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An energy-efficient juice concentration technology by ethylene hydrate formation

Shifeng Li [a,b,*], Fang Qi [a], Kaige Du [a], Yanming Shen [a], Dongbin Liu [a], Lihui Fan [a]

[a] Liaoning Provincial Key Laboratory of Chemical Separation Technology, Shenyang University of Chemical Technology, Shenyang 110142, China
[b] Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang 110016, China

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ABSTRACT

This work first reported ethylene as hydrate formation guest gas for facilitating orange juice concentration process. Ethylene hydrate with orange juice equilibrium conditions under this process were measured by employing the classic isochoric pressure search method. Based on the obtained equilibrium conditions, the effects of feed ethylene pressure and temperature on dehydration ratio were investigated. The gas consumption curves were recorded and distinctly from that CO_2 hydrate formation process in the presence orange juice, which could be caused by the multiple nucleation of ethylene hydrate crystal. The dehydration ratio increased with the increase of the feed ethylene pressure. Maximum dehydration ratio of 92.8% was found at 4.43 MPa. Dehydration ratio ranged from 52.5% to 61.8% in the temperature range of 0.5–10.0 °C. The results demonstrated that ethylene hydrate formation can be an efficient technology on water removal for orange juice concentration.

1. Introduction

Hydrates (also called clathrate hydrates) are nonstoichiometric crystalline inclusion compounds form through the combination of water and suitably sized "guest" molecules, typically under low temperature and elevated pressure conditions. In gas hydrates, water molecules form lattice structures with several interstitial cavities, consisting of hydrogen-bonded polyhedral water. Structure I, II and H hydrates are the common types of gas hydrate structure, depending on the sizes of the guest molecules and conditions. Theoretically, fully loaded structure I hydrate contains up to 164 volumes of gas (STP) per volume of hydrate [1].

Early in 1934, natural gas hydrates have been found to be responsible for blocking gas pipelines. It is still an important industrial problem causing safety hazards to personnel and production equipment until to 1990s [2]. Meanwhile, hydrates as a means of storing mass and energy has gradually attracted intensive attentions with higher energy density [3–5]. Most recently, great efforts have been put into hydrate-based separation technology which is based on the selective partitioning of the components in hydrate phase and in gas phase [3,6–9]. With the growing greenhouse effect, capture of CO_2 by hydrate formation has received much recent interest [6–10]. For reducing the hydrate formation pressure, tetrahydrofuran (THF) was first chosen as hydrate promoter [11]. Hereafter, some new additives such as quaternary ammonium salt (for example, TBAB [12] and TBAF [13]), quaternary phosphonium salt (TBPB) [14], cyclopentane [15], tributylphosphine oxide (TBPO) [16], as hydrate promoters were used to reduce the pressure of hydrate formation. Besides hydrate formation promoters, some porous materials such as porous silicone gel [17], porous glass bead [18], polyurethane foam [19], and emulsion [20] were also applied to enhance the kinetics of hydrate formation process. Another, attractive hydrate-based separation technology is aqueous solution concentration process [21–25], such as desalination, juice concentration. From the 1940s to date, numerous studies have been undertaken to design desalination processes [21–23], treat wastewater [26], or recover biological components [27] via gas hydrates formation. However, with the risk of polluting the juice during the separation, the above-mentioned liquid phase hydrate promoters applied in the gas separation process would not be suitable for juice concentration. So an effective, environmentally friendly hydrate formation promoter would be the key for implementing juice concentration process. Early in 1965, Huang et al. [28] first provided the concept by hydrate-based technology on juice concentration process and investigated concentration of apple, orange, and tomato juices via CH_3Br and CCl_3F hydrate. With satisfied concentration results, the concentration process diminished the color and flavor of most substances, and frequently imparted a slightly bitter aftertaste.

* Corresponding author at: Liaoning Provincial Key Laboratory of Chemical Separation Technology, Shenyang University of Chemical Technology, Shenyang 110142, China.
E-mail address: li.shi.feng@163.com (S. Li).

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Subsequently, propane and xenon as hydrate formation gas were used for hydrate-based aqueous solution concentration [24,29]. Though recently some advances in aqueous solution concentration have achieved, there still remain numerous challenges (environmentally hazardous or costly) that limit the practical use [30]. Most recently, we have developed a novel hydrate-based juice concentration by CO_2 hydrate formation [25,31]. However, the CO_2 hydrate formation pressure is relatively higher and the maximum dehydration ratio is just about 50% under experimental conditions. Even though the apparent advantage of CO_2 hydrate approach over cryogenic one is that separation process can be operated around the ice point [20], it would not be avoided that more energy consumed under higher CO_2 pressure. Hence, it is necessary to explore an efficient hydrate former or formation promoter for reducing the compression work of juice concentration process and increasing dehydration ratio.

