The use of dry ice to maintain high CO_2 levels in CA transports of low-respiring produce

A recipe to maintain high CO_2 in reefer container shipments of table grapes or other fruits.

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Colophon

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Summary

The growth of *Botrytis cinerea* is one of the main post-harvest issues in table grapes and many other fruits. Slow-release SO_2 (sulphur dioxide) pads are therefore routinely used in reefer container transport of grapes. There are downsides to SO_2, and hence reasons to search for alternatives. An atmosphere with approximately 12 % CO_2 (carbon dioxide) seems the most promising alternative to SO_2. The respiration rate of grapes is too low to achieve 12 % CO_2 in reefer containers. Hence an additional source of CO_2 is needed. This source can be dry ice. The aims of this research are:

1. To develop an approach to rapidly raise CO_2 to 12 % in CA reefer containers and subsequently maintain CO_2 at 12 % for multiple weeks, using dry ice as a source of gaseous CO_2.
2. To experimentally verify the technical feasibility of the approach.

An approach has been developed to maintain CO_2 at 12 % in CA reefer containers for multiple weeks, using dry ice as a source of gaseous CO_2 gaseous. The approach consists of combining:

1. A reefer container with a CO_2 sensor and an autovent set to regulate CO_2 to 12 % by closing then vent when measured CO_2 is too low and opening the vent when it is too high.
2. A mass of fast-release dry ice, placed in the container without any insulation, sufficient to rapidly raise CO_2 to 12 %.
3. A mass of slow-release dry ice, placed in the container in a heavily insulation box, sufficient to maintain CO_2 at 12 % during the expected duration of the trip, with the box insulation value tailored to compensate for the anticipated rate of CO_2 leakage from the container.

The technical feasibility of the approach has been verified in two consecutive experiments in an empty 40 ft. reefer container.

Practical application seems economically feasible, but of course some risks remain. The most significant foreseen risks are the unknown container air leakage rate, the fact that the treatment is strictly limited to the period where the container doors are closed, and the unknown efficacy of the treatment on different types of grapes and different initial infections with *Botrytis*.

Because of the promising results a patent application has been filed.

Content

1 Introduction

The growth of *Botrytis cinerea* is one of the main post-harvest issues in table grapes (Chervin *et al.*, 2012) and many other fruits. The effectivity of SO_2 (sulphur dioxide) as a fungicide against *Botrytis cinerea* is unrivalled. Slow-release SO_2 pads are therefore routinely used in reefer container transport of grapes (see *e.g.* Lichter *et al.*, 2008). Yet there are downsides to SO_2, and hence reasons to search for alternatives. Chervin *et al.* (2012) list a whole series of tried alternatives to SO_2. CO_2 (carbon dioxide)seems the most promising alternative to SO_2 (*e.g.* Retamales *et al.*, 2003; Crisosto *et al.*, 2002a; Crisosto *et al.*, 2002b; Artés-Hernández *et al.*, 2004; Teles *et al.*, 2014; Rosales *et al.*, 2013). From all this research on the effect of CO_2 it appears that an atmosphere with approx. 12 % significantly suppresses the growth of *Botrytis cinerea*, while mostly staying below the limit where harm is done to the grapes.

The respiration rate of grapes is too low to achieve 12 % CO_2 in reefer containers. Hence an additional source of CO_2 is needed. This source can be dry ice.

The use of dry ice as a source for CO_2 fumigation for storage of dry food, esp. seed products like grain, is known. Put dry ice and grain together in a container. Let the dry ice sublimate in the container and accumulate high CO_2 atmosphere, then close the lid of the storage container. See *e.g.* Harrison & Andress (1998).

The use of dry ice for cryogenic cooling is old and well-known, but has a very limited application range in chilled transports. Two objections are: the sublimation temperature of -78.5 °C may harm the chilled produce, and the unintended build-up of a modified atmosphere must be prevented (see *e.g.* Vigneault *et al.*, 2009).

Jeyasekaran *et al.* (2008) report on the use of dry ice as a combination of coolant and CO_2 fumigant for the MA packaging of fresh fish exported from India.

To the best of our knowledge there are no reports on the use of dry ice to maintain high CO_2 concentrations in MA/CA environments for the storage/transport of fruit.

The aims of this research are:

1. To develop an approach to rapidly raise CO_2 to 12 % in CA reefer containers and subsequently maintain CO_2 at 12 % for multiple weeks, using dry ice as a source of gaseous CO_2.
2. To experimentally verify the technical feasibility of the approach.

The research has been carried out in an independent way by Wageningen Food & Biobased Research, commissioned by Bakker Barendrecht, VEZET, Albert Heijn and Maersk Line. The commissioning companies jointly financed the research, with financial support by Foundation TKI Horticulture (the Dutch Ministry of Economic Affairs) (project number 623 909 0301, TKI number 1406-031).

2 Theory

The theory is explained with reference to Fig. 1, depicting the experimental system. It sketches a reefer container (1). The red arrow indicates the return air flow (2) from the cargo space into the reefer unit. The blue arrow indicates the supply air flow (3) from the reefer unit into the cargo space. The airflow in the container is maintained by evaporator fans (4). The pressure drop over the evaporator fans is the driving force for fresh air exchange through an autovent (5), from which the degree of opening can be manipulated by the controller (6) based on the measurement signal of a CO_2 sensor (7) in the return air flow. To rapidly build-up an atmosphere with 12 % CO_2 after closing the container doors an amount $m_{co2}^{solid,fast}(t_0)$ of dry ice is placed in the container without any insulation: the fast-release portion of dry ice (8). To maintain the atmosphere at 12 % an amount $m_{co2}^{solid,slow}(t_0)$ of dry ice is placed in the container in a heavily insulation box: the slow-release portion of dry ice (9). Only during the experiments all dry ice is placed on a scale (10) to monitor the dry ice weight change.

The insulation value U_{box} of the box containing the slow-release portion of dry ice is designed such that the release rate of gaseous CO_2 from the box equals the anticipated loss of gaseous CO_2 from the container due to container air leakage, minus the anticipated CO_2 production rate by the cargo.

Ever more reefer containers are equipped with CO_2-regulated autovents (here denoted as AV+). In AV+ a CO_2 sensor in the return air flow measures CO_2, and relays the reading to a controller. When the measured CO_2 exceeds the CO_2 set point $CO_{2,set}$ the controller opens the autovent at 75 m^3/h, and close it again when measures CO_2 drops below $CO_{2,set}$ minus 0.8 %. To avoid CO_2 concentrations higher than intended the reefer unit's AV+ system regulates CO_2 to 12 %.

