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Adsorption separation for high purity propane from liquefied petroleum gas in a fixed bed by removal of alkanes

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ABSTRACT

The process for high purity propane production via adsorption separation of propane from liquefied petroleum gas (LPG) was investigated at ambient temperature and atmospheric pressure under dynamic conditions in a fixed bed. Breakthrough curves for LPG adsorption on 4A, 5A, 13X and NaY zeolite pellets and granular activated carbon were measured. The length of unused bed (LUB) values for isobutane and butane adsorption in fixed beds with different adsorbent samples were determined by analyzing breakthrough curves. Effects of bed height (5–10 cm) and flow rate (60–100 mL/min) on adsorption characteristics of propane, isobutane and butane onto activated carbon were also examined. Among all these five adsorbent samples, activated carbon exhibited the highest adsorption capacity and the best separation performance, and the concentration of propane in the outlet gas could reach as high as 99.7% (volume fraction). Besides, the LUB value of activated carbon fixed bed was the smallest, which indicated that activated carbon fixed bed was more suitable for adsorption separation of propane from LPG. Adsorption dynamics also showed that relatively lower flow rate and relatively longer bed length were favorable for removal of isobutane and butane from LPG. The Yoon–Nelson model provided a good fit to the experimental data and there was a nice agreement between the numerical simulations and the corresponding data obtained from experiments. All the correlation coefficients in fitted equations exceeded 0.98, indicating a good confidence level for the fit.

1. Introduction

Global warming and depletion of the ozone layer are the major environmental issues today [1,2]. The use of R12 (dichlorodifluoromethane) and R134a (1,1,1,2-tetrafluoroethane) as refrigerants in refrigeration industry contribute a lot to greenhouse effect and/or ozone depletion in spite of their excellent cooling characteristics. From the environmental point of view, it is essential to find substitutes for these traditional refrigerants [3]. Hydrocarbons and in particular, R290 (propane of high purify, normally higher than 99.5% (volume fraction)), are known as excellent refrigerants which have negligible ozone depletion potential and pretty low global warming potential [4]. Also, R290 has several positive characteristics such as non-toxicity, good miscibility with mineral oils and acceptable compatibility with common materials employed in refrigeration equipment [5].

Liquefied petroleum gas (LPG) are mixtures of hydrocarbon gases (normally C1–C4) usually used as fuel in heating appliances, cooking equipment and vehicles. The composition of LPG may differ from country to country and from season to season [6], but generally its main constituent is propane. LPG is inexpensive and commercially available in local markets, so the process for refining green refrigerant R290 from LPG by purification is a front subject with both theoretical significance and engineering value [7].

Various treatment processes such as cryogenic distillation [8], absorption [9], membrane separation [10] and adsorption [11] have been proposed for the purification of propane from hydrocarbon mixtures. The adsorption process has become a major unit operation in chemical and petrochemical industries. Furthermore, fixed bed adsorption for separation and purification has been widely used in industrial applications due to its advantages of large capacity, easy operation and low energy consumption [12].

Breakthrough characteristics of the fixed bed play a dominant role in the evaluation of the efficacy of an adsorbent under flowing gas conditions [13]. Therefore, it is of great importance to study breakthrough curves for light hydrocarbons on different adsorbents. Kawakami et al. [14,15] provided a method for purification of propane from LPG at 0.50–0.60 MPa and with molecular sieve 4A adsorbing ethane and propene while with activated carbon adsorbing isobutane and butane. Approximately 99.9% (volume fraction) of the propane was obtained from the LPG which had

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an initial propane concentration of 98.4% (volume fraction). Cho et al. [16] discussed adsorption separation, purification apparatus and the process for obtaining high purity isobutane by removing paraffins (methane, ethane, propane and butane) and olefins (isobutene, 1-butene and 2-butene) from light hydrocarbon mixtures containing isobutane with zeolite 5A and carbon molecular sieve adsorbents. Ahmed at al. [17,18] studied breakthrough curves of methane, ethane and propane mixture and the possibility of propane separation from the gas mixture on 4A molecular sieve zeolite as well as effects of the feed flow rate, feed concentration and composition of adsorbate on propane purity and productivity.

Although a number of researchers have reported the adsorption separation of light hydrocarbons, only a few articles have focused on the adsorption dynamics of separation of propane from LPG or its performance in a fixed bed absorber. In this work, the adsorption of LPG onto five adsorbents (4A, 5A, 13X, NaY zeolite pellets and granular activated carbon) have been studied at ambient conditions in a fixed bed. The dynamics measurements of propane, isobutane and butane on granular activated carbon have been performed to investigate effects of different operation parameters such as flow rate and bed height on the separation of propane from LPG. Adsorption models have been employed to simulate breakthrough curves of propane, isobutane and butane. Moreover, some characteristic parameters from models have been analyzed to test their validity against the experimental data. The performance of those adsorbents on separation of propane from LPG in lab-scale enables us to collect necessary information for industrial scale applications of refining green refrigerants R290 from LPG.

