Removal of Glucose from Water Via Gaseous CO_2 Injection and Hydrates Formation: Process Feasibility as a Function of the Initial Glucose Concentration in Water

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The production of gas hydrates is a widely recognised technique for impurities removal from waste water. Similar to ice, hydrate crystals cannot include ions and other impurities dissolved in water. Therefore, their formation, separation from the liquid phase and following dissociation, leads to the production of two distinguished liquid phases: the first, obtained from hydrate dissociation, which theoretically consists of demineralised water; the second, or the remained water, having a concentration of impurities higher than its initial values. However, mainly due to the stochastic nature of the hydrate formation process, the feasibility of such a strategy has not been completely validated yet, especially for substances different from ions. This study investigates the possibility of forming carbon dioxide hydrates to remove glucose (at different initial concentrations) from water. In order to achieve a satisfying treatment of water, two parameters were investigated: the effective capability of hydrates to produce decontaminated water and the abundancy of treated water, or the quantity of hydrates produced as a function of the initial glucose concentration in the liquid phase.

Keywords: gas hydrates; CO_2 reuse; waste water treatment; process efficiency; glucose separation.

1. Introduction

In addition to the production of energy, since the second mid of the past century, clathrate hydrates started being considered as promising solution for carbon dioxide capture and final disposal, within solid cages which can be easily stored in suitable geological sites. The storage of carbon dioxide can be advantageously coupled with the production of methane from natural hydrate reservoirs: the capture of carbon dioxide molecules occurs at milder thermodynamic conditions than those required for methane molecules. Therefore, the production of carbon dioxide hydrates is favoured and, if that gas is injected within sediments containing methane hydrates, the exchange, between the two molecules, within the existing water cages, is concretely possible (Wei et al., 2022; Kvenvolden 1993). The so-called replacement process, allows to enhance the production of methane and contributes to the preservation of water cages, thus reducing the deformation of soils and the overall environmental impact of the extracting process.

The formation and dissociation processes can also be advantageously applied in several fields, such as storage and transportation of energy gases (Wang et al., 2016; Veluswamy et al., 2016), gas mixture separation, food concentration, cold energy storage, water desalination and, more in general, removal of contaminants from waste water (Montazeri and Kolliopoulos, 2022; Bhatti et al., 2020; Priscilla et al., 2020).

The main hindrance containing the diffusion of hydrate-based process is their relatively low efficiency, mostly related to the stochastic nature of their formation process. The efficiency can be improved by using chemical additives, both promoters or inhibitors, capable to optimize the formation and dissociation processes, by acting on their thermodynamics, kinetics or both. Unfortunately, chemical additives introduce some further variables to consider; among them, higher costs, issues related to their availability. In addition, most of these additives are environmental unfriendly. Therefore, chemical additives must be recovered after their usage, with consequent further costs, due to separation and recovery processes. To overcome this impediment, during the last decades, greener additives have been proposed and tested (Rasoolzadeh et al., 2022), such as ionic liquids

Babamohammadi et al., 2015), amino acids (Zhang et al., 2018), deep eutectic solvents (Hansen et al., 2020) and sugar-derived substances (Methio et al., 2016).Sugar-derived compounds are extremely costless, water soluble and completely biodegradable. They mainly act as thermodynamic inhibitors, due to their hydroxyl (-OH) functional group, which interacts with water molecules, thus reducing the capability of these latter molecules to hydrogen bonding among each other (Mohammadi et al., 2008).The presence of hydroxyl groups impedes to sugar molecules to be involved in the production of hydrates. Therefore, the production of hydrate structures in sugar-containing systems, allows to produce fresh water, resulting from the separated dissociation of the solid phase, and to concentrate sugar in the liquid phase which did not participate to the process.

This study aims to experimentally verify if the production of hydrates can be considered as viable option for purification of waste water containing sugary organic compounds. Here, glucose was taken into account. Carbon dioxide hydrates were firstly formed in demineralised water; then glucose was added to the system at different concentrations, in order to identify the range of concentrations capable, at the same time, to ensure abundant production of hydrates and high removal efficiency.

