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CO₂ Hydrate Slurries for Rapid Chilling of Fresh Food Products

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ABSTRACT

For rapid chilling fresh products we propose the immersion in melting carbon dioxide hydrate crystals, produced at +8 °C and 30 bar. We compare the chilling time of a specific fresh product from 30 to 4 °C making use of a “shock freezer” (2 m/s air velocity, air at -10 °C) and applying a slurry of CO₂ hydrate crystals. Furthermore the effect of these two methods on the weight loss of the product is compared. Then the chilling of chicken products through the proposed method is experimentally verified, including microbiologic contamination of samples chilled through high-speed dry air, immersion in melting water and immersion in CO₂ hydrate slurry. Finally the economic advantages and practical applicability of the proposed method are evaluated.

1. INTRODUCTION

James et al. (2006) have reviewed studies related to the chilling of fresh products. The goal of chilling is always to limit the growth of pathogenic and food spoilage microorganisms. It has been proven that chilling reduces the number of both types of microorganisms on the surface of fresh products. In Europe dry air is the preferred chilling method. This method is believed to have clear microbiological advantages but James et al. (2006) show that the published data do not support this belief and direct contact chilling methods might even have larger microbiological advantages. The rate of chilling has some influence on the taste, texture and appearance of the fresh product. Very rapid chilling will generally lead to robust structure while very slow chilling can produce soft texture. Pederson (1979) has compared the costs of different chilling methods in Denmark. When only energy costs were considered, the cost of a countercurrent water immersion chilling system was one fifth that of an air chilling method. Slush ice is often preferred in immersion systems since cooling takes place without freezing damage of the product while the heat removal takes place at a low temperature. For 70% slush ice content of the slurry, the cooling time is lowest while with 35% slush ice the highest weight gain is attained (around 5%). When air is used, short chilling times require low air temperatures and high air velocities. James et al. (2006) report for a specific product a chilling time (38 to 4 °C) 150 minutes with 0.75 m/s and air temperature 1 °C, 60 minutes with 4.1 m/s and -7 °C, and 17 minutes with -40 °C. Short chilling times impose low air temperatures and so low evaporating temperatures and high energy consumption of the primary refrigeration cycle.

In this paper a method for the continuous production of hydrate crystals of carbon dioxide is first introduced. Then, the immersion of fresh products in melting carbon dioxide hydrate crystals, produced at +8 °C and 30 bar is proposed for rapid chilling of fresh products. First the chilling time of a specific fresh product from 30 to 4 °C through a “shock freezer” (2 m/s air velocity, air at -10 °C) and applying a slurry of CO₂ hydrate crystals is compared. Also the effect of these two methods on the weight loss of the product is compared. Then the chilling of chicken products making use of the proposed method is experimentally verified. Also the microbiologic contamination of samples chilled using high speed dry air, immersion in melting water and immersion in CO₂ hydrate slurry are compared. Finally the economic advantages and practical applicability of the proposed method are evaluated.

The research project also includes comparable experiments with carrots, veal and pork. In this paper only the chicken experiments will be reported.

2. PROTOTYPE CONTINUOUS CO₂ HYDRATE GENERATOR

2.1 Fluidized bed CO₂ hydrate slurry generator

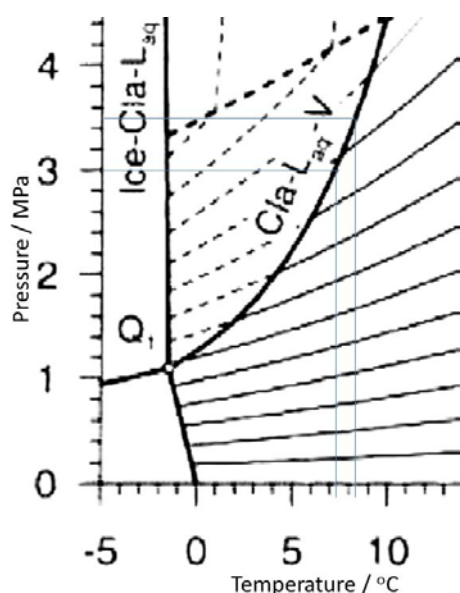


Fig. 1 – Carbon dioxide – water system showing the formation line of hydrates (Cla-L_{aq}-V).

