Proposal of a Method for Maintaining the Quality of Agricultural Products under the Cold Environment

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Food quality control is important for food companies such as restaurants and consumers. Vegetables release heat energy by breathing even after harvesting. When the storage temperature rises, respiratory heat increases, and as a result, sugar decomposition progresses, and nutrients decrease. Therefore, it is possible to keep the quality of food by storing it at a low temperature. In this study, to confirm that cold storage reduced the respiratory heat of foods, we measured respiratory heat of food at low-temperature preservation by each temperature. To measure the respiratory heat of food at low-temperature preservation, we created an experimental device that can be sealed, kept at low-temperature, and can control temperature. Then, we put the food in the device, and measured the change in CO2 concentration immediately after the food was placed and 1 hour after the food was placed by each temperature. Finally, by using the measured data, we calculated the respiratory heat. As a result, low-temperature preservation can reduce respiratory heat, and it was found that the quality of food can be kept.

Key Word
Food quality control, Natural refrigerant, Respiratory heat, Sugar content, Life cycle assessment

1. Introduction
Air conditioning and refrigeration equipment have become indispensable in our daily lives. Refrigerants are used as a heat transfer medium in these devices. In other words, it is no exaggeration to say that refrigerants are an essential part of our lives.

However, there is a close relationship between commonly used refrigerants and environmental issues. One of the environmental problems is global warming. Global warming is caused in part by the increasing emission of greenhouse gases such as CO2. The amount of greenhouse gas emissions in Japan has been gradually decreasing year by year, however, if we look at the breakdown of greenhouse gas emissions, only four gases including chlorofluorocarbons (CFCs) have increased 1). The reason for the increase in CFCs emissions is that hydrochlorofluorocarbons (HCFCs) refrigerants, which contain ozone-depleting substances and were developed in 1928, were replaced by hydrofluorocarbons (HFCs) refrigerants, which do not contain ozone-depleting substances, in 1987 2). Since HFCs refrigerants have extremely high Global Warming Potential (GWP), it is now considered necessary to replace the conventional refrigerants with non-freon natural refrigerants that have extremely low GWP.

On the other hand, energy for cooling and heating
is generally supplied by heat pumps that utilize the evaporative heat and condensation load of refrigerants. Generally, the performance of heat pumps is evaluated by an index called Coefficient of Performance (COP). When a heat pump is used, the higher the COP, the more it is expected to contribute to energy saving and reduction of environmental load. The electricity used for devices that use heat pumps accounts for about 20% of the electricity consumed by air conditioners and refrigerators, and consideration for the environment is required.

To solve the above problems, a natural refrigerant, GF-08, was developed. GF-08 is a non-flammable natural refrigerant composed of propane and propylene, and according to the IPCC AR5 report, GF-08 has a lower environmental impact than the HFCs currently in use, with a GWP per unit of CO₂eq. emission of 3, which is smaller than the GWP of HFCs.

Table 1 below summarizes the characteristics of GF-08 compared to existing refrigerants. In addition, a demonstration experiment when GF-08 was introduced to air conditioning revealed that the power consumption of air conditioning equipment could be reduced by about 30%.

Focusing on the superiority of this performance, research is being conducted for its introduction in refrigeration and freezing fields. Oki et al. compared the performance and environmental impact of conventional refrigerant R410A and GF-08 when introduced into refrigerated warehouses. The results suggested that the annual energy consumption could be reduced by 5.2% in the performance evaluation and the annual CO₂eq. emission could be reduced by 8.6% in the environmental impact evaluation compared to R410A. Kataninwa et al. compared the performance and environmental impact of conventional refrigerants R404A and GF-08 when introduced into prefabricated refrigerator-freezers. As a result, the performance evaluation suggested that the annual power consumption could be reduced by about 28.6% and the environmental impact evaluation suggested that the annual CO₂eq. emissions could be reduced by about 27.1% compared to R404A. However, GF-08 is still not a manufacturer-designated refrigerant in Japan. Thus, its current distribution amount is lower in comparison to conventional refrigerants. Moreover, the safety of GF-08 against flame is the almost same level as conventional refrigerants.

