Research Article
A Novel Orange Juice Concentration Method Based on C_2H_4 Clathrate Hydrate Formation

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Abstract: A novel orange juice concentration method by C_2H_4 hydrate formation was presented. The experiments were carried out in a high-pressure stirred reactor. The changes of temperature and pressure during C_2H_4 hydrate formation were discussed under different pressure (2.10 and 4.43 MPa). Dehydration ratio was defined in order to evaluate the separation efficiency. It was found that secondary nucleation happened under higher initial pressure. The dehydration ratios were 20.2 and 99.3% with initial pressure at 2.10 and 4.43 MPa, respectively. The results demonstrated that removal of water by formation of C_2H_4 hydrate is a potential technology for orange juice concentration.

Keywords: C_2H_4, concentration, fruit juice, hydrate, separation

INTRODUCTION

Fruit juice concentration is recognized word-wide as a way to preserve and reduce transport cost. Despite recent advance in fruit juice concentration such as evaporation, membranes (ultrafiltration, reverse osmosis and membrane distillation) and freeze concentration and so on, there remain numerous challenges (Jiao *et al.*, 2009; Jesus *et al.*, 2007; Guignon *et al.*, 2012; Aider and de Halleux, 2008).

In recent years, hydrate separation technology has attracted scientific interest in the field of CO_2 capture (Eslamimanesh *et al.*, 2012; Fan *et al.*, 2009; Li *et al.*, 2009), hydrogen or methane recovery (Liu *et al.*, 2014; Zhong and Englezos, 2012) and desalination (Javanmardi and Moshfeghian, 2003; Park *et al.*, 2011). 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 (Sloan and Koh, 2008). The basic principle of aqueous concentration by gas hydrate is that under suitable conditions of temperature and pressure, the gas with water forms solid clathrate hydrate which can be removed from the concentrated solution by mechanical separation. Since gas hydrate can be formed above 0°C, energy consumption becomes smaller than that in freezing (Eslamimanesh *et al.*, 2012; Fan *et al.*, 2009; Li *et al.*, 2009). Despite recent advances in hydrate separation technology, there is little report on aqueous concentration via hydrate formation, especially in application in juice concentration (Huang *et al.*, 1966; Purwanto *et al.*, 2001; Andersen and Thomsen, 2009). In fact, as early as the 1960s, Huang *et al.* (1966) utilized CH_3Br and CCl_3F hydrate to concentrate apple, orange and tomato juices. No difficulty was encountered in removing approximately 80% of the water from the substrates. However, the concentration process diminished the color and flavor of most substances and frequently imparted a slightly bitter aftertaste. Because the hydrate gas is not environmental friendly, the practical use of juice concentration by CH_3Br and CCl_3F hydrate formation is limited. Until to 2001, Purwanto *et al.* (2001) proposed concentration of coffee solutions by use of xenon hydrate. Andersen and Thomsen (2009) investigated the possibility of using gas hydrates for concentration of sugar juice. It was found that the process is not suitable for sugar production, but could be interesting for concentration of heat sensitive, high value products.

To our knowledge, there is no report on orange juice concentration via formation of C_2H_4 hydrate and the study of C_2H_4 hydrate formation processes are not clear. Therefore, the purpose of this study is to develop a novel orange juice concentration method via C_2H_4 hydrate formation and investigate the processes of pressure and temperature changing with time in different initial pressure.

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Table 1: The contents of reducing sugars, total acid, vitamin C, soluble solid and water content of orange juice used in this study

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%

MATERIALS AND METHODS

Materials: C_2H_4 gas (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.

Method:
Apparatus: The basic experimental setup was adopted from Li *et al*. (2010) with modifications made to facilitate the higher pressure applications (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 was designed to be operated at pressure 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 Pt100 resistance thermometers (Westzh WZ-PT100) within 0.1 K accuracy which are placed in the middle and bottom of the reactor, respectively, were used to monitor the temperature of the reactor. A pressure transducer (Senex DG-1300) within 0.01 MPa in accuracy measured the pressure inside the reactor. The pressures and temperatures of the reactor were recorded by data logger (Agilent 34972A).

Procedure: 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 C_2H_4 was charged into cell until 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 finished (the system pressure was stable), the stirrer was stopped.

The molar number of gas consumed: The molar number of gas that has been consumed during hydrate formation can be calculated as follows Eq. (1) (Li *et al*., 2009):

$$\Delta n = n_f - n_e = \frac{P_f V_g}{z_f RT} - \frac{P_e V_g}{z_e RT} \tag{1}$$

where, z is the compressibility factor calculated by SRK equation of state, subscripts f, e refer to the feed gas and equilibrium gas. The volume of gas was assumed constant throughout the hydrate formation process
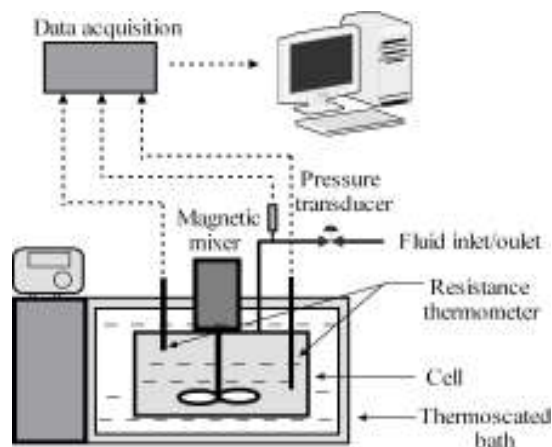

Fig. 1: Schematic of the experimental apparatus

(volume changes due to the phase transitions were neglected).

