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Development of novel wet sublimation cascade refrigeration system with binary mixtures of R744/R32 and R744/R290

Michał Sobieraj

Warsaw University of Technology, Faculty of Building Services, Hydro and Environmental Engineering, 20 Nowowiejska Street, Warsaw 00-653, Poland

A R T I C L E   I N F O

Keywords:
- Carbon dioxide
- CO₂
- Dry ice
- Experimental
- Propane
- Refrigeration
- Sublimation

A B S T R A C T

The use of carbon dioxide (R744) in refrigeration systems is usually limited by its triple point temperature of −56.5 °C; an objective of this study was to extend the range of this natural refrigerant to include low-temperature applications. A novel wet sublimation cascade refrigeration system was developed using low-GWP mixtures of R744 with hydrocarbons (HCs) and hydrofluorocarbons (HFCs) as low-temperature refrigerants. With propane (HC-290) and difluoromethane (HFC-32) serving as solvents for solid carbon dioxide, temperatures as low as −72 °C were obtained in a closed cycle system with mixtures containing 67% CO₂ by mass. Visualisation experiments were performed to illustrate the crystallisation of a supersaturated carbon dioxide solution. The excess solute was visible as clouding or crystals, depending on the saturation level of the solution. High heat transfer rates, up to 3465 W m⁻²K⁻¹, were obtained in the sublimator/evaporator section, resulting in low wall superheat values, indicating potential industrial applicability of the carbon dioxide-based slurry-like fluid. The pressure-mole fraction and temperature-mole fraction diagrams were constructed to study the system parameters working with binary mixtures. Moreover, vapour pressures of the binary mixtures of R744/R290 and R744/R32 at the temperature of −72.5 °C were experimentally obtained.

1. Introduction

Halogenated hydrocarbons were widely used in the refrigeration industry in the 20th century. Recently, the availability of synthetic refrigerants has been greatly reduced by the EU 517/2014 (F-gas) regulation [1]. In air-conditioning and commercial refrigeration, hydrofluorolefins (HFOs) are promoted as low global warming potential (GWP) alternatives [2]. Carbon dioxide (R744) is used as a refrigerant in centralised transcritical systems for food storage in supermarkets [3] and hydrocarbons (HCs) are used mostly in smaller hermetic units [4,5]. These working fluids cover only part of the industry demand for refrigeration. Although low and ultra-low temperature (ULT) systems are not within the scope of the current F-gas regulation, there may be an indirect impact from the EU legislation on the availability of HFC low-temperature refrigerants. With HFC quotas introduced to the common EU market, the price of refrigerants with the highest GWP has increased rapidly. For this reason, the decreased availability of R23 (GWP 14800), a key refrigerant in ULT refrigeration, may be an important issue in the near future [6]. Although there has been improvement from earlier generations of ULT refrigerants, as from R13 to R23 and R508b, and more environmentally friendly HC refrigerants (R170, R1150) or lower GWP HFCs, i.e. R41 [7,8], the flammability of these refrigerants limits their use in some applications.

