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Effects of hydrogen content on nitrogen expansion liquefaction process of coke oven gas

Wensheng Lin *, Lin Zhang, Anzhong Gu

Institute of Refrigeration and Cryogenics, Shanghai Jiao Tong University, Shanghai 200240, China

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ABSTRACT

Coke oven gas (COG) is a by-product when producing coke from coal. Producing liquefied natural gas (LNG) is an efficient way of utilizing COG. The amount of hydrogen in COG affects liquefaction process significantly, because its thermal properties are quite different from the other compositions (methane, carbon monoxide, etc.) of COG. Based on nitrogen expansion liquefaction process, a series of liquefaction processes of COG containing different amount of hydrogen are simulated in this paper. It turns out that the hydrogen content exerts a great influence on the unit power consumption and the liquefaction rate of the processes. In order to ensure very low concentration of hydrogen in LNG product, distillation is added to the process. The processes with or without distillation are compared. Furthermore, for the processes with distillation, the liquefaction process is integrated with distillation separation of hydrogen to upgrade the quality of LNG. Simulations indicate that LNG can be produced by improved nitrogen expansion processes with acceptable energy consumption. The unit power consumption increases with the increase of hydrogen content of COG and the increase of the methane recovery rate. And the unit power consumption of the process with distillation is about 10% lower than that of process without distillation, when the methane recovery rate is fixed.

1. Introduction

Coke oven gas (COG), a by-product from coking plants, is emitted at a level of 0.300–0.350 N m^3/kg of coal [1]. Along with the development of the coke industry, a large amount of COG has not been utilized properly [2]. In China, for example, there is about 120×10^9 N m^3 COG available each year according to the overall coke output in 2010. But in fact, the utilization amount of COG is very small, leading to serious environmental pollution and energy waste.

Besides the easiest way of using COG as a fuel for industrial users, such as an iron and steel works, or for power generation in boilers or turbines, the most usually suggested way of COG utilization is to produce synthetic gas from it, and often, to further produce hydrogen or some other products from syngas [3–7]. Steam reforming or catalytic oxidation are usually adopted to achieve this. As the results given in [7], coke oven gas appears to have the lowest energy consumption to produce hydrogen for all the investigated alternatives of hydrocarbon-based feedstocks; moreover, in terms of CO_2 emissions, COG is superior to other options.

Although these suggested systems sound efficient, they are usually complicated ones with chemical reactions at very high temperature or at catalytic circumstances. Alternatively, a relatively simple way of utilizing COG by producing liquefied natural gas (LNG) from it is suggested in this paper. In areas where natural gas resources are very limited, such as in China, producing of LNG from COG provides an efficient way of transmitting fuel gas from coke plants to gas consumers. Hydrogen, separated from the liquefaction–distillation process, can be another product after further purification.

The liquefaction processes of COG are quite different from those of conventional natural gas, mainly because of their very different compositions. COG contains some nitrogen, carbon monoxide, and, a lot of hydrogen. Gao et al. [8–10] have studied the effects of nitrogen on the liquefaction processes of coalbed methane. The effects of carbon monoxide are similar to those of nitrogen, because their thermal properties are similar in many aspects. The amount of nitrogen and carbon monoxide in COG are not very large, their influences to the liquefaction processes are not very significant, as there is usually some nitrogen in conventional natural gas. However, because of the huge difference of thermal properties between hydrogen and the other components of COG, hydrogen has great influences on the processes. Furthermore, in order to ensure very low concentration of hydrogen in LNG product, distillation is added to the process.

A series of nitrogen expansion liquefaction processes of COG containing different amount of hydrogen at different methane

* Corresponding author. Tel.: +86 21 34206533; fax: +86 21 34206814.
E-mail address: linwsh@sjtu.edu.cn (W. Lin).

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recovery rates are simulated in this paper with Aspen HYSYS software. Also, the processes with or without distillation are compared.

2. Pre-simulation

A typical composition of COG is 54–59%H_2, 24–28%CH_4, 3.5–7%CO, 1–3%CO_2, 3–5%N_2 and other impurities [11]. In most cases, hydrogen content varies from 45% to 65%. Before liquefaction, carbon dioxide and other impurities will be removed, and the remaining components are hydrogen, methane, carbon monoxide and nitrogen.

Among the components of the cleaned COG, methane, carbon monoxide and nitrogen have similar critical point and normal boiling temperature. These temperature points of hydrogen are much lower. In principle, it is possible to separate hydrogen out from COG with partial liquefaction and flash separation, without the assistance of distillation. However, very little hydrogen contained in product has great impact on the temperature of product. Fig. 1 shows the bubble point temperature of methane/hydrogen mixture at 0.1 MPa. When the hydrogen content goes up from 0% to 0.4%, the bubble point temperature decreases about 18 °C. So removing hydrogen from product can not only improve the product quality, but also help to increase the liquefaction temperature, leading to the reduction of unit power consumption. Considering this, distillation is added to the liquefaction process.