2. Materials and Methods

A lab-scale reactor was used for the experimental phase. The reactor is entirely made with 316SS, has cylindrical shape and internal volume equal to 1 L. Technical details about the reactor are visible in Figure 1.
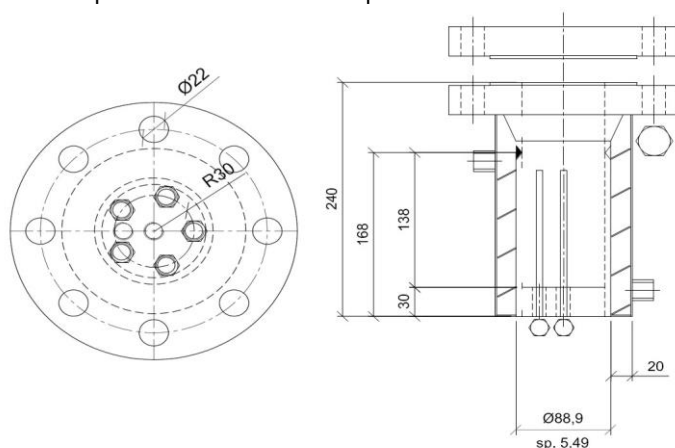

Figure 1: Geometrical details about the reactor used for experiments.

The system is equipped with sensors to measure the internal temperature and pressure. In detail, Tyoe K thermocouples (having class accuracy 1) were used for temperature, while a digital manometer, model MAN-SD (accuracy equal to ± 0.5 of full scale) was considered for pressure. The reactor was directly connected with CO_2 cylinder and the whole system was positioned within a cooling room, to control temperature from the external. More details about the experimental apparatus are available elsewhere in literature (Rossi et al., 2021). About materials, the reactor was filled with 0.744 L of pure quartz sand and 0.236 L of demineralized water, mixed with glucose at different concentrations. The porous sediment consists of spherical grains, having diameter between 90 and 150 µm. The mean porosity of the sediment, was measured with a porosimeter, model Thermo Scientific Pascal 140, and is equal to 34%. Finally, Ultra-high-purity carbon dioxide (>99.99%) was used for the experiments.

2.1 Experimental procedure

The following glucose concentrations were tested: 50, 10, 5 and 1.5 g/L. The optimal concentration was defined by considering the highest value possible, still allowing to abundant production of hydrates. The system was then characterized by defining the dissociation P-T values. Then, hydrates were formed again, with the optimal range of concentrations selected. After formation, hydrates were separated from the liquid phase and dissociated. The resulting water was finally analyzed to detect the concentration of glucose in it contained. The formation and dissociation of gas hydrates was carried out according to previous studies and more details are already available in literature (Gambelli, 2022; Gambelli et al., 2022; Gambelli et al., 2023).

The concentration of glucose was measured as a function of the quantity of C (carbon) observed. Water extractable organic C (WEOC) was measured with a C analyzer (model Multi N/C 2100 S analyzer).

3. Results and Discussion

The following figures (2 – 5) describe the formation and dissociation of carbon dioxide hydrates at the various glucose concentrations tested in this study. As expected, glucose acted as inhibitor for the production process. The entity of such inhibiting effect was then defined by measuring the amount of hydrates formed for each concentration selected.
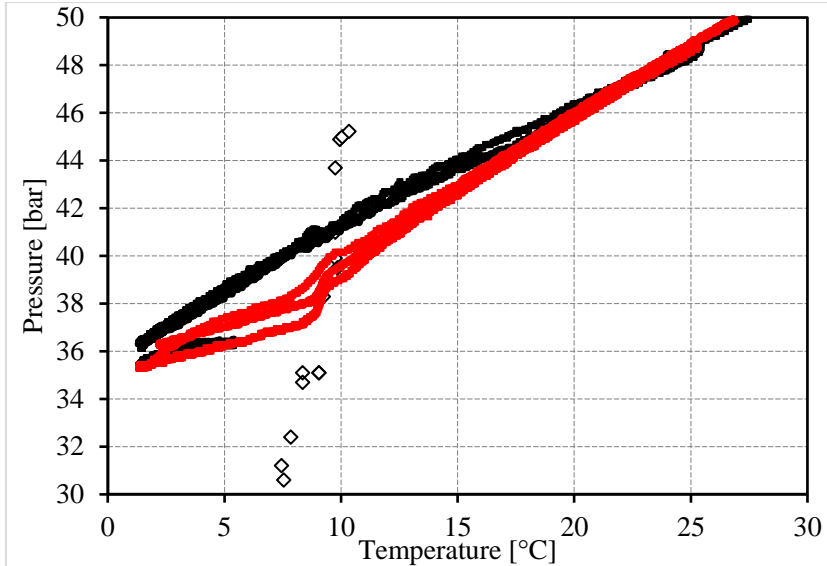