There are no direct substitutes for greenhouse gases such as R23, R116, and R14. Carbon dioxide (R744), a natural non-flammable refrigerant with a sublimation temperature of −78 °C, can be used. According to Bansal [9], CO₂ with superior thermophysical properties, is one of the most promising low-temperature refrigerants. Nasruddin et al. [10] performed a multi-objective optimization of a cascade system operating with a binary mixture of ethane/CO₂ in the low stage. The optimal mass fraction of CO₂ to obtain the evaporation temperature of −55 °C was found to be 0.68. Zhang et al. [11] experimentally studied a two stage cascade system with propylene (R1270) in the high stage and CO₂ in the low stage. An evaporation temperature of −52 °C was achieved. However, in the context of the abovementioned studies, the use of carbon dioxide is currently limited by its triple point temperature (−56.5 °C) because there are technical difficulties associated with its solid phase (dry ice). However, there have been some attempts to use sublimated CO₂ as a refrigerant. Huang et al. [12] investigated a staged CO₂ sublimation cycle. Yamaguchi and Zhang [13] conducted a series of experiments using a solid CO₂ flow. Low heat transfer coefficients [14] and accumulation of solid particles leading to flow blockage [15] have been reported. To solve these problems, Di Nicola et al. [16] suggested...
using a mixture of CO₂ and a refrigerant with a low melting temperature that acts as a solvent for dry ice. Niu and Zhang [17] were successful using a mixture of R744/R290 as a replacement for R13 in the low stage of a cascade system, achieving a temperature of −68 °C. Sobieraj and Rosinski [18] used a mixture of R744/R600a in an auto-cascade cycle, achieving an evaporation temperature of −63.5 °C. When the temperature of the solution was sufficiently low, crystallisation occurred, leading to an increase in the heat transfer coefficient [19]. An analogy to the influence of nanoparticles on the heat transfer may be applied to clarify the effect of crystallisation. As stated by Wen [20], the nanoparticles may not only lead to an increased bubble generation and wettability, but can also influence interfacial properties in the solid–liquid-gas system. All these factors are thus strictly related to the triple line regime. It is therefore of a great importance that the dispersion system in present work is achieved without any additives to the system. Solid particles appear only where they are desired, and disappear after the sublimator section, without affecting the other components of the system, which makes this solution very effective. The flow of a super-saturated solid R744 solution may be considered as a wet sublimation process. There are few research papers in the literature on ULT refrigeration with CO₂. To date, the application range of wet sublimation cycles has not been studied.

The main aim of this study was to develop a wet sublimation cascade refrigeration cycle (WSCS) to provide a reasonable substitute for high-GWP synthetic refrigerants.

2. Experimental description

2.1. Vapour pressure and solubility of carbon dioxide in liquid solvents

Volatile liquids with low solidification temperatures can be considered as solvents for dry ice. It is common practice to use a mixture of dry ice with ethanol or acetone in laboratory cooling baths to improve the heat transfer conditions [21,22]. The same concept can be applied in vapour compression refrigeration cycles. However, a suitable solvent is not easily found as the operation regime of a vapour compressor cycle is strict. A substance acting as a solvent should possess the following characteristics:

- suitable vapour pressure curve
- compatibility with construction materials and compressor oil
- low viscosity
- low flammability and toxicity
- low global warming potential

Alcohols such as methanol, ethanol, and ketones (e.g. acetone) are disqualified because they are flammable, toxic, and may cause damage to the insulation of the compressor motor wiring [23]. Moreover, these substances exhibit extremely low vapour pressures at low temperatures. Saturation pressure is another important factor to be considered. It is known that boiling heat transfer depends strongly on the reduced pressure [24]. Lower pressure produces lower heat transfer coefficients. Thus, it is favourable to use a solvent with a relatively high saturation pressure such as R41 or R170. Another important factor is the temperature glide during the evaporation (sublimation) process. Solvents with a higher vapour pressure and a lower normal boiling point (NBP) decrease the temperature glide and can form an azeotrope. Cox et al. [25] suggested the use of a mixture of R744/R41 with virtually no temperature glide.

Di Nicola [16] proposed a variety of low-GWP synthetic fluids as solvents for dry ice including R125, R41, and R32. Difluoromethane (R32), which is classified as a mildly flammable refrigerant, was chosen as a possible HFC, mostly for its good thermophysical properties [26], relatively low GWP, and good availability. Another study by Di Nicola et al. [27] suggested the use of natural HC refrigerants such as ethane R170, ethylene R1150, propylene R1270, propane R290, and dimethyl ether RE170. It was reported that a cascade system operating with a recuperative liquid/suction heat exchanger attained the highest COP when a mixture of R744/R290 was used as the working fluid. Thus, propane R290 was selected as the high-boiling compound. Fig. 1 presents the vapour pressure curves for pure refrigerants R744, R290, R32, and their mixtures, and the bubble (liquid) and dew (vapour) curves of the binary mixtures. The liquid curves of the mixtures are similar to the liquid curve of R23, indicating potential applicability as a substitute for HFC-23. The vapour curve is not similar, indicating high-temperature glide. However, when applied to a specifically designed system, this effect can be avoided by using a recuperative heat exchanger (RHX), making the system capable of near-isothermal refrigeration over a vapour quality range [18]. Another factor to consider is the solubility of solid carbon dioxide in the solvent. When using CO₂ as a refrigerant in pressure–temperature conditions below the triple point of R744, the solubility of solid carbon dioxide (dry ice) in a liquid solvent should be considered.

