Food and Bioprocess Technology (2021) 14:1758–1762
https://doi.org/10.1007/s11947-021-02656-5

COMMUNICATION

A Future Road Map for Carbon Dioxide (CO_2) Gas Hydrate as an Emerging Technology in Food Research

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Received: 31 January 2021 / Accepted: 22 April 2021 / Published online: 3 May 2021

Abstract

Gas hydrates constitute of gas as a guest molecule in hydrogen-bonded water lattices. This review covers ongoing hydrate research in food technology with a spotlight on carbon dioxide (CO_2) application as a hydrate. The application of gas hydrates in the concentration of juices, desalination, carbonation, and food preservation has been covered in the review. One of the applications of CO_2 hydrate technology was in the concentration of orange juice which gave a dehydration ratio (DR) of 57.2% at a pressure of 4.1 MPa. Similarly, one study applied it for the tomato juice concentration and had a DR of 65.2%. The CO_2 hydrate rate constants recorded were 0.94×10^{-8} and 1.65×10^{-8} J^{-1} mol^2 s^{-1} at a feed pressure of 1.81 and 3.1 MPa respectively. Hence, CO_2 hydrate can be used effectively for the juice concentration as well as for other applications too. The review will cater insights on the generic trends of hydrates in food research with respect to their kinetics properties and their role in food applications. Despite the fact that there are no technology stoppers to exploit CO_2 hydrates, a downright technological quantum leap is the need of the future in this riveting field. Thus, the perspectives and key challenges in food research are also discussed. The food applications of CO_2 gas hydrates are still very scarce so there is an urge to carry through more theoretical and experimental analysis to elucidate various applications of hydrates in food and to positively validate its sustainability.

Keywords CO_2 hydrates · Thermodynamics · Kinetics · Food applications

Introduction

In the last decennium, gas hydrate research has gained attention in different fields. Inspiringly, the research not only hones in the formation of gas hydrates but also as a plausible cutting edge separation technology. Giant strides of gas hydrates in a number of fields have been leading-edge; these fields, especially in food research, consist of desalination, aqueous solution concentration, and waste minimization. The concentration of fruit juices, enzymes, and fluid solutes by gas hydrates has been described by some researchers (Huang et al. 1966).

Gas hydrates are crystal/cage-like structure which forms between water and guest (carbon dioxide, methane, and ethane) molecules at temperature 273 K and 1–10 MPa pressure range depending on the guest molecules (Hassanpouryouzband et al. 2020). They are the point of attraction in research because of their ingenious applications in an outstretched lineup of a scientific and industrial frame of reference (Uchida et al. 1999). The antediluvian era research on gas hydrates chiefly has an upper hand on researches related to gas pipeline blockage, energy recovery, improved flow assurance, and refrigeration. Nevertheless, in recent times, the aggrandizement in food research was ablaze by the gas hydrate applications to CO_2 capture/storage, separation of gas, and desalination of water. In recent times, experiments fostered by theory-based calculations bring out a significant increase in the worthiness of the gas hydrate applications, which necessitate more food technology development with a new blueprint. This could not be followed through without collaborative attempts among researchers in food and engineering.

Thus, the review comprehends the advances in gas hydrates with a spotlight on CO_2 gas hydrates, especially the practical applications in food such as juice concentration, carbonation, and desalination to date which were applied over the commonly used techniques such as freeze-drying, thermal evaporation, and reverse osmosis. The review also highlights how this gas hydrate technology can be used in several other applications in the near future.

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Gas Hydrates

Gas hydrates comprise basically of three structures, viz. cubic structure I (sI), cubic structure II (sII), and the hexagonal structure (sH). The water molecule arrangement for each structure is different with different cavity diameters (7.91 Å in sI 5^{12}, 7.82 Å in sII 5^{12}, 11.58 Å in sH $5^{12}6^8$ cage) to reside the molecules of gas. The formation of hydrate structure depends upon the chemical nature of gas, pressure, and temperature conditions (Hassanpouryouzband et al. 2020).