On the other hand, Alessandro et al. employed R404A, R407F, and R410A as comparative refrigerants to evaluate the environmental impact of a commercial refrigeration system equipped for medium and low-temperature food storage. The results showed that R404A has the highest CO₂eq. emission and R410A has the lowest under the condition of a set temperature of 10 °C. In addition, analysis of the entire life cycle of the refrigeration system has shown that the use stage contributes significantly to the overall environmental burden, and that indirect emissions from the power consumption of the refrigeration equipment are significant.

However, there is a problem that these environmental impact assessments in the refrigeration field have not been conducted considering the cooled materials. Especially in the refrigeration field, it is important to consider the quality of food products, because the cooling performance of different refrigerant types has a significant impact on power consumption, and at the same time, the storage environment has a significant impact on the quality of food products.

Quality control of food products is also very important for companies dealing with food products, such as restaurants, and for consumers. From the standpoint of a company, it is essential to minimize the deterioration of quality in the inventory that is stored and managed. Therefore, from the standpoint of a company, it is very important to prevent food wastage, food accidents, food poisoning, and other quality-related issues. On the other hand, the same thing can be said from the standpoint of consumers. In a questionnaire survey on vegetables conducted in 2013, 75.5% of respondents answered, “for health”, surpassing “because I like” (58.8%) (see Fig. 1). Also, in a questionnaire conducted in 2017, 40% each selected “delicious,” “rich in dietary fiber,” “to keep fit,” and “to take vitamins, minerals, etc.”. Therefore, many people are becoming more health conscious and are mindful of the quality of vegetables, for example, for the sake of their bodies, and the quality of food will be a very important factor for companies and consumers.

| Name                      | R404A     | R410A     | GF-08     |
|---------------------------|-----------|-----------|-----------|
| Normal boiling point [°C] | -4.62E+01 | -5.14E+01 | -4.49E+01 |
| Critical temperature [°C] | 7.21E+01  | 7.14E+01  | 9.31E+01  |
| Critical pressure [MPa]   | 3.73E+00  | 4.90E+00  | 4.40E+00  |
| Critical density [kg/m³]  | 4.87E+02  | 4.60E+02  | 2.24E+02  |
| Global warming potential [kg-CO₂eq./kg] | 3.92E+03 | 2.09E+03 | 3.00E+00 |
To control the deterioration of quality, it is necessary to preserve the food in an appropriate manner. Preservation methods to prevent deterioration of food quality include cold treatment (freezing, refrigeration), dehydration, drying (dry storage, salting, syruping, etc.), and addition of preservatives.

In this study, we focused on the preservation method in cold storage. In general, the main form of vegetables purchased for home consumption is fresh, and cold storage is commonly used.

One of the main characteristics of vegetable storage is that vegetables breathe to continue their life activities after harvesting, and when they breathe, they consume energy sources such as sugars, emit CO₂, and at the same time release heat energy (respiratory heat). Therefore, this respiratory action leads to a decrease in freshness and quality 10).

The amount of respiratory heat varies from food to food and can be judged to some extent depending on which part of the plant the vegetable is made from and at what stage of maturity it is. Leafy vegetables such as spinach, which is a leaf at the peak of its growth, are generally said to have a high respiratory rate 11). By suppressing the respiration rate, the rate of sugar decomposition can be reduced, and the quality of the product can be suppressed, while at the same time release heat energy (respiratory heat). Therefore, this respiratory action leads to a decrease in freshness and quality 11).

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The measurement of carbon dioxide emissions from respiration of the artifacts under cold storage was carried out using the device shown in Fig. 2. The device is divided into a cooling room and a vegetable storage room, which are connected to each other. For cooling in the cooling room, Peltier elements were used to cool the cooling room, and the air cooled in the cooling room is blown to the vegetable storage room to cool the storage room. For heat retention after cooling, the outside and inside of the device are covered with insulating material to improve the heat retention performance. Also, the silicone cover and curing tape were used to improve the sealing property. Carbon dioxide was measured with CO₂-9904SD (see Table 2).

The measurement procedure is as follows.
(1) Put the spinach into the device.
(2) Measuring the initial carbon dioxide concentration.
(3) Place for 1 hour while keeping the temperature constant.
(4) Measuring the carbon dioxide concentration after 1 hour.

