Open Cycle Joule-Thomson Cryocooling by Mixed Coolant

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ABSTRACT

Mixed coolants are conventionally employed for the closed cycle Joule-Thomson mode of cryocooling. Here, the potential of mixed coolants is utilized for reducing the pressure of operation. Numerous experimental and theoretical studies of closed cycles have been reported. However, the preferred compositions for closed cycle mixtures at low pressure are not the same as for elevated pressure open cycle use. Elevating the charging pressure is essential for the open cycle mode of cryocooling since it enables one to store more coolant in the vessel and prolong the mission. However, the reported experience with open cycle mixed coolants is quite rare. Traditionally, open cycle J-T cryocoolers employ pure coolants: nitrogen and argon for the 80 K and 90 K range, respectively. The present study is an experimental demonstration of a mixed-coolant open cycle system for the same temperature range, performing at elevated pressures. This mixture combines the advantages of nitrogen and argon: it reaches the lower temperature of nitrogen but still cools down as fast as argon. The examined mixture includes more than 80% of nitrogen (by volume) and hydrocarbons.

INTRODUCTION

Common applications of open-cycle Joule-Thomson cryocoolers include autonomous functioning infrared sensors[1,2,3] for missiles, night vision devices, and cryosurgical machines.[4,5,6] Traditionally, open-cycle cryocoolers employ pure coolants at elevated pressure for two reasons: (a) to enhance the Joule-Thomson effect, and no less significant, (b) to store more gas in a given vessel volume in order to prolong the duration of the mission.

Nitrogen is the most commonly used gas, with a normal boiling point of 77.2 K. The alternative coolant is argon, which has a higher normal boiling point of 88.3 K. The specific cooling capacity, $\dot{Q}/\dot{n}$, of a Joule-Thomson cryocooler, in the general case of mixed and pure coolants, is the minimum enthalpy difference due to the pressure difference between the streams (P_{IN}, P_{OUT}), while scanning all temperatures along the recuperator,

$$\dot{Q}/\dot{n} = \Delta h_T = \underset{T}{\text{MIN}}\left[h\left(P_{OUT},T\right) - h\left(P_{IN},T\right)\right] \tag{1}$$

where $\dot{Q}$ and $\dot{n}$ represent the cooling power and the mass flow rate of coolant. The Δh_T is the integral isothermal Joule-Thomson effect. Pure coolants have their minimum (pinch point) value at the warm end (ambient temperature). Argon reaches Δh_T values of about 1.8 kJ/mole vs. 1.2 kJ/mole for nitrogen, at room temperature. Therefore, argon tolerates smaller flow rates and enjoys a lower

cutoff pressure. Each of these parameters, potentially, extends the duration of the mission for any given size vessel. In addition, argon cools down faster than nitrogen at similar conditions.

For cryocooling in the range of 80 K, mixing nitrogen with higher boiling point components raises the integral Joule-Thomson effect for similar pressure and temperature, but still may suppress the boiling point of the mixture close to that of nitrogen. The more common employment of mixed coolants is for the closed-cycle Joule-Thomson mode of cryocooling. Here, the potential of mixed coolants is utilized for reduction of the pressure of operation. A closed cycle cryocooler employs a compressor to pressurize the coolant on site. Reducing the operating pressure, but still enjoying a reasonable specific cooling capacity, Δh_T, is the central issue. For pressures as low as 2.5 MPa, a single stage compressor might be adequate—as developed by Longsworth [7]— following the original pressure reduction proposal of Alfeev, Brodyansky, et al.[8] That significantly simplifies the system, makes it more reliable, and reduces its cost[9] in comparison with two- and three-stage compression systems. As well, the lower pressure might be significant when the cryocooling system is combined with another mechanism like gimbals[10]. Other examples of low pressure practice and various compositions of mixed coolants are described by Longsworth, et al.[11], Boiarsky, et al.[12], and Alexeev, et al.[13]

Hydrocarbon additives are superior candidates in comparison to other non flammable components of higher normal boiling points and higher Δh_T, but of relatively low melting points. One may add more hydrocarbons and still not be threatened by solidification of the mixture while cooling down to the range of 80 K. Flammable versus nonflammable components were discussed in the patents of Khatri and Boiarski[14] and of Boiarski et al.[15]   Flynn, et al.[16] protected their proposal for mixtures of inert components.