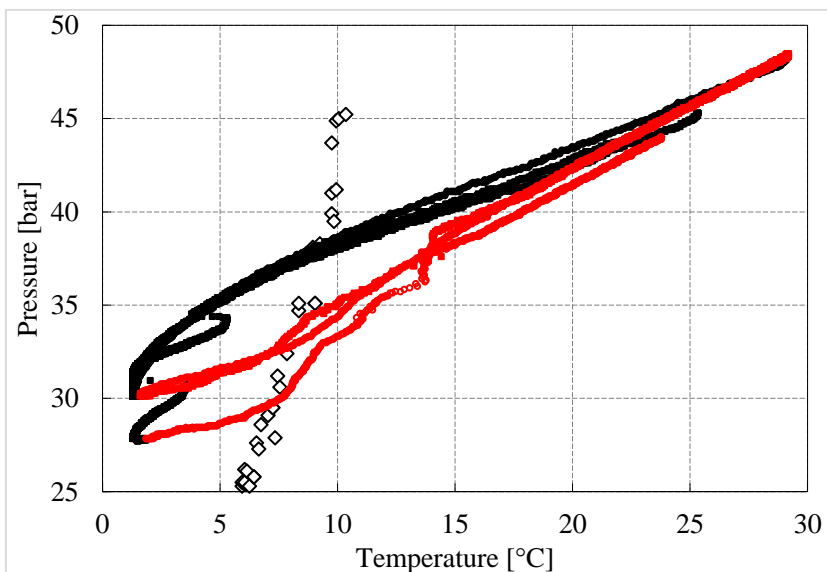*Figure 2: Formation (in black) and dissociation (in red) of CO_2 hydrates, in presence of 50 g/L glucose.*

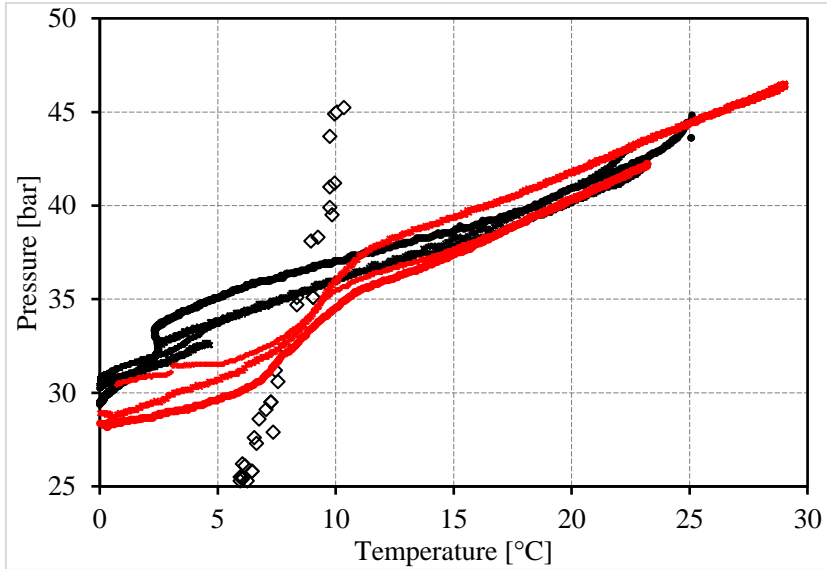*Figure 3: Formation (in black) and dissociation (in red) of CO_2 hydrates, in presence of 10 g/L glucose.*

