Fachtagung "Experimentelle Strömungsmechanik"
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Experimentelle und numerische Untersuchung von Hydratbildung in einem zylindrischer Reaktor

Experimental and numerical investigation of hydrate formation in a cylindrical reactor

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Food technology, gas hydrate, fruit juice, cylindrical reactor, computational fluid dynamics

Abstract

Despite the ongoing pandemic, the market of fruit juices is projected to keep expanding in years to come. To fulfill the expanding global demand, innovative preservation and concentration technologies are crucial. However, they are difficult to develop and preservation techniques relying on thermal treatments either modify or even deteriorate precious substances present in fruit juices. In contrast to that, novel non-thermal food preservation methods became attractive for the scientific community, since they enable the conservation of food properties and sensorial characteristics such as flavor, color, and mouthfeel. Gas hydrate (GH) are ice-like crystalline solids, where small, non-polar molecules are trapped inside cages formed by hydrogen-bonded, water molecules at "elevated pressure" and low temperature. Due to its inertness, CO_2 serves as an ideal compound for gentle processes for concentrating juices. Besides, the energy requirements of the whole process can be drastically reduced. Therefore, the CO_2 gas hydrates technology is regarded more and more like a novel fruit juice concentration and preservation one. In the present work, we first report experimental results of hydrate formation inside a cylindrical reactor. Besides, we present the results of numerical simulation of the rate of CO_2 gas hydrate formation in a reactor of the same size. Numerical simulations not only allow a deep understanding of the whole process but also provide useful information regarding its optimization.

Introduction

As the human population becomes more and more conscious about their health and well-being, they also become aware of their choice of food and drinks. Due to their capabilities to provide various health benefits through different nutrients, fruit juices are currently having a rising demand as healthy and nutritious drinks (Caswell 2009). Currently, the global juice market keeps expanding at an 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

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preservation and concentration technologies become more and more crucial to fulfill the global demand. Preservation techniques relying on thermal treatments have resulted in the change or even deterioration of precious substances contained in the fruit juices. Thus, novel non-thermal food preservation methods, such as CO_2 gas hydrate technology, have emerged as an interesting alternative, since they enable 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 a general understanding, 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 are interconnected with hydrogen bonds (Koh et al. 2011). As CO_2 gas is safe and has been widely applied in the food processing industry, CO_2 gas hydrate technology seems to be a gentle, novel technology to concentrate fruit juices.

A conventional evaporation process requires temperatures up to 80 °C and needs an energy demand of 180–2,160 kJ/kg water to reach a concentration degree between 65% and 85%. However, this process leads to a loss of heat-sensitive and volatile components, like, for instance, vitamins, aroma compounds, and other valuable substances (Cheryan 2006; Guignon et al. 2012; Jiao et al. 2004). During the freeze concentration, the process requires an energy demand that ranges between 936–1,800 kJ/kg water but it can only achieve a degree of concentration of 55% (Ashurst 2016). The application of CO_2 gas hydrate technology provides a more energy-efficient process with an energy demand that varies between 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 enabling the severance of water molecules from the fruit juices.

In the present work, we investigate the process of hydrate formation inside a small cylindrical reactor both numerically and experimentally. On the one hand, experiments accommodate the first-hand observation for the base of the modeling and numerical simulation. In addition, they also provide and give hints about possible deviation from the idealized simulation environment. On the other hand, numerical simulations provide clear insights into the process of hydrate formation, since they permit to study in detail the complex phenomena of mass transfer and reaction that lead to the formation of hydrate. Besides, the choice of a simple geometry and hydrate formation under creeping flow conditions allow us to isolate and comprehensively investigate the mechanism of hydrate formation.

Experimental set-up

In this work, we investigate the CO_2 hydrate formation. All the experiments were carried in a cylindrical pressure optical cell up to 350 bar with a volume of 12 mL equipped with four sapphire glasses for optical access and a cooling mantle to maintain and control the temperature with the help of a circulating chiller (ThermoScientific™ Arctic A28).