STATE OF THE ART

Judging by the reported experience with high-pressure mixed-coolants for open-cycle Joule-Thomson cryocooling, it seems that this mode of cryocooling is less common in practice. Little and Paugh[17] report an attempt at fast cooldown while precooling a final stage of nitrogen by a 30 MPa mixture of 28.8% nitrogen balanced by methane, ethane, and propane. Maytal et al.[18] optimized a mixture of 30 MPa. Their analysis showed that it is possible to find a ternary mixture of nitrogen with hydrocarbons that exhibits a higher Δh_T than argon, but with a boiling point close to nitrogen. A further study of Maytal et al.[19] explored the upper limit of pushing Δh_T for 80 K cryocooling by allowing up to eight components mixed with nitrogen and pressurizing up to 50 MPa. This analysis showed that ternary mixtures optimized at 30 MPa actually represent quite well the global optimum, even for higher pressures.

Vetrovec[20] proposed an open cycle high pressure thermal management system for a high-average power solid state laser as a series of short single-shot expansions. He mentions the possibility of replacing nitrogen or argon by a ternary mixture of nitrogen, ethane, and propane at the composition of reference 18.

Sobel[21] focused on the possibility of reaching a temperature below 80 K, down to 27 K. He proposed a mixture of argon and neon for open-cycle cryocooling below 80 K at charge pressures up to 80 MPa. These mixtures are not flammable. However, to suppress the boiling point of the mixture significantly below 80 K would require a substantial fraction of neon. Since neon has a negative Joule-Thomson effect at room temperature, the Δh_T of the mixture will be significantly below that of argon and might even become negative.

Hingst[22] expressed an opposing interest: he tolerated higher temperatures, which are up to 90 K and also up to 100 K. His mixed coolants for open cycle cryocooling are pressurized up to 80 MPa. Basically, the compositions are as those of Alfeev, et al.[8] for closed-cycle and low-pressure operation, with the nitrogen or argon share below 70%, balanced by hydrocarbons. Hingst describes experiments for extending the run by a flow-regulated cryocooler, fed by ternary and quaternary mixtures of 30% nitrogen supplemented by hydrocarbons. Warming the pressure vessel during the operation enabled further extension of the run time. In addition, Hingst tested two binary mixtures in the same experiment, including 56% of argon or 70% of nitrogen. In general, binary mixtures have a less stable boiling temperature than a ternary or quaternary mixtures. He did not

focus on the cooldown period in comparison to other coolants, nor on discharge through a fixed orifice cryocooler.

The flammability of the kind of mixtures of Alfeev et al. and of Hingst has been recognized and discussed by Little[23] and Vogt, et al.[24]. They got rid of the flammability by adding a flame retarding component which is bromotrifluoromethane (CF_3Br), also known as a refrigerant R13b1 ("Helon"). A few percent of it turned a flammable mixture of nitrogen with a substantial share of hydrocarbons into a non flammable one. Similarly, Hingst[22] dealt with the flammability of his mixtures by adding 3% to 15% of heptafluoropropane or 3 to 20% of tetrafluoromethane (CF_4).

THE PROPOSED MIXTURES

The hereby proposed group of open-cycle and elevated-pressure mixtures contain a higher share of nitrogen or argon (at least 78%) than the previously studied mixtures. The additional two or three balancing components are: methane, ethane, propane, and 1-butene. The following arguments, some of them discussed in references[18,19], articulate the advantages of this group of mixtures:

1. The $\dot{Q}/\dot{n}$ values of ternary optimized mixtures at the elevated pressure range may theoretically approach about 2.5 kJ/mole, which is significantly higher than nitrogen and even higher than argon. This is only about 20% below the highest optimized value (about 3.15 kJ/mole) of eight-components mixtures. The higher boiling point components have higher Δh_T than nitrogen. In spite of the small molar fraction, their contribution is significant due to the elevated pressure of the mixture (at the relevant ambient temperatures). However, elevating their share to the level of low pressure optimized mixtures would suppress their $\dot{Q}/\dot{n}$.

2. Elevating the charge pressure to the range of about 60 to 70 MPa is somewhat "over-pressurizing," and suppresses the $\dot{Q}/\dot{n}$ by about 20%. However, that is a reasonable compromise with the desire to store more coolant in the reservoir. In addition, for small pressure vessels and especially for flow regulated cryocoolers, pressure might significantly drop during the cooldown process, and, as a result, approach the peak value of $\dot{Q}/\dot{n}$.

3. However, ternary mixtures tolerate about half the size of recuperator (in terms of NTU) than optimized mixtures with eight components and about two thirds of that of six-component mixtures. This is explained by the smaller temperature difference between the streams of eight-component optimized mixtures. Even though, it is still about twice the required NTU for nitrogen and about four times larger than that required for pure argon. The compactness is of special relevance when applying miniature Joule-Thomson cryocoolers, and especially on gimbaled mechanisms.