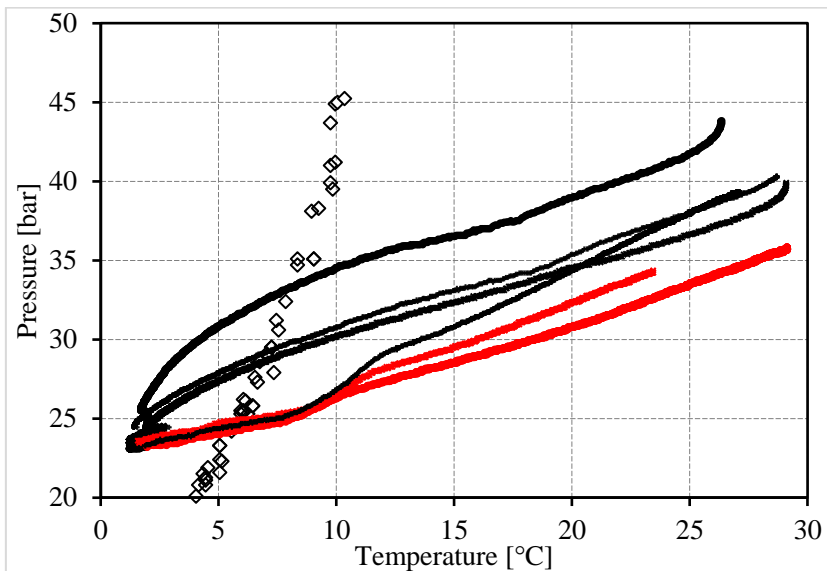*Figure 4: Formation (in black) and dissociation (in red) of CO_2 hydrates, in presence of 5 g/L glucose.*

Figure 5: Formation (in black) and dissociation (in red) of CO_2 hydrates, in presence of 1.5 g/L glucose.

Table 1: Pressure measured after the process completion and moles of hydrates formed.

Initial glucose concentration [g/L]	Lowest pressure [bar]	Moles of hydrates formed [mol]
50	35.31 ± 0.19	0.19 ± 0.02
10	30.12 ± 2.27	0.26 ± 0.3
5.0	29.42 ± 0.47	0.27 ± 0.05
1.5	23.39 ± 0.12	0.34 ± 0.02

The results highlighted that glucose surely worked as inhibitor for the process but, at the same time, its presence also delayed the dissociation of water cages. While the inhibiting effect was always observed and did not change significantly between the different groups of experiments, this latter effect, due to the addition of glucose to the system, was observed mainly at the highest concentrations, then it gradually disappeared with the lowering of glucose content within the system. In correspondence of the lowest concentrations, the process showed the characteristic peaks of temperature, associated to the exothermicity of the process and indicating massive production of hydrates. That assumption was then confirmed by calculating the moles of hydrates formed,

showed in Table 1.At concentrations equal or lower than 10 g/L, also the inhibiting action was found to decrease (with concentration) and the system gradually approached the phase equilibrium curve of pure carbon dioxide hydrates, shown with black dots in the figures above. Based on this latter assumption and on the quantities of hydrates formed (see Table 1), the three lowest glucose concentrations, respectively equal to 10, 5 and 1.5 g/L, were selected to evaluate the removal of glucose achievable with the hydrate formation process.

For the scope, carbon dioxide hydrates were formed again and then separated from the liquid phase. Once separated, hydrate samples were melted and the resulting water analyzed. Two samples for each concentration were collected and their respective C content was determined. The results are shown in Table 2. In the Table, the results were provided as weight percentage. In particular, the three concentrations selected, or 10, 5 and 1.5 g/L, respectively correspond to 1.0, 0.5 and 0.15 w/w%.

Table 2: Concentration of glucose in the water mixture obtained from the melting of hydrate samples.

$(C_6H_{12}O_6)_{INITIAL}$ w/w%	Conc. Sample 1 w/w%	Conc. Sample 2 w/w%	Mean concentration w/w%
1.0	0.128	0.139	0.131
0.5	0.082	0.083	0.079
0.15	0.045	0.055	0.046

Each sample collected proved the selectivity of the hydrate formation process. The production of a crystalline lattice containing carbon dioxide and its following dissociation, allowed to obtain two liquid mixtures having widely different glucose concentrations. Glucose mainly remained in the portion of water which did not participate to the production of crystalline cages, while the water resulted from the dissociation of water, showed a content in glucose almost one order of magnitude lower than the initial concentration of the system.