In the past, among others Meewisse and Infante Ferreira (2001) and Pronk et al. (2003, 2010) have investigated the production of ice slurry in fluidized bed heat exchangers. A similar approach has been used to design and construct a system for the continuous production of CO₂ hydrate crystal slurry. The operating conditions are however quite different, limiting an easy application of similar design rules. First of all the operating pressure is in the range 25 to 35 bar delivering some challenges with respect to pumping, but also addition and extraction of flows. The relevant range of equilibrium between CO₂ hydrate crystals and aqueous CO₂ solution and aqueous CO₂ solution plus CO₂ vapor is illustrated in Fig. 1 (Diamond and Akinfiev, 2003).

The Cla-L_{aq}-V line indicates the hydrate – aqueous solution – vapor equilibrium line. To its left a slurry of hydrate crystals can be formed. The lines at 30 and 35 bar indicate when hydrates formation will start, respectively, at about 7.3 and 8.3 °C. Since the process allows for crystal formation at temperatures above 0 °C and so to make operation of the primary refrigeration cycle at temperatures above this temperature possible, operating under high pressures in this range will be required in the system. A phase transition at around 8 °C makes evaporating temperatures of the primary refrigeration cycle of 4 to 6 °C possible and so gives significant energy saving advantages in comparison to ice slurry production systems with evaporating temperatures in the range -5 to -8 °C.

An additional challenge is that the slurry must be brought to atmospheric pressure so that it can be applied to the fresh products. For this purpose a special discharge section has been implemented in the prototype system which is intermittently and automatically depressurized and discharged to atmospheric pressure. Since the depressurization is an adiabatic process and some of the captured CO₂ will escape and vaporize, this will have an effect on the properties of the extracted slurry. Except for specific requirements imposed to the pump which circulates the slurry through the fluidized bed, the continuous injection of gaseous CO₂ into the aqueous solution also requires the application of static mixers which guarantee that the gaseous CO₂ is homogeneously dispersed through the solution.

Fig. 2 shows the prototype fluidized bed CO₂ hydrate slurry generator. The fluidized bed is installed vertically and has a disengaging section on the top. The fluidized bed is 1.9 m height and is surrounded by a falling film of evaporating R134a. The discharge section is located in the left corner of the frame, in between the two blue valves. The vertical vessel close to this section is the, high pressure, slurry storage vessel. The fluidized bed is a stationary fluidized bed and has an internal diameter of 88.9 mm. The fluidized particles are stainless steel particles with diameter of 2 mm. The bed porosity is 85%. The increase in crystals concentration with time could be derived from the solution density change in time. In “continuous operation” conditions, the same amount of CO₂ and water removed by extracting the slurry was continuously added so that the crystals concentration could be maintained at a selected level. More details of the prototype have been reported by Zhou et al. (2015a,b).

