Physical Chemical view of typical pressurized cold sprays on the market

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Abstract Cold sprays are suitable for many situations. A typical cold spray is composed of a valve, a can and contents. The payload for cold spray serves as a propellant at the same time. R-134a and LPG are common payload for cold spray. The pressure rise with temperature in the can is probed and cooling effect in for the two kinds of payloads are determined and compared. Cooling spray is hardly enough for cooling internal atmosphere in car. Spraying time under 3s is recommended on injury cases.

Introduction

In the summer, there are times when one opening the car door and a heat wave directly coming over the face. On the football pitches, the instant cooling is always essential for a swollen ankle or a broken knee. Under those conditions, the cold sprays are suitable choices for dealing with the hot atmosphere and an injured sportsman.

Technically, cold spray (freeze spray or vapocoolant) is a type of aerosol spray product containing a liquified gas used for rapidly cooling in medical and industrial applications.

The concept of an aerosol spray tank can be date back to 1790 as self-pressurized carbonated beverages appeared in France. Then in 1899, Helbling and Pertsch patented aerosols pressurized using methyl and ethyl chloride as propellants.[1] Nowadays, the pressurized aerosol spray cans are filled with various kinds of payload.

This article aims at introducing the basic principles of the cold spray, analyzing and build up models for distinct conditions of applications. Comparison and discussion are combined throughout.

Containers and contents

The container is composed of two main parts, involving the valve and the can. According to the pieces of metal crimped, the can is classified into one-piece can to three-piece can. Aluminum and steel are common materials for the can.

The contents are generally made up of the payload and propellant. In cold spray, the payload itself can serve as a propellant at the same time. For the cold spray, Liquefied Petroleum Gas (LPG) and 1,1,1,2-Tetrafluoroethane (R-134a) are two typical payloads, according to the market research on JD. Two representative cold sprays are manifested in Figure 1. The content of R-134a spray is roughly pure substance except for negligible amount of essence, while the content of LPG spray is a complicated mixture of alkanes, alkenes, etc. Their chemical and physical properties are presented in table 1.

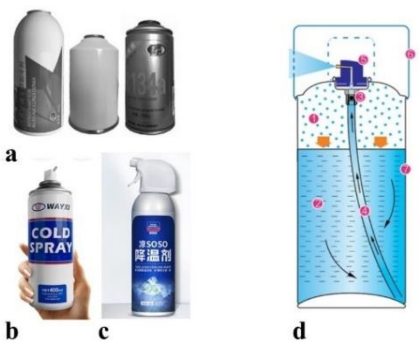

Figure 1: The image(a) shows the three kinds of cans. From left to right, they are one-piece, two-piece, three-piece can. The image(b) displays a three-piece LPG cold spray, and (c) displays a one-piece R-134a cold spray. The image(d) shows a typical structure of a spray cans the liquid and gas are in a phase equilibrium.

Properties (298K,1atm)	**$\Delta_{vap}H$ (kJ /mol)**	**P* (kPa)**	**BP (K)**	**MW (g/mol)**	**Density (kg/ m^3)**
R-134a	20.29	665.3	246.5	102.03	670
Propane	14.79	953.3	230.9	44.10	493
iso-Butane	22.39	213.7	272.7	58.12	583

Table 1:Chemical and physical properties of relevant substances, $\Delta_{vap}H$ is the vaporization enthalpy, P^* is the satirized vapor pressure, BP stands for boiling point, MW for molecular weight. Density refers to liquid density.

Thermodynamic analysis of contents

There supposes to be an equilibrium between liquid phase and gas phase in the pressurized spray can. According to the properties of the contents, they are in the gas phase in room temperature(298K) and atmospheric pressure (1 atm).

Pure substance spray: R-134a Cold Spray

When the propellant and payload is the same substance, physical transformations of pure substances should be considered.

Fixing the temperature, the pressure in the can is fixed in the meantime. According to the phase rule:

$$f = C - \phi + 2 \tag{1}$$

$$C = S - R - R' \tag{2}$$

where the 'f' is the freedom, '2' represents the temperature and pressure, 'C' is the number of components, which depend on the number of substance (S) and restrains (R, R'). In the pure case of pure substance with fixed room temperature: $f = 0$, thus the pressure is fixed which means the pressure does not vary with the remained volume of substance throughout the using period as long as liquid exist.

Pressure of the can in different temperature around room temperature can be calculated. From the conditions of phase equilibrium, the Clapeyron equation for liquid-vapor boundary can be derived:

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T\Delta_{vap}V} \tag{3}$$

If assume ideal gas behaviors and $V_l << V_g = \Delta_{vap}V$, Clausius-Clapeyron equation for the variation can be derived:

$$\frac{d\ln p}{dT} = \frac{\Delta_{vap}H}{RT^2} \tag{4}$$

Mixture spray: LPG Cold Spray

LPG is mostly composed of propane (>90%, volume proportion, hereinafter similar) and butane (>4%). To simplify the model, postulate is reasonable that the LPG is made up of 95%propane and 5% butane (95.6% and 4.4% in mole percentage). Given that propane and butane have the similar structure, Raoult's Law is selected for a direct and quick insight. Figure 3 presents the pressure change with the change of mole percentage of propane.