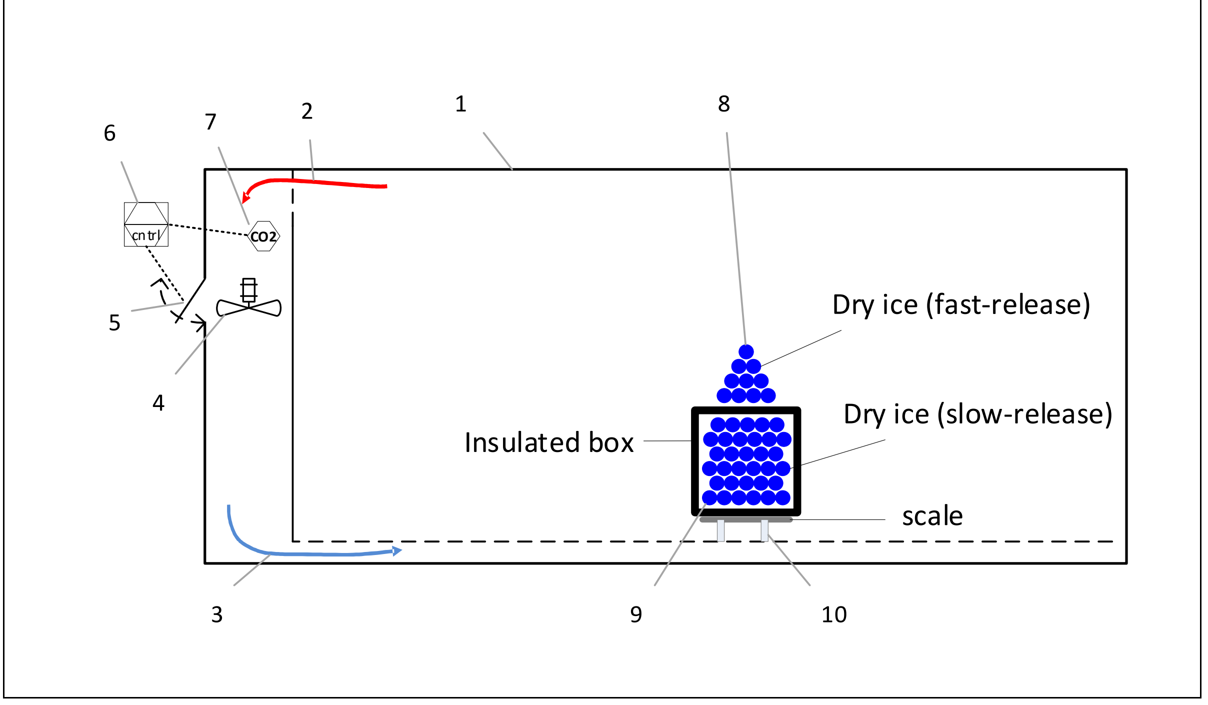

Fig. 1, schematic drawing of dry ice in reefer container (scale is only there in experimental set-up).

The parameters $m_{co2}^{solid,fast}(t_0)$, $m_{co2}^{solid,slow}(t_0)$ and U_{box} are calculated in relation to the CO_2 mass balance over a container:

Accumulation of CO_2 in container = CO_2 losses to ambient+ respiratory CO_2 production + CO_2 slow release + CO_2 fast release

In mathematical terms:

$$\rho_{CO2} \times \frac{V_{air}}{100} \times \frac{dx_{CO2}}{dt} = \rho_{CO2} \times \phi_{air}^{leak} \times \frac{(CO_2^{amb} - x_{CO2})}{100} + \frac{m_{fruit} \times r_{resp} \times 0.34}{1000} + (\dot{m}_{CO2}^{prod,slow} + \dot{m}_{CO2}^{prod,fast}) \quad [\text{kg.h}^{-1}] \quad (1)$$

See Table 1 for the nomenclature. In the above equation 0.34 is a conversion factor from respiratory heat production r_{resp} in W/tonne to CO_2 production rate in [(mg CO_2)/(kg prod.).h].

The mass $m_{co2}^{solid,fast}(t_0)$ is the amount of dry ice needed to raise x_{CO2} from the initial CO_2^{amb} to the target value of 12 %:

$$m_{co2}^{solid,fast}(t_0) = \frac{\rho_{CO2} \times V_{air} \times (12 - 0.04)}{100} = 16.4 \quad [\text{kg}] \quad (2)$$

The rate $\dot{m}_{co2}^{solid,fast}$ at which this mass sublimates shall be as high as possible, hence it should be placed inside the container without any insulation around it.

In the maintenance phase, after completion of the initial rise to 12 %, the CO_2 production rate should balance the loss of CO_2 due to air leakage minus the possible respiratory CO_2-production, i.e.

$$\dot{m}_{CO2}^{prod,slow*} = \phi_{air}^{leak} \times \frac{(x_{CO2} - CO_2^{amb})}{100} \times \rho_{CO2} - m_{prod} \times r_{resp}/1000 \quad [(\text{kg } CO_2).\text{h}^{-1}] \quad (3)$$

Solving the above equation for the target value $\dot{m}_{CO2}^{prod,slow*}$ of $\dot{m}_{CO2}^{prod,slow}$ in an empty container, assuming an air leakage rate of 0.7 m^3/h, yields:

$$\dot{m}_{CO2}^{prod,slow*} = 0.7 \times \frac{(12 - 0.04)}{100} \times 1.98 = 0.17 \quad [\text{kg.h}^{-1}] \quad (4)$$

Once the required production rate $\dot{m}_{CO2}^{prod,slow*}$ is known the required initial mass $m_{co2}^{solid,slow}(t_0)$ follows from

$$m_{co2}^{solid,slow}(t_0) = t_{final} \times 24 \times \dot{m}_{CO2}^{prod,slow} \quad [\text{kg}] \quad (5)$$

For a 12 days shipment this is

$$m_{co2}^{solid,slow}(t_0) = 12 \times 24 \times 0.17 = 48 \quad [\text{kg}] \quad (6)$$

To adjust the slow-release production rate $\dot{m}_{CO2}^{prod,slow}$ the initial mass $m_{co2}^{solid,slow}(t_0)$ is packed in an insulated box with specific heat leakage rate U_{box}. CO_2 has a freezing point of -78.5 °C, hence during sublimation the dry ice temperature T_{dry_ice} inside the box is -78.5 °C. The set temperature T_{set} of the container is 0 °C. The required box heat transfer coefficient U_{box}^* is the only unknown in

$$\dot{m}_{CO2}^{solid,slow*} \times L_{dry\_ice} \times \frac{1000}{3600} = U_{box}^* \times (T_{set} - T_{dry\_ice}) \quad [\text{W}] \quad (7)$$

and hence

$$U_{box}^{*} = \frac{\dot{m}_{CO2}^{prod,slow*} \times L_{dry\_ice} \times \frac{1000}{3600}}{T_{set} - T_{dry_{ice}}} = \frac{0.17 \times 571 \times \frac{1000}{3600}}{0 - -78} = 0.34 \qquad [W/°C] \quad (8)$$

The U-value of a box follows from its dimensions, and the heat conduction coefficient λ_{box} of the material of which it's made:

$$U = \sum_{s=1}^{6} \frac{\lambda_{box}}{d_s} \times L_s \times W_s \qquad [W/°C] \quad (9)$$

Obviously the box's internal length, width and height must suffice to contain $m_{co2}^{solid,slow}(t_0)$, which leaves λ_{box} and the 6 wall thicknesses as design parameters. The natural approach is to first calculate $m_{co2}^{solid,slow}(t_0)$, then calculate the required box dimensions to contain $m_{co2}^{solid,slow}(t_0)$ and then calculate the required wall thicknesses to achieve the required U_{box}^{*}.