2. Experimental

2.1. Materials

Commercial granular activated carbons (GAC) with average particle diameter of 0.9 mm were supplied by Shanxi Xinhua activated carbon Co., Ltd. The zeolite 13X and NaY were manufactured by Anhui Mingmei Minchem Co., Ltd and Dalian absorbent Co., Ltd, respectively. The zeolite 4A and 5A were both purchased from Tianjin Kemeiou Chemical Reagrnt Co., Ltd. All zeolites in this work were spherical grain with average diameter of 4 mm and all adsorbent samples were milled and sieved to size of 250–425 μm. Before adsorption breakthrough experiments, zeolite pellets 13X, NaY, 4A and 5A were degassed at 300 °C for 4 h in air and cooled to ambient temperature while GAC was put in an oven at 110 °C for about 12 h.

LPG was obtained from Guangzhou Huakai Oil and Gas Co., Ltd. The specific LPG mainly contained propane with small concentration of methane, ethane, propene, isobutane and butane. The composition for the test LPG by volume fraction was: propane, 97.05 ± 0.10%; ethane, 0.17 ± 0.01%; isobutane, 2.16 ± 0.01%; butane, 0.54 ± 0.01%; all other constituents, 0.08%. Therefore, the concentration of methane, propene and corrosive substance (e.g. sulphur, mercaptans and water) were very low.

2.2. Characterization

The pore structure characteristics of adsorbents were determined by N_2 adsorption–desorption at 77 K with a Micromeritics ASAP 2020 automatic adsorption instruments. Prior to the measurement, samples were outgassed at 200 °C in a vacuum system for 4 h. The specific surface areas were calculated from adsorption branches using the BET (Brunauer–Emmett–Teller) equation. The micropore, mesopore and total volumes were determined via *t*-plot, BJH (Barret–Joyner–Halenda) and single point method, respectively. The micropore and mesopore size distribution of all adsorbents were calculated via DFT (Density Functional Theory) and BJH method (determined from the adsorption branch of the N_2 isotherms).

2.3. Adsorption separation measurements

Adsorption experiments of LPG were performed in a stainless steel tube (20 mm i.d.). The breakthrough tests of LPG were carried out at ambient temperature (298 ± 1 K) and atmospheric pressure with flow rate of 60, 80 and 100 mL/min and bed height of 5, 8, 10 cm, respectively. The inlet gas flow rate was measured by a rotameter. The inlet and outlet concentrations of methane, ethane, propane, butane and isobutane were monitored by a gas chromatography (Aglient 7890A, USA) equipped with a flame ionization detector (FID) and a GS-GasPro capillary column using N_2 as carried gas. The data for ethane from effluent stream of adsorption column were measured at 1 min sampling interval while those for butane and isobutane were analyzed at 2 min sampling interval until breakthrough of all adsorbate species were completed. The experimental results (breakthrough carves) were expressed in the form of variations of C/C_0 verse time (C and C_0 refer to the concentration of outlet and inlet gas respectively). In this work, when the concentration of adsorbate was detected above 0.5% of the corresponding C_0, it was regarded that the breakthrough point was reached.

3. Mathematical models

Successful design of a fixed bed adsorption process requires prediction of the concentration–time profile or breakthrough curve for the adsorbate. The maximum adsorption capacity of an adsorbent is also needed for rational design. Several models have been used to fulfil those purposes.

3.1. The length of unused bed (LUB)

In the design of an adsorption column which can obtain a high sorbent productivity as well as a high product purity, a short LUB is desired. This length represents the length of the mass-transfer zone, which is the part of the column where the adsorbent is not completely used and but where adsorption is still occurring [19]. The LUB is defined by [20]

$$\mathrm{LUB} = \left(1 - \frac{t_b}{t^*}\right)L \tag{1}$$

where L is the length of the bed (m), t_b is the breakthrough time (s) at which the outlet concentration reaches its maximum permissible level and t^* is the stoichiometric time (s) which can be obtained by drawing a vertical line on breakthrough curve at a time when the used adsorbent capacity equals the unused adsorbent capacity [21]. A single dynamic adsorption experiment which generates the entire breakthrough curve is sufficient to enable t_b and t^* to be determined since

$$t_b = \int_0^{t_b} \left(1 - \frac{C}{C_0}\right) dt \tag{2}$$

$$t^* = \int_0^{\infty} \left(1 - \frac{C}{C_0}\right) dt \tag{3}$$

And t^* can be also regarded as the adsorption time for reaching the half of the equilibrium concentration for a symmetrical breakthrough curve, it is the time at which C/C_0 equals 0.5 [22].