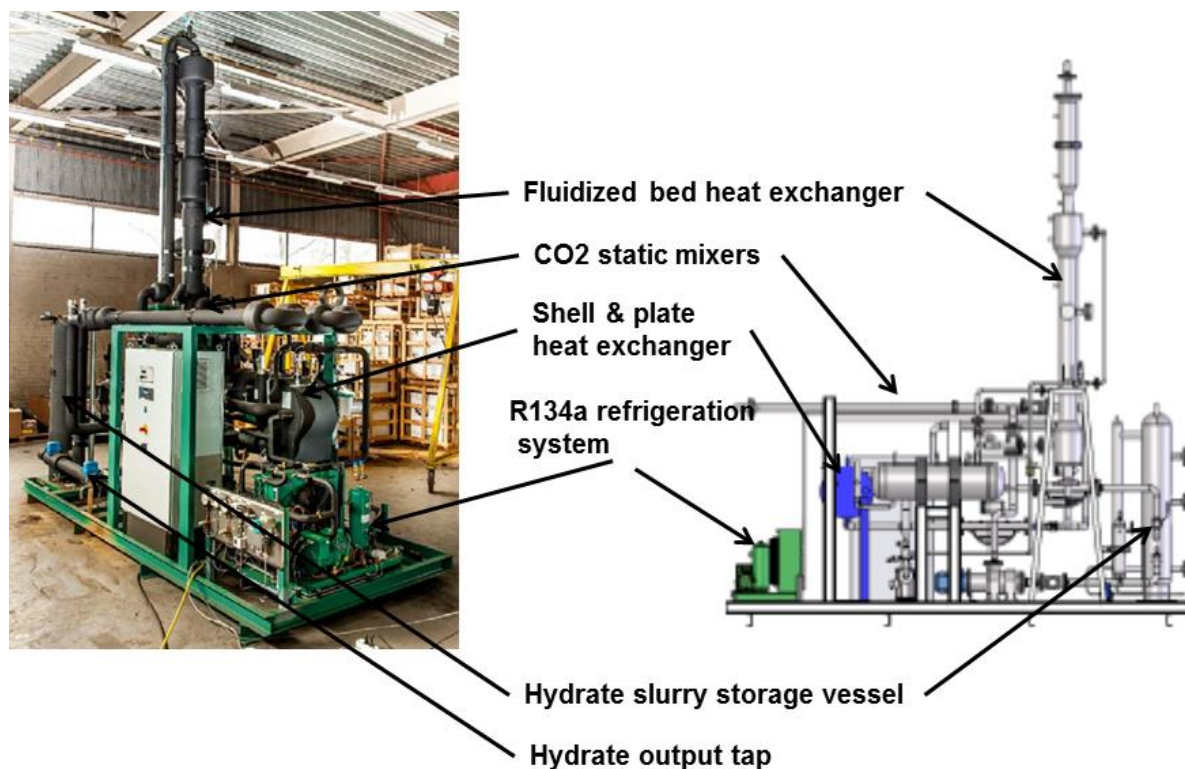


Fig. 2 – Prototype fluidized bed CO₂ hydrate slurry generator.

A second hydrate generator in the system is a Vatherus IQ-plate PSHE 4/3 HH-36/1/1 with a solution flow of 6.5 m³/h. R134a evaporates on the other side of the plates of this shell and plate heat exchanger. Hydrates will grow on the plate surface and will be removed by the (high velocity) solution flow. This second generator is much more promising for industrial purposes because of its compact construction and its operation free of fluidized steel particles. A manageable growth of the hydrates is still part of the ongoing R&D program. The CO₂ hydrates used in the experiments discussed in this paper have all been produced with the fluidized bed generator.

2.2 Experimental performance of the prototype

The consumption of CO₂ during the formation of the hydrate slurry has been investigated under several operating conditions. Before extracting slurry from the system, first the concentration of solids was increased until the desired level. Fig. 3 (left) illustrates how the density of the slurry (starting from a CO₂ –water solution) increases with time. The right hand side of Fig. 3 shows that densities up to ca. 1025 kg/m³ could be attained what corresponds to ca. 40% hydrate crystals in the slurry.

