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Modelling of CO_2 Frost Formation and Growth on a Flat Plate

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Cryogenic separation is one of many CO_2 capture technologies developed for upgrading biogas or for CO_2 separation from flue gases. In order to better understand the CO_2 frosting phenomena, in this paper, CO_2 frost growth is modelled considering deposition on a flat plate. The frost layer is modelled as a porous medium with heat and mass transfer occurring on the surface and within the frost layer. Simulations are conducted for CO_2 separation from CH_4+CO_2 (biogas) and N_2+CO_2 (flue gas) mixtures, frost thickness and density were assessed. The modelling results are compared to experimental data found in literature and it is for the first time possible to have detailed and accurate model of heat and mass transfer for CO_2 frosting. Multiple heat transfer correlations were assessed and improvement of accuracy between calculated and experimental results has reached 80 %. For CH_4+CO_2 mixtures, a sensitivity study is carried out. The drivers of frost formation are mainly plate temperature and inlet CO_2 concentration, and to lesser extent the gas temperature.

1. Introduction

Thermodynamic systems with heat transfer towards or from a cold plate with frost formation are important for many applications. Among them is the cryogenic separation of CO_2 from the biomethane CH_4. Biomethane is a renewable clean energy source that can be used for heating, electricity generation and transportation (Scarlat et al., 2018). Cryogenic separation is in competition with other processes for biogas upgrading like the absorption using a solvent, based on the solubility of acid components of biogas, adsorption using Pressure Swing Adsorption (PSA) and separation using a membrane based on molecule size and chemical potential. Cryogenic processes separate components based on their saturation temperature which is different for each element in the biogas mixture. Even though cryogenic separation is an expensive investment, it enables high purity of methane (98 %) to be reached, no use of chemicals in biogas facilities, and an easier liquefaction of methane by adding little extra energy, which is not the case for the other technologies (Awe et al., 2018). According to the phase diagram of CO_2, at atmospheric pressure, carbon dioxide goes from its gaseous phase to its solid phase directly without it being liquefied. In the literature, most of the frost formation studies focus on water vapour contained in humid air, few studies can be found about CO_2 frosting: Song et al. (2012) studied CO_2 frosting on a Stirling machine, Tuinier et al. (2010) studied CO_2 frosting on dynamically operated packed beds. Literature review shows a lack of studies concerning CO_2 frosting compared to water vapour therefore the aim of this article is to better understand the growth (in thickness and density) of the CO_2 frost and how to model it accurately. First, the frost growth will be described from an observational point of view, the model is defined and validated by comparison to available experimental results, and finally a parametric study is conducted to define the drivers of mass and heat transfer while frosting.

2. Fundamentals and mathematical modeling of frost formation

Frost formation is considered a complex phenomenon to describe especially in its first few seconds of occurrence. Thermo-physical properties of frost vary continuously during the development of the solid layers and the temperature at the interface gas-frost surface varies with time and position, leading to variations in the saturation conditions. Na and Webb (2004) and Dave et al. (2017) studied water vapor deposition and compared their models to experimental results. Their explanation of the frost formation mechanism can be considered in order to better understand frosting of CO_2 contained in biogas, which follows the same analogy.

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In the following section, CO_2 frosting from flue gases (N_2-CO_2) is studied as base case. Flue gases containing CO_2 are cooled down by convection over a flat cold plate until reaching the temperature of deposition of CO_2 at its partial pressure (Figure 1a). Frost appears and its thickness and density are constantly increasing. At the beginning the increase rate is at its maximum but the frost accumulation reduces the thermal conductivity from the plate to the frost-gas surface. The more the thickness increases, the temperature at the frost surface increases and less CO_2 is frosted. At early deposition stage, the frost is porous, the gas diffuses into it and deposits inside the pores. This increases the density of the frost and generates layering of solids with time.

