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Experiment on the separation of tail gases of ammonia plant via continuous hydrates formation with TBAB

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ARTICLE INFO

Article history:
Received 13 February 2015
Received in revised form
18 March 2015
Accepted 23 March 2015
Available online xxx

Keywords:
Hydrate
Separation
Ammonia
Tail gases
TBAB

ABSTRACT

We used hydrate separation method in this paper to recover H_2 and N_2 from tail gases of ammonia plant in the presence of tetra-n-butylammonium bromide (TBAB). The formation condition of $H_2/N_2/CH_4$/TBAB hydrates was measured by pressure search method. Then the continuous separation of $H_2/N_2/CH_4$ via hydrates formation was conducted in the presence of TBAB, and a two-stage separation process was proposed to increase the recovery of H_2 and N_2. The influences of experimental pressure, temperature and gas flow on the separation results were investigated. The results show that the total concentration of H_2 and N_2 in the unhydrated gas (recovered gas) is 95.28 mol%, and the total recovery of H_2 and N_2 is more than 90%. This work supplies the preliminary ideas and fundamental data for the industrial application of hydrate separation method.

Introduction

As we all know, a lot of tail gases will be discharged in the ammonia synthesis process. The main components of the ammonia plant tail gases (short for tail gases) are H_2, N_2, CH_4, and some other gases such as Ar, etc [1–3]. Generally, the total concentration of H_2 and N_2 in the tail gases is about 80–95 mol %, and the emission of the tail gases is up to 180–200 Nm^3 per ton of ammonia [4]. However, the tail gases are usually burned in the flare system because the presence of CH_4 makes it difficult and risky to be processed [5]. It undoubtedly results in the huge waste of resource and pollution of atmosphere. Now, the discharge of the tail gases in Tarim Oilfield Petrochemical Company (TOPC) is about 238 Nm^3 per ton of ammonia. At a rough estimate, if 90% of H_2 and N_2 in the tail gases are recycled to the synthesis section, the output of ammonia could be increased by 348,000 tons, i.e., the production capacity could be increased by 7%. Consequently, it is necessary to separate the tail gases and recover H_2 and N_2.

Gas hydrates or clathrate hydrates are nonstoichiometric crystalline compounds consist of the small guest molecules trapped in a cage of water molecules networked together by hydrogen bonds [6]. In the semi-clathrate hydrates produced in the presence of Tetra-*n*-butylammonium bromide (TBAB), some part of the hydrogen-bonded water lattice is broken and

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http://dx.doi.org/10.1016/j.ijhydene.2015.03.111

the anionic part of the hydrate former (Br-) is confined in the network [7,8]. Hydrates have the potential for many industrial applications: Flow Assurance in Petroleum Industry [9–13], CO_2 Capture and Sequestration [14–23], Separation of Close-Boiling Point Compounds [24–32], Water Desalination [33], Gas (H_2 and CH_4) storage [34–36], etc.

In this work, we use hydrate separation method to recover H_2 and N_2 from tail gases. The method is believed very appropriate for the separation of H_2-containing gas mixtures, because H_2 forms hydrate much more difficultly than the common gases [37,38]. Furthermore, hydrate separation method is also considered as a safe approach to deal with CH_4-containing gas mixtures due to the presence of water [39]. However, most of the existing studies on the separation of gas mixtures via hydrates formation were conducted using batch operations, resulting in the limitation of practical application of the method. Consequently, we developed a continuous separation process [40] of tail gases via sequential hydrates formation and dissociation in the presence of TBAB. The concentration of CH_4 in the recovered gas after separation should be lower than 5 mol% to meet the requirement of the ammonia synthesis plant of TOPC.

Experimental work

Measurement of the formation condition of $H_2/N_2/CH_4/$TBAB hydrates

Materials and apparatus

The tail gases are supplied by Beijing Bei Temperature Gas Company. The compositions of the tail gases are H_2: 66.47 mol %, N_2: 25.33 mol% and CH_4: 8.20 mol%, which are given from TOPC and determined by gas chromatograph (Agilent 7890). The uncertainty of the gas compositions is within ±0.05 mol%. Analytical-grade TBAB with the purity of 99.0 mol% is purchased from Tianjin Fuchen Chemical Reagents Factory. Deionized water is prepared in our laboratory by SZ-93 water distillation unit.