The procedures (1) to (4) were performed at four different temperatures (10, 15, 20, and 25 °C). The number of spinaches was 15 sets (1 set = 27 g).
2.2 Measuring sugar content

As evaluation of quality, the sugar content was measured. In this study, the sugar content was measured as Brix value using a sugar meter (MASTER-53P, ATAGO CO., LTD.) (see Fig. 3). The sugar content was measured in the following four patterns: 10°C, 15°C, 20°C, and 25°C, respectively. Using the incubator (LH-30-8CT, NIPPON MEDICAL & CHEMICAL INSTRUMENTS CO., LTD.), the sugar contents were measured at the designed temperatures. Each test has a double trial, and storage duration was four hours at constant. Eq. (1) shows that glucose is decomposed during respiration of vegetables.

However, sucrose is measured by the sugar meter in this study. Sucrose is one of the components of glucose, and when sucrose decreases, glucose is also considered to be decreasing.

2.3 Calculation of respiration rate

The measured values were recorded as the difference in CO₂ concentration, and the respiration rate R (the amount of CO₂ emitted per hour) was calculated using the following equation.

\[
R = \frac{\Delta ppm}{22.4} \times \frac{273.15}{273.15 + T} \times \frac{P}{1013} \times \frac{V}{M}
\]

where \(R\) [mg-CO₂/kg/h], \(\Delta ppm\) [ppm], \(M\) [g/mol], \(T\) [K], \(P\) [hPa], and \(V\) [m³] are Respiration rate, Difference in CO₂ concentration in one hour at storage temperature, Molecular weight of CO₂ (=44), Storage temperature, Gas pressure during storage, and Volume of the storage room.

3. Measurement Results and Discussion

3.1 Respiration Rate

The Arrhenius equation was used as the temperature-dependent equation for product respiration to organize the measurement results. The Arrhenius equation is often used as a chemical reaction rate equation.

\[
R = R_0 e^{-\frac{a}{T}}
\]

where \(R_0\) and \(a\) are Product-specific coefficients and Product-specific temperature coefficient.

The coefficients were determined by the least-squares method by applying the Arrhenius equation to the temperature-dependent respiratory rate of the spinach measured. The Arrhenius equation has already been used to evaluate the temperature dependent respiratory rate of agricultural products, and the studies of Tano et al. and Barbosa, Lisiane das Neves et al. have used the Arrhenius equation to estimate respiratory rate and evaluate the effect of temperature on respiratory rate.

Fig. 4 shows the results of analyzing the temperature dependence of the respiration rate of spinach using the Arrhenius equation. Since the measured values follow the Arrhenius plot, it is likely that accurate values could be measured from the measurements of respiratory heat in this study. Note that the heat transfer coefficient in this apparatus was 0.0708 W/m²/K.

3.2 Respiratory Heat

The respiratory heat was estimated by converting to mol from the measured change in CO₂ concentration and based on Eq. (1). The results showed that the lower the temperature, the more the respiratory heat was suppressed.
It was suggested that the quality deterioration could be suppressed by cold storage. This is not spinach, but a study by Nei et al.\textsuperscript{18} pointed out that one of the main factors promoting quality deterioration of fresh vegetables is the consumption of respiratory response. Therefore, it can be said that there is a close relationship between respiratory heat and quality.

### 3.3 Change of sugar content

Fig. 5 shows the change in sugar content of spinach at different temperatures. It was found that the sugar content decreases with time in each temperature range. In other words, it can be concluded that glucose is decomposed by respiration. It was also found that the amount of sucrose was not degraded in a lower temperature storage condition. Therefore, it was suggested that the storage control at a low temperature would encourage to hold the lighter respiratory, that is, protect the sugar content reduction.

4. Cooling performance by refrigerant

#### 4.1 Vapor Compression Refrigeration Cycle

Vapor compression refrigeration cycles are used in most of the refrigeration equipment for cold storage, such as refrigerators and freezers. Based on the vapor compression refrigeration cycle, a model was developed to calculate the performance of the refrigerant against the heat demand. The physical property data of the refrigerants required for the calculations were obtained using REFPROP ver10.0\textsuperscript{19}.

