EXPERIMENTAL STUDY OF CONCENTRATION OF TOMATO JUICE BY CO2 HYDRATE FORMATION

Article Highlights
- Novel tomato juice concentration process using CO2 hydrate formation is presented
- Tomato juice has a small effect on CO2 hydrate formation
- The maximum dehydration ratio can reach 63.2% with feed pressure of 3.95 MPa
- The rate constant increased with increasing the feed pressure

Abstract
A new tomato juice concentration technology using CO2 hydrate formation is presented. The CO2 hydrate equilibrium conditions were measured by the isochoric pressure search method and tomato juice concentration experiments were carried out in a high-pressure stirred reactor. Moreover, the dehydration ratio was defined and CO2 hydrate formation rate constants were calculated with different feed pressures. The effects of feed pressure, temperature, and juice volume on the dehydration ratio were investigated. The results show that the tomato juice used in this work has almost no effect on CO2 hydrate phase equilibrium conditions, but can accelerate CO2 hydrate formation. The dehydration ratio increased with increasing the feed pressure from 1.81 to 3.95 MPa; the maximum dehydration ratio reached 63.2% at a feed pressure of 3.95 MPa, and the optimum tomato juice volume was 80 mL. These results demonstrated that removal of water with the help of CO2 hydrate is an efficient technology for tomato juice concentration.

Keywords: concentration, separation, clathrate hydrate, carbon dioxide, tomato juice.
Despite recent advances in hydrate separation technology, there are few reports on aqueous concentration via hydrate formation, especially in juice concentration [20-22]. In fact, as early as the 1960s, Huang et al. [20] utilized CH$_3$Br and CCl$_3$F hydrate to concentrate apple, tomato, and tomato juices. No difficulty was encountered in removing approximately 80% of the water from the substrates. Because the hydrate formation gas is not environmentally friendly, the practical use of juice concentration by CH$_3$Br and hydrate formation gas is limited. In the subsequent 40 years there had been no reports on on fruit juice concentration via gas hydrate formation until 2001, when Purwanto et al. [21] proposed concentration of coffee solutions by use of xenon hydrate. They determined the induction time and size distribution of gas hydrate and found that longer time was required for higher concentration of solution to form xenon hydrate and higher temperature and lower xenon pressure yielded the larger size of xenon hydrate. Recently, Andersen and Thomsen [22] investigated the possibility of using gas hydrates for concentration of sugar juice. They found the process was not suitable for sugar production, but could be interesting for concentration of heat sensitive, or high value products. Most recently, Purwanto et al. [23] designed a novel higher pressure container to concentrate coffee solution by formation of Xe hydrate. The ingenious designs of the higher pressure container could contribute to the development of separation process continuously.

To our knowledge, there is no report on tomato juice concentration via formation of CO$_2$ hydrate. Therefore, the purpose of this work is to develop a novel tomato juice concentration method via CO$_2$ hydrate formation and investigate the effect of feed pressure, temperature, and volume of juice on the concentration efficiency in order to establish the optimum operating conditions and explore practical applications of the technique in the future.

**EXPERIMENTAL**

**Materials**

CO$_2$ gas (99.99%) was purchased from Beijing AP BAIF Gases Industry CO., Ltd (China) and tomato juice was supplied by Kagome (Taiwan). The contents of reducing sugars, total acid, vitamin C, soluble solid and water content of tomato juice are listed in Table 1.

![Tomato juice hydrate concentration experiment](image)

**General procedure**

**CO$_2$ hydrate phase equilibrium.** The basic experimental setup was adopted from Li et al. [24] with modifications made to facilitate the higher pressure applications. 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 temperature of the reactor was controlled by circulating the coolant from a thermostat (Tianheng THCD-306) with a stability of ±0.01 K inside the jacket around the cell. Two Pt100 resistance thermometers (Westzh WZ-PT100) within 0.1 K accuracy measured the pressure inside of the reactor. The pressures and temperatures of the reactor were recorded by data logger (Agilent 34972A). The hydrate equilibrium conditions were measured by the isochoric pressure search method [25]. The cell containing liquids (approximately 120 mL) was immersed into the temperature-controlled bath. Carbon dioxide gas was then supplied from a gas cylinder through a pressure-regulating valve into the evacuated cell until the pressure inside the cell was increased to the desired level. After the temperature and pressure were stabilized, the valve in the line connecting the cell and cylinder was closed; then, the stirrer was started. Subsequently, the temperature was gradually decreased to form the hydrate. Hydrate formation in the cell can be detected by a decrease in pressure and an increase in temperature. The temperature was then increased with steps of 0.1 K. At every 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 [25]. 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.

