Potential Application of Innovative Gas Hydrate Technology in Fruit Juices Concentration Process

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ABSTRACT

Novel non-thermal food preservation has gained more interest in the scientific community in lieu of the thermal preservation ones as it enables the conservation of food properties and sensorial characteristics. Furthermore, thermosensitive substances contained in the food can also be preserved. In this study, CO\textsubscript{2} gas hydrate technology used as novel fruit juice concentration and preservation will be presented alongside with two reactor designs studied for the possibilities of the fast hydrate formation and separation processes between the concentrated juices and water.

1. INTRODUCTION

As human population becomes more and more conscious about their health and well-being, they also become aware about their choice of food and drinks. Due to their capabilities to provide various health benefits through different nutrients, fruit juices are currently have rising demand as healthy and nutritious drink. (Caswell 2009) Currently, the global juice market keeps expanding at the annual growth rate of 3\% and still expected to have even a higher growth rate. (Rajauria and Tiwari 2018) However, due to their perishable nature, innovative preservation and concentration technologies become more and more crucial in order to fulfill the global demand. Preservation techniques relying on thermal treatments have resulted in the change or even deterioration precious substances contained in the fruit juices. Thus, novel non-thermal food preservation, such as CO\textsubscript{2} gas hydrate technology, has emerged as an interesting alternative as it enables the conservation of food properties and sensorial characteristics, such as flavor, color and mouthfeel. Furthermore, thermosensitive substances, e.g. vitamins, polyphenol content and microbial load are also preserved.

As general understanding, gas hydrates (GH), also known as clathrates, are crystalline solids that are formed when water and gas come into contact under “elevated” pressure and low temperatures. The gas molecules (“guest molecules”) are enclosed in the water molecule cages (“host molecules”) which is interconnected with hydrogen bonds. (Koh et al. 2011) As CO\textsubscript{2} gas is considered to be safe and has been widely applied in the food processing industry, CO\textsubscript{2} gas hydrate technology seems to be a gentle, novel technology to concentrate fruit juices.
Conventional evaporation process requires the temperatures up to 80 °C and has energy demand of 180–2,160 kJ/kg water (depending on the system) to reach concentration degree between 65% and 85%. However, this process leads to a loss of heat-sensitive and volatile components (vitamins, aroma compounds and other valuable substances (e.g. polyphenols)). (Cheryan 2006; Guignon et al. 2012; Jiao et al. 2004; Miyawaki 2003; Taylor 2007) During the freeze concentration, the process requires an energy demand of 936–1,800 kJ/kg water but can only achieve a degree of concentration of 55%. (Miyawaki 2003; Taylor 2007; Schwartzberg 1990) The application of CO$_2$ gas hydrate technology provides a more energy-efficient process with an energy demand of 252–360 kJ/kg water. In this case, the products can theoretically reach a degree of concentration up to 99%. (Li et al. 2015) Due to the nature of the gas hydrates as well as due to their small cavity sizes, only the CO$_2$ and water can make the gas hydrate, thus enable the severance of water molecules from the fruit juices.

In this presented work, phase equilibrium of three fruit juices (two mostly consumed juices, i.e. orange and apple juices, and sea buckthorn juice, which is dubbed as “superfood” due to their richness in vitamins and other active ingredients) are investigated. Furthermore, the attempts to concentrate the juices in two different type reactors, bubble column and spray tower, will also be presented.

2. DEVELOPMENT OF EQUILIBRIUM CURVES

For the development of the gas hydrate equilibrium curve for different systems investigated, all experiments were carried in a cylindrical pressure optical cell (up to 350 bar) with the volume of 12 mL equipped four sapphire glasses for optical access and a cooling mantle to maintain/control the temperature with the help of a circulating chiller (ThermoScientific™ Arctic A28).

The hydrates are formed using 7 mL commercially available fruit juices, cooled down to 273.65 ± 0.5 K followed by the injection of high purity CO$_2$ (99.95%) pressure into the pressure cell. The hydrate was then left for ca. twelve hours to be fully grown prior to the dissociation procedure. The pressure and temperature are monitored continuously using pressure transducer (Omega PX409-2.5 KAUSBH) within a relative uncertainty lower than 1%, while the whole experiment was also recorded using a 1920 × 1080 CMOS color camera (IDS UI-3590CP-C-HQ Rev. 2) equipped with a macro lens (Canon EF 180mm f/3.5 L Macro USM Lens). The experimental setup for hydrate experiments is depicted in figure 1.
During the dissociation experiment following the hydrate formation, the system was subjected to a slow temperature increase with the rate of 0.5 K over 10 minutes followed by keeping the temperature value constant for another 110 minutes. The temperature ramps were repeated until the gas hydrate was fully dissociated.