Uncertainties in the preceding calculation:

1) The true container air leakage rate is unknown.
2) The volume of air in a stuffed container is not exactly known.
3) It is unknown how much gaseous CO_2 may be absorbed by the fruit stuffed in the container.
4) Dry ice sublimates at -78.5 °C, but the air temperature inside the slow-release box is unknown, and stratification in the box may be severe, esp. when the remaining amount of dry ice diminishes.

Table 1, nomenclature

symbol	description	unit	value [unit]
ρ_{CO2}	density of gaseous CO_2 @ 0 °C and ambient pressure	kg/m^3	1.98
$\dot{m}_{CO2}^{prod,fast}$	fast-release CO_2 production rate	kg/h	
$\dot{m}_{CO2}^{prod,slow}$	slow-release CO_2 production rate	kg/h	
CO_2^{amb}	ambient CO_2 concentration	%	0.04
$m_{co2}^{solid,fast}(t)$	mass of fast-release portion of dry ice at time t	kg	
$m_{co2}^{solid,slow}(t)$	mass of slow-release portion of dry ice at time t	kg	
ϕ_{air}^{leak}	air leakage rate (with a priori assumed value)	m^3/h	0.7
d_s	thickness of box side s	m	
H_c	internal height container	m	2.60
L_c	internal length container	m	11.59
L_{dry_ice}	latent heat of sublimation of dry ice	kJ/kg	571
L_s	length of box side s	m	
m_{fruit}	mass of fruit in container	tonne	0
r_{resp}	respiration rate of the carried fruit	W/tonne	

t_0	initial time	h	0
T_{dry_ice}	temperature of sublimating dry ice	°C	-78.5
t_{final}	final time till which CO_2 is to be maintained at 12 %	days	
T_{set}	container set temperature	°C	0
T_{set}	container set temperature	°C	0
U_{box}	specific heat leakage rate of the box containing the slow-release portion of dry ice	W/°C	
V_{air}	air volume inside container	m^3	69
V_c	internal volume container	m^3	69
W_c	internal width container	m	2.29
W_s	width of box side s	m	
x_{CO2}	CO_2 concentration in container	%	
λ_{box}	heat conduction coeff. of box' wall material	$W.m^{-1}.°C^{-1}$	

3 Experiment 1

3.1 Experiment 1: materials and methods

Experiment 1 was performed in ambient conditions. In this first experiment dry ice was placed on a scale in a 40 ft. HC reefer container (Fig. 2, Table 2, Table 3) equipped with AV+ atmosphere control. The scale (Fig. 3, Fig. 4) recorded the weight of dry ice + packaging at a 5 min. log interval. A Dansensor (Fig. 5, Fig. 6) logged the CO_2 concentration inside the container at a 7 min. log interval. The Dansensor was placed outside the container and sampled the atmosphere through a small air sampling tube.
The purchased amount of dry ice was 70 kg, it was delivered in three normally insulated small EPS boxes (Table 4) of equal weight. Before the start of the experiment already 6 kg had sublimated, leaving 64 kg of dry ice at the start of the experiment. At the start of the experiment two small boxes, containing together 43 kg of dry ice ($m_{co2}^{solid,slow}(t_0)$ = 43 kg), were placed in a heavily insulated large box. The large insulated box was tailor-made from 5 cm thick EPS foam panels purchased from the local lumberyard (Table 5). The third normally insulated small box was then placed on top of this large box ($m_{co2}^{solid,fast}(t_0)$ = 21 kg), and its lid was removed. Together this was all placed on a scale (Fig. 7) in the container. A CA door curtain was installed (Fig. 8) before closing the container doors. See Table 6 for a further specification of test conditions.

Fig. 2, test container

Table 2, photos of tested container type plates

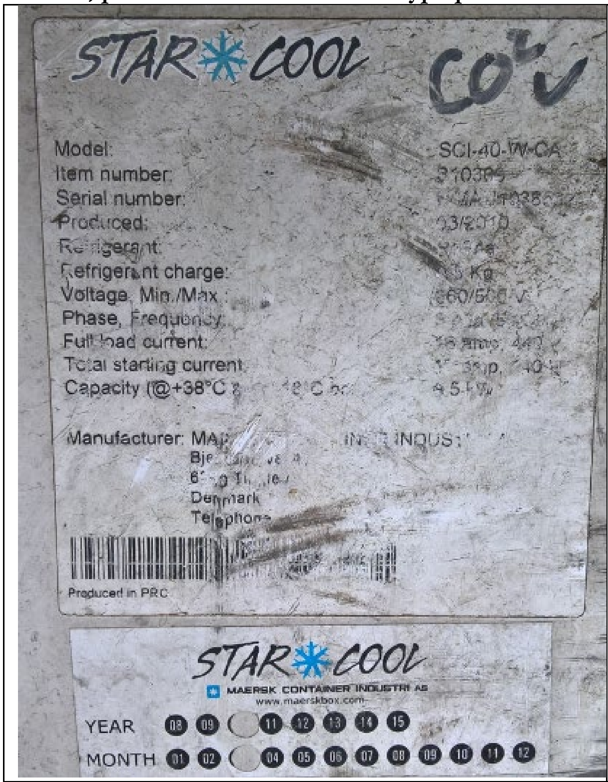

Table 3, characteristics of equipment used in tests

	manufacturer	man. date	model no.	identification no.	last PTI
container	N/A	N/A	N/A	MMAU103858[2]	N/A
unit	Starcool	March 2010	SCI-40- -W-CA	Unreadable	24 May 2016
box	MCI Qingdao	Febr. 2010	MQRS-40HS-062A	MMAU103858[2]	N/A

Fig. 3, scale

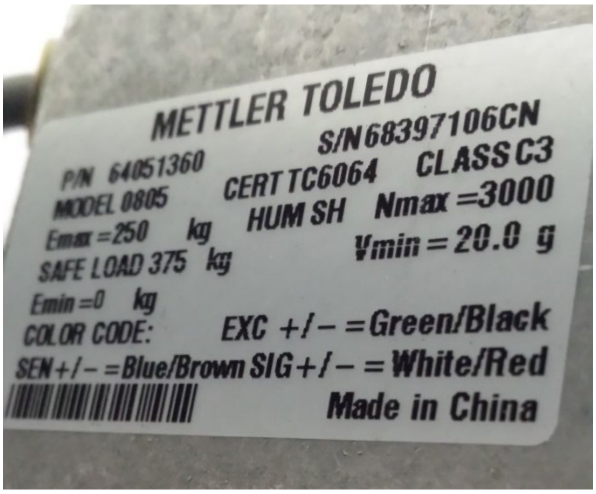

Fig. 4, scale type plate

Fig. 5, Dansensor CO_2 logger

Fig. 6, Dansensor type plate

Table 4, specifications of small internal EPS box, containing dry ice

Parameter	Value
external dimensions	L x W x H = 380 x 380 x 380 mm
internal dimensions	L x W x H = 310 x 310 x 310 mm
thickness of all sides	35 mm
Specified thermal resistance	Unknown, assumed λ = 0.039 $W.m^{-1}.°C^{-1}$, though probably a bit lower.
Calculated U-value of small box (with closed lid)	0.44 $W.°C^{-1}$

The calculated U-value in both Table 4 and Table 5 assumes an air-to-wall heat transfer coefficient α = 5 $W.m^{-2}.°C^{-1}$ at all sides of the boxes, both internally and externally.