Although some sources suggest that the solubility of dry ice is independent of the solvent [27], an in-depth analysis was conducted based on the available literature. Kurata et al. [28] experimentally studied the solubility of solid carbon dioxide in light hydrocarbons such as butane, propane, and ethane. Similar studies with HFC refrigerants as solvents were conducted by a research group led by Di Nicola [29,30]. Considering the experimental data, Fig. 2 illustrates the solid–liquid equilibrium (SLE) for mixtures of R744/R290 and R744/R32. Both mixtures contained the same amount of R744 (67% by mass).

The solubility of solid CO₂ denoted as x₂ decreases with a decrease in the temperature of the solution. The trend is obvious, and similar with different solvents. However, the solubility of the solute depends greatly on the type of solvent, as shown in Fig. 2. A solution of solid carbon dioxide in R32 with a CO₂ mole fraction of 0.7 (67% by mass) achieves a saturation state at −72 °C, a solution of R744 in R290 reaches this condition at −62 °C.

It has been suggested in previous studies [17,25,27] to use such a refrigerant mixture composition to avoid the formation of solids in the stream caused by supersaturated solution conditions. In this study, an opposite approach is presented to increase the applicability range of R744 under low-temperature conditions. Under appropriate temperature–pressure conditions, solid carbon dioxide is present, and the carrier fluid participates in the heat transfer. A supersaturated carbon dioxide solution in which crystallization occurs indicates a wet sublimation process [19]. To study the feasibility of a wet cascade system, an experimental setup was designed and constructed.

A comparison of the thermophysical properties of R744, R32, R290, and their mixtures with HFC-23 is presented in Table 1. Both R290 and R32 are flammable refrigerants, classified as A3 and A2L, respectively. Although the dilution effect of CO₂ can suppress the flammability, based on Le Chatelier’s method [33] and experimental results by Tian et al. [34], the proposed mixture of propane and carbon dioxide exhibits flammability until the concentration of the inert CO₂ is as high as 91.5%.
Thus, the studied R744/R290 mixture is still classified in the A3 group. However, calculations based on the method by Yang et al. [35] indicate that a mixture of R744/R32 can presumably be non-flammable with a CO₂ content of at least 52%. With this approach, the proposed mixture containing 67% R744 is classified in the A1 group.

Evaluation of novel mixtures should also include the analysis of the vapour and liquid curves for boundary conditions given by the condensation temperature and evaporation pressure. For this reason, the mixtures of R744 with R290/R32 were further investigated based on p-x and T-x plots.

Fig. 3 depicts differences in dew and bubble curves of the studied mixtures with R744 mass composition of 67%, at a constant pressure of 1.5 MPa. The temperature glide, ΔT_g, is higher with R744/R290 and the required condensation temperature is lower, being close to −24 °C, compared to −20 °C for R744/R32.

When a constant condensation temperature of −25 °C is assumed, as shown in Fig. 4, it can be noted that the bubble pressure, being close to 1.40 MPa, is higher for R744/R290. At the same time, the condensation

![Fig. 1. Saturation pressure of selected refrigerants.](image1)

![Fig. 2. Solid carbon dioxide solubility in liquid R290 and R32.](image2)

Table 1
Comparison of refrigerant properties [31,32].

<table>
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<th></th>
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<th>R744</th>
<th>R32</th>
<th>R290</th>
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<td>M</td>
<td>70.0</td>
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<td>52.0</td>
<td>44.1</td>
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<td>NBP [°C]</td>
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<td>−51.7</td>
<td>−42.1</td>
<td>−83.3/-</td>
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<td>t_ptr [°C]</td>
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<td>−56.5</td>
<td>−136.8</td>
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<tr>
<td>t_c [°C]</td>
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<td>78.1</td>
<td>96.7</td>
<td>48.9</td>
<td>47.6</td>
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<td>A1</td>
<td>A2L</td>
<td>A3</td>
<td>A1</td>
<td>A3</td>
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</table>

* Onset of crystallisation.