Close to the phase equilibrium line, the increasing temperature causes the dissociation of some of the hydrate, and thus CO\(_2\) gas is released. As a result, the pressure of the system is increased, resulted in the hydrate being stabilized again. These alternating processes (hydrate dissociation and hydrate stabilization due pressure increase) continue until the amount of CO\(_2\) gas in the system was no longer enough to maintain stable hydrate structures.

In order to determine the phase equilibrium lines, the pressure and temperature at which the hydrate dissociated were points of interest and based on those points, the equilibrium lines of system of interest can be established. Furthermore, using those points, the hydrate dissociation enthalpy can then be calculated using the Clausius-Clapeyron equation (equation (1))

\[
\ln P_{eq} = -\frac{\Delta H_d}{z \cdot R} \cdot \left( \frac{1}{T_{eq}} \right) + c
\]

Where \( P_{eq} \) is the equilibrium pressure in bar, \( T_{eq} \) is the equilibrium temperature in K, \( \Delta H_d \) is the dissociation enthalpy in kJ/mol, \( z \) is the compressibility factor (unity for ideal gas) and \( R \) is the gas constant (= 8.314·10\(^{-3}\) kJ/(K·mol)). The application of the Clausius-Clapeyron equation for these multi component systems (i.e.
fruit juices) is thermodynamically correct if the system under consideration is univariant which is the case for simple hydrate. (Sloan Jr and Koh 2007)

The expansion of the equilibrium line to commercial juices, represented by common 100% orange juice, 100% apple juice and 100% buckthorn juice, were carried out also in the pressure cell. The juices were tested without any treatment beforehand. The contents of the juices tested in this work can be read in Table 1.

**Table 1. Relevant values and parameter for commercial orange juice (average values)**

<table>
<thead>
<tr>
<th>Constituent/Parameter</th>
<th>Orange Juice*</th>
<th>Apple Juice*</th>
<th>Sea Buckthorn Juice**</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH value</td>
<td>3.2 – 4.3</td>
<td>~ 3.5</td>
<td>~ 2.7</td>
</tr>
<tr>
<td>°Brix</td>
<td>11.18 – 13.54</td>
<td>11.18 – 14.01</td>
<td>6.4 – 22.74</td>
</tr>
<tr>
<td>Ethanol</td>
<td>max. 3.0 g·L⁻¹</td>
<td>0.05 – 0.27 g·L⁻¹</td>
<td>N/A</td>
</tr>
<tr>
<td>L-Ascorbic Acid</td>
<td>23 – 66 mg·L⁻¹</td>
<td>0.7 – 2.0 mg·L⁻¹</td>
<td>360 – 2,500 mg/100 g</td>
</tr>
<tr>
<td>Total carotenoid content</td>
<td>max. 15 mg·L⁻¹</td>
<td>30 – 60 µg·L⁻¹</td>
<td>2.0 – 34.5 mg/100 g</td>
</tr>
</tbody>
</table>

* (Souci et al. 2000; Lozano 2006; WERTE 1987)
** (Singh et al. 2003-<2014>; Li and Beveridge 2003)

The equilibrium line for all systems under investigations alongside with the data reported in the literature for water/CO₂ can be seen in figure 2 (for orange juice), figure 3 (for apple juice) and figure 4 (for sea buckthorn juice) below.

*Figure 2: Equilibrium curve of commercial orange juice compared with the value of water/CO₂ system from references. (Sloan Jr and Koh 2007; Carroll 2014)*
Figure 3: Equilibrium curve of commercial apple juice compared with the value of water/CO$_2$ system from references. (Sloan Jr and Koh 2007; Carroll 2014)

Figure 4: Equilibrium curve of commercial sea buckthorn juice compared with the value of water/CO$_2$ system from references. (Sloan Jr and Koh 2007; Carroll 2014)
The dissociation enthalpy for different CO$_2$/fruit juice systems were found to be in the range of value reported for CO$_2$/water system (between 80 kJ/mol and 90 kJ/mol) are depicted in table 2, hinting that the hydrate formed, only consist of water and carbon dioxide. (Sloan Jr and Koh 2007; Carroll 2014) The shift of the equilibrium lines can be explained due to the interactions of several substances (e.g. pectin, proteins, carboxyl) contained inside the fruit juices that acted as inhibitors for the hydrate formation.