CO_2 Hydrates

CO_2 hydrates are constituted as structure I (sI) among the other structures (sII and sH). The structure and number of cages in a unit cell rely upon the size of cages, i.e., either M-cage or S-cage (M - medium and S - small). The sI structure has 6 medium size cage comprising 12 pentagonal and 2 hexagonal faces ($5^{12}6^2$), and 2 small size cage comprising 12 pentagonal faces (5^{12}). The cage structure also has water molecules held by hydrogen (H-) bond with an internal void per cage containing guest molecules at particular temperature and pressure (Li et al. 2009; Peters et al. 2013). Thus, CO_2 hydrates are represented by the formula $CO_2.nH_2O$ where n is the hydration number. CO_2 molecules can also constitute large cages (L) in sII hydrate structure with propane and cyclopentane ($5^{12}6^4$). Moreover, at temperatures 273–283 K, the phase equilibrium pressure of CO_2 hydrate is more than 10 and 200 MPa less than that of O_2 and H_2 hydrates respectively (Ota et al. 2005).

Food Applications

In recent times, several food applications of gas hydrates have been reported. One of the first applications of gas hydrates was in 1966 by Huang et al. for the concentration of juices. They inspected concentrating the tomato, apple, and orange juice by CH_3Br and CCl_3F hydrates. Their results indicated color and flavor loss with a bitter aftertaste in juices. Other gas hydrate applications available to date such as desalination, food preservation, and carbonation are described in a more detailed view in the next few sections.

The liquid foods are mostly concentrated either by freeze-drying, thermal evaporation, or reverse osmosis. However, inappropriate selection for the concentration process may lead to unfavorable changes in the nutritional and sensory attributes of the product (Adnan et al. 2018). Operation of gas hydrate technology in that event has the aspects of being an upbeat alternative because of mild temperature and higher concentration levels. The gas hydrates were used for the concentration of sugar syrup, but due to large volumes at high pressure, the process was found unsuitable. Moreover, it was also suggested that gas hydrates can be used to concentrate sensitive products, mostly liquids Andersen and Thomsen (2009). Looking over to the research done, until now the gas hydrates have been used for the concentration of liquid foods such as coffee and juices (Claßen et al. 2020; Li et al., 2015a, b; Purwanto et al. 2014; Seidl et al. 2019). However, no one reported with respect to the product stability and quality as Huang et al. (1966).

Gas Hydrate for the Concentration of Coffee Solution Under High Pressure

Purwanto et al. (2014) used xenon (Xe) gas hydrate for the concentration of coffee solution at 9 °C with a Xe partial pressure of 0.9 MPa. An increase in stirring rate resulted in more Xe hydrate formation which was small in size, but an increase in temperature to 14 °C lowered the concentration efficiency as the dissolution of Xe gas in coffee solution was increased. Thus, Xe or other gas hydrates might be effectively used for the concentration of other liquid solutions too.

CO_2 Gas Hydrate Technology for the Concentration of Juices

Apple Juice

CO_2 hydrate technology was used for the concentration of apple juice at a pressure range of 30–80 × 10^5 Pascal and a temperature range of 274–283 K (Seidl et al. 2019). The apple juice concentration was achieved 21–27° Brix indicating 60% of the juice was trapped inside the gas hydrate. The dissociation enthalpy (DE) of the apple juice was 52 J·mol^{-1} which lied in the range of other DE reported for a H_2O-CO_2 system. Thus, the correct evaluation of this technology depends upon the phase equilibrium lines of juices, and bubble column effect on the gas hydrate formation/separation. Moreover, the numerical modeling in terms of simulation (temperature, pressure, and velocity) for the concentration product should also be done. Another study was performed by Claßen et al. (2020) for the concentration of apple juice to high sugar content at 35 bar pressure. The juice was concentrated until 45° Brix and the formation of hydrates was somewhat interfered due to the chemical composition of the juice when 30° Brix was achieved.

Orange Juice

CO_2 hydrate technology was also used for the concentration of orange juice by means of an isochoric pressure search method (Li et al. 2015a). The effects of temperature, pressure of feed, stirring speed, and juice volume on the dehydration ratio (DR) were explored. An increase in DR was observed with the increase in the pressure of feed. A maximum DR of 57.2% was achieved at pressure 4.1 MPa of feed, while DR was constant (45.8%) at a temperature range of 274–279 K. The DE for the orange juice was 86.5 kJmol^{-1} while the rate constant had a value of 0.6×10^{-8} mol^2 s^{-1} J^{-1} at 1.9 MPa but it increased (1.9×10^{-8} mol^2 s^{-1} J^{-1}) when the feed pressure was increased to 4.1 MPa. Hence, CO_2 hydrate can be used effectively for orange juice concentration.

