Carbon Dioxide Hydrate Inhibition and Energy Requirements in Systems Relevant to Gas Hydrate-based Fruit Juice Concentration

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Abstract—Hydrate-based technology has emerged as a possible alternative preserving technology in the juice industry. This is due to the technology's favourable advantages over well-known concentration technologies, including low energy requirements and food freshness preservation. As the juice industry is currently experiencing increasing demand from consumers, the industry's energy demand has risen sharply. In this context, hydrate-based juice concentration has been identified as a less energy-intensive process still preserving product quality. However, phase equilibrium data are essential to design and analyse such a process. Experimental dissociation conditions measurements for grape/pineapple/bitter melon juice were investigated at different water cuts and dissociation conditions (*P-T*). The study revealed inhibitory effects as pressure shifted to higher values while temperature shifted to lower values. The Clausius-Clapeyron equation was used to determine the enthalpy of dissociation at reported experimental dissociation conditions for investigated systems to assess the energy requirements of CO_2 hydrate-based technology. This study revealed that it is possible to use CO_2 hydrate-based technology as an alternative technology for juice concentration.

Keywords—Fruit juice; gas hydrate dissociation; carbon dioxide; molar dissociation enthalpy **r**enewable energy, blue energy, reverse electrodialysis, water, Southern Africa.

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I. INTRODUCTION

The world's population is expected to reach 9.8 billion people by 2050. As it continues to grow, there is a growing concern about ways to prevent food shortages as food production needs are predicted to increase by 50%. Growing demand for juice has contributed to rising food shortages and energy demand challenges. Additionally, a 45% increase in energy demand by 2050 will lead to an energy crisis as fossil fuel reserves are depleting. Since current juice concentration technologies are heavily reliant on energy, this energy crisis has profoundly impacted the juice industry. Uncontrolled increase of fossil fuel consumption would amount to ignoring environmental regulations as well as international regulations meant to protect the environment (Net-Zero carbon emissions) [1–3].

It takes energy to grow, process, package, distribute, store, prepare, and dispose of food. Due to UN initiatives and environmental legislation, the juice industry has attempted to reduce its energy consumption. As an alternative to thermal evaporation (180 to 2160 kJ/kg water), well-proven energy conservation technologies (such as freeze-drying and membrane) were used, which led to a quick return on investment. Although these technologies do not use carbon-based energy resources and preserve bioactive juice content, they still have high energy requirements (refrigeration and thermal energy). CO_2 gas hydrate technology remains the most promising alternative to practical and well-established technologies, including thermal evaporation and freeze-drying (936 to 1800 kJ/kg water). Low energy consumption (252 to 360 kJ/kg water) and juice preservation are the advantages of this technology.

The milder conditions required by CO_2 hydrate technology are better suited to fruit juice concentration than conventional methods. A new technology enabling the storage of CO_2 gas in hydrate form presents opportunities for reducing CO_2 emissions by maximising the use of abundant CO_2 gas. Upon lowering carbon emissions, it is considered that alternative energy resources or cold thermal storage options, or carbon-capture, utilisation and storage (CCUS), may be required. CCUS and cold storage have been made possible by gas

hydrate technology. As a result, CO_2 hydrate technology has gained popularity in numerous industries as a popular renewable energy resource. As a result, these CCUS and purification methods are believed to benefit the gas industry. Other sectors can directly purchase purified CO_2 for cold thermal energy storage from this industry. Cold thermal energy storage can benefit various industries, including the juice industry.

As the juice industry is currently using freeze concentration as a more efficient means of removing water while preserving juice bioactive, CO_2 hydrate technology offers a similar benefit. However, the ice formation steps are replaced by gas hydrate nucleation steps in gas hydrate technology. Therefore, to conserve energy without destroying bioactive contents in liquid foods such as juices [4,5,14,6–13] and coffee [15–17], it is feasible to incorporate high concentrations of CO_2 into liquid foods using gas hydrate-based technology. To the best of our knowledge, there is limited research contribution to the study of hydrate-based juice concentration as an alternative to evaporation. In this study, the investigation of CO_2 hydrate-based technology in the juice concentration process was carried out. The experimental hydrate phase equilibrium measurement for juice systems (pineapple/grape/bitter melon) at different water cuts is reported in this study.

II. EXPERIMENTAL SECTION

A. Materials

This study utilised ultrapure Millipore-Q water, fruits, and carbon dioxide (CO_2) gas. A laboratory within this research group produced ultrapure Millipore water. Afrox (South Africa) supplied the CO_2 gas, which was food-grade quality. The fruits (grapes, pineapple, and bitter melon) were bought from a Food lovers' supermarket in KwaZulu-Natal (South Africa, Durban).

B. Experimental set up and procedure

Following an isochoric pressure-search method, a newly developed apparatus was used to measure the hydrate phase equilibrium in dilute juice systems. Detailed descriptions of the experimental setup can be found elsewhere [18,19]. In this context, the following experimental procedure will give a brief description. The present study used the isochoric pressure search method to determine the hydrate dissociation conditions for CO_2 hydrate in a dilute or pure juice solution.