4. A ternary mixture of halogenated hydrocarbons or other non flammable components would have a significantly lower $\dot{Q}/\dot{n}$. (Even an eight-components mixture with halogenated hydrocarbons has a somewhat lower $\dot{Q}/\dot{n}$ than a ternary mixture with hydrocarbons[19]).

COOLDOWN AND CRYOCOOLING EXPERIMENTS

The System

The single shot, fast cooldown system included a 150 cm³ pressure vessel, repeatedly charged by the coolants to feed an open-cycle miniature Joule-Thomson cryocooler with a fixed-orifice, assembled in an evacuated encapsulation (dewar). The cryocooling instantaneous temperature was measured at the cold end and recorded. The cooling capability lasts until the cooled object warms up. The charge and discharge was repeated three times to compare the three coolants: nitrogen, argon and the proposed mixture. Each coolant was tested at similar conditions; two levels of pressures and ambient temperatures.

The Tested Mixture

The composition of the particular mixture as tested below was inspired by the optimization study[18] and its verification[19] by Maytal et al. The reported optimized ternary composition of nitro-
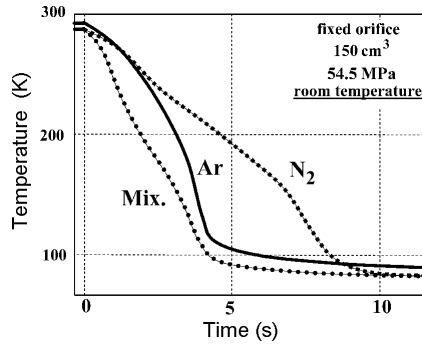
Figure 1. Comparison of cooldown by the mixed coolant, by nitrogen and by argon.
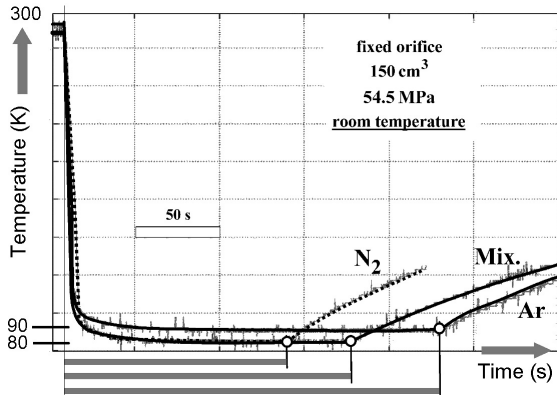

Figure 2. Comparison of cryocooling periods with mixed coolant vs. nitrogen and argon.

gen, ethane and propane is (0.8, 0.12, 0.08), by volume. In order to increase the temperature difference at the pinch point by about 10 K, it was proposed as part of the same study to somewhat deviate from the optimum and include less hydrocarbons. So the chosen composition by volume became (0.83, 0.10, 0.07) and that is also the blend of the present experiments. In addition, it serves for reduction of the flammability potential. It is the same candidate composition as mentioned in reference 20.

Operation at Room Temperature

Figure 1 displays the cooldown process attained by each of the coolants using a charging pressure of 54.5 MPa. Note that the mixture is faster than argon and also reaches indeed the boiling point of nitrogen. Cooldown terminates within 3.5 s with the mixture, and within about 4 s with argon. Nitrogen doubles the cooldown period to about 7.5 s.

Figure 2 focuses on the run time of each coolant. The mixed coolant runs longer (173 s) than nitrogen (132 s) but shorter than argon (215 s). The cutoff pressures behave similarly: 2.4 MPa for the mixed coolant, which is between 1.2 MPa for argon and 2.87 MPa for nitrogen.

Operation at Elevated Ambient Temperature

The entire system, including the encapsulated cryocooler and the charged pressure vessel, before and during the discharge process, stays at the elevated ambient temperature. The pressure in the vessel at the elevated ambient temperature is 64 MPa. While elevating the temperature, the pressure in the vessel rises too, thus the charging pressure at room temperature has to be correspondingly lower. The ambient temperatures were 87, 82 and 75°C with the mixed-coolant, argon, and nitrogen, respectively.
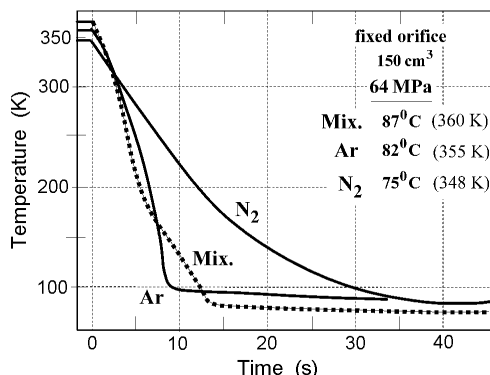
Figure 3. Comparative experiments at elevated ambient temperatures, including the encapsulated cryocooler and the pressure vessel. The pressure of the gas in the vessel is 64 MPa, at each temperature.