Table 5, specifications of large external EPS box, containing two small boxes with dry ice

Parameter	Value
external dimensions	L x W x H = 1000 x 500 x 700 mm
internal dimensions	L x W x H = 800 x 400 x 400 mm
thickness of floor and lid	150 mm
thickness of long side walls	50 mm
thickness of short side walls	100 mm
Specified thermal resistance of 50 mm thick panels from which it is built up	1.30 $m^2.°C/W$ (i.e. $\lambda = 0.039\ W.m^{-1}.°C^{-1}$)
Calculated U-value of large box	0.64 $W.°C^{-1}$
Calculated U-value of large box + small box inside	0.34 $W.°C^{-1}$

The calculate U-value U_{box} of the large box + the small box inside is 0.34 $W.°C^{-1}$, exactly equal to the theoretical target value for U_{box} (eqn. 8).

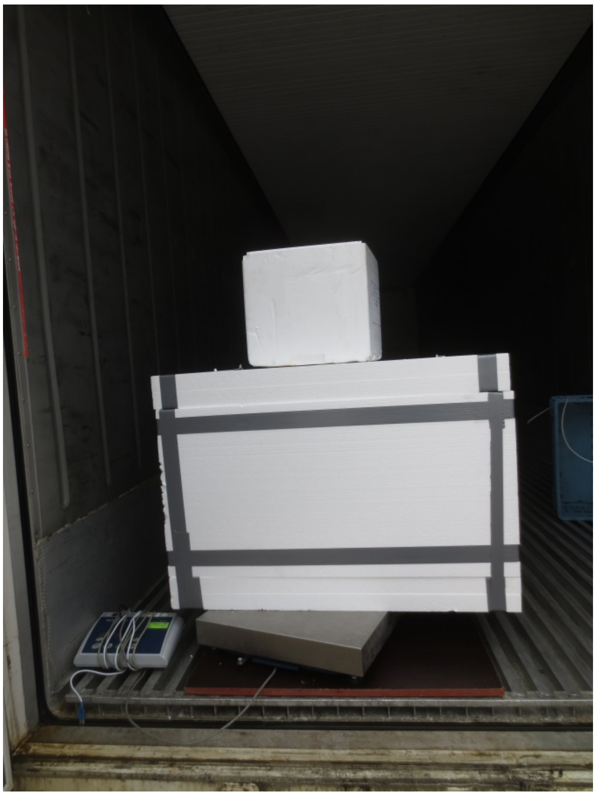

Fig. 7, small dry ice carton without lid on top of large heavily insulated carton containing two small dry ice cartons, together placed on a scale at container's door-end.

Fig. 8, door curtain used.

Table 6, test conditions

Parameter	Value
container identification number	MMAU103858[2]
control mode	QUEST
Tset	0.0 °C
Text	15 ~30 °C (uncontrolled, truly ambient)
fresh air exchange	closed
atmosphere control method	AV+ @ $CO_{2,set}$ = 12 %
CA door curtain installed?	yes
drain holes	closed
power supply	400 V / 50 Hz
software version	0354r7
log interval of dry ice weight	5 min.
log interval of Dansensor CO_2 measurement	7 min.
log interval of reefer unit datalog	15 min.
CO_2 logger	PBI Dansensor Checkmate II (Fig. 5, Fig. 6)
scale	Mettler Toledo 0805 (Fig. 3, Fig. 4)
$m_{co2}^{solid,fast}(t_0)$	21 kg
$m_{co2}^{solid,slow}(t_0)$	43 kg

3.2 Experiment 1: results

Fig. 9 presents the CO_2 concentrations recorded by the Dansensor, and the reefer unit's CO_2 sensor. The recorded dry ice mass is presented in Fig. 10. Due to human error the recording of the Dansensor and the scale stopped around day 12, about two days before all dry ice had sublimated. The recording of CO_2 by the reefer unit continued till the end of the experiment on day 17.