#### 4.2 Comparison of cooling rates

The amount of respiratory heat varies with the temperature in the storage environment at the time, and at the same time the latent heat of the refrigerant itself varies with temperature. In this study, we calculated the amount of latent heat under the same conditions as when the respiratory heat was measured and compared the rate at which the respiratory heat was removed, i.e., the cooling rate. When spinach was put into a refrigerator at room temperature (25 °C), it was assumed that only the respiratory heat was to be removed by the refrigerator to check the difference in cooling rate until the product temperature reached the set temperature (10 °C) depending on the refrigerant. The specific heat of spinach was assumed to be 0.94 kcal/kg/°C. As a result, it was found that cooling using GF-08 reached the set temperature about 2.5 times faster than that using R404A (see Fig. 6). The reason why GF-08 has a faster cooling rate than R404A is that the latent heat of evaporation of GF-08 is higher than that of R404A when focusing on the physical properties of each refrigerant. The latent heat of evaporation can be determined by the difference between the enthalpy of saturated vapor and the enthalpy of saturated liquid in each refrigerant.
refrigerant. In particular, when the temperature is set to 25 °C, R404A has 140 kJ/kg while GF-08 has 335 kJ/kg, which is about 2.4 times higher. This value was calculated using REFPROP 19. This suggests that the quality of the product can be maintained longer when GF-08 is used for cold storage.

5. Environmental Impact Assessment

5.1 LCA

The environmental impact of refrigerants was evaluated based on LCCP (Life Cycle Climate Performance) 20. The purpose of the LCA in this study was to determine the environmental impact of replacing R404A with GF-08 in maintaining the quality of 1 kg of spinach. In accordance with the objective of the LCA in this study, the functional unit is the period of 3 days to reach 5% water loss by transpiration at a storage temperature of T_{set} = 10 °C. In this study, sugar content was measured as an evaluation of quality maintenance, but since the formula for estimating sugar content decrease could not be calculated and there is no clear threshold for sugar content as a definition of quality maintenance, the percentage of water loss, which has a clear threshold 14, was used as the functional unit in this LCA.

5.2 System boundary

In accordance with the purpose of the LCA in this study, the scope of the study covers “refrigerant production,” “use,” and “in-use leakage,” as shown in Fig. 7. For “leakage during use”, we assumed that 15% of the filled volume would leak during one year of use, referring to the leakage rate of commercial refrigeration and air conditioning equipment in use reported by the Global Environment Research Center 21. Since 15% is the leakage rate in one year, the refrigerant leakage rate until the moisture loss ratio reaches 5% will be different. Therefore, the leakage rate until the moisture loss ratio reaches 5% is calculated by dividing 3 days by 365 days, and the leakage rate until the moisture loss ratio reaches 5% is 0.123%, which is calculated by multiplying the annual leakage rate of 15% by 0.00821, which is calculated by dividing 3 days by 365 days.

5.3 Inventory Analysis

The LCCP considers the environmental impact of the refrigerator in which the refrigerant is charged, and the term representing the environmental impact of the refrigerator was deleted because it is not in line with the purpose of environmental impact assessment in this study. Therefore, CO_{2eq,ref} the CO\textsubscript{2}eq. emission of the entire life cycle of the refrigerant, was calculated by summing Eq. (5) to (7). The values of these variables are shown in Table 4. For the estimation of the refrigerant circulation of R404A and GF-08, the model developed in section 4 was used and calculated, respectively. In the refrigerant production stage, the amount of CO_{2eq} emitted during the production of 1 kg of refrigerant was used as the reference for R404A 22. The data for GF-08 was obtained by adding up the production stages of propane and propylene using SimaPro (ver. 9.1.0.8), which was then used as the production stage emissions for GF-08. The possible reasons for the high CO_{2eq} emissions of R404A in the manufacturing stage are that R404A is a

| Name     | Unit       | R404A | GF-08 |
|----------|------------|-------|-------|
| CO_{2eq} | kg         | 374E-01 | 145E-01 |
| ALR      | %/year     | 1.23E-01 | 1.23E-01 |
| RFM      | kg CO_{2eq}/kg | 1.36E+02 | 1.00E+00 |
| EC       | kWh        | 147E+01 | 144E+01 |
| EM       | kg CO_{2eq}/kWh | 4.57E-01 | 4.57E-01 |
| GWP      | kg CO_{2eq}/kg | 3.92E+03 | 3.00E+00 |