The cooldown results are displayed in Figure 3. The cooldown pattern of the mixture is quite close to that of argon, although the ambient temperature of argon was lower by 5°C. The mixture reaches the boiling temperature of nitrogen or somewhat above because of the back pressure. Nitrogen at only 75°C failed to reach its boiling point, and after about 40 s, it starts to warm up. The periods of cryocooling were 140 s with the mixture, and 90 s with argon.

FLAMMABILITY TESTS

The flammability of the proposed mixed coolant was examined in the following manner: the tested mixture was charged into a vessel at a moderate pressure of about 0.3 MPa at room temperature. A delicate burner adjusted by a needle valve was used to discharge a slight jet of the mixture. This stream was released upon a burning piece of wood. It was assumed that the open fire would assist the evoking of potential flammability more intensively than a series of electrical sparks. The attempts in this experiment to ignite and burn the jet of the proposed mixture failed. Vogt et al.[24] checked flammability of a mixed coolant in a similar manner. They connected a Bunsen burner and a reignitor to the exhaust of an operating Joule-Thomson cryocooler. The reignitor provided high voltage sparks.

For gaining confidence in this flammability test procedure, a case study was conducted on three flammable nitrogen mixtures with a higher share of hydrocarbons. The mixtures were tested before and after diluting each of them by a few percent of a flame retarding component: it was below 10% bromotrifluoromethane as defended by Vogt et al.[24] and applied by Little[23] (4.7%). These nitrogen mixtures included a share of 55%, 60% and 65% by volume of hydrocarbons. All were ignited and burned, and were thus indicated as flammable according to the present test procedure. The content of bromotrifluoromethane was gradually elevated in each of them. Only by approaching concentrations of 5%, 4% and 9.5% respectively, did the flammability of all the mixtures disappear. It was not possible to ignite and burn any of the mixtures.

However, it should be emphasized that the proposed mixture is regarded as flammable by the calculation method of the ISO 10156 standard.

DISCUSSION

1. **The expected features of the proposed mixture were demonstrated experimentally using a real open-cycle system** consisting of a miniature fixed-orifice, fast-cooldown cryocooler and a relatively small pressure vessel. The mixed coolant is as "fast" (cooldown) at room temperature as argon, but as "cold" as nitrogen. At an ambient temperature of about 85°C the cooldown period of both is similar.

2. **One might say that the mixture is non-conditionally superior over nitrogen**. For the same cryocooling temperature, the mixture cools down faster and runs for a longer period. However, the superiority of the mixed coolant over argon gas is conditioned. The mixture's temperature is lower than of argon, and its cooldown is faster or similar at elevated ambient temperature. However, the run time of the mixture is shorter. For applications that focus on fast cooldown or when the cooled object requires the lower temperature of boiling nitrogen, the mixture might be advantageous.

3. **The discharge period through a fixed orifice cryocooler is not simply dependent on the Δh_T of the different coolants**; i.e. the one of higher Δh_T doesn't necessarily have a longer run period. The run time with the proposed mixture was longer than with nitrogen but shorter than with argon, although the Δh_T of the mixture is larger than that of argon. There are some other parameters that affect the run time like: the choked molar mass flux of real gases, which depends on the critical temperature and pressure, the instantaneous temperature and pressure in the vessel, and the stored amount of gas in the vessel corresponding with the compressibility. For instance, at similar conditions there are more moles of argon stored in the reservoir than of nitrogen and of the mixed coolant. Another relevant parameter in case of relatively short periods of discharge is the fraction of liquefaction of the coolant and the actual size of the liquid plenum in the evaporator. A larger plenum might prolong the run to lower values of cut off pressure. Argon liquefies a larger fraction of the stream than nitrogen and also, presumably, than the mixture.

4. **The discharge period through a flow-regulated cryocooler should be a planed experiment for approving the proposed mixture.** A fine and proper flow regulation would match the instantaneous flow rate to the instantaneous pressure, the associated specific cooling capacity and heat load. It has the potential of better utilizing the higher Δh_T. The discharge through a fixed orifice cryocooler does not respond instantaneously to the elevated Δh_T. Therefore, one should expect that a flow-demand cryocooler would operate longer with a mixed coolant than with argon (as indeed is reported with other mixtures[22]). However, it should be noted that a regulating mechanism, when calibrated for one coolant, might not be optimal for another one.

5. **Although, according to the ISO standard[25] the proposed nitrogen mixture with 17% hydrocarbons is regarded as flammable**, the attempts in this present study to ignite a free delicate jet of this mixture and cause it to burn, failed.

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