Thus, the studied R744/R290 mixture is still classified in the A3 group. However, calculations based on the method by Yang et al. [35] indicate that a mixture of R744/R32 can presumably be non-flammable with a CO₂ content of at least 52%. With this approach, the proposed mixture containing 67% R744 is classified in the A1 group.
According to Fig. 4, while the bubble curve of R744/R32 blend shows almost linear behaviour following Raoult’s law, the curve of R744/R290 shows a positive deviation. This phenomenon is related to the polarity of the molecules of R290 and R32, which are designated as non-polar and polar, respectively.

Despite substantial research work on modelling of multi-component CO₂ mixtures [36–38], the calculation methods for the mixtures containing R290 or R32 in the temperature range of −56.5 to −78.4 are lacking. The results reported in the literature are either focused on CO₂–CH₄ mixtures [39,40] or do not cover the specific fluid [41] or the temperature range [42]. The mixture model of Kunz and Wagner [43] incorporated in REFPROP [32] can be applied only to the temperature of 216 K corresponding to the triple point conditions of CO₂, and can be conditionally extrapolated to lower values. However, as stated by NIST “The REFPROP program does not know the location of the solid–liquid interface for a mixture”. Therefore, a question arises whether the predicted SLE curves are reliable since the conditions experienced are quite distant from the triple point of pure CO₂. An in-depth study was thus conducted in the present work to examine the SLE behaviour over a range of solvents and compositions. An additional experimentation was performed to study the solid–liquid behaviour of the mixtures. The experimental setup included: a dry ice–ethanol–acetone bath, a copper cylinder with an internal volume of approx. 40 cm³, pressure and temperature measurement apparatus and a data acquisition system. An uncertainty of ± 0.05 bar and 0.2 K applies to the measurements of pressure and temperature, respectively. The experimental procedure was to fill the abovementioned copper cylinder with an appropriate amount of R744 and R290 or R32, based on the partial vapour pressure of each component. The cylinder was then put in a thermally-insulated flask containing dry ice bath at −72.5 °C. The saturation pressures of pure substances R744, R290 and R32 were also measured to verify the

![Fig. 3. Temperature–mole fraction diagram for blends of R744 and R290/R32 at 1.5 MPa.](image)

![Fig. 4. Pressure–mole fraction diagram for blends of R744 and R290/R32 at −25 °C.](image)
As shown in Fig. 5, the highest pressure with R290 was 0.186 MPa at the mole fraction, \( x_2 \), of 0.3. Experimental data derived of Jensen and Kurata [28], represent the pressure of 0.184 MPa with a mole fraction of approx. 0.29, indicating also the saturation state of the solution. That is, the maximum mole fraction of solid CO\(_2\) that can dissolve in propane at –72.5 °C, is close to 0.29. The vapour pressure for mole fractions of 0 to the saturation state of 0.3 could be presumably described with Raoult’s law, as \( p \sim x_1 p_1 + x_2 p_2 \). Then, the pressure decreases linearly until \( x_2 \) of 0.8. The pressure – composition relationship in this area can be expressed as \( p \sim p_1 + p_s \), meaning that the vapour pressure of the saturated solution of dry ice in R290 is close to the sum of pressures of saturated solvent and saturated dry ice. Simulations, based on Kunz-Wagner model (KWO) known as GERG-2008 EoS [43], were also performed. The model is based on a multi-fluid approximation explicit in the reduced Helmholtz free energy, in which the residual part of the Helmholtz free energy of the mixture is calculated using the reduced mixture density and the inverse reduced temperature. The composition-dependent reducing functions for density and temperature are calculated based on the mixing rules, using the binary interaction parameters, GammaT and BetaT, that fitted to data for binary mixtures [44].

The results of the calculations are presented in Fig. 5. When standard mixing parameters (\( \text{GammaT} = 1.0336, \text{BetaT} = 0.90877 \)) were used, the model seemed to be able to predict the vapour pressure in undersaturated region, but overestimated the saturation pressure of the oversaturated solution.

