

## ABSTRACT

The constant rise in energy costs is one of the major challenges confronting the fruit juice industry. As a result, it is in the industry's interest to find environmentally friendly measures that reduce energy consumption while cost-effectively maintaining product quality. In this industry, multi-effect evaporation is used as a traditional technique to reduce the water content of fruit juices. Because of the need for steam, this process is highly energy-intensive. An alternative technology based on renewable energy resources is required to reduce the industry's energy demand while increasing revenues and contributing to the UN's 2050 net-zero carbon emission targets. It is in this context that hydrate-based technology has emerged as a promising approach to meeting the food industry's energy demands and product quality challenges. It is a technology with the potential to contribute to sustainability while also establishing itself as a viable alternative to current juice concentration processes.

This study aimed to investigate gas hydrate-based concentration as an energy-saving process in the fruit-juice energy. However, the rationale and economical design of this hydrate-based fruit juice concentration process would require the knowledge of the equilibrium hydrate forming conditions and their formation kinetics. For this reason, measurements of hydrate phase dissociation conditions and hydrate formation kinetics were conducted experimentally.

The isochoric pressure-search experimental method used a newly developed static high-pressure stainless-steel equilibrium cell to measure the hydrate-vapour-liquid phase equilibrium data. Experimental measurements on hydrate phase equilibrium conditions on a known test system were conducted to test the validity and reliability of the experimental apparatus, calibrations, and method used. This includes gas hydrate dissociation points (P and T) for the CO<sub>2</sub> + H<sub>2</sub>O test system. The experimental method and measurements were accurate and reliable, as shown by the agreement between the results and the literature measured within the acceptable uncertainty. Subsequently, novel systems measured include experimental hydrate phase equilibrium conditions of three systems involving juices (System 1: CO<sub>2</sub> + grape juice; System 2: CO<sub>2</sub> + pineapple juice; System 3: CO<sub>2</sub> + bitter melon juice) at varying juice water cuts from (88.5 to 98.3 ± 2.53) wt.% were generated. In the experimental dissociation conditions reported for the hydrate phase, the temperatures and pressures ranged from 272.6 to 282.3 K and from 1.17 to 3.85 MPa.

Based on the hydrate phase equilibrium measurements undertaken in this study, it was discovered that the juice systems under consideration have considerable inhibitory effects on hydrate formation. The results showed that reducing the water cut from (98.3 to 88.5 ± 2.53) wt.% could shift the hydrate phase equilibrium conditions toward higher pressures and lower temperatures.

A further study examined the effect of different driving forces (temperature, pressure and subcooling) and juice water cuts on hydrate formation kinetics using a novel experimental kinetic measurement of the binary CO<sub>2</sub> and grape/pineapple or bitter melon juice mixture. The kinetics of hydrate formation is fundamentally affected by the interaction between hydrate and dissolved. Insights into the potential commercialisation of hydrate-based technology can be gained through such measurements.

Considering this fact, the conclusions of this comprehensive study, including measurements of hydrate phase dissociation conditions and kinetic experiments of hydrate formation, were crucial for calculating the optimum conditions of the proposed fruit juice concentration process.

Also included in this research was the optimisation of dissociation conditions and kinetic data from three (3) different juice systems forming carbon dioxide hydrates. This was done to close the gap between the measured data and its applicability. A historical data design using response surface methodology (RSM) was used to determine optimal conditions from prediction models for the dissociation and formation of hydrates in the presence of pineapple, grape, and bitter melon juices. An examination of the effects of the RSM input variables, such as the system temperature  $T = (274.15 \text{ to } 276.15) \text{ K}$ , the juice concentration (88.5 to 97.4) wt.%, and the pressure  $P = (3.0 \text{ to } 4.2) \text{ MPa}$ , on the dehydration ratio (DHR) and apparent kinetic rate constant ( $K_{app}$ ) is presented in this study.

Lastly, this study evaluated the feasibility of fruit juice concentration technology via hydrate formation as opposed to the multi-effect evaporation method. A preliminary analysis of the estimated energy consumption at optimum conditions for the hydrate-based concentration process was conducted for comparison purposes. The analysis suggests that hydrate separation technology requires between 4864.04 to 5006.66 kJ of cooling per stage to concentrate fruit juices. Comparatively to a multi-effect evaporator, this cooling process requires 48 to 52 % less energy. While these findings may seem promising, it is still necessary to determine the size and quality of crystals before hydrate-based concentration technology is implemented in the fruit juice industry. As such, methods for accurately determining the final concentration of the solution must be developed.