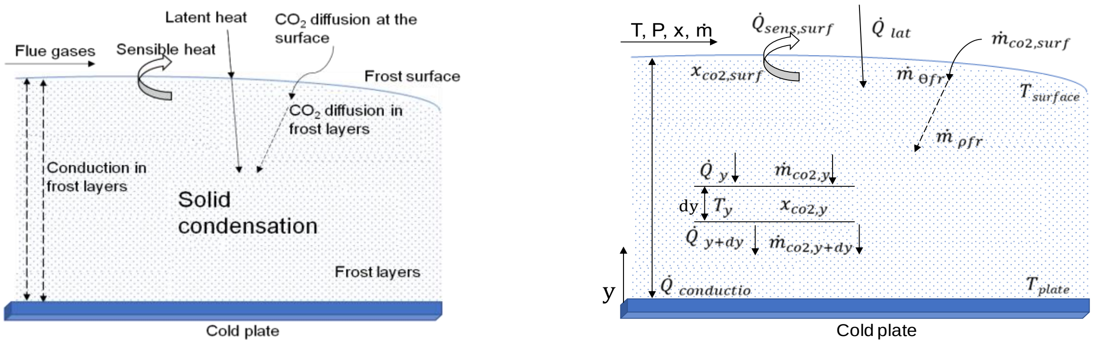

Figure 1: (a) Description of heat and mass fluxes during deposition, (b) Conservation of mass and energy on the surface and inside frost

The frosting model describes the heat transfer between the flue gases, the frost surface, the frost layers and the plate as well as the mass transfer of CO_2 from its gas phase in the flue gases to its solid phase on the plate. This model predicts the variation of thickness, the density of frost and the sensible and latent heat transferred in the system. The plate is considered at constant cryogenic temperature, the flue gases passing above the plate are cooled down to the point where they reach the temperature of deposition of CO_2 at its given partial pressure. As long as a difference in concentration between the flue gases and the frost surface exists, frost is formed. The study of frost growth evolution can be carried out using an analogy between mass and heat transfer or using the equations of molecular diffusion, energy and mass balance and state equations. These two models can be coupled (Brèque and Nemer, 2016) and were both considered in the development of the frosting model described in this article.

In Figure 1b, the model is presented with 3 zones: the flue gases over the flat plate with heat and mass transfer, the frost layer where heat and mass transfer are a result of gas diffusion, and the interface between the flue gases and the frost surface. The assumptions below are found in literature and are considered:

- Modelling neglects the nucleation phase. The existence of a very thin and low-density uniform frost layer is considered over the plate at time t = 0 s (Lee et al., 1997).
- The model is 1D. The frost layer is discretised in the direction normal to the plate (Lee and Ro, 2005).
- Temperature at the flue gases-frost interface is considered equal for the gas and solid phases.

2.1 Energy and mass balance during frosting

The flue gases

At the frost surface, the convective sensible heat exchanged $\dot{\boldsymbol{Q}}_{\boldsymbol{sens,surf}}$ over surface $\boldsymbol{A}$ is calculated as follows:

$$\dot{Q}_{sens,surf} = h_c . A . \left(T_{flue_{gases}} - T_{surf}\right) \tag{1}$$

The mass of CO_2 that frosts at the surface can be calculated by establishing an analogy between the heat and mass transfer. The CO_2 concentration in the flue gases $x_{co2/n2}$ and its saturation temperature are represented by a psychrometric diagram built especially for this particular case:

$$\dot{m}_{co2,surf} = h_m . A . \rho_{flue\_gases} . (x_{co2/n2} - x_{surf}) \tag{2}$$

Inside the frost layer

As mentioned before, frost is formed on the surface and inside the frost layers where the mass flow of CO_2 frosted can be calculated using Fick's law for the diffusion of matter:

$$\dot{m}_{CO2,\rho} = D_{eff} . A . \rho_{flue\_gases} . \frac{dx}{dy} \tag{3}$$