The experimental and simulation results of the mixture of R744/R32 are presented in Fig. 6. According to the literature [29], the solution reaches the saturation state \( x_2 \) of 0.7 at –72.5 °C. The pressure increases linearly and can be expressed as \( p \sim x_1 p_1 + x_2 p_2 \) until it reaches its maximum value of 0.188 MPa at \( x_2 = 0.7 \). In the oversaturated region the pressure decreases linearly until the pressure of pure CO\(_2\). REPROP XR0 linear model shows good agreement with experimental data in the undersaturated region.

### 2.2. Experimental setup

Fig. 7 shows a schematic of the experimental setup. A two-stage refrigeration system was developed based on rotary hermetic compressors. A vapour compression system with an air-cooled condenser operating with R404A was used as the high-temperature stage to remove the heat load for the condensation of the refrigerant mixture in the low-temperature stage via a coaxial tube in a tube evaporator-condenser made of 1/4" OD tube in a 1/2" OD tube with a length of 6000 mm. The high-temperature stage was designed with sufficient cooling capacity to produce a condensation temperature ranging from –20 °C to –25 °C. As the main focus of this study is the low-temperature stage, the performance of the high-temperature stage was disregarded. The low-temperature stage consisted of an R290 hermetic compressor with a displacement of 17.3 cm\(^3\). The compressor was intended for operation with high back pressure (HBP); thus, it was equipped with a heavy-duty motor with a nominal input power of 795 W according to ASHRAE HBP and was not designed for low evaporation temperatures.

The path of the refrigerant mixture is shown in Figs. 7 and 8. The compressed refrigerant enters an oil separator, a Coriolis-effect mass flow meter, and is directed to an air-cooled desuperheating heat exchanger to lower the vapour temperature (2 → 3) before the refrigerant mixture is introduced to the cascade condenser (CHX) where the mixture is condensed (3 → 4) to a slightly subcooled liquid, with a subcooling degree of \( \Delta T_{CHX} \). Further subcooling, \( \Delta T_{RHX} \) (4 → 5), occurs in the recuperative heat exchanger (RHX) made of two coiled copper tubes with an inner diameter of 2.0 mm and a length of 2350 mm, each placed in a 22 mm OD tube shell.

An electronic expansion valve with a 1.0 mm orifice diameter was used for throttling the refrigerant mixture (5 → 6). After the throttling process, the refrigerant entered the visualisation section to observe the flow through a boro-silica glass tube with an inner diameter (ID) of 7.6 mm and a length of 250 mm. The outlet of the first visualisation tube was connected to the inlet of an evaporator consisting of two copper tubes with an inner diameter of 8 mm and a length of 480 mm. The evaporator tubes were wrapped with a silicon electric heating cable with a total input power of 500 W and insulated well with 75 mm of Armaflex insulation, with thermal conductivity of 0.035 W/mK. The outlet of the evaporator was connected to a lower visualisation tube, showing the flow pattern of the refrigerant after partial evaporation. The suction (vapour) side of the RHX was connected between the visualisation.
section and the suction port of the compressor, partially superheating the vapour (7 → 1). The vapour was compressed (1 → 2).

Fig. 9 shows the visualisation section, a hermetically sealed steel chamber with thick polycarbonate glass as an inspection window and boro-silica glass tubes interconnected between the inlet and outlet of the evaporator. The flow was recorded using a high-speed 1000 FPS CMOS camera. The characteristics of the system components are presented in Table 2.

Temperature was measured at the locations specified in Fig. 7 with miniature PT100 resistors with an uncertainty of 0.1 K. To obtain the temperatures of the outer wall of the evaporator tube, miniature PT100 resistors, bonded with a thermal glue, were placed along the evaporator tube every 75 mm, starting 25 mm from the inlet. The discharge and suction pressures were measured with piezoelectric transducers with measuring ranges of −1 to 9.3 bar and 0 to 30 bar respectively. The relative combined standard uncertainties were calculated with a coverage factor of 2, resulting in an approximately 95% confidence interval, as per JCGM [45]. The combined uncertainty in the heat transfer coefficient results from the uncertainties in the measurements of the electrical power delivered to the test section and the temperatures of the wall and refrigerant. The expanded uncertainty in the heat transfer coefficient is in the range of 0.9% to 8.3%.