Because of the extremely low boiling point temperature of hydrogen, lower temperature is needed to liquefy COG than to liquefy conventional natural gas. As shown in Fig. 2, under different methane recovery rate x (which is defined as the molar flow rate ratio of methane in LNG product to methane in COG feed gas), the temperature of COG before throttling decrease with the increase of hydrogen content. As a result, the nitrogen expansion liquefaction process is used in the present research, because it can provide very low temperature.

3. Simulation details

3.1. The Liquefaction process

From the above analysis, the process should provide lower temperature to liquefy COG than to liquefy conventional natural gas. Generally, natural gas is cooled to about −160 °C before throttling. However, as shown in Fig. 2, when methane recovery rate is higher than 95%, COG should be cooled to below −185 °C before throttling, it means that the lowest temperature of liquefaction process is about −190 °C, 25 °C lower than the process for natural gas.

To achieve this, the nitrogen expansion liquefaction process for conventional natural gas should be modified for liquefying COG. In the conventional liquefaction process, after the first stage expansion, nitrogen is heated by natural gas and then undergoes the second stage expansion, and the ideal thermodynamic process in T–s diagram is 1–2–3–4–5 as shown in Fig. 3. In another process, developed for coalbed methane liquefaction by Gao et al. [10], after the first stage expansion, nitrogen is further cooled before the second stage expansion, and the ideal thermodynamic process is 1–2–3–4′–5′ in Fig. 3. Obviously, the lowest pressure of Gao's process is much higher than the conventional process, when the lowest temperature of process is fixed. It means that Gao's process can provide lower temperature than the conventional process, under the condition of ensuring the pressure of the liquefaction process is higher than atmosphere pressure, which is important for the safe and stable running of liquefaction system. So Gao's process is used for the present study.

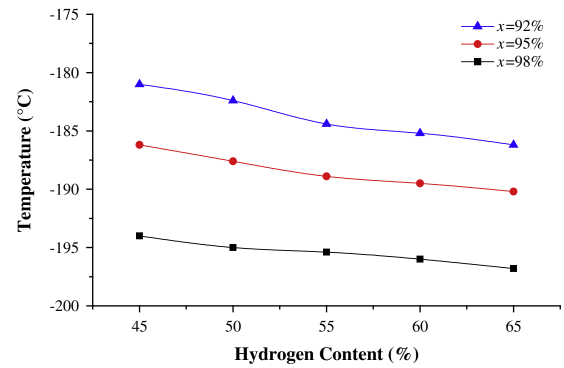

Fig. 2. Temperature of COG before throttling.

For the nitrogen cycle in Fig. 4, nitrogen firstly undergoes two stages of compression and cooling by a water cooler, and then it is cooled in heat exchanger HEX-101. After the first stage expansion it is further cooled in heat exchanger HEX-102. Finally, it supplies cold energy for the two heat exchangers after the second stage expansion. In order to ensure very low concentration of hydrogen in LNG product, distillation is added to the process. The pressurized feed COG is cooled in heat exchanger HEX-101 and HEX-102, then it is throttled to low pressure. Finally, it is separated into high quality LNG and hydrogen-rich tail gas.

Additionally, for the processes with distillation, the nitrogen cycle is integrated with the distillation column. Because the nitrogen flow 205 has the lowest temperature in all the flows hotter than reboiler, it is used to heat the reboiler of the distillation column. In this way, nitrogen is further cooled before it goes to the second stage of expansion, while the reboiler obtains the required heat.

A simpler process without distillation is also studied in this paper to investigate if it is capable of producing LNG with little

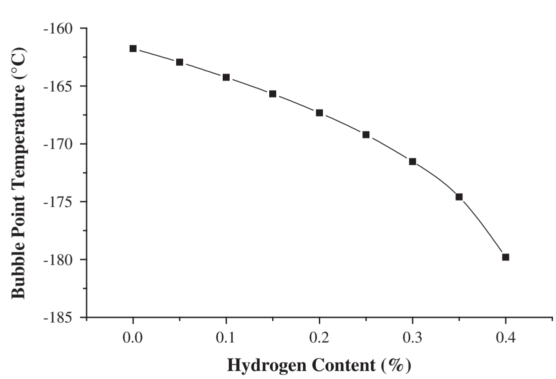

Fig. 1. Bubble point temperature of methane/hydrogen mixture at 0.1 MPa.

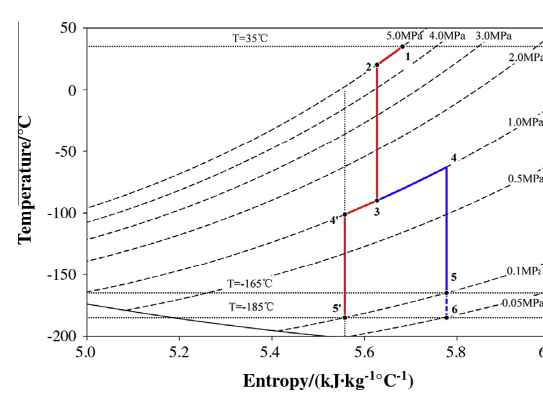

Fig. 3. The ideal thermodynamic processes of two processes in T–s diagram.