The hydrates are formed using 7 mL deionized water, 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 overnight to be fully grown. The pressure and temperature are monitored continuously using a 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

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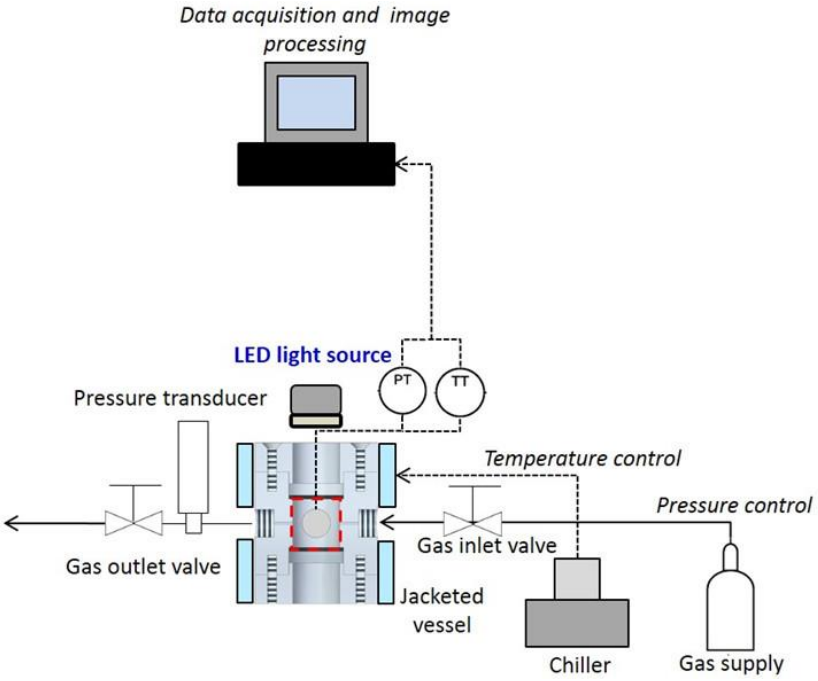

Fig. 1: Sketch of the experimental setup for CO_2 hydrate formation

with a macro lens (Canon EF 180mm f/3.5 L Macro USM Lens). The experimental setup for hydrate experiments is depicted in Fig. 1**.**

Results and discussion: experiments

Once the cooled water was subjected to this elevated pressure, the hydrate starts to form at any spot where there is a contact surface between CO_2 and water. As hydrate formation is an exothermic process, the hydrate growth is enhanced at the spot where the temperature is low. Hence, the rapid hydrate growth rate can be observed on the surface where the temperature is the lowest, i.e., the surfaces of the optical cell which are in direct contact with the cooling fluid, including the glass surface. This course of hydrate formation can be seen in Fig. 2. Even though no further change can be visually detected after 120 minutes, the hydrate is assumed to keep on growing at the bulk of the liquid where it has no direct contact with the CO_2. The hydrate that was formed in the beginning was porous and as the hydrate grows over time, the hydrate structure became more compact. This phenomenon can be observed by the fact that the CO_2 pressure inside the reactor continuously decreases. The pressure profile during the hydrate growth can be seen in Fig. 3. The preliminary experiments carried out in this work are aimed to provide results that can be used for numerical simulations. Those will later allow a deeper understanding of the whole hydrate formation and growth process, and they will provide necessary information to design and optimize more complex processes in the future, i.e., fruit juice concentration, water desalination, etc.