The effective diffusion coefficient D_{eff} is limited by the porosity of the CO_2 frost layer. Since the frost densifies as more frost is formed, a new term called the mass absorption rate α_{co2} is introduced (Lee et al., 1997) and calculated according to Eq(4). Frost density is calculated according to Eq(5).

$$\alpha_{co2} = \frac{d\dot{m}_{CO2,\rho}}{dy}/A \tag{4}$$

$$\alpha_{co2} = \frac{d\rho_{fr}}{dt} \tag{5}$$

The heat transfer by conduction inside the frost layer follows Fourier's law:

$$\dot{Q}_{cond\_fr} = k_{eff,fr}\,.A\,.\frac{dT_{fr}}{dy} \tag{6}$$

On the frost-bulk interface

As mentioned before, the mass flow rate of CO_2 frosted can be divided into two parts: $\dot{m}_{\rho fr}$ which represents the mass of diffused CO_2 from the surface into the frost, this mass flow increases the frost density; the second part $\dot{m}_{\theta fr}$ which increases the frost thickness corresponds to the condensation of CO_2 on the surface.

$$\dot{m}_{\rho fr} = D_{fr}.A\,.\rho_{flue\_gases}.\left(\frac{dx_{flue\_gases}}{dy}\right)_{surf} \tag{7}$$

The CO_2 concentration gradient $(dx_{flue\_gases}/dy)_{surf}$ is calculated as y tends to θfr, hence at the frost surface. Using Eq(2) the mass flow rate of CO_2 responsible for thickness growth $\dot{m}_{\theta fr}$ can be calculated. This flow rate can then be considered to calculate the increase in frost thickness:

$$\frac{d\theta fr}{dt} = \frac{\dot{m}_{\theta fr}}{A\,.\rho_{fr}} \tag{8}$$

The thermal transfer to the surface is described by the following equations:

$$\dot{Q}_{fr} = -\dot{Q}_{sens,surf} + \dot{m}_{\theta fr}.H_{sv,co2} \tag{9}$$

$$\dot{Q}_{fr} = k_{eff,fr}.A\,.\left(\frac{dT}{dy}\right)_{surf} \tag{10}$$

$H_{sv,co2}$ is the latent heat of sublimation of CO_2. $k_{eff,fr}$ is the effective thermal conductivity of CO_2 frost.

2.2 Thermophysical properties

In order to determine the nature of the gas flow, the Reynolds number must be calculated. This requires knowing of the viscosity. Moreover, the convective heat transfer is function of the heat transfer coefficient which is function of the Reynolds number and the gas thermal conductivity. In this study, transport properties are found using REFPROP for different compositions of the mixture. The diffusion coefficient is another key parameter that is used to determine a fraction of the mass flux of solidified CO_2. In this study, the method proposed by Fuller et al. (1966) will be used. The CO_2 effective conductivity frost is not found in the literature like in the case of water vapor frosting, but it is function of its density. Therefore, the thermal conductivity of CO_2 frost will be estimated using the results found in an experiment by Shchelkunov et al. (1986):

$$k_{eff,fr} = \frac{0.27 \times \rho_{fr}}{2386.037 - \rho_{fr}} \tag{11}$$

2.3 Transfer coefficients

Heat transfer

When it comes to classical known geometries, correlations for heat transfer coefficients give good predictions of the heat transfer involved but in the presence of frost the surface geometry change can have a major effect on the heat transfer coefficient which will affect directly the convective sensible heat transfer as well as the mass transfer coefficient which will be used to estimate the mass flux of solid CO_2 frost formed on the surface of the plate. In Table 1, the two correlations presented will be compared while validating the model in order to choose the best fit for the continuing of this study.