Dehydration ratio: The content of water in hydrate phase is important for evaluating the dehydrate ratio of C_2H_4 (defined as ratio of water in the hydrate phase and in the initial orange juice). Because it is difficult to directly determine the water cut in hydrate phase in the presence of residual concentrate orange juice, the following assumption C_2H_4 "reacts" with water to form C_2H_4 hydrate based on following reaction Eq. (2) were adapted:

$$C_2H_4(g) + n\,H_2O\,(l) \rightarrow C_2H_4 \bullet nH_2O\ (H) \tag{2}$$

where, n is the hydrate number of C_2H_4 hydrate, according to experimental result of Falabella (1975), the hydrate number of C_2H_4 hydrate (n) under this study is approximately equal to 6.76. Therefore, the Dehydrate ratio (D) can be calculated as following Eq. (3):

$$D = \frac{n \times \Delta n \times W_{H_2O}}{m_f} \times 100\% \tag{3}$$

where,
W_{H_2O} = Molar mass of water
m_f = The mass of water in initial orange juice

RESULTS AND DISCUSSION

Figure 2 shows the typical processes of pressure and temperature changing with time in initial pressure of 2.10 MPa. During the C_2H_4 hydrate formation, the
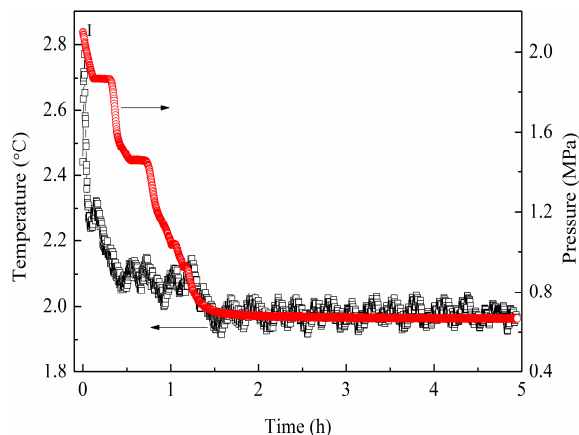
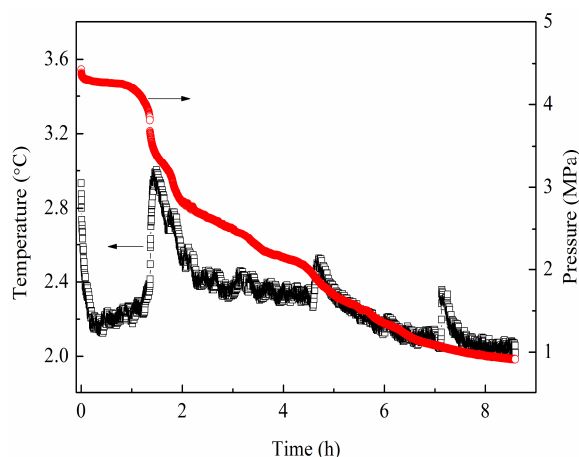Fig. 2: Temperature and pressure as a function of time with initial pressure at 2.10 MPa

Fig. 3: Temperature and pressure as a function of time with initial pressure at 4.43 MPa

pressure decreased gradually and achieved constant after about 1.5 h. However there were not obvious temperature changes during orange juice concentration process. These results demonstrated that the C_2H_4 hydrate formation process was gent under lower initial pressure. Based on the formula of (3), the theoretical dehydration ratio was 20.2%.

The trends of the pressure and temperature during orange juice concentration process with initial pressure at 4.43 MPa are shown in Fig. 3. As we can see that the during C_2H_4 hydrate formation, there are three obvious temperature rises, due to intense exotherm of hydrate formation. And the pressure decreased gradually in the whole process except in the first hydrate formation step. Upon comparison of Fig. 2 and 3, we found that secondary nucleation happened under higher initial pressure. The reason was why that with higher initial C_2H_4 pressure, the concentration of C_2H_4 dissolved in orange juice increased. Therefore, the concentration of water clusters around dissolved C_2H_4 molecules could be kept a higher level based on the labile cluster nucleation hypothesis (Sloan and Koh, 2008), which

caused the phenomenon of secondary nucleation. In addition, the theoretical dehydration ratio calculated by formula (3) was 99.3%.

Orange juice concentration by C_2H_4 hydrate formation was presented. During the C_2H_4 hydrate formation, the pressure decreased gradually and then achieved constant in both initial pressures. It was found that secondary nucleation happened in higher initial pressure. The dehydration ratios were 20.2 and 99.3% with initial pressure at 2.10 and 4.43 MPa, respectively. The results demonstrated that removal of water by formation of C_2H_4 hydrate is a potential technology for orange juice concentration.

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