Ethylene is an important industrial gas and also a special gas that it forms hydrates over a relatively wide range of temperature covering the critical temperature of 282.6 K [32]. Therefore, the potential application of ethylene hydrates for storage or separation have attracted intensive research interest. Up to now, researches on ethylene mostly focus on ethylene hydrate formation conditions [20,38] and separation ethylene from gas mixture [32–37]. These finding suggested that the hydrate formation pressure of ethylene at the same temperature is considerably less than those of CH_4, C_2H_6, CO_2, and so on [1,32–37]. To the best of our knowledge, it has never been reported that ethylene can be used as hydrate former for juice concentration process. In this work, ethylene, as common industrial gas and effective hydrate former was investigated in orange juice concentration process. Changes of pressure and temperature during ethylene hydrate formation and effects of feed gas pressure and temperature on the concentration efficiency were studied in this work to explore the possible practical applications of this technique in the future.

2. Experimental methods

2.1. Materials

Ethylene (99.95%) was purchased from Dalian GuangMing Special Gas Products CO., Ltd (China) and orange juice was supplied by Beijing Huiyuan Group (China). The contents of reducing sugars, total acid, vitamin C, soluble solid and water content of orange juice are listed in Table 1.

2.2. Apparatus and methods

The basic experimental setup used in this study is the same apparatus from our previous work [25,31] with modifications to facilitate the higher pressure applications shown in Fig. 1. It mainly consisted of a stainless-steel reactor (volume 300 mL) equipped with a magnetic stirrer (Nantong Feiyu Science and Technology exploitation CO., China). The reactor can be operated up to 25 MPa. The reactor was submerged into a thermostat (Tianheng THCD-306) with a stability of ±0.01 K to control the temperature. Two Pt-100 resistance thermometers (Westzh WZ-PT100) within 0.1 K accuracy placed in the middle and bottom of the reactor respectively monitored the temperature of the reactor with interval of 10 s. A pressure transducer (Senex DG-1300) with the accuracy of 0.01 MPa was used to measure the pressure inside the reactor. The pressures and temperatures of the reactor were recorded by data logger (Agilent 34972A).

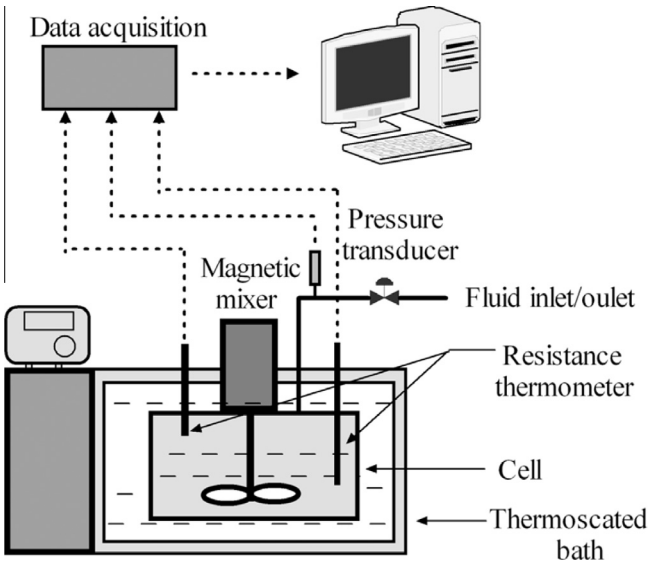

Fig. 1. Schematic diagram of the experimental apparatus for hydrate formation.

2.3. Ethylene hydrate phase equilibrium

The hydrate equilibrium conditions were measured by an isochoric pressure search method [25]. The reactor containing liquids (approximately 120 mL) was immersed into the temperature-controlled bath. Ethylene gas was then loaded from gas cylinder through a pressure-regulator into the evacuated cell to the desired level. After temperature and pressure leveling off, the valve in the line connecting the cell and cylinder was closed, and then the stirrer was started. Subsequently, temperature was gradually decreased to form the hydrate. Hydrate formation in the cell was detected by a sharp pressure drop and an exothermic peak. The temperature was then increased with steps of 0.1 K. At every temperature step, the temperature was held constant for 4 h to achieve equilibrium state in the cell. In this way, a *P-T* diagram was obtained for each experimental run, from which the hydrate dissociation point was determined. Consequently, the point at which the slope of the *P-T* curve plots sharply changed was considered as the hydrate dissociation point at which all hydrate crystals have dissociated.

2.4. Concentration of orange juice

After 80 mL orange juice solution was introduced into the evacuated reactor, the reactor was cooled to the desired value (typical at 275.2 K). When the cell temperature was stabilized, the reactor was vacuumed to ensure the absence of air, and then ethylene gas was charged into cell up to the given pressure. Then the stirrer was started to initiate hydrate formation (500 rpm). During experiment the temperature and pressure were recorded. After hydrate formation completing (the system pressure was stable), the stirrer was stopped.

Table 1
The contents of reducing sugars, total acid, vitamin C, soluble solid and water cut of orange juice used in this work.

Orange juice	Reducing sugar (g/100 g)	Total acid (g/kg)	Vitamin C (mg/100 g)	Soluble solid	Water cut
Content	4.42	6.08	49.96	10.5%	87.7%