The experimental components, measurement instruments, and their uncertainties are summarised in Table 3.

2.3. Experimental procedure

The following experimental procedure was performed with each low-temperature blend:

(1) The low-stage system was evacuated with a vacuum pump to remove the moisture and non-condensing gases.
(2) Appropriate amounts of higher- and lower-boiling compounds: R32 (50 g) or R290 (50 g) and R744 (100 g), were charged to the low-stage system; the total charge was 150 g.
(3) The high-stage system was turned on to condense the low-temperature refrigerant blend.
(4) Once the high-stage was running, the low-stage was started, and heat load was added to the evaporator.
(5) After the system was in steady operation, the data were recorded every 5 s for further calculations of the system performance.

The opening of the expansion valve remained constant during experiments for a given refrigerant blend and heat load on the evaporator. After experiments for a given heat load, the system was turned off until the pressures equalised, and then restarted to provide similar conditions in the case of a dry ice build-up somewhere in the system, which was occasionally observed.

2.4. Data reduction

The assessment of the proposed novel wet sublimation cascade refrigeration system included discharge, condensation, evaporation, and suction parameters, and an analysis of the cascade heat exchanger (CHX) and recuperative heat exchanger (RHX) performance.

The subcooling of the refrigerant leaving the CHX was defined as...
Δ\(T_{CHX}^{sc}\) = \(t_{bubble}(\text{p}_2)\) - \(t_4\)  

\(\Delta T_{RHX}^{sc} = \Delta T_{bubble}(\text{p}_2)\)  

\(\Delta T_{sh} = \frac{T_6 + T_7}{2}\)  

\(\alpha_i(L) = \frac{\dot{Q}}{\pi d_i L \Delta T(L)}\)
3. Results and discussion

3.1. System performance

The performance tests of the wet sublimation cycle were conducted with the aforementioned mixtures of R744/R290 and R744/R32 with condensation temperatures ranging from −22.5 to −27 °C. The test conditions, including the discharge and suction parameters, measured mass flows, calculated subcooling $\Delta T_{c,s}$, and superheating degrees $\Delta T_{sh}$ are presented in Table 4.

The temperatures at the inlet of the evaporator, $T_0$ and $T_7$, ranged from −72.3 to −69.9 °C for the R744/R32 blend, and from −72.2 to −71.5 °C for R744/R290. At the outlet, the temperature ranged from −71.0 to −65.9 °C and from −71.9 to −64.8 °C for R32 and R290 blends, respectively.

However, the use of R290 promoted lower evaporator inlet temperatures, the temperature glide was greater, ranging from 0.3 K with lower heat loads to 6.6 K with higher heat loads. Nevertheless, the average evaporation temperature was always slightly lower for the R744/R290 blend, as shown in Fig. 16.

The wall temperatures were higher with R290 as the secondary mixture compound. The temperature difference, the wall superheat, ranged from 4.2 to 11.2 K, and was significantly lower (3.0–7.9) when R32 was used in the blend. Thus, the resulting heat transfer coefficient of the wet sublimation process reached 1922 $\text{W m}^{-2} \text{K}^{-1}$ for R744/R32 and 1388–2430 $\text{W m}^{-2} \text{K}^{-1}$ for R744/R290. The flow boiling heat transfer coefficients with CO$_2$ at $-30$ °C obtained by Zhao and Bansal [46] for low mass and heat fluxes of 100 kg m$^{-2}$s$^{-1}$ and 10 kW m$^{-2}$15 kW m$^{-2}$ ranged from 4000 to 6000 W m$^{-2}$K$^{-1}$. Pure refrigerants usually exhibit higher boiling heat transfer coefficients than mixtures [47,48]. Moreover, refrigerants with higher vapour partial pressures such as R32 exhibit higher boiling heat transfer coefficients than lower vapour pressure blends, respectively. Although the use of R290 promoted lower evaporation temperatures, the change in temperature of the vapour pressure of R32 is higher than R744/R32 mixture was minimal. The vapour pressure of R32 is higher than R744/R290, and from R744/R32 and from 1.38 to 1.61 MPa with R744/R290. There is a linear increase in the discharge pressure when more heat load is delivered to the evaporator, resulting from increased heat flux on the condenser for a given heat transfer surface. Nevertheless, the discharge pressure was always approximately 0.15–0.2 MPa greater when R290 was used, which is strictly related to the dew/bubble curves of the mixtures shown in Fig. 1. The curve for R744/R290 is much steeper than the curve for R744/R32. For a saturation (bubble-point) temperature of $-25$ °C, the difference in the saturation pressure is approximately 0.14 MPa, which is close to the experimentally obtained value.

