



# Preparation of high purity propane from liquefied petroleum gas in a fixed bed by removal of sulfur and butanes



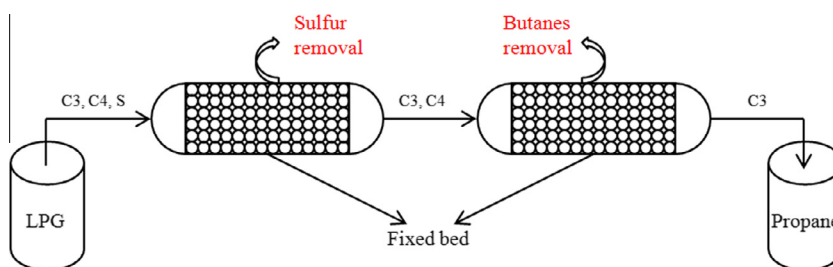
Huan Xiang, Huiping Zhang, Pengfei Liu, Ying Yan\*

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China

## HIGHLIGHTS

- High purity propane was prepared from LPG in a fixed bed.
- Sulfur compounds in LPG were removed by adsorption over zeolite 13X and NaY efficiently.
- Butanes (i-butane and n-butane) in LPG were removed by adsorption over activated carbon efficiently.

## GRAPHICAL ABSTRACT



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## ABSTRACT

High purity propane was prepared from liquefied petroleum gas (LPG) in a fixed bed by removal of sulfur and butanes (i-butane and n-butane). First, sulfur compounds were removed from LPG by fixed bed adsorption over three commercial zeolites (13X, NaY and 5A). Then, adsorption dynamics of propane, i-butane and n-butane on activated carbon were investigated by evaluating effects of the feed flow rate, bed length and temperature on breakthrough curves. Breakthrough curves for sulfur, propane and butanes adsorption were analyzed by Yoon–Nelson model. The experimental results indicated that zeolite 13X and NaY presented better desulfurization performance than zeolite 5A at the temperature of 303 K, feed flow rate of 20 mL/min and bed length of 15 cm. Breakthrough curves for sulfur, propane and butanes fitted relatively well to Yoon–Nelson model. The Yoon–Nelson model is strongly valid for breakthrough curves of n-butane, with all correlation coefficient exceeding 0.96. Butanes were more selectively adsorbed on activated carbon than propane. The adsorption selectivity of activated carbon for these three adsorbates decreased in the order of n-butane > i-butane > propane. Activated carbon had been proved to be a desirable adsorbent to remove butanes from LPG to prepare high purity propane under experimental conditions.

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## 1. Introduction

Refrigerators are one of the major energy consuming domestic appliances in household environment [1]. Chlorofluorocarbons (CFCs) were used as refrigerants in most of the domestic refrigerators and other small refrigeration units for many decades because of their excellent cooling characteristics. However, CFCs, such as R12, were found to cause global warming and damage the strato-

spheric ozone layer due to their chlorine chemical effect [2]. In contrast, hydrocarbons, another kind of refrigerant, have been demonstrated to be energy efficient and environment-friendly [3–6]. Hydrocarbons have no ozone depletion effect and global warming effect (see Table 1). They are also universally available in large amounts at low price.

Among all hydrocarbons, propane (R290) is found to be the most convenient refrigerant in small refrigerators [3]. As a new environment-friendly refrigerant, R290, with its total sulfur content below 2 ppm, is comprised of at least 99.5% propane. Since large amounts of propane are contained in LPG (see Table 2), LPG

\* Corresponding author. Tel./fax: +86 2087111975.

E-mail address: [yingyan@scut.edu.cn](mailto:yingyan@scut.edu.cn) (Y. Yan).

**Table 1**  
Properties of some refrigerants [7,8].

Refrig.	Chemical formula	Molecular weight (kg/kmol)	Natural	ODP	GWGP (100 yr)
R12	CCl <sub>2</sub> F <sub>2</sub>	120.9	No	0.82	8100
R134a	CH <sub>2</sub> FCF <sub>3</sub>	102.0	No	0	1300
R290	C <sub>3</sub> H <sub>8</sub>	44.0	Yes	0	0
R600	n-C <sub>4</sub> H <sub>10</sub>	58.1	Yes	0	0
R600a	i-C <sub>4</sub> H <sub>10</sub>	58.1	Yes	0	0

is considered to be a potential feedstock to manufacture R290 due to its local availability and relatively low price. In addition, the key issues in producing R290 from LPG lie in removing sulfur compounds and hydrocarbons other than propane, especially butanes, which are also seemed as main components of LPG.