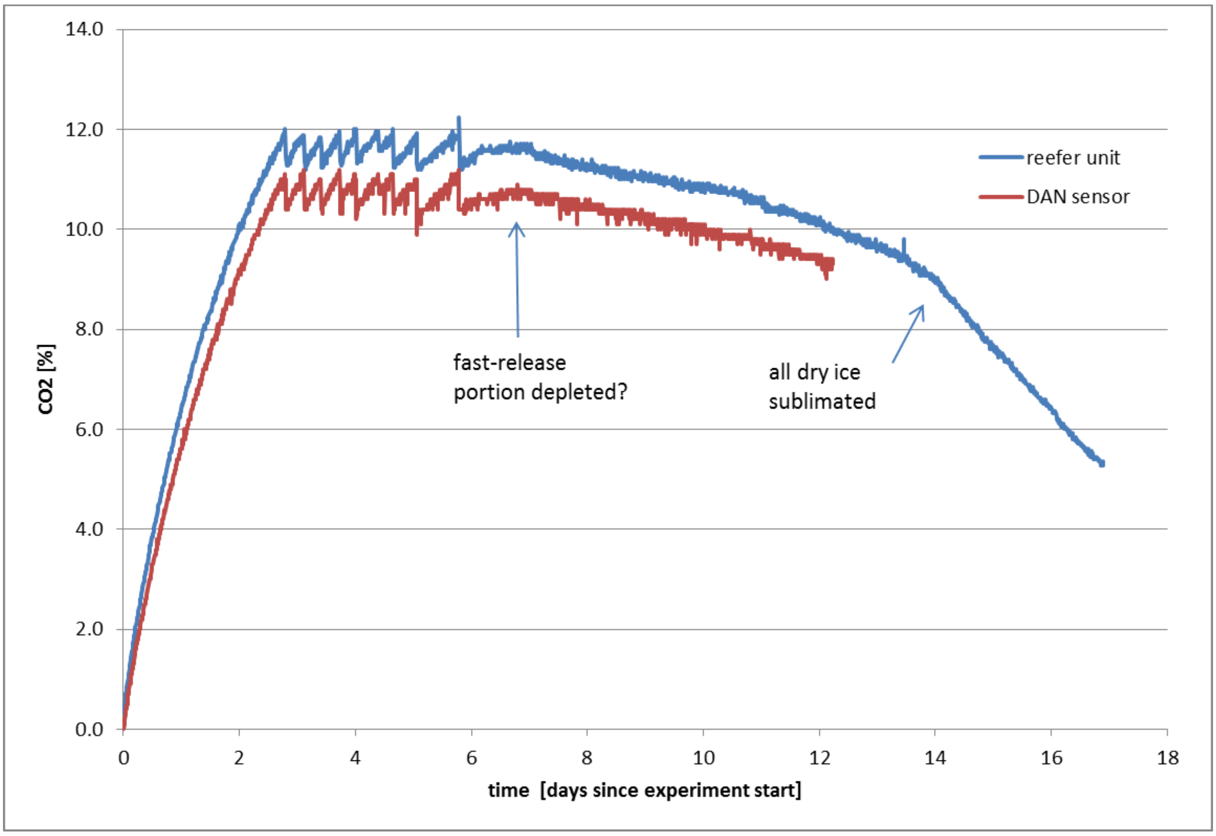

Fig. 9, CO_2 recorded by Dansensor and by unit sensor

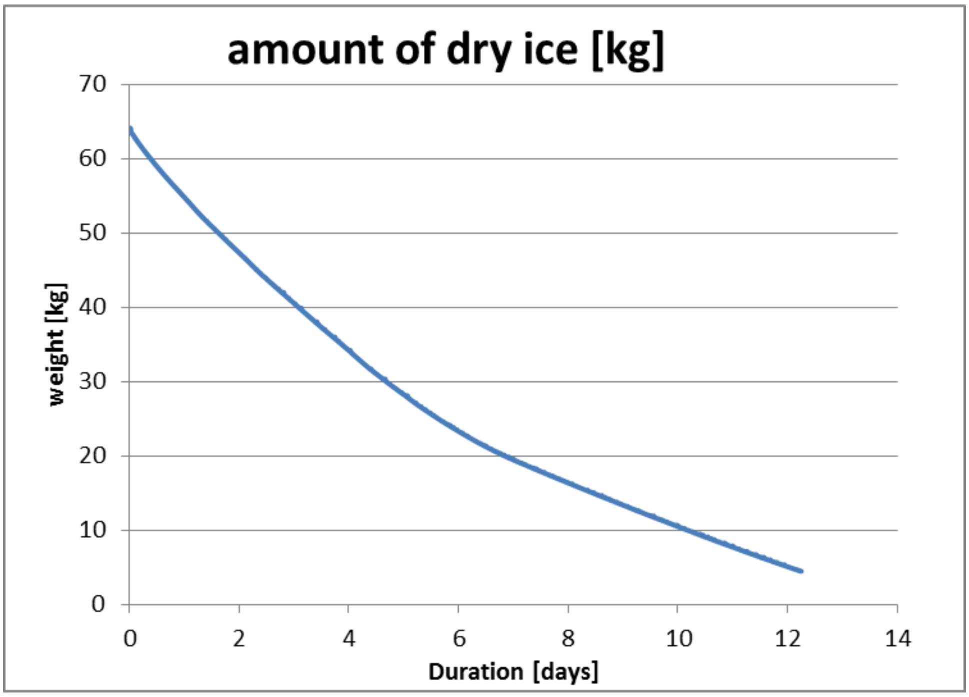

Fig. 10, weight of remaining dry ice

3.3 Experiment 1: discussion

Some observations in the recordings for CO_2 and dry ice mass:

1) Duration till CO_2 reaches 12 % for the first time: 2.8 days (see Fig. 9). Apparently the fast release rate $\dot{m}_{co2}^{solid,fast}(t)$ is not so fast. Two ways to accelerated this:
   a. This is probably because $m_{co2}^{solid,fast}(t_0)$ was left in a small insulated box without lid (Fig. 7). A more thorough removal of insulation would be to just pour out the contents of the box on the T-bar at the door-end. That will certainly yield a faster atmosphere build-up.
   b. The experiment was in an empty container. A stuffed container contains much less air. Hence CO_2 is expected to rise faster, but it's unclear how much CO_2 may be absorbed in the fruit.
2) One would expect a sharp inflection point in the recorded dry ice weight (Fig. 10) when $m_{co2}^{solid,fast}(t)$ reaches 0 kg. That sharp inflection point does not occur. A weak inflection seems to occur around day 6 (Fig. 10), which more or less coincides with the moment when the CO_2 concentration starts to decline (Fig. 9).
3) Between day 3 and 6 there are 9 sharp drops in CO_2 concentration (Fig. 9). That's because in that period AV+ opens the fresh air inlet 9x.
4) From day 3 till 6 CO_2, measured by the reefer unit, is maintained between 11.2 and 12 %. This is because the AV+ system does not regulate CO_2 *around*, but just below, the set target value of 12 %. To maintain measured CO_2 around 12 % set the AV+ target value for CO_2 at 12.4 %.
5) There is an offset between the Dansensor's and the reefer unit's CO_2 recording (Fig. 9). Most likely this is due to an offset in the unit's CO_2 sensor. This illustrates the need for a proper calibration procedure for the unit's CO_2 sensors in this measurement range.
6) Extrapolation of the recorded dry ice weight recordings since day 6 (Fig. 10) indicate that all dry ice had sublimated on day 14. This coincides with an inflection point in the CO_2 readings recorded by the reefer unit (Fig. 9). Hence the results show that the rate of CO_2 release from the slow-release portion of dry ice, $\dot{m}_{CO2}^{prod,slow}$, was too slow to maintain CO_2 at 12 % between day 6 and 14 in Fig. 9. Apparently, at least after day 6, a less insulated box (U_{box} larger) was needed to maintain CO_2 at 12 %.

Based on this last observations it was decided to repeat the experiment with a larger value for U_{box}. The optimal U_{box}, at least for that period, is calculated below.

Step 1. Both on day 6 and 8 x_{CO2} was around 10.5 % (Fig. 9). Hence in that period $\dot{m}_{CO2}^{prod,fast}(t) + \dot{m}_{CO2}^{prod,slow}(t)$ was close to optimal. In that period the mass of dry ice declined from 23.3 to 16.4 kg. The actual rate of CO_2 release in that period $\dot{m}_{CO2}^{prod,fast}(t) + \dot{m}_{CO2}^{prod,slow}(t)$ was:

$$\dot{m}_{CO2}^{prod,fast}(t) + \dot{m}_{CO2}^{prod,slow}(t) = \frac{(23.3-16.4)}{2\times 24} = 0.15 \quad [\mathrm{kg.h^{-1}}] \quad (10)$$

Because of the weak inflection point in the dry ice weight curve (Fig. 10) around day 6 $\dot{m}_{CO2}^{prod,fast}(t)$ may have been larger than 0 during a part of the period. Therefore $\dot{m}_{CO2}^{prod,slow}(t)$ is assessed from a period where $\dot{m}_{CO2}^{prod,fast}(t)$ is certainly 0 kg/h: day 7 till 12.2.