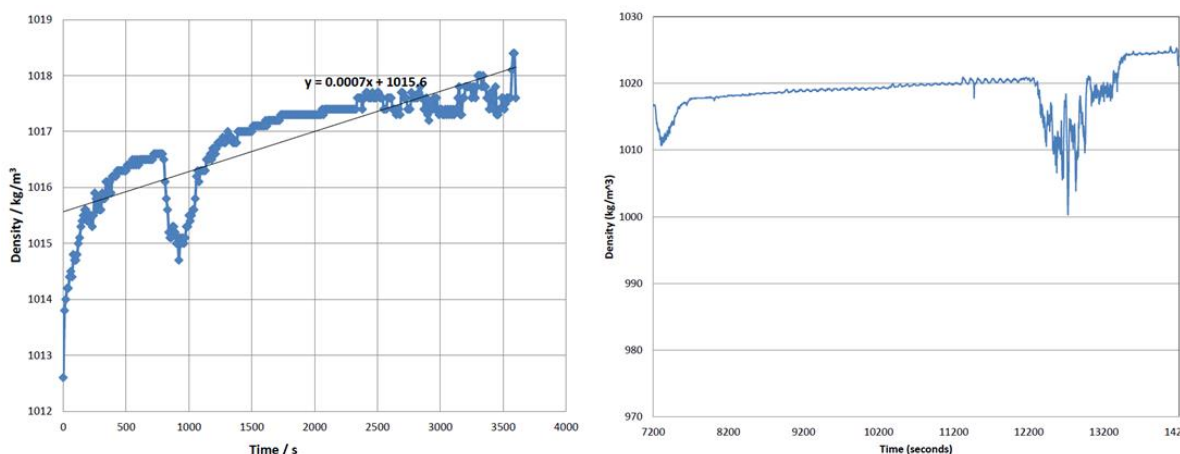


Fig. 3 – Slurry density as a function of time. Initial density increase (left) and densities which could be attained (right). The density is an indication of the solids concentration in the slurry (Zhou et al., 2015a).

Fig. 4 shows the CO₂ consumption and operating conditions of the system for a period of stable operation in which CO₂ addition and slurry removal are balanced.

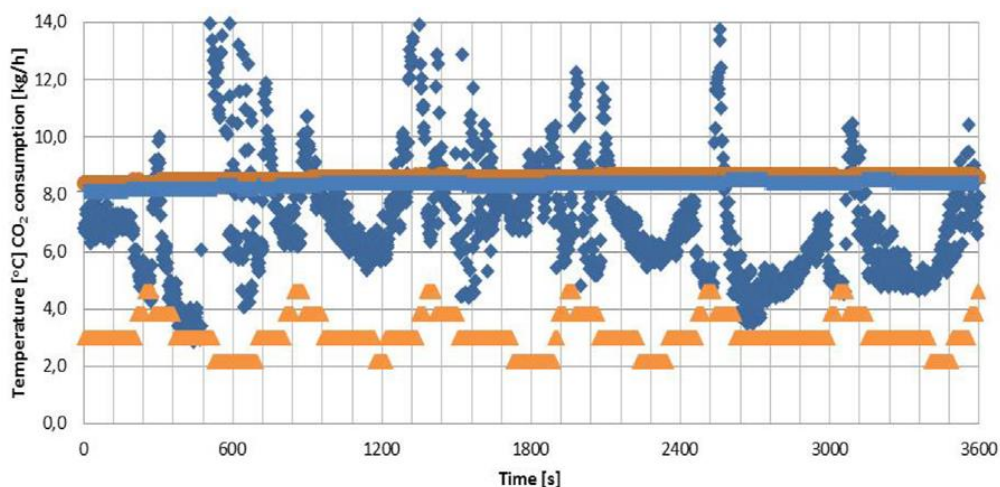


Fig. 4 – CO₂ consumption (dark blue); evaporating temperature (orange); slurry in / out (orange)

Fig. 4 shows that while the slurry in and outlet temperatures are around 8 – 8.5 °C, the evaporating temperature varies between 2 and 4.5 °C. By applying a compressor speed control, the evaporating temperature has been made much more stable in later experiments. During these experiments approximately 7 kg/h CO₂ gas was being added to the system and being captured in the cavities of the hydrate crystals.

It should be remarked that, although the average overall temperature difference was quite small (approximately 5 K), the overall heat transfer coefficient during hydrate formation was quite high: around 1800 W/m²K. This indicates an internal heat transfer coefficient of around 6500 W/m²K, making the fluidized bed hydrate slurry generator an attractive design for these applications. This value is significantly higher than predicted making use of Haid's (1997) correlation.

3. CHILLING TIME SHOCK CHILLER VS IMMERSION IN CO₂ HYDRATE SLURRY

Quick chilling of products making use of immersion in CO₂ hydrate slurries is expected to have the following advantages:

1. reduce the number of both pathogenic and food spoilage microorganisms on the surface of fresh products (longer shelf life);

2. reduce the weight loss of product (economic loss) in comparison with chilling with dry air which also reduces the robustness of the fresh products (quality and economic loss);
3. slow down the growth of microorganisms due to high concentration of CO_2 around product.