Grid generation and simulation details

We performed numerical simulations of hydrate formation in a small cylindrical vessel with diameter $d = 2.48\,cm$ and height $H = 2.48\,cm$ using ANSYS CFX®. The pressure within the cylindrical vessel is kept constant at $p = 3.7\,MPa$. At the beginning of the simulations, the top half of the cylinder is filled with CO_2 gas, while the bottom half of it is filled with water. The domain is covered with a structured grid obtained by employing a simple O-grid. The mesh has been generated utilizing the commercial software

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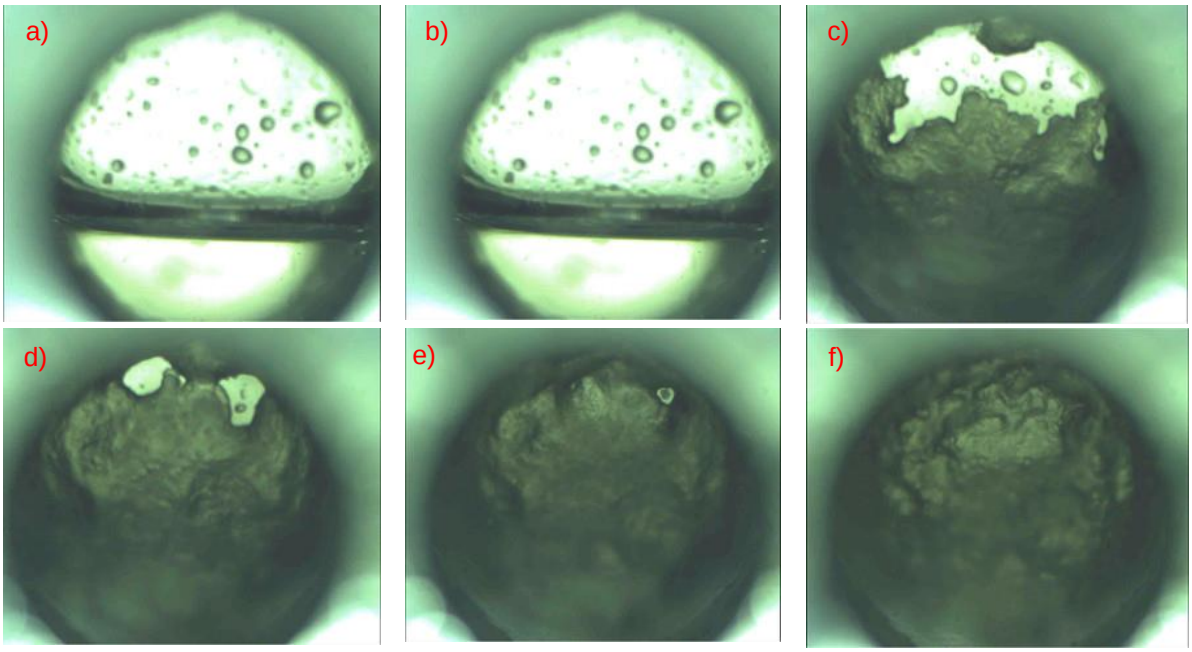

Fig. 2: Hydrate formation and growth at a) t=0 min, b) 5 min, c) 15 min, d) 30 min, e) 60 min, and f) 120 min