Tomato Juice

CO_2 hydrate was also used by Li et al. (2015b) for the tomato juice concentration which gave a maximum DR of 65.2% at pressure 3.95 MPa of feed. Also, the DR increased when the feed pressure was increased from 1.81 to 3.95 MPa. The CO_2 hydrate rate constants recorded were 0.94×10^{-8}, 1.65×10^{-8}, and 2.01×10^{-8} J^{-1} mol^2 s^{-1} at a feed pressure of 1.81, 3.1, and 3.95 MPa respectively.

Despite the fact that there has been advancement in the field of hydrate concentration, there exists another stumbling block for its application in the industry, which is the time facet. One of the studies by Safari and Varaminian (2019) found that kinetics of CO_2 gas hydrate formation was inhibited by the sugar, while another study by Andersen and Thomsen (2009) reported no significant change in CO_2 hydrate formation kinetics for the same. Furthermore, the average time of hydrate formation to yield maximum concentration was in hours which was quite impractical when one has to deal with large quantities (1000 kg/s) of liquid food/juice (Adnan et al. 2018). Hence, in the near future, such limitations must be overcome by decreasing the time of induction and increasing the growth rate of hydrates.

Desalination by Gas Hydrate Technology

Gas hydrate technology in comparison to thermal distillation, reverse osmosis (RO), and pressure-driven technologies for the desalination of H_2O has several merits in terms of energy required cost of production, and the environmental effect (Youssef et al. 2014). The thermal distillation method requires more making it quite expensive, while in RO technology with the passage of time the accumulation of salts on surface membrane keeps on increasing, ultimately leading to fouling (Han et al. 2017). One of the positive discoveries with gas hydrate was reported by Park et al. (2011) who altogether made a process design for separating hydrate crystals from the brine (concentration) solution with the application of a pelletizer (dual cylinder having pistons). This process not only extracted gas hydrate from the brine but also removed the water left from the hydrate slurry. Thus, 78% of H_2O salinity was removed efficiently with the application of gas hydrate. Moreover, the efficiency of the salt removal was equivalent to the cation radius (ionic) in the specified order $K^+ > Na^+ > Mg^{2+} > B^{3+}$. Further examination by a Raman spectrometer explained that the minerals dissolved in seawater had no effect on the structure of hydrates. Thus, the hydrate process for desalination efficiency can be improved further if multisteps are involved during the hydrate process (Park et al. 2011). Taking forward to the research, Kang et al. (2014) used a similar design to examine the cation (Cl^-) and anion (SO_4^{2-}) removal. It was found that the cation and anion removal efficiency was almost the same (76%). New advancement in H_2O desalination with gas hydrates was now focused on the identification of the guest molecules which have the ability to form hydrates at high temperature and above the freezing point of water, thereby making it more convenient in terms of energy demand McCormack and Niblock (2000). Cyclopentane at atmospheric pressure and 280.9 K temperature was identified as hydrate former for the process of desalination having low energy requirements Cha and Seol (2013). Adding to the above findings, Han et al. (2017) found a highly powerful H_2O desalination technique using hydrate of cyclopentane which removes approximately 63% of the ions after hydrate formation. Moreover, if successive washing with H_2O was done at temperatures of 274 and 277 K, then the salt removal efficiency increased to 72 and 83% respectively. Furthermore, the effects of derivatives of cyclopentane for promoting CO_2 hydrate formation with H_2O were also reported (Hong et al. 2019). The cyclopentanone, a derivative of cyclopentane, had the smallest induction time with the highest conversion yield for the gas hydrate desalination process. Another promising attempt to decrease the energy demand for gas hydrate H_2O desalination process was done by He et al. (2018). The findings deduced application of liquefied natural gas instead of refrigeration cycle can decrease the energy consumption to 0.6–0.8 kWh m^{-3} which is equivalent to 18–24% of the energy demand for the RO process.