3.1 Chilling time

Fig. 5 (left) shows the calculated surface temperature of a meat product of cylindrical shape with a diameter of 10 cm both when a shock freezer with cold dry air of -10°C and when immersion in CO_2 hydrate slurry are applied to the product. Fig. 5 (right) shows the expected core temperature of the same product.

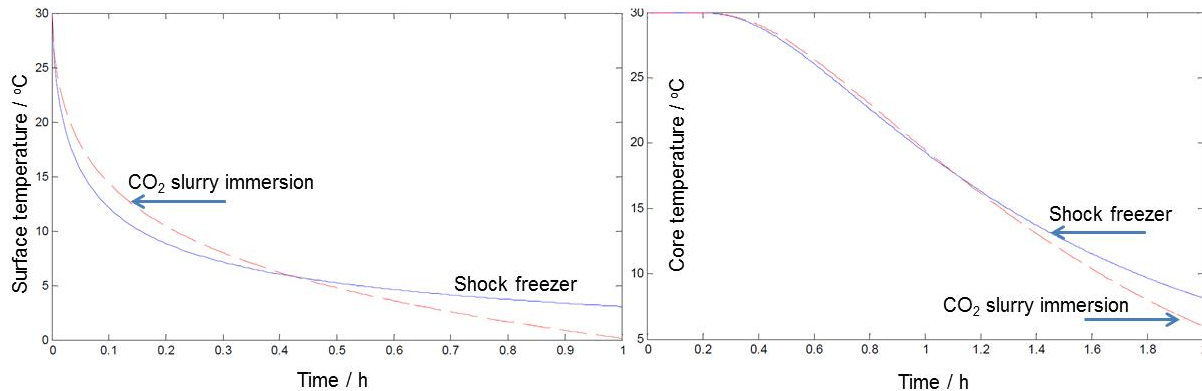


Fig. 5 – Comparison of the predicted surface (left) and core (right) temperature of a meat product with a diameter of 10 cm when chilled by two alternative methods (Broeze et al. (2015)).

Fig. 5 shows that the surface cooling with the melting CO_2 hydrate crystals goes quicker than the cooling with chilled air. This is expected since the heat transfer coefficient of the melting crystals is significantly higher than of the forced air flow. Since microorganism growth starts at the product surface and also weight loss is associated with the surface temperature, the supremacy of the immersion in CO_2 hydrate slurry is evident.

3.2 Weight loss

Carciofi and Laurindo (2007) have demonstrated that immersion of meat in a chilled bath leads to a mass increase so that a mass increase is expected when immersion in CO_2 hydrate slurry is applied. Fig. 6 (left) shows the experimental weight gain determined by these authors: weight gain of about 2% can be expected. The right hand side of Fig. 6 shows the weight loss predicted by Broeze et al. (2015) for the same product when shock chilling is applied with dry air of -10°C and an air velocity of 2.0 m/s. When shock freezing is applied after two hours of operation (needed to reach the core of the product) the weight loss is about 2.5%. Again the use of CO_2 hydrate slurry seems to be quite advantageous.