Table 1: Correlations for convective heat transfer coefficients

Heat transfer coefficient		Flow nature and geometry	References
$h_c = \frac{0.034.Re_{Dh}{}^{0.8} \times k_{flue\_gases}}{D_h}$	(12)	Two parallel plates with frost. 6,000 < Re < 50,000	Yamakawa et al. (1972)
$h_c = \frac{0.021.Re_{Dh}{}^{0.8} \times Pr^{0.6} \times k_{flue\_gases}}{D_h}$	(13)	Flow in a duct over a horizontal plate with frost. Re > 10,000	Dientenberger et al. (1979)

D_h represents the hydraulic diameter in this study, that is to take into account the effect of the frost thickness on the velocity so the Reynolds number. k_{flue_gases} is the thermal conductivity of the flue gases.

Mass transfer

The Lewis number enables the linkage between the heat and mass transfer coefficients. It represents the ratio of mass to thermal diffusion and it will be calculated using the thermos-physical properties of the flue gases:

$$Le = \frac{k_{flue\_gases}}{D_{flue\_gases} \times \rho_{flue\_gases} \times C_{p,flue\_gases}} \quad (14)$$

The linkage between the mass and heat transfer can be expressed as follows:

$$h_m = h_c/(\rho_{flue\_gases}.c_{p,flue\_gases}.Le^{\frac{2}{3}}) \quad (15)$$

3. Simulation and results

3.1 Model validation

Very little data can be gathered concerning frost formation and growth of CO_2. An experimental study was led by Shchelkunov et al. (1986) where he used a horizontal cold flat plate and a flow of N_2+CO_2 at different inlet conditions. In this work, the two heat transfer correlations proposed will be compared for three experimental cases from Shchelkunov's results. Frost thickness and density are the quantities that will be compared.

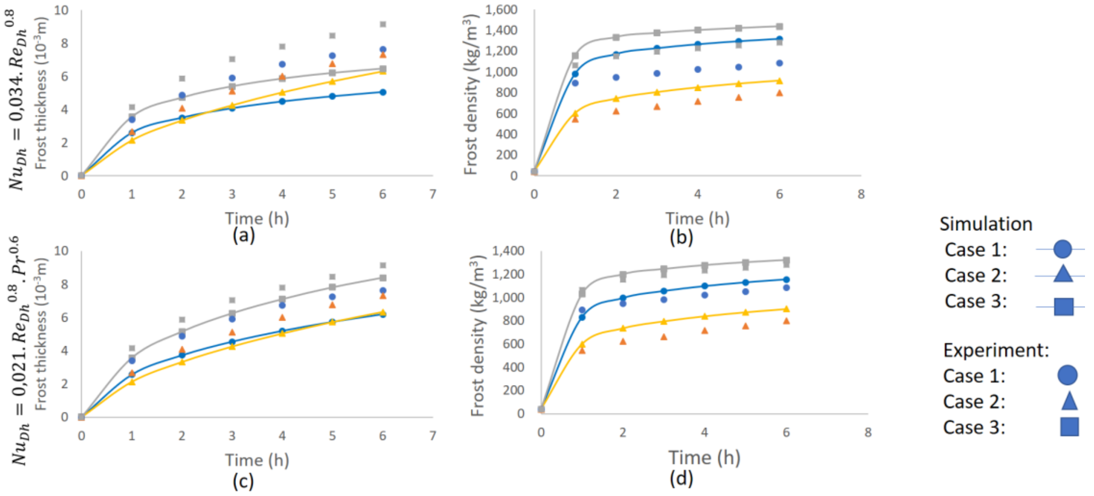

Figure 2: Comparison of frost thickness and density growth between simulation and experimental results for different heat transfer coefficients

Results in Figure 2 show the effect of the correlation choice of heat transfer coefficient. For both cases, frost thickness and density increase continuously with time. The increase rate is high at the beginning of frosting, then the frost thickness creates a thermal barrier limiting the temperature at the surface of the frost thus increasing its temperature. Transfer coefficient equations in each case affect directly the convective sensible heat transfer as well as the mass of CO_2. Shchelkunov's experiment was used to correlate the thermal conductivity of the CO_2 frost which affects the conduction heat transfer inside the frost layer responsible for the temperature distribution in the frost. Results show an underestimation of frost thickness (7-20 %) and an over estimation of the density (3-19 %) but for all three cases, the frost evolution with respect to the initial conditions set follow the same direction in the simulation as in the experiment. The Dietenberger et al. (1979) correlation gives the best estimation of frost growth.