<table>
<thead>
<tr>
<th>Component</th>
<th>Reducing sugar, g/100 g</th>
<th>Total acid, g/kg</th>
<th>Vitamin C, mg/100 g</th>
<th>Soluble solid, %</th>
<th>Water content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>2.51</td>
<td>3.31</td>
<td>16.85</td>
<td>5.5</td>
<td>94.2</td>
</tr>
</tbody>
</table>
umed to ensure the absence of air, and then CO₂ was charged into cell until the given pressure. Then, the CO₂ intake valve was closed and the stirrer was started to initiate hydrate formation (500 rpm). During the experiment, the temperature and pressure were recorded. After hydrate formation finished (the system pressure was stable), the stirrer was stopped.

**Calculation method**

**The moles of gas consumed.** The number of moles of CO₂ gas that has been consumed during hydrate formation can be calculated as [14]:

\[
\Delta n = n_f - n_e = \frac{p_f V_f}{z_f R T} - \frac{p_e V_e}{z_e R T}
\]  

(1)

where \(z\) is the compressibility factor of CO₂ gas calculated by the SRK equation of state, and subscripts \(f\) and \(e\) refer to component of the feed gas and equilibrium gas. The volume of CO₂ gas was assumed constant throughout the hydrate formation process (volume changes due to the phase transitions were neglected).

**Dehydration ratio.** The content of water in hydrate phase is important for evaluating the dehydration ratio of CO₂ (defined as the ratio of water in the hydrate phase and in the feed tomato juice). Because it is difficult to determine the water cut in hydrate phase in the presence of residual concentrated tomato juice, the following assumption and calculation were adapted:

CO₂ connects with water to form CO₂ hydrate based on the following reaction equations:

\[
\text{CO}_2(g) + n\text{H}_2\text{O} (l) \rightarrow \text{CO}_2 \cdot n\text{H}_2\text{O} (H)
\]

(2)

where \(n\) is the hydrate number of CO₂ hydrate. According to theoretical calculation result of Mckov and Sinanoğlu [26] and Raman spectroscopic analyses data of Uchida et al. [27], the hydrate number of CO₂ hydrate in this work is approximately equal to 7.24. Therefore, the dehydration ratio \((D)\) can be calculated by the following formula:

\[
D = 100 \frac{n w_{\text{H}_2\text{O}}}{m_t}
\]

(3)

where \(w_{\text{H}_2\text{O}}\) is molar mass of water, and \(m_t\) is the mass of water in feed tomato juice.

**Hydrate formation rate constant.** The hydrate formation rate can be expressed in terms of fugacity difference during formation and at equilibrium [28,29]. In this study, the chemical potential difference was used as the driving force and the apparent gas uptake rate \((\frac{dn}{dt})\) is expressed as:

\[
\left(\frac{dn}{dt}\right) = aK^*(\mu_t - \mu_e)
\]

(4)

\[
\frac{1}{K^*} = \frac{1}{k_t} - \frac{1}{k_c}
\]

(5)

where \(a\) is the interfacial area, \(K^*\) is the overall kinetic constant, \(\mu_t\) and \(\mu_e\) are chemical potentials of the guest molecule in the gas phase and in the hydrate phase, respectively, \(k_t\) is the crystal growth constant, and \(k_c\) is the mass transfer coefficient in the liquid phase.