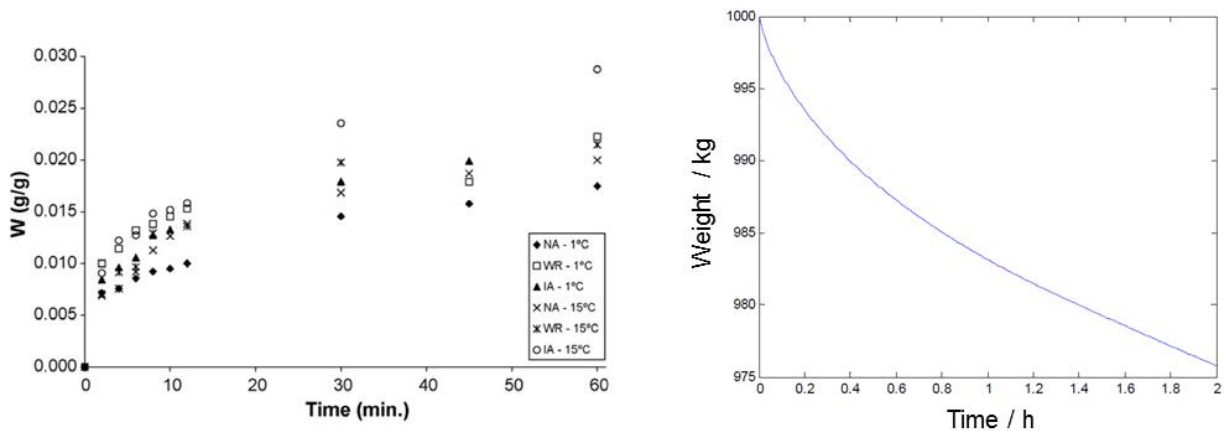


Fig. 6 – Comparison of the predicted weight gain (left) when immersion chilling is applied (Carciofi and Laurindo, 2007) and weight loss (right) when shock freezing is applied (Broeze et al., 2015).

3.3 Concentration of CO₂ around product

Since the CO₂ captured in the hydrates during melting leads to a reduction of the pH of the melting slurry, it is expected that the melting CO₂ hydrate crystals will slow down the growth of microorganisms in the immersion bath.

4. EXPERIMENTAL CHILLING TIME FOR IMMERSION IN CO₂ HYDRATE SLURRY

Three situations have been considered for the rapid chilling of chicken products. For each situation 10 products have been processed. The evaluated situations are:

1. Shock chilling with air temperature a few degrees below freezing point in a chilling tunnel;
2. Immersion of a few kilogram of product in melting CO₂ hydrate slurry;
3. Immersion of a few kilogram of product in ice-water.

The product (chicken breast) has approximately the shape of a cylinder with 5 cm diameter. When immersed in CO₂ hydrate slurry, the core of the product cooled down from 20 to 7 °C in 20 to 30 minutes while the shock chilling process required about 10 minutes more. This is illustrated in the left hand side of Fig. 7. The right hand side of Fig. 7 shows the surface temperature of the product.

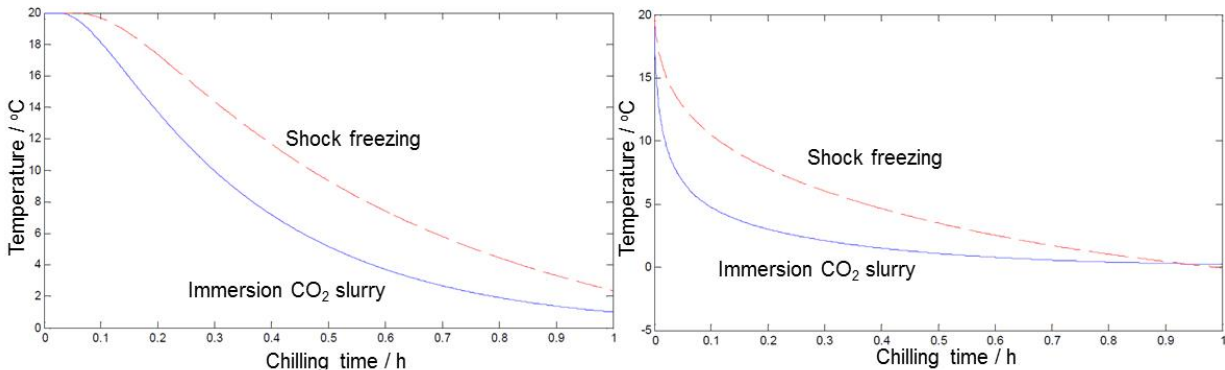


Fig. 7 – Comparison of the experimental chilling time of the chicken product. Core temperature (left); Surface temperature (right) (Broeze et al., 2015).