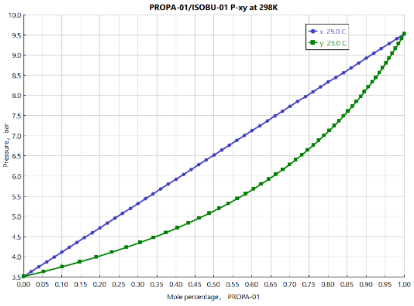

Figure 1:The pressure varies with mole percentage of propane (drawn by Aspen).

Application: Safety

When a cold spray put in the car under hot sun, the temperature can rise up to 40℃. The pressure can be computed by an integration of equation (4) with the assumption that $\Delta_{vap}H$ is constant.

For R-134a, the pressure rises to 984.6kPa, nearly 50% higher than the pressure in room temperature, which is a risk for safety. For LPG cold spray it is basically same. That is why, according to the market research, almost all kinds of cold spray are recommended to keep in fresh place under 40℃.

Cooling Model

Given that the phase transformation happened in room temperature and atmospheric pressure, the heat absorbed is equal to the total change of enthalpy:

$$Q = \Delta_{vap}H * n_{eff} \qquad (5)$$

where n_{eff} represents the effective mole number. Hence the temperature change can be calculated with the thermal capacity. The n_{eff} in two conditions is determined. In order to simplify the model, the throttling effect of liquid is not taken into consideration.

Constraint space

For a certain constraint space such the internal space of a vehicle. The n_{eff} is equal to the total volume of liquid sprayed out:

$$n_{eff} = F * t \qquad (6)$$

where the F refers to the flow flux and t refers to projection time**.**

Target area at a distance

For a surface at a certain distance, the amount of payload finally reaching the target area need calculating. If assuming that no liquid has evaporated before reaching the target aera, and the spray is projected conically and evenly with a spherical front. The n_{eff} can be derived:

$$n_{eff} = \frac{A}{2\pi R^2(1 - cos\alpha)} * F * t \qquad (7)$$

As Figure 4 shows the A is the area of target surface, R is the distance from nozzle to target surface and α is the angle of scattering. The $2\pi R^2(1 - cos\alpha)$ item represents the overall area of scattering surface.

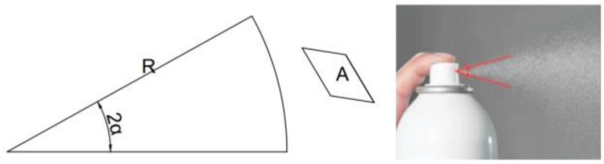

Figure2: The spray is projected conically and evenly with a spherical front.

Application: Cooling the cars and the injured

For a typical car, the internal space is around $5m^3$. The figure for air density and constant-pressure heat capacity are $1.29\text{kg}/m^3(F)$ and $1.00\text{kJ}/(\text{kg}\cdot℃)(C_p)$, and the spray flux may around 4mL/s(F). By combining the equation (5) and (6), the volume, thus the projection time, needed for cooling a 40℃ car into 25℃ can be calculated. The results are shown in the table 2. The amount needed for cooling the whole car is above net capacity biggest container.

For a sportsman with ankle injuries or knee broken where wounded skin area is $50\ cm^2(A)$ and a 14℃ instant cooling needed, if the spray projects payloads at a distance of 30cm(R) and a scattering angle of $30°(2\alpha)$, the volume and time can be determined. If human skins have an average thickness of 1mm and heat capacity like water, the result is shown in the table 2. Commonly, a cooling within 3s is recommended through the market research, which is consonant with the results. The LPG spray seems to have a faster cooling effect while the R-134a spray is milder.

Results	$V_c(mL)$	$t_c(s)$	$V_s(mL)$	$t_s(s)$
R-134a spray	726	182	13.9	3.48
LPG spray	575	144	11.0	2.76

Table 2:Results of the applications.

Conclusion

With the theoretical and practical analysis above, the pressure and cooling effect are probed by building model. The pressure in the aerosol spray can hardly change throughout the using process according to the phase rule. The pressure can rise dramatically with a temperature difference of 15℃, thus it is more secure to put the spray in a fresh place. It is beyond the capacity for the spray to cooling the whole internal air of a car, while sufficient for skin cooling. A spraying time under 3s is recommended otherwise the skin may be damaged with frostbite. The LPG spray freeze objects faster whereas the R-134a is milder. However, the real situations are more complicated, hopefully, a straight-forward and helpful insight has been made for understanding the cold spray.

Reference

[1] Aerosol spray dispenser. (2022, December 23). Wikipedia. Retrieved February 2, 2023, from https://en.wikipedia.org/wiki/Aerosol_spray_dispenser.

[2] 赵烨，郑苏录 ＆ 宓宏.(2018).制冷剂气雾罐及其使用. 化工生产与技术 (06),44-45+48+10.