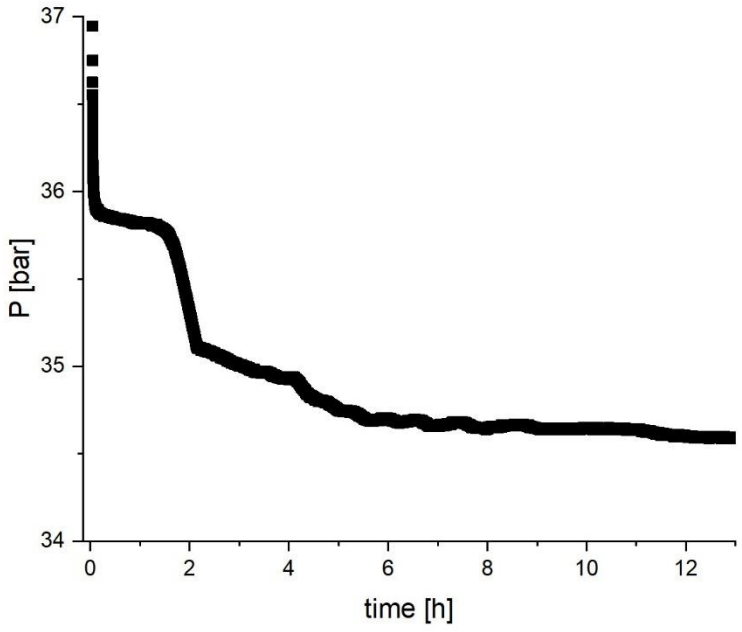

Fig. 3: Pressure profile over time during the hydrate formation and growth period

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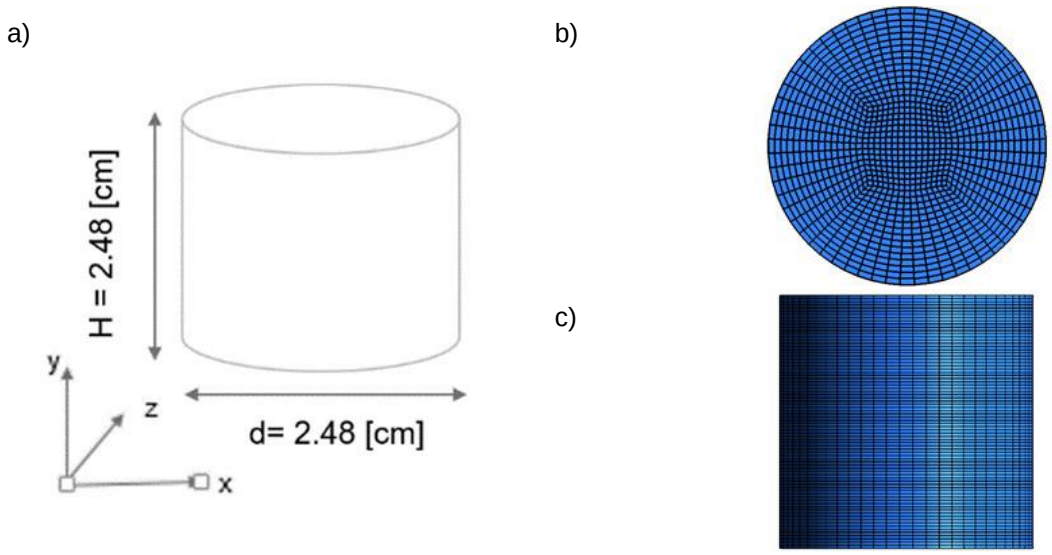

Fig. 4: a) Sketch of the cylindrical vessel with dimensions, b) view of the meshed bottom face of the reactor, c) side view of the meshed lateral surface of the vessel

ANSYS ICEM® CFD 18.1 and has 88875 hexahedral elements. We set a no-slip boundary condition for the velocity of CO_2 and water on the bottom and the lateral walls of the cylinder. In addition, the temperature of the walls is kept fixed at $T = 274.15\ K$. We specify an opening boundary condition for the top of the cylinder with also a fixed temperature $T = 274.15\ K$. By setting an "opening" boundary condition, the software applies an outlet boundary condition if a fluid (i.e., CO_2) exits the domain while it computes the static pressure from the total one if fluid enters the domain. The cylindrical domain and the mesh are depicted in Fig. 4. We simulate until the final time $t = 1500\ s$, by using an adaptive time step ranging from a minimum $\Delta t = 10^{-5}\ s$ up to a maximum $\Delta t = 10^{-2}\ s$. The maximum number of inner iterations after which the time step is decreased is 15, while the minimum number of inner iterations before which the time step is increased is 5. The increasing factor is 1.06 while the decreasing factor is 0.8.