Since the difference in chilling time (10 minutes) is small in comparison to the time between slaughter and chilling which was between one and two hours due to practical reasons, no significant difference was encountered between the microorganisms contamination for the three applied methods. This is illustrated in the left hand side of Fig. 8. It can be expected that when the delay between slaughter and chilling process is shortened then significant differences can be measured. To illustrate this, the chilling of a pork product using the three methods is also given in the right hand side of Fig. 8. From the chicken product experiments the impact of the lower pH in the melting CO₂ hydrate slurry could not be identified: the contamination did not reduce in comparison to the alternative methods however the hydrates had not a negative effect on the product quality. Nevertheless, the pork product experiments show a substantial reduction of the microbiological contamination indicating a shelf life increase of at least one day when the CO₂ hydrate slurry is applied.

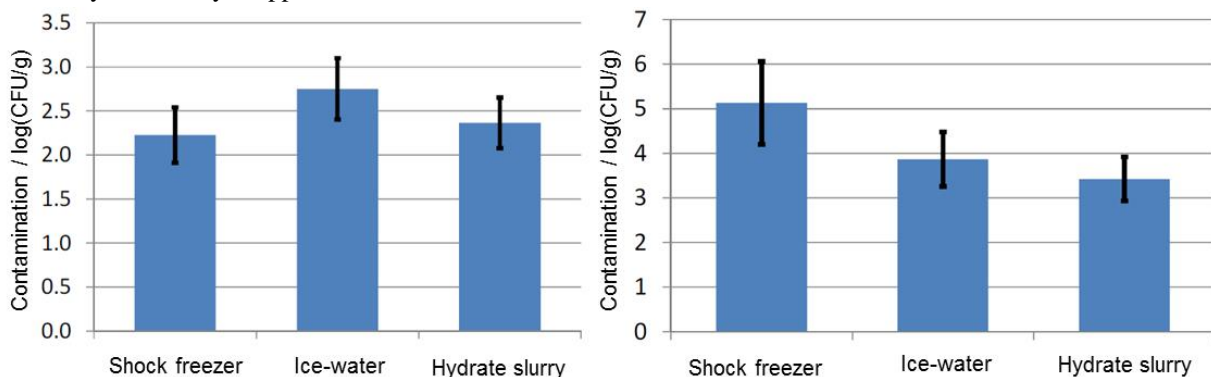


Fig. 8 – Comparison of the experimental microorganisms contamination of the chicken product (left) and pork product (right) (Broeze et al., 2015).

Air chilling is associated with significant weight loss of products. Weight loss leads, for some products, to a loss of robustness of the product. Application of melting CO₂ hydrate slurry or melting ice-water prevents weight loss and even leads to weight increase of the product. The production of ice-water requires evaporating temperatures below 0 °C while the hydrate slurry can be produced with evaporating temperatures of 3-4 °C.

5. ECONOMIC ADVANTAGES AND APPLICABILITY

In Fig. 9 a schematic overview is given of the system including the primary refrigeration loop. In case of shock freezing the secondary loop consists of an air flow which is forced along the products. Since the air should have a temperature lower than 0 °C, evaporation must take place at -10 °C or even lower temperatures. The ice-water production will require an evaporating temperature below 0 °C (-3 °C) while the CO₂ hydrate generation requires +4 °C. Assuming that the primary refrigeration cycle uses R134a as the refrigerant, the compressor has an isentropic efficiency of 70% and that the condensation temperature +30 °C is then the results listed in Table 1 apply. Assumed is a system with a cooling capacity of 500 kW and which operates 8000 h/year.

Table 1 – Comparison of energy consumption and related emissions for the alternative systems.

System	COP	W _c [kW]	E [MWh]	Cost [Euro]	Savings [%]	CO _{2eq} [ton]
Shock freezing	3.78	132	1056	68640		528
Ice-water	4.51	111	888	57720	15.9	444
Hydrate slurry	6.52	76.5	612	39780	42.0	306

Table 1 shows that the hydrate slurry system leads to 42% electric energy savings and 42% CO₂ emissions savings, significantly larger impact than of using an ice-water system.