Under the conditions of this study, \(1/k_c\) could be eliminated by vigorous stirring (500 rpm) in the reactor (\(1/k_t >> 1/k_c\)). So the hydrate rate can be expressed by:

\[
r_t = \left(\frac{dn}{dt}\right) = ak_t(\mu_t - \mu_e) = ak_t R T \ln \frac{f_f}{f_e}
\]

(6)

\[
r_t = \left(\frac{\Delta n}{\Delta t}\right) = \frac{V_g}{R T} \left(\frac{f_f - f_e}{f_f - f_e}\right)
\]

(7)

where \(f_f\) and \(f_e\) are the fugacity of the gas phase and the hydrate phase at equilibrium condition, respectively, calculated by SRK equation of state. \(V_g\) is the volume of the gas phase and \(\Delta t\) is the time to reach equilibrium for hydrate separation process. Since it is difficult to separate the terms \(a\) and \(k_t\) from the experimental results for the fugacity change, the hydrate rate constant is expressed as:

\[
ak_t = \frac{V_g}{(RT)^2} \frac{(f_f - f_e)}{\Delta t \ln(f_f / f_e)}
\]

(8)

**RESULTS AND DISCUSSION**

Figure 1 shows the curve of CO₂ gas-liquid equilibrium and CO₂ hydrate phase equilibrium. So, the temperature and pressure conditions of tomato juice concentration experiments were chosen in the ellipse region between the two curves.

Firstly, to elucidate how the water cut of tomato juice (94.2 wt%) affects CO₂ hydrate phase equilibrium, hydrate phase equilibrium conditions for CO₂ in water and tomato juice systems were measured in the presence of pure water and tomato juice by an isochoric pressure search method. The phase equilibrium data are given in Figure 2. From Figure 2, it is apparent that the CO₂ hydrate phase equilibrium curve in the presence of tomato juice agrees roughly with that in water. Therefore, it can be concluded that the tomato juice has nearly no effect on CO₂ hydrate phase equilibrium conditions because the most of tomato juice (94.2 wt.%) is water and the most of the
residuals (fructose and soluble solid) have little effect on equilibrium temperature and pressure of CO₂ hydrate formation [22].

Then the tomato juice concentration experiments were carried out with different feed pressure. In this work, the feed pressure of CO₂ gas varied from 1.80 to 3.95 MPa. As shown in Figure 3, the dehydration ratio calculated using Eq. (3) increased with the feed pressure increasing. The maximum dehydration ratio can reach 63.2% with a feed pressure of 3.95 MPa. The results clearly indicate that higher dehydration ratio can be obtained with higher feed pressure because of more hydrate formation. However, although higher feed pressure was more beneficial for concentration efficiency, the higher feed pressure would need higher cost compression work.

The effect of hydrate formation temperature on dehydration ratio was also studied. Figure 4 shows the dehydration ratio as a function of temperature with the feed pressure of 3.46 MPa. As we can see, the dehydration ratio increased with decreasing of temperature in the range of 274.8-279.8 K. Although lower temperature is favorable for tomato juice concentration, the lower temperature would need higher refrigeration energy consumption. Comparing the results in Figures 3 and 4, we can conclude that increasing feed pressure is more efficient for tomato juice concentration than reducing temperature.

The effect of tomato juice volume on dehydration ratio was studied at 275.8 K and 3.46 MPa. As shown in Figure 5, the dehydration ratio first increased up to 65.2% and then decreased when tomato juice volume increased from 40 to 120 mL. With increasing tomato juice volume the mass of removed water accordingly increased. The increase in tomato juice volume from 40 to 120 mL will decrease the free volume space in the reactor. With the same feeding pressure, due to the different free volume space, the amount of CO₂ will be different. So when the volume
of tomato juice is 40 mL, the liquid volume just accounts for approximately one-thirteenth of the reactor. Because the stirrer stays in a fixed position, the mix of CO₂ gas and tomato juice could be insufficient, which causes the dehydration ratio to decrease. Therefore, considering the mass of removed water, the optimum tomato juice volume is 80 mL.

![Figure 5. Dehydration ratio as function of tomato juice volume.](image)