Fig. 13 shows the compressor discharge temperatures for the mixtures with different heat loads. When R290 was used, the discharge temperatures ranged from 76 °C to 82 °C. Although the condensing pressure with R32 was lower under similar heat load conditions, the discharge temperatures were higher, ranging from 78 °C to 83 °C. The discharge temperature rise ranged from 1.7 to 2.4 K. The intrinsic properties of the refrigerants and their mixtures used in this study play an important role in the evaluation of the compression process and should be considered as the dominant parameters affecting overall system performance. The specific heat ratio $k = c_p/c_v$ exhibits significant differences, as shown in Table 5.

Propane R290 has a much lower specific heat ratio than R32, with both fluids treated as higher-boiling compounds of the mixture; R744 has the highest specific heat ratio. The specific heat ratio, or adiabatic index, describes the isentropic process according to Poisson’s equation:

$$T_2 = T_1 \left(\frac{p_2}{p_1}\right)^{(k-1)/k}$$

Thus, the maximum gas temperature after the compression process depends on the k index and the pressure ratio of $p_2/p_1$. It is evident from Table 5 that R32 in a mixture with R744 presumably produces the highest discharge temperatures, which was demonstrated in the experiments, although the pressure ratio seemed more favourable.

The compressor used in this study was designed specifically for use with propane R290 as per ASHRAE HBP conditions with an evaporation temperature of 7.2 °C, a condensing temperature of 54.4 °C, and liquid and suction gas temperatures of 46.1 °C and 35 °C, respectively. The nominal pressure ratio was determined to be 3.205, and the resulting discharge temperature was approximately 81 °C, assuming isentropic compression. The experiments revealed that the internal overheating protection activated at approximately 90 °C, switching off the compressor.

Table 4

<table>
<thead>
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<th>$Q_{ev}$ [W]</th>
<th>$m$ [g s$^{-1}$]</th>
<th>$p_1$ [MPa]</th>
<th>$t_0$ [°C]</th>
<th>$t_7$ [°C]</th>
<th>$t_1$ [°C]</th>
<th>$\Delta T_{sh}$ [°C]</th>
<th>$\Delta T_{c,s}$ [°C]</th>
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<td>R744/R32</td>
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<td>R744/R290</td>
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<td>0.178</td>
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<td>−13.8</td>
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<td>−71.0</td>
<td>−68.4</td>
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<td>300</td>
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<tr>
<td>257</td>
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<td>0.167</td>
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<td>−71.9</td>
<td>−27.0</td>
<td>26.9</td>
<td>−27.0</td>
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</table>
However, dissipating a large amount of heat during the compression process degraded the overall compressor performance.

A literature survey revealed that the optimisation of hermetic compressors was a complex problem when using non-standard mixtures as refrigerants [50]. Lee at al. [51] examined the use of an air-conditioning scroll compressor in a J-T cryocooling cycle with a multicomponent mixture. Compressor failure occurred when no additional cooling was used. Song et al. [52] reported compressor overheating in a cascade system working with R508B. A specially designed compressor was used by Bai et al. [53] in an R290/R170 J-T cycle to solve overheating problems, obtaining discharge temperatures lower than 100 °C during steady-state operation.

3.2. Flow visualisation

Flow visualisation experiments were conducted to highlight triple-phase flow phenomena. Different flow characteristics were observed depending on the mixture components and the pressure–temperature conditions.