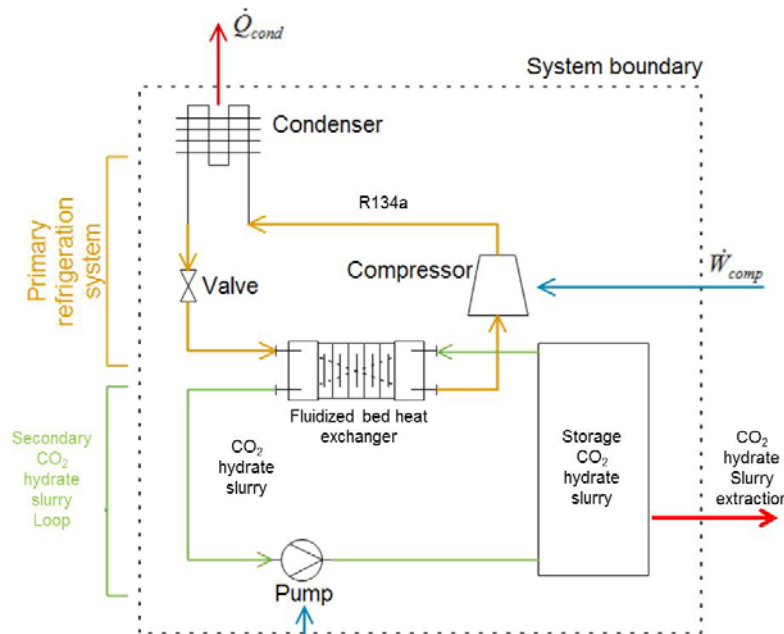


Fig. 9 – Schematic of the primary refrigeration cycle which produces the chilling agent for the process.

method reduces the chilling time from 35 minutes for shock freezing to 25 minutes, a reduction of almost 30%. In this way it is possible to increase the production capacity making use of the same facilities.

The concentration of hydrates is 26%. (Zhou et al. 2015a). This concentration is equal to 6 mass percent of CO₂. The enthalpy of the concentration is 100 kJ/kg.

The requested cooling load of meat products cooled from 38 to 4 °C is 115 kJ/kg of product. For cooling 1 kg of meat, 1 kg solution is requested. This is equal to 60 gram of CO₂ per kg meat. The CO₂ price is equal to €0.10-0.20 / kg. The extra cost of the CO₂ consumption is equal to €0.01 / kg meat. (Lobregt 2015). The energy saving per kg meat is not enough to compensate the CO₂ consumption Preventing a product dehydration of 2%, with an average meat price of € 2.00 / kg, results in a cost reduction of € 0.04 / kg product. This cost reduction is 4 times larger then the costs associated with the CO₂ consumption.

Additional advantages of the hydrate-slurry system are associated with the chilling time. The hydrate slurry chilling

6. CONCLUSIONS

A prototype has been developed and realized for the continuous production of CO₂ hydrate slurry. The prototype could

- Continuously deliver hydrate slurry at environmental pressure (continuous addition of CO₂ gas + water and slurry removal);
- Operate with high concentrations of hydrate crystals (up to 40% concentration);
- Operate with small overall temperature differences between slurry and primary evaporating refrigerant (4 to 5 K);
- Operate with a high overall heat transfer coefficient (1800 W/m²K).

The prototype has been used to produce hydrate slurry which has been used for the chilling of fresh products. The product tests have indicated that

- Chilling times are approximately 30% shorter than for shock freezing systems;
- The microorganisms contamination is at least comparable for shock freezing, ice-water and hydrate slurry chilling methods for the product investigated. The contamination level was mainly determined by the period between slaughtering and start chilling which was large for these experiments;
- Due to the shorter chilling time, for shorter processing times between slaughtering and chilling, a significant reduction in microorganisms contamination can be expected;
- Immersion of the product in melting hydrate slurry prevents weight loss and so reduces the costs associated with weight loss.

For the whole system including primary refrigeration cycle it has been concluded that

- Both electric energy and related CO₂ emissions are reduced by 42% in comparison with shock freezing systems.
- The cost savings associated with the reduced dehydration of the product are 4 times larger than the costs of the consumed CO₂.

NOMENCLATURE

CO _{2eq}	equivalent CO ₂ emissions	(ton)
COP	coefficient of performance	(-)
Cost	Yearly costs of energy	(Euro)
E	electrical energy consumption	(MWh)
W	power requirement	(kW)

Subscript

c	compressor
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