Table 2. Dissociation enthalpy of hydrates formed from various systems (water and fruit juices)

<table>
<thead>
<tr>
<th>System</th>
<th>$\Delta H_d$/ kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ / Water$^*$</td>
<td>85.19</td>
</tr>
<tr>
<td>CO$_2$ / Orange Juice</td>
<td>85.32</td>
</tr>
<tr>
<td>CO$_2$ / Apple Juice</td>
<td>86.64</td>
</tr>
<tr>
<td>CO$_2$ / Sea Buckthorn Juice</td>
<td>89.38</td>
</tr>
</tbody>
</table>

* (Sloan Jr and Koh 2007)

3. GAS HYDRATE JUICE CONCENTRATION BY BUBBLE COLUMN

In order to obtain juice concentrates, one possible way is to operate a CO$_2$ bubble column. Compared to a static system the thereby achieved mixing of the two phases, gas and juice, is remarkably enhanced which leads to faster reaction rates and therefore gas hydrate formation. For the concentration process pressures of 30 – 45 bar and temperatures of 0 – 10 °C were applied in a 1.5 L high pressure reactor (Figure 5). The reactor is equipped with sapphire glasses, a cooling jacket with a circulating chiller (Lauda-Brinkmann® L002326 Proline RP 855), a LED (Toshiba G4 1.2W warm white) which is placed near the reactor lid and an endoscope camera (Voltcraft BS-22 HD). Furthermore, a pressure sensor (B + B Sensors DRTR-AL-10V-R100B) and thermocouples are installed to continuously measure and record (MC Measurement Computing USB-2408) the hydrate formation process. The experiments comprised apple juice and varying volumes thereof in the range of 450 – 750 mL. Additionally, the length of the experiments had been varied (1 – 24 h).
For the analysis on the influence of different pressures on the gas hydrate formation and therefore the concentration process, each experiment had a duration of two hours and was carried out with 600 mL apple juice (10.4 °Brix). In both, the lower (30 – 37.5 bar) and higher (42.5 – 45 bar) pressure ranges, the respectively concentrated juice contained just around 12 – 15.5 °Brix while the application of 40 bar showed the best results with an average of around 20 °Brix.

After an experiment duration of 24 h at 40 bar, 450 mL of apple juice was too little to receive any concentrate in this set-up, whilst 750 mL juice led to a volume of around 230 mL concentrate, unfortunately with only an average of 16 °Brix. The optimal volume of apple juice for this type of reactor had been demonstrated to be between 500 and 600 mL which led to a concentration up to ca. 28 °Brix.

Concerning the length of the experiments, it can be stressed that the longer the bubble column is running the higher the degree of concentration of the apple juice, but also the lower the yield. A typical experiment within the bubble column is shown in figure 6.
4. GAS HYDRATE JUICE CONCENTRATION BY SPRAY TOWER

To allow detailed observations of hydrate formation via spraying, a 1.1-liter stainless steel pressure vessel was designed. Figure 7 shows the vessel and periphery needed for the whole process. The autoclave is temperature controlled by a mantle cooling and equipped with a total of five borosilicate windows (not depicted) with a diameter of 30 mm. Two of them are located at the very bottom and the others at the very top with a spacing of 180° and 90° respectively. Liquid is supplied by a piston pump (EcoSmart, LEWA) and injected through a nozzle (LNN 0.4, Spraying Systems Co.) resulting in a droplet size of approx. 25 μm according to the supplier. The feed temperature is permanently kept constant by multiple chillers for the feed storage tank and the piping from the pump to the reactor. A stainless-steel sieve was placed on top of the bottom lid for separation of the formed hydrate and the unreacted liquid. It retains the hydrate crystals whilst the residual fluid can pass and be sampled.