Step 2. From day 7 till 12.2 the dry ice weight decays linearly (Fig. 10) and $\dot{m}_{CO2}^{prod,fast}(t) = 0$. Hence $\dot{m}_{CO2}^{prod,slow}(t)$ can be calculated from the weight measurements:

$$\dot{m}_{CO2}^{prod,slow}(t) = \frac{(19.5-4.6)}{5.2\times24} = 0.12 \qquad [\text{kg.h}^{-1}] \quad (11)$$

Step 3. Take the value for $\dot{m}_{CO2}^{prod,slow}(t)$ calculated above and insert it in eqn. 8 to calculate the apparent value for U_{box} between days 7 and 12.2:

$$U_{box} = \frac{\dot{m}_{CO2}^{prod,slow}\times L_{dry\_ice}\times\frac{1000}{3600}}{T_{set}-T_{dry\_ice}} = \frac{0.12\times571\times\frac{1000}{3600}}{0--78.5} = 0.24 \qquad [\text{W/°C}] \quad (12)$$

A priori it was calculated that U_{box} = 0.34 W/°C would suffice to achieve $\dot{m}_{CO2}^{slow}(t)$ = 0.17 kg/h, which would suffice to maintain x_{CO2} = 12 %. The data show that $\dot{m}_{CO2}(t)$ = 0.15 kg/h suffices to maintain x_{CO2} = 10.5 %, thus confirming that achieving $\dot{m}_{CO2}^{slow}(t)$ = 0.17 kg/h would indeed suffice to maintain x_{CO2} = 12 %, and hence that the target value U_{box}^{*} = 0.34 W/°C is good.

Step 4. Unfortunately the difference between calculated U_{box} (0.34 W/°C) and apparent U_{box} (0.24 W/°C) remained to be explained at that time. Therefore, anticipating the same error ratio, it was decided to aim for:

$$U_{box}^{2*} = U_{box}^{*}\times\frac{calculated\ U_{box}}{apparent\ U_{box}} = 0.34\times\frac{0.34}{0.24} = 0.47 \qquad [\text{W/°C}] \quad (13)$$

Step 5. Using eqn. 9 the dimensions of the large insulated box are redesigned. See Table 7.

4 Experiment 2

4.1 Experiment 2: materials and methods

Only the experimental parameters that differ from experiment 1 are listed in Table 7 and Table 8.

Table 7, specifications of large external EPS box, containing two small boxes with dry ice

Parameter	Value
external dimensions	L x W x H = 900 x 500 x 500 mm
internal dimensions	L x W x H = 800 x 400 x 400 mm
thickness of floor and lid	50 mm
thickness of long side walls	50 mm
thickness of short side walls	50 mm
Calculated U-value of large box + small box inside	0.46 W.°C^{-1}
$m_{co2}^{solid,fast}(t_0)$	16 kg
$m_{co2}^{solid,slow}(t_0)$	50 kg

Table 8, test conditions

Parameter	Value
atmosphere control method	AV+ @ $CO_{2,set}$ = 12.4 %

A temperature logger is taped to the lid inside one of the boxes containing the slow release portion of dry ice. The aim of this logger is to gain insight in the possible vertical stratification of air temperature inside the boxes.

Fig. 11, fast release portion poured out on top of large heavily insulated carton containing two small dry ice cartons, together placed on a scale at container's door-end

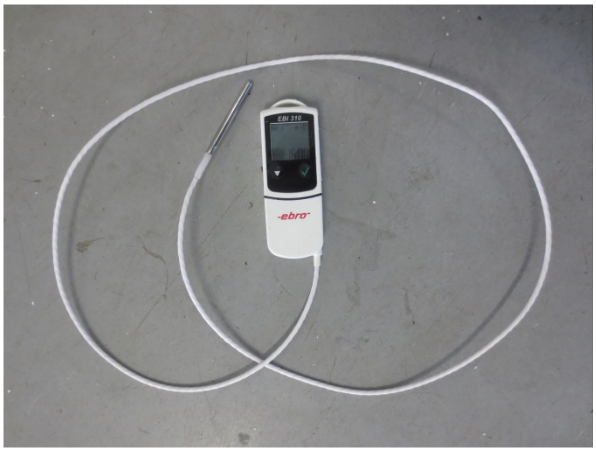

Fig. 12, temperature sensor taped to the lid inside one of the boxes containing the slow release portion of dry ice

4.2 Experiment 2: results

Fig. 13 presents the CO_2 concentrations recorded by the Dansensor, and the reefer unit's CO_2 sensor. The recorded dry ice mass is presented in Fig. 14.