- Material
- Electricity
- Fuel

\[ \text{CO}_{2eq} = \text{Material} + \text{Electricity} + \text{Fuel} \]

\[ \text{CO}_{2eq} = \text{Power Consumption} + \text{Leakage} \]

\[ 15 (\%) / \text{year} \]

\[ 0.123\% (\%) / 3 \text{days} \]
mixed refrigerant consisting of three components, R-125, R-134a, and R-143a, and all three refrigerants have fluorine in common. Therefore, fluorine is thought to be the reason for the higher CO₂eq emissions during the manufacturing stage compared to GF-08, a hydrocarbon refrigerant. This is because the GWP value of fluorine was calculated using SimaPro (ver.9.1.0.8) and was 1.4 times larger than that of GF-08. The literature also reports that fluorinated intermediates and refrigerants are also leaked during the manufacturing process, and their atmospheric release also has an effect. Therefore, we considered that R404A, which has a large GWP value, is highly affected by leakage. The energy consumption of each refrigerant, EC was calculated using the model developed in section 4, and the energy consumption required to maintain the quality of spinach was calculated. The calculation formula is Eq. (8). ECstorage is the power consumption required to cool 1 kg of spinach at 25 °C to the set temperature of 10 °C. ECrespiration is the power consumption when only the respiratory heat of the spinach is used as heat demand. For the CO₂eq emission intensity of electricity, we referred to the values reported by TEPCO.

\[
\text{CO}_\text{eq. Ref} = \text{CO}_\text{eq. Manufacturing} + \text{CO}_\text{eq. Use} + \text{CO}_\text{eq. Leakage}
\]

\[
\text{CO}_\text{eq. Use} = EC \times EM
\]

\[
\text{CO}_\text{eq. Leakage} = C \times \text{GWP} \times \text{ALR} \times \frac{3}{365}
\]

\[
\text{EC} = \text{ECstorage} + \text{ECrespiration}
\]

where C [kg], ALR [%/year], RFM [kg-CO₂eq/kg], EC [kWh], EM [kg-CO₂eq/kWh], and GWP [kg-CO₂eq/kg] are Refrigerant Circulating Volume, Leakage Rate, Refrigerant Manufacturing Emissions, Energy Consumption, CO₂eq Emissions per kWh of Energy, and Global Warming Potential.

The CO₂eq emissions due to respiration of spinach were calculated using Eq. (1). Finally, the CO₂eq emissions due to the respiration of spinach were added to CO₂eqRef to obtain the total emissions, and the environmental impact assessment was conducted.

5.4 Environmental Impact Assessment

The results of the environmental impact assessment are shown in Fig. 8. As can be seen from the figure, in maintaining the quality of 1 kg of spinach for 3 days, cooling with GF-08 can reduce CO₂eq by about 88.7% compared to R404A. Focusing on the energy consumption required to maintain the quality of the product, we found that we can reduce about 2.5%.

6. Conclusion

The purpose of this study was to propose a method for maintaining the quality of spinach using GF-08, a non-CFC natural refrigerant, and to evaluate its environmental impact.

To evaluate the effect of temperature change on the quality of spinach, a demonstration system was constructed. We placed spinach in the demonstration device and measured the change in CO₂ concentration to calculate the respiratory heat. At the same time, we measured changes in the sugar content of the spinach and evaluated the quality maintenance.

The measured respiratory heat was used to compare the cooling rates of R404A and GF-08, and then to compare the environmental impact of reducing CO₂eq emissions by suppressing respiratory heat and reducing greenhouse gas emissions by replacing the refrigerant.

In the measurement of respiratory heat, the calculated respiratory rate R followed the Arrhenius plot, so it was likely that the measurement was accurate. The heat of respiration was found to be suppressed as the storage temperature decreased. In the sugar content measurements, it was found that the degradation of the sugar was remarkably fast, suggesting that more rapid cooling was needed. In comparison of cooling rate, it was suggested that the spinach can be more rapidly cooled by using GF-08 for refrigerated storage instead of R404A. In the environmental impact assessment, it was found that the cooling of 1 kg of spinach for 3 days using GF-08 reduced CO₂eq by about 88.7% compared to R404A. Focusing on the energy consumption required to maintain the quality of spinach, we found that CO₂eq emissions could be reduced about 2.5%.

In conclusion, by using GF-08 for refrigerated storage of vegetables, it could be able to lead to long preservation because of rapid suppressing the respiration of vegetables, by more rapid cooling than using R404A. In addition, it
could be suggested that the quality of vegetables can be kept with reducing the environmental impact and saving energy.

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