Each experimental run was commenced by: (1) cooling the storage tank, the pressure vessel and the feed piping to the desired value; (2) flushing the vessel three times with CO₂ to remove any residual air; (3) setting the pressure to the desired value by supplying CO₂; and then (4) starting the pump and opening the stop valve located between the feed line and the nozzle to allow the fluid to burst through the nozzle. During each run the pressure and temperature are constantly being measured.
Figure 7: Experimental set-up for hydrate formation using spray tower

For each experiment, the conversion ratio and the respective driving force are calculated in accordance to equation (2) and equation (3):

$$\eta = \frac{m_{hydrate}}{m_{injection}} \cdot 100\%$$  \hspace{1cm} (2)

Where \( \eta \) is the conversion ratio in %. This equation corresponds to the ratio of the mass of the hydrate formed to the total mass injected to the system through the spray system. The latter was measured by letting the formed hydrate dissociate completely and weighing the residuals. The driving force at a certain temperature \( T \) and pressure \( P \) in comparison to the equilibrium pressure \( P_{eq} \) is defined as the molar Gibbs free energy \( |\Delta g| \) (the absolute value was taken to render the expression positive):

$$\Delta g = \Delta u \cdot (P - P_{eq}) + R \cdot T \cdot \sum x_i \ln \left( \frac{f_{i,eq}}{f_{i,exp}} \right)$$  \hspace{1cm} (3)

Where \( f_{i,eq} \) and \( f_{i,exp} \) are the respective fugacities of component \( i \) (only CO\(_2\) here) in the gas phase at equilibrium and experimental conditions and \( x_i \) is the mole fraction of component \( i \) in the gas phase. Equations of state (EOS) can be used to calculate these parameters, here Peng-Robinson EOS was applied. \( \Delta u \) represents the difference in the molar volume of water in hydrate and the molar volume of liquid water. Last, \( R \) is the ideal gas constant at 8.314·10\(^{-3}\) kJ/(K·mol). For a more thorough explanation the reader is referred to Daniel-David et al. (Daniel-David et al. 2015)

Preliminary experiments with a water spray at conditions specified in Table 3 showed rapid hydrate formation as depicted in Figure 8.
Figure 8: Gas hydrate formation within sprayed water. Residual water formed initial hydrates as seen in (1). The window is located directly above the bottom lid and the spray comes from the top lid. Timestamps: $t_1=0\ s$, $t_2=20\ s$, $t_3=45\ s$ and $t_4=90\ s$.

Hydrates start to form immediately after the water is leaving the nozzle and start to accumulate on top of the sieve in the form of fine droplets covered by a hydrate shell. From picture (3) to (4) one can see that at progressed time the formed hydrate becomes more and more like a slurry and less rigid. This phenomenon comes from the poor heat removal via the gas phase whilst the hydrate formation being an exothermic reaction. (Sloan Jr and Koh 2007) It results in an increased reactor temperature, in the depicted case from 0.75 °C up to 5.5 °C and therefore reducing the overall dimensionless driving force $\frac{|\Delta g|}{R\cdot T}$ from 0.918 to 0.031. Apparently, water injection then happens at a higher rate as the hydrate formation, resulting in a less rigid product. For further experiments the amount of total sprayed mass was there for reduced in order to prevent uncomplete hydrate formation.

Table 3: Experimental condition in the spray tower system for different system

<table>
<thead>
<tr>
<th>Feed</th>
<th>P / bar</th>
<th>T / °C</th>
<th>Total Mass Sprayed / g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>33</td>
<td>0.75</td>
<td>200</td>
</tr>
<tr>
<td>Apple Juice</td>
<td>33; 30</td>
<td>-1; 0; 1</td>
<td>100</td>
</tr>
<tr>
<td>Orange Juice</td>
<td>33; 30</td>
<td>-1; 0; 1</td>
<td>100</td>
</tr>
</tbody>
</table>

* For each experiment the volume flowrate was set to constant value of 3.5 l/h, the experiment was stopped after spraying the specified mass and each run was conducted three times. Apple and orange juices had an initial sugar content of 10°Brix and 11°Brix respectively.
The formation of apple and orange juice hydrate was more closely studied by varying the applied formation pressure and temperature to investigate their influence on hydrate conversion rates. Figure 9 shows the respective conversion rates of apple juice into hydrate relative to the applied pressure and temperature, while in figure 10, the same is depicted for orange juice.

**Figure 9:** Conversion rates of apple juice at 30 and 33 bars at different temperatures as indicated with their respective measurement uncertainty.