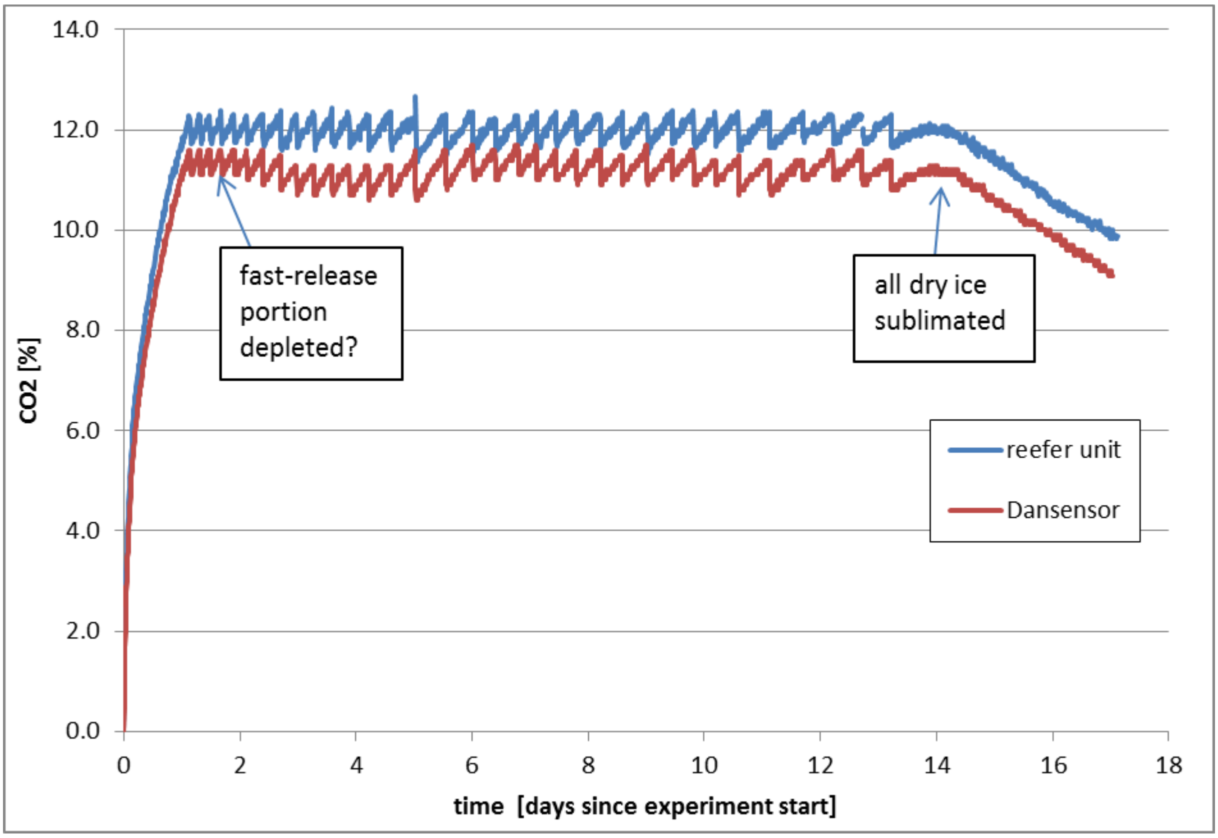

Fig. 13, CO_2 recorded by Dansensor and by unit sensor

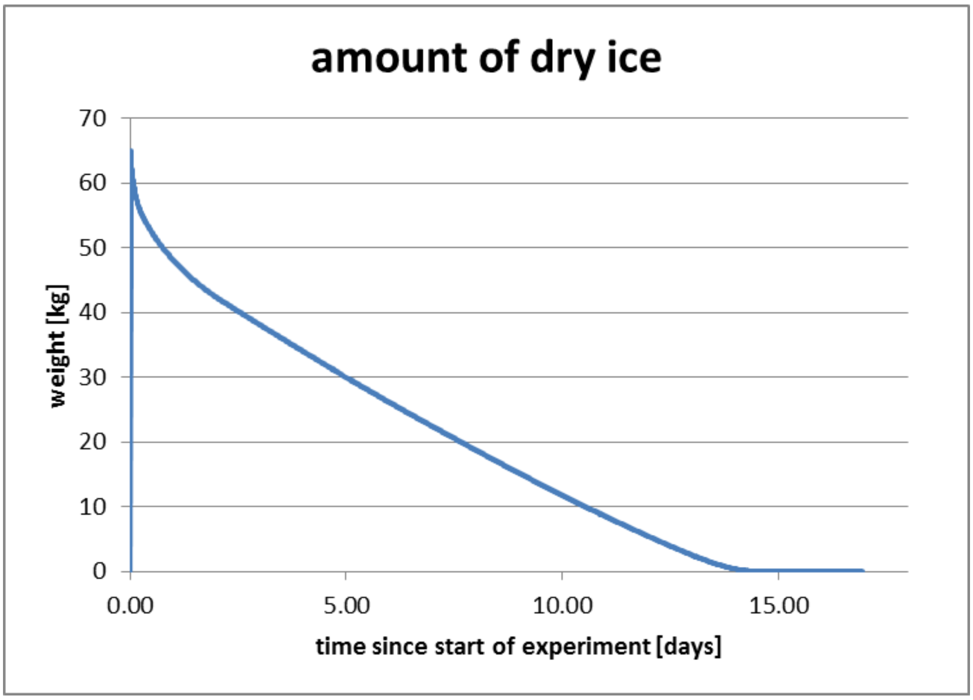

Fig. 14, weight of remaining dry ice

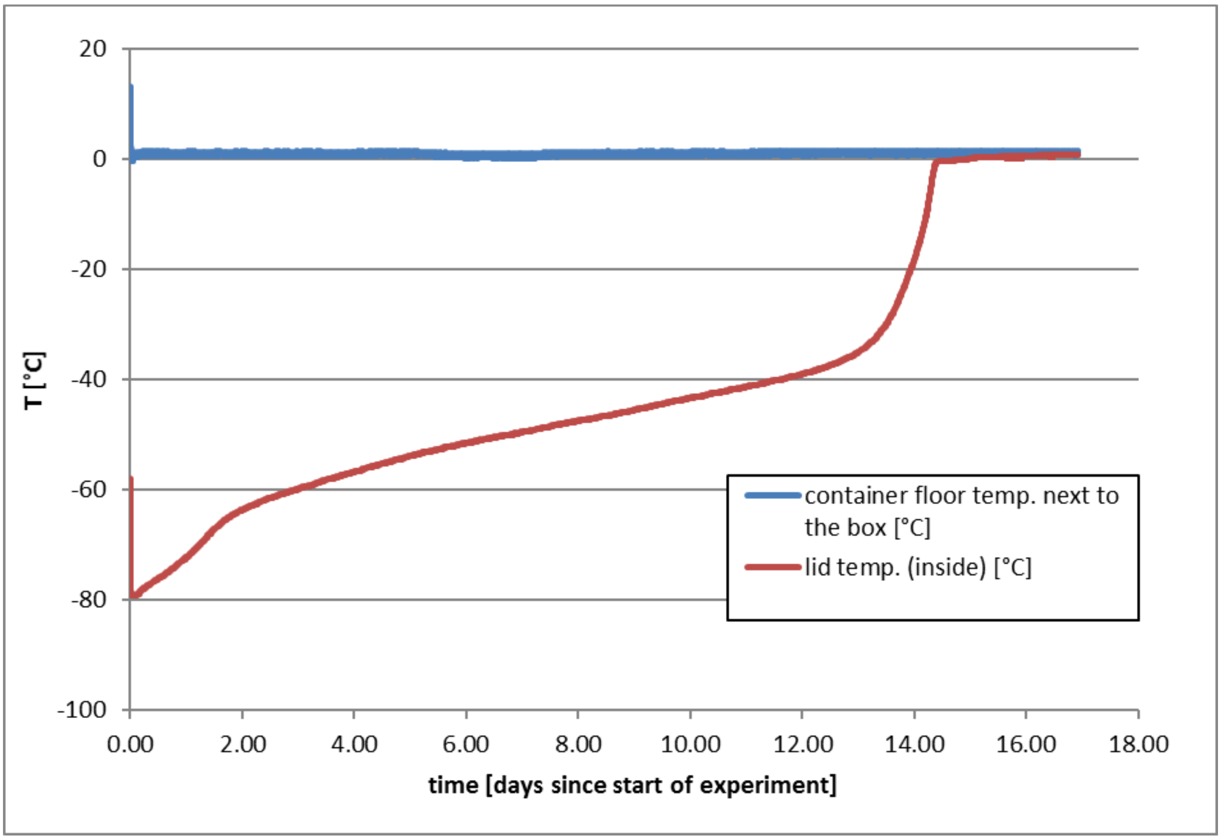

Fig. 15, temperatures recorded around the dry ice box: on the container floor next to the box, and air temperature against the lid inside the box

4.3 Experiment 2: discussion

Some observations in the recordings for CO_2 and dry ice mass:

1) Duration till CO_2 reaches 12 % for the first time: 1.1 days (see Fig. 13). Apparently the fast release rate $\dot{m}_{co2}^{solid,fast}(t)$ of the dry ice poured on top of the slow-release box (Fig. 11) is a lot faster than in experiment 1, where it was left in a small insulated box without lid (Fig. 7).
2) From day 1 till 14 CO_2, measured by the reefer unit, is maintained between 11.6 and 12.4 %, with an average of 12.0%. Apparently the change in set point from 12.0% in experiment 1 to 12.4% in experiment 2 is effective in raising the average CO_2 concentration to 12.0%.
3) Like in experiment 1 there is an offset between the Dansensor's and the reefer unit's CO_2 recording (Fig. 13).
4) A sharp inflection point in the dry ice weight curve (Fig. 14) occurs around day 14. This coincides with the moment the CO_2 concentration starts to decline (Fig. 13). That clearly is the moment when all dry ice has sublimated.
5) The CO_2 concentration only started to drop after all dry ice had sublimated. Hence the results show that the rate of CO_2 release from the slow-release portion of dry ice, $\dot{m}_{CO2}^{prod,slow}$, sufficed to compensate for the loss of CO_2 from the container due to air leakage. Apparently,

the less insulated box used in experiment 2 solved the issues of decreasing CO_2 since day 6 in experiment 1 (compare Fig. 9 to Fig. 13).