3.2 Sensitivity study of frost growth of CO2 contained in biogas

A sensitivity study of the effect of inlet conditions and plate temperature on the frost thickness and density evolutions during the frosting process is carried out. Biogas (CH_4-CO_2) passes over a cold plate (30 cm x 15 cm) and CO_2 frosts on its surface. Different CO_2 concentrations, plate temperatures and inlet biogas temperatures will be studied, and frost growth compared.

Table 2: Operating conditions for sensitivity study cases

	$x_{co2/biogas}$ (kg/kg)	T_{cold_plate} (°C)	T_{biogas} (°C)
Case 1	0.6;0.5;0.4	-128	-80
Case 2	0.5	-138; -128; -118	-80
Case 3	0.5	-128	-85; -80; -75

In part (a) of Figures 4-5-6 shown below, frost thickness will be compared for the three different values given to the parameter studied in each case and in part (b) density will be compared.

3.2.1 Case 1: Concentrations of CO_2

Varying the CO_2 concentration in the biogas affects mainly the total mass flux of CO_2 frosted (Eq(2)) and the mass flux of CO_2 frosted inside the frost layers (Eq(3)) but less than the total mass of frosted CO_2. The difference between these two fluxes gives the mass flux of CO_2 frosted at the surface which will increase for a higher concentration the frost thickness by about 11 % (Figure 3a). Heat exchange surface in Eq(8) is considered constant in this study. The frost density is calculated using the mass absorption rate α (Eq(5)) which is function of the mass flow of CO_2 frosted inside frost layers and it increases in a non-uniform rate for a higher CO_2 concentration (Figure 3b). Although an increase in the frost density reduces the thickness growth, the effect of a higher concentration on the mass flow of CO_2 frosted is more important.

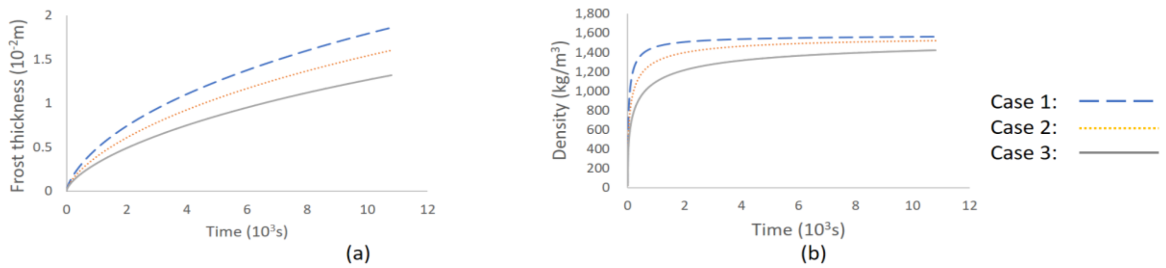

Figure 3: CO_2 frost growth for different mass concentration: (a) frost thickness, (b) frost density

3.2.2 Case 2: Plate temperatures

Lower plate temperatures decrease the temperature at the frost surface. This decreases the CO_2 saturation point hence increasing the CO_2 concentration difference in Eq(2) which will increase the total mass flow of CO_2 frosted. This will result in higher values for the frost (Figure 4a), just like case 1 with CO_2 concentration change, the increase rate in thickness is also close to that of case 1 and is about 11 %. As for the density, it decreases for lower plate temperatures because lower temperatures in the frost result in lower saturation vapour concentration in CO_2 inside the frost layers. This will reduce the amount of CO_2 frosting inside the frost layer thus reducing the density.

