybrid technology (L-V+S-V separation): In the hybrid technique, conventional cryogenic distillation networks are used in conjunction with de-sublimation based packed bed separators as shown in Fig. 1. The hybrid technique is suitable for separation of a natural gas mixture containing heavier hydrocarbons with high CO_2 content and at high-pressure applications as the efficiency of the process is increased due to a combination of the conventional distillation process and non-conventional packed bed based process (Maqsood *et al*., 2014).

Maqsood *et al*. (2014) presented a techno-economic evaluation of cryogenics network for CO_2 removal from NG with different feed compositions. Equipment sizing and cost estimation have been carried out by the

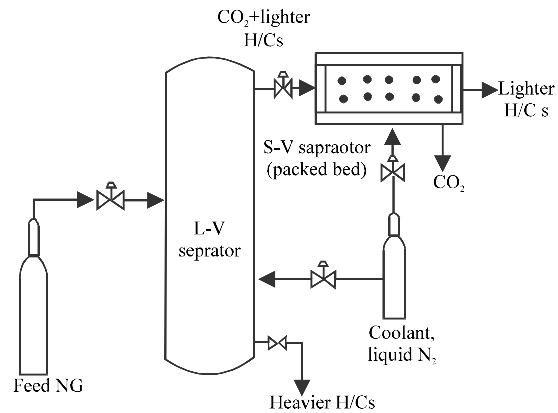

Fig. 1: Schematic of hybrid cryogenic separation process for NG purification involving heavier hydrocarbons

cryogenic networks using the correlations provided in the literature (Maqsood *et al*., 2014). Ganguly *et al*. proposed different efficient cryogenic distillation sequences for purification of NG having a medium and high concentration of CO_2 contained. Calculations for conventional and hybrid distillation column sequences were performed using the heuristic and evolutionary strategies. It was found that hybrid cryogenic network required considerably lower energy and showed a significant reduction in capital cost of the columns compared to the conventional cryogenic network (Maqsood *et al*., 2014). Recently, Maqsood *et al*. (2014) performed simulation work on NG separation components containing Heavier Hydrocarbons (HHCs) and feed gas containing 50 and 72% CO_2 content (Maqsood *et al*., 2014).

CONCLUSION

Natural gas needs to be purified from impurities before it can be used as a fuel for commercial purposes. The presence of CO_2 in natural gas affects the calorific value of the gas and can also cause corrosion in the pipelines. Cryogenic separation technique is advantageous as it does not involve chemical reactions and CO_2 can be captured at high pressure as well as atmospheric pressure. The product carbon dioxide is very pure and can be piped as a liquid. Cryogenic separation technique is classified into conventional, non-conventional and hybrid. The conventional process includes liquid-vapor based distillation or extractive distillation technologies, e.g., natural gas liquefaction. Non-conventional method deals with solid-vapor desublimation, e.g., CO_2 separation from biogas mixture. In the hybrid technique, conventional cryogenic distillation networks are used in conjunction with de-sublimation based packed bed separators. The main advantages of the hybrid process are reduced energy requirement, reduced equipment size and elimination of additive requirement.

ACKNOWLEDGEMENT

The researchers would like to thank Universiti Teknologi Petronas for financial support in the form of Yayasan Universiti Teknologi PETRONAS (YUTP) grant No. 0153AA-E16.

REFERENCES

Ali, A., K. Maqsood, A. Redza, K. Hii and A.B. Shariff *et al*., 2016. Performance enhancement using multiple cryogenic desublimation based pipeline network during dehydration and carbon capture from natural gas. Chem. Eng. Res. Des., 109: 519-531.

Ali, A., K. Maqsood, N. Syahera, A. Shariff and S. Ganguly, 2014. Energy minimization in cryogenic packed beds during purification of natural gas with high CO2 content. Chem. Eng. Technol., 37: 1675-1685.

Atkinson, T.D., J.T. Lavin and D.T. Linnett, 1988. Separation of gaseous mixtures. US. Patent and Trademark Office, Washington, DC., USA.

Berstad, D., P. Neksa and R. Anantharaman, 2012. Low-temperature CO2 removal from natural gas. Energy Procedia, 26: 41-48.

Clodic, D. and M. Younes, 2002. A New Method for CO2 Capture: Frosting CO2 at Atmospheric Pressure. In: Greenhouse Gas Control Technologies, Gale, J. and K. Yoichi (Eds.). Elsevier, Kyoto, Japan, ISBN:0-08-043325-1, pp: 155-160.

Clodic, D., R. El-Hitti, M. Younes, A. Bill and F. Casier, 2005. CO2 capture by anti-sublimation thermo-economic process evaluation. Proceedings of the 4th Annual Conference on Carbon Capture and Sequestration, May 2-5, 2005, Hilton Alexandria Mark Center, Alexandria Virginia, pp: 2-5.

Donnelly, H.G. and D.L. Katz, 1954. Phase equilibria in the carbon dioxide-methane system. Ind. Eng. Chem., 46: 511-517.

Garg, S., A.M. Shariff, M.S. Shaikh, B. Lal and H. Suleman *et al*., 2017. Experimental data, thermodynamic and neural network modeling of CO2 solubility in aqueous sodium salt of l-phenylalanine. J. CO2 Util., 19: 146-156.

Karen, H.W.W., 2013. Cryogenic multiple bed dehydration and CO2 separation during purification of natural gas. Master Thesis, Universiti Teknologi Petronas, Seri Iskandar, Malaysia.

Maqsood, K., A. Ali, A.B. Shariff and S. Ganguly, 2014d. Synthesis of conventional and hybrid cryogenic distillation sequence for Puri?cation of natural gas. J. Appl. Sci., 14: 2722-2729.

Maqsood, K., A. Mullick, A. Ali, K. Kargupta and S. Ganguly, 2014a. Cryogenic carbon dioxide separation from natural gas: A review based on conventional and novel emerging technologies. Rev. Chem. Eng., 30: 453-477.

Maqsood, K., A.H. Ali, A.M. Shariff and S. Ganguly, 2014b. Techno-Economic Evaluation of Cryogenic Networks for Separation of CO_2 from Natural Gas. In: Applied Mechanics and Materials, Ahmed, I. (Ed.). Trans Tech Publications, Switzerland, pp: 635-638.

Maqsood, K., J. Pal, D. Turunawarasu, A.J. Pal and S. Ganguly, 2014c. Performance enhancement and energy reduction using hybrid cryogenic distillation networks for purification of natural gas with high CO_2 content. Korean J. Chem. Eng., 31: 1120-1135.

Partoon, B., O. Nashed, Z. Kassim, K.M. Sabil and J. Sangwai *et al*., 2016. Gas hydrate equilibrium measurement of Methane+Carbon Dioxide+ Tetrahydrofuran+Water system at high CO2 concentrations. Procedia Eng., 148: 1220-1224.

Schach, M.O., B. Oyarzun, H. Schramm, R. Schneider and J.U. Repke, 2011 . Feasibility study of CO_2 capture by anti-sublimation. Energy Procedia, 4: 1403-1410.

Tuinier, M.J. and M.V.S. Annaland, 2012. Biogas purification using cryogenic packed-bed technology. Ind. Eng. Chem. Res., 51: 5552-5558.