At the beginning of the experiment, the hydrate cell was cleaned and washed with deionised water. The hydrate cell was then placed in a temperature-controlled bath. In this experiment, the temperature-controlled unit named LTC4 (supplied by Grant Instruments, United Kingdom) set the bath temperature outside the hydrates' equilibrium temperature (T = 293.15 K). The hydrate cell was placed under vacuum for approximately 30 minutes at 0.062 MPa. An amount of 40 mL of solution was injected into the vessel, and a vacuum was applied for 3 to 5 minutes. Impurities or air that may have

entered the vessel were removed with this method. The temperature of the vessel was allowed to stabilise. After that was completed, the stirrer was set to 500 rpm. Carbon dioxide was used to load the hydrate cell to its desired pressure. As the hydrate cell temperature and pressure stabilised, the high-pressure equilibrium cell temperature was gradually decreased. As a result of hydrate formation, the pressure suddenly dropped and crystals formed in the reactor. When the pressure had stabilised, the high-pressure equilibrium cell temperature was raised at a rate of 0.1 K per hour until the hydrates had dissociated entirely. During each increment, the system temperature was maintained constant for approximately 3-4 h to stabilise the pressure. Hydrate dissociation occurs when the pressure versus time plot gradients changes dramatically, and the heating (dissociation) and cooling (formation) curves coincide.

III. RESULTS AND DISCUSSION

Considering that the piece of equipment used in this study was brand new, it was necessary to examine its reliability and validity before generating the data on hydrate phase equilibrium. As intensive studies had already been performed on this mixture under hydrate forming conditions, the binary test system consisted of carbon dioxide and pure water (CO_2 + H_2O). Numerous hydrate data are available in the literature for this system. Gas hydrate dissociation points (P and T), under liquid water (L_w) + hydrate (H) + CO_2 vapour (V) equilibrium, for the CO_2 + H_2O test system were measured. A comparison of hydrate dissociation data was also carried out with the literature data [13,20,21]. Fig. 1 presents the experimental data measured in this study and a graphical representation of the same data. The experimental data and the literature data agree for the carbon dioxide + H_2O test system, as shown in Fig. 1.
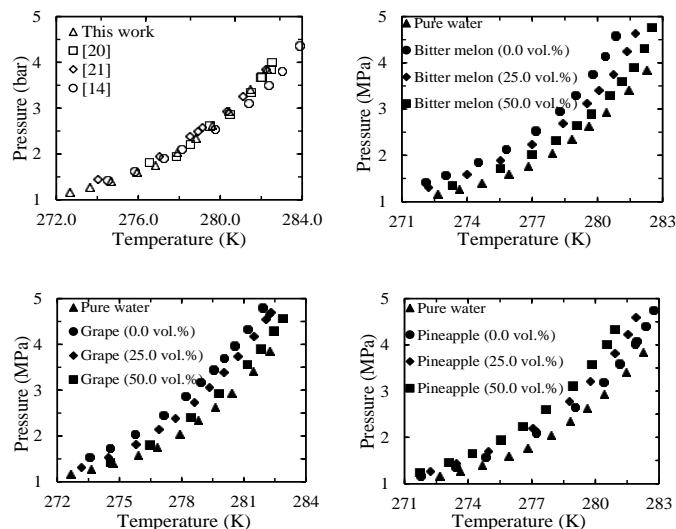

Fig. 1. Experimental dissociation data for carbon dioxide gas hydrate in the pure water [14,20,21] and juice systems.

As shown in Fig. 1, the investigated systems indicated that

the slight increase in equilibrium temperature results in a drastic increase in dissociation pressure. This observed behaviour indicates the possibility of obtaining erroneous dissociation data. Thus, this was prevented by increasing system temperature stepwise by 0.1 K every hour until the equilibrium dissociation point was obtained. It was observed that investigated systems possessed inhibitory effects. This was observed through a shift dissociation curve to lower temperatures and higher-pressure zones. This behaviour confirms the intermolecular interactions between dissolved juice constituents. Moreover, this suggests that the compression costs for these proposed systems will be higher. The authors suggest further experimental investigation on dissolved juice constituents to understand the inhibitory effects observed in this study.

This study also investigated the effect of water cuts as this information is useful for designing a hydrate-based juice concentration process. It was observed that the inhibitory effects due to intermolecular interactions of juice constituents were weakened with an increase in water cut. This suggests that further experimental studies on the strength of each involved juice constituent will be vital in developing the thermodynamic model.

The investigated systems' energy requirements were assessed by estimating the experimental enthalpy of dissociation of CO_2 hydrates using the Clausius-Clapeyron relation and presented in Table 1. The average dissociation enthalpies values for grape, pineapple, and bitter melon investigated juice systems in CO_2 were 67.83 ± 1.5, 64.19 ± 1.5 and 63.44 ± 1.5 kJ/mol of CO_2, respectively. Moreover, it was observed that these values increased slightly. This observed behaviour may be attributed to molecular interactions between CO_2 molecules and the hydrate lattice, which suggests the requirements of higher-pressure and lower temperature conditions to form hydrate.

TABLE I
Enthalpy of formation for hydrates of CO_2

System	Enthalpy (kJ/kg-CO_2)	Reference
CO_2 + H_2O	67.66 ± 1.5	This study
	68.2	[22]
CO_2 + Grape	67.83 ± 1.5	This study
CO_2 + Pineapple	64.19 ± 1.5	This study
CO_2 + Bitter melon	63.44 ± 1.5	This study

IV. CONCLUSION

The addition of water moved the curve to lower pressure and higher temperature region when compared to pure juices. The further shift to even higher temperatures and lower pressures was observed when water additions increased. The observed inhibition effects may not be ignored when predictive thermodynamic models are developed to calculate the dissociation points for the investigated systems. Based on this observed behaviour, it is advisable to undertake experiments and modelling studies on fresh juices rather than commercial (supermarket) juices containing some additives.

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