The first visualisation tests were performed with a mixture of R744/R32 to show the moment of transition from undersaturated to saturated flow conditions. When the temperature of the solution was sufficiently low (-72 °C), crystallisation occurred, as shown in Video 1 and Fig. 14c. Crystallisation indicated that the solid carbon dry ice solution was saturated. A further decrease in temperature led to an increase in the solid fraction that could not be dissolved in the solvent. The mole fraction of solid carbon dioxide is expressed as [19]

$$\phi_{CO_2} = (1 - X)(\Delta x)$$  (7)

Depending on the saturation conditions of the solution, which are determined by the mole fraction of solid carbon dioxide $\phi_{CO_2}$, the excess solute is visible in the form of clouding (Fig. 15) or crystals (Fig. 16).

Fig. 15 and Fig. 16 illustrate the flow of the R744 mixtures under almost identical conditions, with a 67% mass fraction of CO₂ in each case. The temperature and pressure conditions were –72.2 °C and 0.65 to 0.67 bar.

The solid mole fraction of the R744/R32 mixture was close to zero and clouding was visible, indicating the onset of crystallisation and the saturation of the solution. When the solution was saturated, the flow exhibited a stratified wavy pattern compared to the available maps for two-phase flows [54]. However, when the R744/R290 mixture was
examined under similar conditions, crystals were present in the stream, with a $\phi_{\text{CO}_2}$ of 0.4, indicating heavy oversaturation of the solution. The flow pattern was much more sophisticated. The crystals tended to form larger structures that filled the entire cross-section of the visualisation tube (Fig. 17 and Video 2) and were pushed by the pressure difference through the length of the tube and the evaporator section.

With identical compositions and flow conditions, the mole fraction of solid carbon dioxide was much higher for the R744/R290 mixture, confirming that the solubility of carbon dioxide in its solid phase (dry ice), is much lower in propane (R290) than in difluoromethane (R32).

4. Conclusions

A novel wet sublimation cascade refrigeration cycle was developed in this study, indicating the possibility of using carbon dioxide (R744) as a low-temperature refrigerant. An experimental facility was built and different mixtures of CO$_2$ were tested. Propane R290 and difluoromethane R32, both environmentally friendly refrigerants, were used as the higher-boiling compounds. It was the purpose of this study to investigate the effect of the solvent on the system performance. Although, R290 and R32 possess quite similar thermophysical properties, the main difference is the solubility of solid dry ice. Unlike previous studies in the literature, this study focused on the saturated and over-saturated states of the solution formed by solid carbon and solvents. The mixture compositions were selected to operate under the corresponding pressure–temperature conditions to produce crystallisation. The differences in the solubility of solid carbon dioxide in different solvents (HFC and HC) were demonstrated, both theoretically and experimentally. Temperature–composition graphs were constructed to illustrate the solubility. A visualisation section was designed in this study to observe the crystallisation phenomenon and the flow regimes. It was found that the flow characteristics were dependent on the solution state. The excess

<table>
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<th>Table 5 Specific heat ratios of refrigerants and mixtures.</th>
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<tr>
<td>Refrigerant</td>
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<td>Specific heat ratio</td>
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</table>

Fig. 12. Discharge pressure.

Fig. 13. Discharge temperature.
solid carbon dioxide was visible as clouding or crystals, acting as a slurry-like liquid with high heat transfer capabilities down to $72^\circ C$. The mole fraction of the excess undissolved solid CO$_2$ was much more visible with R290. Although the mean evaporation temperatures were similar in mixtures with R290 and R32, the wall superheat was always lower when R32 was used, mainly due to its higher partial pressure and superior thermophysical properties in low temperature and pressure conditions. The temperatures achieved in the refrigeration cycle in this study were similar to the sublimation temperature of dry ice at atmospheric pressure ($-78^\circ C$). Thus, it can be concluded that a WSCR system operating with CO$_2$ can be considered as an alternative to standard cascade systems with HFC-23 or HFC-508B in the lower-temperature stage.

Similar mass compositions of each blend were selected in this study to examine the influence of the solvent and crystallisation on the system performance. On the other hand, it would be interesting to study the system performance with both mixtures achieving crystallisation at the same temperature. Such tests, with R744/R32 mixture composition being unchanged (67/33) and that of R744/R290 being (30/70) are to be performed in the nearest future.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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References