Sulfur compounds, such as H<sub>2</sub>S and mercaptans, coming from crude oil and odorized gas added for safety regulations, are widely existed in LPG. As sulfur can cause corrosion to equipments, LPG must be thoroughly desulfurized in producing R290. For the removal of sulfur compounds from hydrocarbon fuels, three kinds of methods are commonly adopted, hydrodesulfurization (HDS), selective catalytic oxidation (SCO) followed by adsorption and adsorption desulfurization. HDS is operated at elevated temperature (300–400 °C) and pressure (40–50 bar) and requires high hydrogen to feedstock ratio [11,12]. Because of the large energy cost of compressing hydrogen, HDS is categorized as an impractical way in fuel processors. Moreover, the conversion of olefin to alkane results in massive losses of olefin during the HDS process. While SCO does not require additional hydrogen compared to HDS, it needs an extra unit to separate unconverted oxygen and nitrogen from hydrocarbon fuels [13]. In contrast, adsorption desulfurization does not need any hydrogen and is usually operated at relative low temperature and pressure. Hence, it is a promising and applicable method in removing sulfide from LPG. Up to present, activated carbon [14,15] and zeolite [16–18] are two of the most widely studied adsorbents for desulfurization. Takatsu et al. [19] studied the adsorption of sulfur compounds in LPG on activated carbon, CuO/ZnO/Al<sub>2</sub>O<sub>3</sub>, Ag-exchanged β-zeolite and Ag/CeO<sub>2</sub> at room temperature. Among the tested adsorbents, Ag-exchanged β-zeolite and Ag/CeO<sub>2</sub> presented better adsorption capacity. They also deduced that the larger the negative charge of the sulfur atom, the stronger the coordination bonding between Ag<sup>+</sup> and the sulfur atom of the compounds.

The main processes for light hydrocarbons separation are absorption process, cryogenic process, membrane process, and adsorption process [20,21]. Adsorption separation process has

**Table 2**  
LPG composition by country [9,10].

Country	LPG composition% (vol/vol)			
	Ethane	Propane	Propylene	Butanes
Australia	0–10	0–100	0–45	0–50
Belgium	0–5	50–100	0–50	0–10
Canada		92.5–100	0–5	0–2.5
France	0–5	50–100	0–50	0–5
Hong Kong	0–5	20–40		60–80
Italy	0–5	40–100	0–50	0–50
Korea		10–35		65–90
Mexico		60		40
Netherlands	0–5	50–100	0–50	0–50
New Zealand		60–70		30–40
Poland		20–60		40–80
Singapore	0–5	20–40		60–80
Spain	0–5	87.5–100	0–5	0–5
United Kingdom	0–5	50–100	0–50	0–5
United States		92.5–100	0–5	0–2.5

been widely applied in recovering hydrocarbons with high purity due to its convenience and high efficiency. It is worth mentioning that activated carbon, which has high surface area and large adsorption capacity, has been proved to be an attractive material for adsorbing butane. Marbán et al. [22] studied the breakthrough behavior of activated carbon fiber monolith in n-butane adsorption and proposed a complete breakthrough model to predict its breakthrough profile. The results showed a good agreement between the experimental and the simulated data. Kawakami et al. [23,24] provided an industrially advantageous method and system for obtaining high purity propane from low purity propane. Propane with a purity of 99.99 vol.% or higher was obtained by adsorbing ethane, propylene and butanes (i-butane and n-butane) over activated carbon molecular sieve and activated carbon, respectively. Besides, there is no other literature described the removal of sulfur compounds and butanes from LPG for producing high purity propane by fixed bed adsorption.

To obtain high purity propane (R290) from LPG, sulfur compounds and butanes must be removed. Adsorption is one of the most feasible methods due to its high efficiency. However, it seems difficult to find a material that can remove sulfur and butanes from LPG by fixed bed adsorption simultaneously and efficiently. Therefore, a combined process is a good choice to prepare high purity propane from LPG, as shown in Fig. 1. During this process, high purity propane can be obtained from LPG in the fixed bed by removing sulfur and butanes, respectively.

However, the adsorption process has its own limitations. Since it is a non-stationary process, some kinds of cycle will be needed, where adsorbents can be regenerated or substituted. In the industrial adsorption processes, adsorbent regeneration is by far the most time and energy consuming step. Hence, the method for adsorbents regeneration, such as pressure swing adsorption (PSA) [25] and temperature swing adsorption (TSA) [26], is another crucial issue that must be considered. This study is just a preliminary exploration of preparing high purity propane from LPG by fixed bed adsorption, so the regeneration of used adsorbents is not investigated.

The purpose of the present work is to prepare high purity propane by adsorption separation of sulfur and butanes from LPG in a fixed bed. The removal of sulfur compounds and butanes from LPG over three different zeolites (13X, NaY and 5A) and activated carbon will be studied, respectively. Breakthrough experiments with commercial LPG are carried out to select excellent adsorbents for desulfurization. Furthermore, adsorption dynamics of propane, i-butane and n-butane will be investigated by evaluating effects of the feed flow rate, bed length and temperature on breakthrough curves, and the Yoon–Nelson model is used to analyze breakthrough curves for sulfur, propane and butanes.

## 2. Experimental

### 2.1. Materials

LPG (Guangzhou Huakai Oil and Gas Co., Ltd) was used as adsorbate. The compositions of sulfur, propane, i-butane, and n-butane in LPG were 35 ppm, 97 ± 1%, 0.02%, and 0.01%, respectively. Zeolite 13X (Anhui Mingmei Mining Co., Ltd), NaY (Dalian Adsorbent Factory), 5A (Zhengzhou Tianxiang Inorganic Material Co., Ltd) with a particle diameter of 3–5 mm, and activated carbon (Ningxia Huayang Activated Carbon Co., Ltd) with an average particle diameter of 0.9 mm, were used as adsorbents. Zeolites were crushed and sieved to the required particle size (250–425 μm) before being used in the adsorption experiments.

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