Gas Hydrate Application in Carbonation of Food

CO_2 gas hydrates were used as a carbonation compound in frozen desserts by mixing the CO_2 hydrates with frozen desserts (Peters et al. 2013). The bubbling effect was created due to the CO_2 released during thawing or consumption. Also, a flash freezing technique was brought in for the production in which H_2O was mixed with liquid CO_2 and then sprayed. The CO_2 evaporation after the expansion allowed subcooling of the droplets which are crucial for fast nucleation and growth of hydrates, thus making the hydrate stability much tougher even outside the thermodynamic equilibrium. Still, the research on CO_2 hydrate applications is very scarce in literature so the broader picture in terms of its advantages should be given prime importance.

Prospects and Key Challenges in Food Research

Despite the fact that some research has been done on CO_2 and other hydrates, still the rationale of the entire process is difficult to understand and some crucial challenges need to be decoded. Hence, some points for it are compiled below:

1. An exhaustive study on how the replacement reaction occurs should be elaborated: how H_2O/CO_2 transportation/rearrangement during replacement reaction takes place, whether before the process of exchange the parent hydrate dissociates or not is very well explained and thus requires further insights.
2. Kinetics of CO_2 production from injection: However, some studies reported the rate of CO_2 production, but still it is not clear whether some conditions favor the production and drive the dissociation or there is CO_2 replacement. Also, the CO_2 hydrate formation kinetics via sequestration of CO_2 or guest exchange process is still not answered.
3. Knowledge on mass and heat transfer during the process of exchange: Since the exchange process associates a give-and-take of hydrate dissociation, the mechanism of transport with respect to heat/mass needs to be clarified.
4. Advancement of simulation models: A number of adequate inputs from food research are needed to establish simulation models. The kinetics of hydrates put forward meaningful challenges to food researchers, notably in the modeling part.
5. The time-dependent behavior of hydrates: Different food components exhibit different behaviors even when the same gas hydrate is used because of the presence of promoters and inhibitors during the gas hydrate formation.
6. Way forward towards a more sustainable technology: It is quite obvious that the technology of gas hydrate formation will contribute significantly in the future for the separation processes and it also perhaps has the budding potential to take a way forward towards a more sustainable technology than the existing technologies of separation. Thus, it should be taken into consideration that one of the critical factors in decision-making for surrogate technology to come forward is its economical facet. More clearly stating, the proposed novel method should be economically practicable.

Conclusion

It is irrefutable that sequestering CO_2 as gas hydrates for food research has enormous potential in the near future. Experimental studies in the food sector are quite limited, calling for far-reaching and panoptic future studies. The structural properties of gas hydrates are self-sufficient to open channels for their application in food technology. One of the advantages that these gas hydrates have in food technology is mild conditions required for its formation prompting energy savings and preserving the nutritional/sensory attributes in the food. Recent overture in the science and engineering of gas hydrates is desirous for the unexplored area of food research. These CO_2 gas hydrates can replace existing technologies such as freeze-drying, reverse osmosis, and thermal evaporation for different food products if they are applied effectively. To recapitulate, in order to prove the sustainability in the technology of gas hydrates, experimental calculations (induction time, phase behavior, formation rate) should be supplemented with theoretical work (molecular simulation, kinetic modeling) and economical aspects (cost of production, financial assets) for persuasion of food research in the future.

Acknowledgements This IGF project of the FEI is/was supported via AiF (21084 N) within the program for promoting the Industrial Collective Research (IGF) of the German Ministry of Economics and Energy (BMWi), bases on a resolution of the German Parliament for which the authors are grateful.

Availability of Data and Material Not applicable.

Author Contribution Shubhangi Srivastava: writing - original draft preparation, revision and editing; Bernd Hitzmann: conceptualization, project administration, supervision, writing - review and editing; Viktoria Zettel: supervision, review and editing.

Funding Open Access funding enabled and organized by Projekt DEAL.

Declarations

This article does not contain any studies with human participants or animals performed by any of the authors.

Ethics Approval Not applicable.

Conflict of Interest The authors declare no competing interests.

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