To reveal the effect of feed pressure on hydrate formation kinetics, the CO₂ hydrate formation rate constants were defined and calculated. As shown in Table 2, the CO₂ hydrate formation rate constants calculated using Eq. (8) were $0.94 \times 10^{-8}$, $1.36 \times 10^{-8}$, $1.65 \times 10^{-8}$, $1.82 \times 10^{-8}$ and $2.01 \times 10^{-8}$ $\text{J}^{-1} \text{mol}^2 \text{s}^{-1}$ with feed pressure of 1.81, 2.40, 3.10, 3.46 and 3.95 MPa, respectively. The results showed that the rate constant increased with increasing the feed pressure. It can be explained by the higher feed pressure that a larger driving force was achieved, which is consistent with the two-film model for hydrate formation process [28,29]. Several studies have reported the formation rate of CO₂ hydrate. For example, Uchida et al. [30,31] observed CO₂ hydrate formation process at the interface between water and CO₂ using microscopy and found that the rate-determining process is mainly heat diffusion from the reaction sites. They also studied the effect of addition of NaCl on lateral growth rate of CO₂ hydrate films, and their observations suggested that the hydrate formation rate in NaCl solution is determined by not only the heat transport, but also the mass transport of NaCl. Yang et al. [32] concluded that vigorous inter-phase mixing reduced heat and mass transfer resistances and the global reaction rate may ultimately approached the intrinsic CO₂ hydrate formation rate. Tajma et al. [33] also carried out CO₂ hydrate formation experiments to elucidate the effects of mixing functions of the static mixer on CO₂ hydrate formation. In conclusion, although the presence of tomato juice does not affect the equilibrium conditions of CO₂ hydrate, it can impact the kinetics of the hydrate formation due to the texture in tomato juice. The solid particles in the mixture may serve as nuclei for initiating the hydrate formation, which may accelerate the CO₂ hydrate formation [19,29].

<table>
<thead>
<tr>
<th>Pressure, MPa</th>
<th>$ak f$/$\text{J}^{-1} \text{mol}^2 \text{s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.81</td>
<td>0.94</td>
</tr>
<tr>
<td>2.40</td>
<td>1.36</td>
</tr>
<tr>
<td>3.10</td>
<td>1.65</td>
</tr>
<tr>
<td>3.46</td>
<td>1.82</td>
</tr>
<tr>
<td>3.95</td>
<td>2.01</td>
</tr>
</tbody>
</table>

**CONCLUSIONS**

A novel separation process was developed for tomato juice concentration on the basis of CO₂ hydrate formation. The CO₂ hydrate equilibrium conditions in the presence tomato juice were measured by the isochoric pressure search method. The tomato juice concentration experiments were carried out in a high-pressure stirred reactor under different conditions of feed pressure, temperature, juice volume, and stirring speed. The hydrate equilibrium results show that the tomato juice used in this work has little effect on CO₂ hydrate phase equilibrium conditions, but can accelerate CO₂ hydrate formation. The dehydration ratio increased with increasing the feed pressure and decreasing the temperature. The optimum tomato juice volume was 80 mL and the stirring speed has almost no effect on the dehydration ratio. The CO₂ hydrate formation constants in tomato juice were the same order of magnitude as the results of CH₄ hydrate in the presence of surfactants.

**Acknowledgement**

The authors gratefully acknowledge the National Natural Science Foundation of China (No. 21106085).

**REFERENCES**

Experimental Study of Concentration of Tomato Juice Using CO2 Hydrate Formation

SHIFENG LI1,2, YANMING SHEN2, DONGBING LIU2, LIHUI FAN2, ZHE TAN2, ZHIGANG ZHANG1,2, WENXIU LI1,2, WENPENG LI2

1Liaoning Provincial Key Laboratory of Chemical Separation Technology, Shenyang University of Chemical Technology, Shenyang, Liaoning, China
2College of Chemical Engineering, Shenyang University of Chemical Technology, Shenyang, Liaoning, China

NAUCNI RAD

In the paper, a new technology for concentrating tomato juice using CO2 hydrate formation is presented. The equilibrium conditions of CO2 hydrate are measured using the isochore pressure method. Experiments for concentrating tomato juice were conducted in a reactor under high pressure. Moreover, the dehydration ratio and the formation rate constants of CO2 hydrate under different pressures were defined. The effects of pressure, temperature, and the volume of tomato juice on the dehydration ratio were analyzed. The results show that the tomato juice has almost no effect on the equilibrium of CO2 hydrate, but it can accelerate the formation of CO2 hydrate. The dehydration ratio increases with increasing pressure from 1.81 to 3.95 MPa, and the maximum dehydration ratio can reach 63.2% under a pressure of 3.95 MPa and a tomato juice volume of 80 ml. These results show that water removal using CO2 hydrate is an effective technology for concentrating tomato juice.

Key words: concentration, separation, clathrate hydrate, carbon dioxide, tomato juice.