6) Throughout the experiment there are 34 sharp drops in CO_2 concentration (Fig. 13). That's because in that period AV+ opens the fresh air inlet 34x.
7) From the CO_2 recordings since day 14 the container air leakage rate can be estimated using eqn. 1:

$$\frac{V_{air}}{100} \times \frac{dx_{CO2}}{dt} = \phi_{air}^{leak} \times \frac{(CO_2^{amb} - x_{CO2})}{100} \qquad [\text{kg.h}^{-1}] \quad (14)$$

Read the CO_2 concentrations on day 17 and 14.6 from Fig. 13 and fill out the unknowns to get.

$$\frac{69}{100} \times \frac{9.1-10.9}{17-14.6} = \phi_{air}^{leak} \times \frac{(0.04-avg(9.1,10.9))}{100} \qquad [\text{kg.h}^{-1}] \quad (15)$$

Solving this for ϕ_{air}^{leak} yields

$$\phi_{air}^{leak} = \frac{(0.04-avg(9.1,10.9))}{69} \times \frac{17-14.6}{9.1-10.9} = 0.19 \qquad [\text{m}^3.\text{h}^{-1}] \quad (16)$$

The calculated ϕ_{air}^{leak} of 0.19 m^3/h is distinctly less than the assumed value of 0.7 m^3/h (Table 1), which explains why the fresh air inlet opened 34x.

8) Fig. 15 reveals a strong stratification in air temperature inside the slow-release box, which grew bigger over time. Dry ice is -78.5 °C, so the unmeasured temperature at the floor of the slow-release box was -78.5 °C till all dry ice sublimated. The temperature of the inside of the lid gradually rose during the test (Fig. 15). The initial rise till about day 2 was relatively fast, because in that period the fast-release portion on top of the lid vanishes and hence the outside temperature of the lid rose. Then there was a linear rise from approx. -60 °C on day 2 till -40 °C on day 14. When on approx. day 14 all dry ice had sublimated the temperature inside the box converged to the temperature outside the box.
9) In the discussion of the results from experiment 1 the difference between calculated U_{box} (0.34 W/°C) and apparent U_{box} (0.24 W/°C) remained unexplained. The temperature of the inside of the lid observed in experiment 2 sheds a new light on this. In eqn. 8 the apparent value for U_{box} was calculated using

$$U_{box} = \frac{\dot{m}_{CO2}^{prod,slow} \times L_{dry\_ice} \times \frac{1000}{3600}}{T_{set} - T_{dry\_ice}} \qquad [\text{W/°C}] \quad (17)$$

assuming that T_{dry_ice} is representative of the internal box temperature. The temperature recordings in Fig. 15 invalidate that assumption. Assume an average internal box temperature T_{box} of -56 °C, not unreasonable in view of Fig. 15, to get

$$U_{box} = \frac{\dot{m}_{CO2}^{prod,slow} \times L_{dry\_ice} \times \frac{1000}{3600}}{T_{set} - T_{box}} = \frac{0.12 \times 571 \times \frac{1000}{3600}}{0 - -78.5} = 0.34 \qquad [\text{W/°C}] \quad (18)$$

This is exactly the U_{box}-value calculated upfront in experiment 1 (Table 5). Hence for future applications it is reasonable to trust the design calculations for U_{box}, but a warmer T_{box} of approximately -60 ~ -50 °C shall be used.

5 Overall discussion

The experiments delivered a proof of principle: the test container with CO_2-regulated autovent and door-end curtain properly installed, in combination with dry ice packed in sufficiently tight thermal insulation, was able to maintain CO_2 at 12 %.
www.praxair.nl delivered 100 kg of dry ice for this experiment in The Netherlands. From the invoice the commercial price for supply of 100 kg appears to be € 200.-.
The experiments demonstrate that 200 kg could be enough to maintain 12 % CO_2 for approx. three weeks in an empty container. When the container is stuffed with fruit the additional respiratory CO_2 production might be exploited to reduce the required amount of dry ice.
The successful proof of principle, together with the known market demand and the limited costs, have been reason to apply for patent on the concept (Lukasse *et al.*, 2018).
How to assess the desired slow release rate $\dot{m}_{CO2}^{solid,slow*}$? The dry ice is needed to compensate for CO_2 loss due to air leakage, while the air leakage rate is unknown and depends on many factors. The experiment was designed to counter a possible air leakage rate ϕ_{air}^{leak} of 0.7 m^3/h. Eventually the air leakage rate turned out to be only 0.19 m^3/h. Air leakage tests, when applied at all, are typically done at a 250 Pa over - or under pressure (see *e.g.* ISO1496-2). ISO1496-2 also specifies that reefer containers shall have an air leakage rate of at most 10 m^3/h at a pressure difference of 250 Pa. How those test results and requirements relate to air leakage in practical operating conditions is largely unknown. Air leakage in practical operating conditions depends on many factors, like state of door gaskets, vents, drain holes, the proper installation of a CA-curtain at door-end, stability of temperature control, fluctuations in external air pressure, and wind direction and force. In fact there is not much known about practically occurring air leakage rates, certainly not in in the public domain. For now it seems best to continue to calculate with a possible air leakage rate ϕ_{air}^{leak} of 0.7 m^3/h. In due time experience may teach if it is sensible to reduce this number.

Foreseen risks for practical implementation:

1. In remote areas the costs of dry ice delivery may be higher than € 1.- per kg
2. The reliability of the reefer-unit's CO_2 sensors in the relevant range of approx. 12 % may be insufficient.
3. Does the hassle of loading dry ice in a container pay off?
4. The dry ice + packaging occupies quite some space in the container, space which would otherwise be available to carry fruit.
5. The dry ice is -78.5 °C. Proper measures are needed to avoid freezing injury to some of the fruit.
6. The efficacy of the treatment may vary over different types of grapes. Think of variables like cultivar, harvest time, and sugar content.
7. Container transport is only one link in the supply chain. Supply chains encompass more than only container transport: storage prior to transport, precooling, truck transport to the location of container stuffing, storage after transport and truck transport to final

destination. In practical applications the CO_2 treatment can only be applied in the period where the container doors are closed, while the alternative of SO_2 pads can continue to do its job in the stages before and after the container transport. This disadvantage of CO_2-treatment could become the reason why it is less attractive in some supply chains.

6 Conclusions

An approach has been developed to maintain CO_2 at 12 % in CA reefer containers for multiple weeks, using dry ice as a source of gaseous CO_2 gaseous.
The technical feasibility of the approach has been verified.
Because of the promising results a patent application has been filed (Lukasse *et al.*, 2018).

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