Fig. 1 shows the schematic sketch of the experimental apparatus. It mainly consists of a visual crystallizer, an air bath and a hand-pump. The visual and volume-variable crystallizer has a maximum volume of 420 ml. A magnetic stirrer is fixed at the bottom of the crystallizer to constantly stir the gas and liquid mixture. The air bath, with a compressor power of 1.5 KW, supplies the crystallizer with a constant temperature from 243.15 K to 323.15 K. The hand-pump is used to control the gas pressure in the crystallizer. The temperature inside the crystallizer is measured by a platinum resistance thermometer with an uncertainty of ±0.1 K. The gas pressure in the crystallizer is measured by a pressure sensor with a deviation less than 0.01 MPa.

Method

The method for the measurement of the formation condition of $H_2/N_2/CH_4$/TBAB hydrates has been described in our previous work [41,42]. After the TBAB solution and $H_2/N_2/CH_4$ mixture were introduced into the crystallizer, the air bath was turned on to lower the temperature of crystallizer and keep it at the constant experimental value. Generally, the temperature reduced about 2–3 K per hour from the room value to the experimental value. Then the gas pressure in the crystallizer was increased slowly by turning the hand bump. After a trace of hydrate (only several crystal particles could be seen) formed, the gas pressure and temperature at this moment should remain constant. If the trace of hydrate crystals could exist for 4 h, the current pressure and temperature was regarded as one set of hydrates formation data. If the trace of hydrates crystals totally disappeared in 4 h, then the gas pressure should be increased again until the trace of hydrates crystals regenerated and coexisted with the gas mixture for at least 4 h. The hydrates formation pressure at current temperature was obtained finally then.

Continuous separation of $H_2/N_2/CH_4$ via hydrates formation with TBAB solution

Apparatus

Fig. 2 shows the schematic diagram of the continuous separation apparatus. It is composed of the gas inflow system, the hydration system, the hydrate dissociation system and the liquid circulation system. The gas inflow system consists of gas cylinders, a gas booster pump, a buffer tank and a gas flow controller. The hydration system contains a visual crystallizer

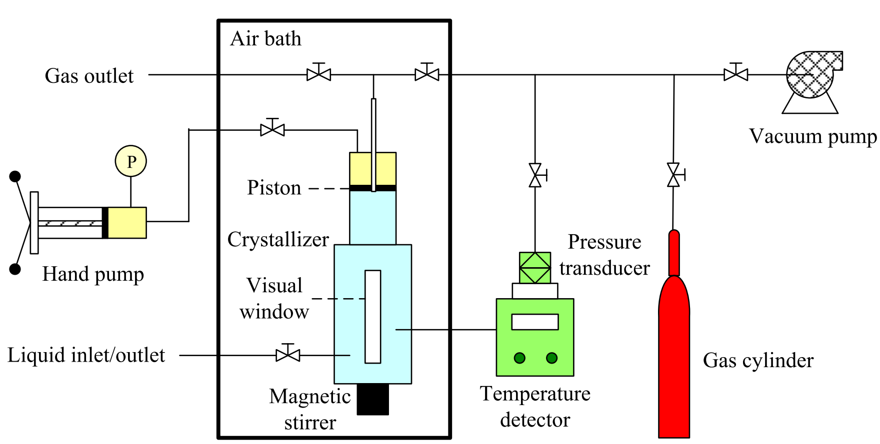

Fig. 1 – Experimental apparatus for the measurement of hydrates formation condition.

Please cite this article in press as: Sun Q, et al., Experiment on the separation of tail gases of ammonia plant via continuous hydrates formation with TBAB, International Journal of Hydrogen Energy (2015), http://dx.doi.org/10.1016/j.ijhydene.2015.03.111