In tests carried out at 1.0 w/w% glucose, the initial concentration dropped from the values as soon indicated, to 0.133 w/w%; in tests made in presence of 0.5 and 0.15 w/w%, it reached respectively 0.079 and 0.046 w/w%.

Even if the removal effect is clear, such a process cannot be considered by its own, since the concentration of glucose in water (the portion obtained from hydrate melting) is clearly not negligible. However, it can be considered as pretreatment method, capable to concentrate the contaminant into reduced volume of water, thus simplifying the next removal processes and also make them cheaper.

The results also indicated that the selectivity decreased with the lowering of glucose initial concentration in water. Based on the values collected in Table 2, the reduction in glucose concentration was equal to 86.9% in tests carried out at 1.0 w/w%, 84.2% in tests made with 0.5 w/w% and to 69.3% in tests having 0.15 w/w% as initial concentration. It should be noted that higher percentages can be reached if the system contains initial glucose concentrations higher than 1.0 w/w%. However, at those concentrations, the quantity of hydrates produced would be excessively contained and, as a consequence of it, the amount of water processed irrelevant. Based on these results, it can be concluded that the best performances are reached in water mixtures having initial glucose concentrations equal to 0.1 – 0.5 w/w%. Within this range of concentrations, the inhibiting effect of glucose is sufficiently weak and the production of hydrates is consequently massive; therefore, the removal efficiency ranged from 84.2% to 86.9%. Since the concentration of glucose, belonging to this latter range, well approximates the carbon content of residual biomasses obtained after anaerobic digestion processes (Cucina et al., 2022), it can be concluded that the hydrates formation process consists of a viable option for the removal of the organic content from waters resulting from biogas and biomethane production.

4. Conclusions

The present study deals with carbon dioxide hydrates production with liquid mixtures containing fresh water and glucose, added to the system at different concentrations. Similar to ice, gas hydrates do not involve contaminants diffused in water in building their crystalline lattice; therefore, their formation process can be advantageously exploited for waste waters treatment. The present research aimed to verify the capability of remove/concentrate glucose via hydrates formation. To be effective, the process must show at the same time:

1) Abundant production of hydrates. Glucose is an inhibitor for the process; excessive concentrations of it would lead to low production of hydrates and, consequently, treatment of only a negligible portion of water;
2) High selectivity. The formation of hydrates is stochastic and the complete exclusion of contaminants is practically impossible (these elements could also remain trapped in the hydrate lattice during its growth, even if not directly involved in its building).

The results produced in this study confirmed the inhibiting action of glucose, which was found to be constant at relatively high concentrations of the additive, and proportional to the initial quantity of it, in correspondence of the lowest concentrations. Conversely, the presence of glucose enhanced the self-preservation capability of the system, thus preventing the melting of hydrates (only within a certain thermodynamic range) when the system

was brought out from the hydrate stability zone. This further effect was proved to be proportional with the initial concentration of glucose. The results revealed that, at glucose concentrations equal to 1.0, 0.5 and 0.15 w/w%, the production of hydrates was elevated. Carbon dioxide hydrates were consequently produced again, at the same concentrations and samples of it were analysed to detect the capability of the system to remove it, form the portion of water involved in the crystalline lattice, and to concentrate it in the portion remained in the liquid state. The removal efficiency was equal to 86.9% at 1.0 w/w% and to 84.2% at 0.5 w/w%. Conversely, at the lowest concentration selected, corresponding to 0.15 w/w%, such efficiency drastically dropped to 69.3%.

The results, allowed to define an optimum range of glucose concentrations where both the productivity of hydrates and the removal capability ensured the suitability of the process for water/glucose mixture treatment. Reflecting these concentrations the carbon content of residual digestates, it can be concluded that the proposed process can be included in bio-refinery chains, for the removal of the organic content from waters resulting from biogas and biomethane production.

Acknowledgements

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