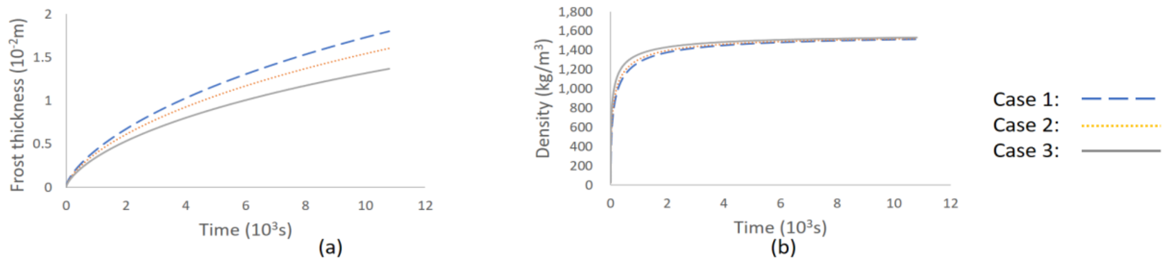

Figure 4: CO_2 frost growth for different plate temperatures: (a) frost thickness, (b) frost density

3.2.3 Case 3: Temperatures of biogas

As for the change in inlet temperature, there is no direct effect on the CO_2 concentration difference at the surface nor in the frost layers, therefore no remarkable change in frost thickness (Figure 5a) and density (Figure 5b) can be seen. Frost thickness increases slightly for lower inlet temperatures because the convective sensible heat decrease has more effect compared to the decrease of conduction heat transfer in the frost layers. The conclusion that can be drawn is that since the mass of CO_2 frosted at the surface will increase, then the thickness will increase too, even if not more than 3 %, at the frost surface.

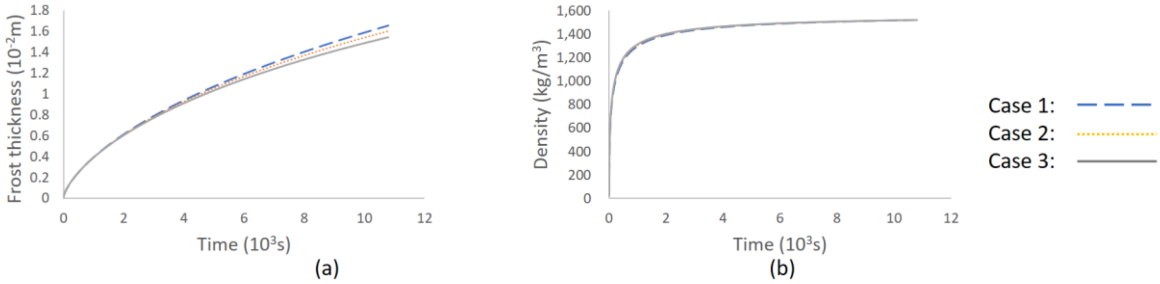

Figure 5: CO_2 frost growth for different inlet temperatures: (a) frost thickness, (b) frost density

4. Conclusion

In this article, CO_2 frosting on a cold flat plate was modelled with values for the transport properties from REFPROP or relations found in literature. Simulation results show accurate fit when compared to existing experimental results. A correlation proposed by Dietenberger et al. was used for the choice of the heat transfer coefficient which will be used to calculate the mass transfer coefficient and eventually the mass flow of CO_2 frosted. A sensitivity study was led on CO_2 frosting from biogas, and results show that for higher CO_2 concentrations, frost grows faster and more in terms of thickness and density. When the plate temperature was reduced, thickness increased because of the decrease of CO_2 saturation vapor concentration at the frost surface but density decreased because of CO_2 concentration decrease in the frost layer. Also, the increase of the gas inlet temperature will reduce slightly the frost thickness while almost not affecting the density. Further works are anticipated to study the effect of transport properties correlations' choice as well as different geometries of heat exchanger.

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