Results and discussion: numerical simulations

Fig. 5 shows contours of instantaneous mass fraction of dissolved CO_2 and CO_2 hydrate at different time steps. For better visualization, they are displayed on a cross-sectional $(x - y)$ plane at $z = 0$. Specifically, Fig. 5a) and b) depict the volume fraction of dissolved CO_2 in water at $t = 65\ s$ and at $t = 565\ s$. As the time progresses, the amount of CO_2 dissolved in the bottom half of the reactor and the amount of dissolved CO_2 at a specific height increase with time, see Fig. 5a) and b). CO_2 hydrate starts growing almost immediately even though a small amount of CO_2 is dissolved in water. This is plausible since hydrate formation may occur even if a very small amount of CO_2 is present in water and the nucleation time is estimated to be of the order of nanoseconds. Moreover, it is clear from Fig. 5c) that hydrate correctly forms only where dissolved CO_2 is present. As the time proceeds, the amount of hydrate formed also increases. To prove that the results of our numerical simulations are qualitatively correct, we compare our outcomes with the experimental findings of (Kvamme et al. 2007). In their manuscript (Kvamme et al. 2007) they investigate methane hydrate (CH_4) formation in a cylindrical vessel. More specifically, they examined two-half cylinders divided by a spacer which leaves two connected compartments. The lower half-section is filled with water and the upper half is filled with methane kept at $p = 8.38\ MPa$. The temperature in their system is maintained fixed at $T = 277.15\ K$. It can be seen from Fig. 4 of the manuscript of (Kvamme et al. 2007), that hydrate starts forming at the interface between methane and water and subsequently grows. This is

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qualitatively similar to our numerical findings, see for instance Fig. 5c) and d). Hydrate formation is a complex process governed by the first and the second law of thermodynamics where the regions with the lowest free energy of the non-equilibrium hydrate film grow at cost of less stable neighboring regions where the availability of hydrate formers is inhibited by the presence of solid hydrate. For this reason, the process of hydrate growth in a system like a cylindrical vessel is very slow due to the presence of a growing hydrate film which inhibits the diffusion of a hydrate former. This is also evident from our simulations since even after approximately 20 minutes (i.e. $t = 1345\ s$), the mass fraction of CO_2 hydrate formed is only approximately 0.15%, see Fig. 5f). (Kvamme et al. 2007; Kvamme et al. 2020) report an induction time of 100 h in their experiments, where the induction time is defined as the time when an "onset of massive hydrate growth" occurs. Specifically, it is clear from Fig. 10 of the manuscript of (Kvamme et al. 2007) that approximately only 4% of methane hydrate is formed after 100 h. Considering that the solubility of CO_2 in water is approximately ten times higher than the one of CH_4 in water (Hashemi et al. 2006) and since the rate of hydrate growth is constant and always lower than the rate of mass transfer of CO_2 in our simulations, one expects to have 4% of CO_2 hydrate after approximately 10 h.

Conclusion

CO_2 hydrate formation has been successfully carried out in an optical cell. Preliminary experiments were performed to obtain results that will be compared in the future with outcomes of numerical simulations. Furthermore, numerical simulations of CO_2 hydrate formation have been carried out and the results have been compared with those available in the literature for the case of CH_4 hydrate formation. The numerical outcomes agree qualitatively well with experimental trials, indicating that hydrate formation in a cylindrical vessel is a very slow process due to the limited mass transfer of the hydrate former in water. In the future, different reactor types will be also investigated numerically.
Novel CO_2 gas hydrate technology is a promising technology that can be potentially applied in the field of food preservation as it offers a unique approach to solve the increasing demand for nutritious drinks coupled with the preservation of the valuable substances contained inside for a healthier lifestyle.