**Figure 10:** Conversion rates of orange juice at 30 and 33 bars at different temperatures as indicated with their respective measurement uncertainty.

The graphs show a general trend that the conversion rate decreases with increasing temperature although the one for apple juice at -1 °C and 30 bar in Figure 9...
is unexpectedly small compared to 0 °C. Overall apple juice shows much higher conversion rates at the same conditions compared to orange juice (67 % maximum conversion compared to 43 %) as well as a stronger dependency on the varied parameters. While a temperature reduction from e.g. 33 bar and 1 °C to 0 °C increases the conversion rate of orange juice by only 2 %, the rate for apple juice increases by 4 %. This behavior is even more prominent at 0 °C to -1 °C. Figure 11 gives a brief explanation of this, it shows the conversion rates for each juice as a function of the dimensionless driving force. It shows that due the different equilibrium lines the driving force for apple juice at the same conditions is always higher than the one for orange juice. Therefore a change in temperature, for example, has a more prominent effect on the conversion rate of apple juice hydrate as it would have on orange juice hydrate. The graph also shows, as previously reported in the literature, that a higher driving force results in a more rapid hydrate formation and therefore in a higher conversion rate. (Ma et al. 2002; Yang et al. 2011)

![Figure 11: Comparison of the conversion rates of apple and orange juice over the dimensionless driving force. The dimensionless driving force $\frac{|\Delta g|}{RT}$ was calculated according to Eq. (3) with the respective values for $P_{eq}$ from the previously reported equilibrium lines. The dashed lines represent the general trend of the calculated values. –A & -O are apple and orange juice respectively. Even though the hydrates were formed at similar conditions, the driving forces are different due to different reference temperatures $T_{eq}$ and pressures $P_{eq}$.](image)

However, as mentioned in the previous paragraph the conversion rate for apple juice at 30 bar and -1 °C is smaller as the driving force would suggest. It has a value of around 0.9, while apple juice at 33 bar and 0 °C is approx. 0.86 and yet has a higher conversion rate. Furthermore, orange juice conversion rates in general showed an unexpected behavior as seen in Figure 10 and Figure 11. Despite increasing driving
force, the yield does not increase significantly unlike apple juice. Currently, the authors cannot explain this behavior and further investigation is needed.

5. CONCLUSIONS

The hydrate formation and dissociation for three commercial fruit juices (orange, apple and sea buckthorn) have been successfully carried out in an optical cell. The value of the hydrate dissociation enthalpy for these three different fruit juices systems were found to be in the same range with the value reported in the references for water/CO$_2$ system, hinting that the hydrate was only composed of water and carbon dioxide. The shift in equilibrium lines was due to the interactions of substances contain in the fruit juices that might acted as inhibitors (and promotors).

In order to be applied in industrial processes, it is critical to have an accelerated gas hydrate formation thus allowing the system to process a large quantities of fruit juices continuously. In this regard, the rate of the formation of the gas hydrate can be improved by increasing the contact area between phases (i.e. CO$_2$ and juice) involved in the process. The application of the bubble column has showed an improved mixing of both phases which led to an improved and accelerated gas hydrate formation and therefore also led to shorter time to produce the desired juice concentration, even under varying conditions.

With a spraying system rapid hydrate formation rates could be achieved, not only for water but also apple and orange juice. A maximum conversion rate of 67 % at 33 bar and -1 °C for apple juice and 43% at 30 bar and -1 °C for orange juice were reported. These values were in the same order of magnitude as reported by other authors (Li et al. 2015) but have been achieved within seconds in the spray chamber compared to hours in a stirred tank reactor. However, the strong exothermic formation reaction and poor heat transfer in the gas phase limited the continuity of the process to several hundreds of grams. Furthermore, orange juice showed an unexpectedly strong restraint if terms of conversion ratio, which cannot fully be explained.

Novel CO$_2$ gas hydrate technology is promising technology to be applied in the field of food preservation as it offers unique approach to solve the increasing demand of the nutritious drinks coupled with the preservation of the valuable substances contained inside for a healthier lifestyle.

FUNDING

This Industrial Community Research (IGF – Industrielle Gemeinschaftsforschung) project is funded by German Federal Ministry of Economics and Technology (BMWi – Bundesministerium für Wirtschaft und Energie), based on a resolution of the German Parliament, via Research Association of the German Food Industry (FEI – Forschungskreis der Ernährungsindustrie e.V.).

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