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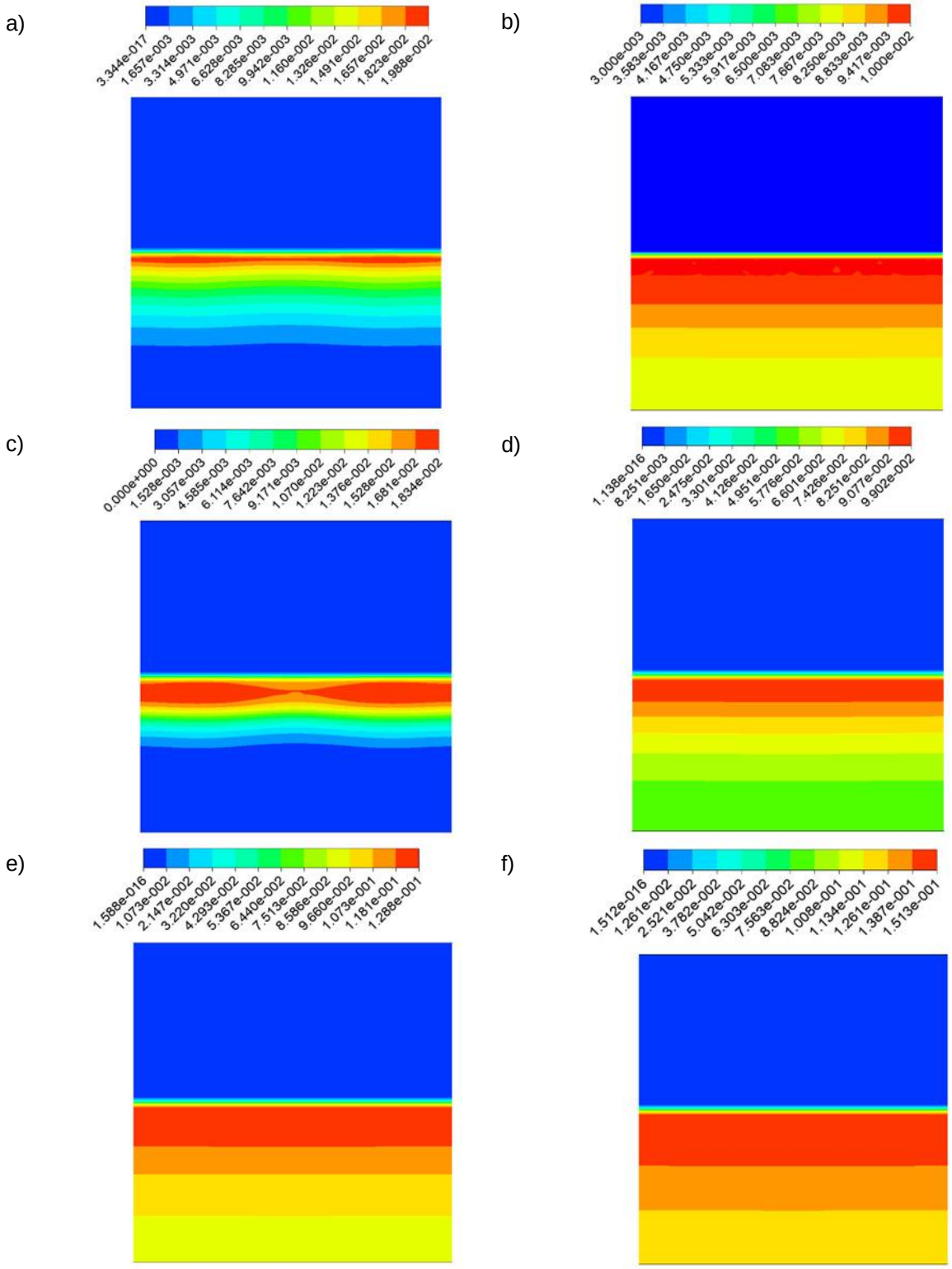

Fig. 5: Contours of a) dissolved CO_2 at t=65 s, b) dissolved CO_2 at t=565 s, c) CO_2 hydrate at t=65 s, d) CO_2 hydrate at t=565 s, e) CO_2 hydrate at t=1005 s and f) CO_2 hydrate at t=1345 s

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