Analysis of working fluids applicable for high-temperature loop heat pipe applications

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Abstract. An objective of this study was to perform an analysis of available working fluids and select those one(s) that will be able to comply with the specific requirements of the ultra-high bypass ratio (UHBR) engine air bleed system and ensure efficient LHP operation. A multi-step approach was applied to analyse more than 700 working fluids and select four potential candidates, taking into account (1) working fluids compliance with EU regulations; (2) working fluids freezing, boiling, and critical points for the operating temperature range; (3) working fluids specific properties that influence the LHP performances. Selected fluids (toluene, acetone, methanol, 1,2-dichlorobenzene) were subjected to accelerated life tests to check their chemical compatibility with AISI 316 stainless steel to be used as the LHP material. Based on the results obtained, the toluene was selected as the working fluid for application in the innovative LHP-based thermal management solution for the UHBR engine air bleed system.

1. Introduction

An aircraft engine bleed system extracts the air from the compressor and supplies it to various locations within the aircraft for the purposes of cabin pressurisation and air conditioning, internal cooling of the engine, airframe anti-icing, etc. In existing turbojet engines, the bleed air system valves are not specially cooled. For their cooling, the so-called “engine compartment air” is used. A new generation of turbojet engines with ultra-high bypass ratio (UHBR) will surpass existing engines in technical, operational and environmental performances, particularly in reduced fuel consumption and, therefore, CO₂ emissions. At the same time, the UHBR engine components will operate in a harsher environment due to increased compression ratio (up to 70 ... 80) and gas temperature in front of the turbine. Thus, the air temperature taken out by the bleed system will also increase significantly. As a result, the air bleed system valves will operate at much higher temperatures.

In the UHBR engines, the “engine compartment” air no longer provides the required cooling of the bleed system valves below 200°C. Therefore, a special cooling system is required to remove the heat from the sensitive elements of the valves and ensure their long-term operability and reliability. The single “cold source” in this part of the engine is the secondary flow air with a temperature up to 100°C. Nowadays, the most effective thermal management systems are based on the two-phase passive heat transfer systems, namely heat pipes (HP) and Loop Heat Pipes (LHP).

LHPs are widely used in spacecraft applications. Among recent works relevant to aeronautics, one can only mention the work on attempts to use LHP in anti-icing systems [1, 2] and in the cooling systems of some engine elements [3]. In the considered systems, the maximum temperature did not exceed 100°C, while the heat was removed to an environment with a temperature below 50°C.
While HP and LHP are mature technologies studied and developed for tens of years, there is no commonly accepted working fluid for HP/LHPs operating at a temperature over 100°C. Therefore, the objective of this study is to perform an extensive analysis of available working fluids and select those one(s) that will be able to comply with the technical requirements for heat dissipation in the harsh environment, ensure efficient LHP operation and meet the aeronautical standards.

After identifying the most suitable working fluids by their properties in the operational temperature range, long term stability and compatibility with the wick and envelope materials should be analysed. It is critically important because the formation of Non-Condensable Gas (NCG) due to incompatibility of LHP materials with working fluid can lead to LHP operation failure [4 - 7].

2. Method and results

To determine the most suitable working fluid, a list of 782 substances was compiled using different databases and information sources. The optimal working fluid must be compliant with a set of various requirements. Firstly, the working fluid must comply with the EU regulations regarding environmental protection and occupational safety. Secondly, the working fluid must have adequate freezing, boiling and critical points for the operating temperature range. Besides, the working fluid should have advantageous heat transfer properties in the operating range and ensure long-term reliable LHP operation. To take all these criteria into account, a multi-stage selection approach was applied.

2.1. Stage 1: Filtering of the initial working fluids list

Firstly, the list was processed to exclude the working fluids banned by the EC regulations No 2037/2000 and 1005/2009 on substances that deplete the ozone layer. Then, the working fluids compliance with the following criteria was checked:

1. General criteria:
   - Compliance with REACH regulations;
   - Global warming potential (GWP) is below 150;
   - Ozone depletion potential (ODP) is lower than 0.1;
   - Ignition temperature is above +220°C.

2. Criteria imperative for the LHP operation:
   - Critical temperature is above +220°C;
   - Boiling temperature is between +50°C and +150°C at pressure p=0.1 MPa;
   - Saturated pressure is above 0.5 bar at +220°C.

Working fluids that did not meet any of the criteria presented above were rejected.

2.2. Stage 2: Working fluids grading

The working fluids were graded according to the criteria that characterise the LHP operation efficiency in a specific environment. The following paragraphs summarise the grading criteria and the pre-selected fluid properties. The maximum score is “5”, the minimum score is “0”. If a fluid received a “0” score for any criteria, it was excluded from further considerations. The total score is the sum of the individual scores for all criteria. The best working fluid is the one with the maximal total score.

The working fluid safety was assessed in line with the NFPA (National Fire Protection Association of the USA) rating. Based on NFPA rating, the following grading of working fluids was used for the purposes of this study.

| Evaluation | $\Pi_{\text{hazard}}$ score |
|------------|-----------------------------|
| “Severe or High hazard for health” | 0 (fluid rejected) |
| “Moderate hazard for health” and “Severe or High flammability” and “Severe and High reactivity” | 1 |
| “None or Slight hazard for health” and “Severe or High flammability” and “Severe or High reactivity” | 2 |
“None or Slight hazard for health” and “Moderate flammability” and “Moderate reactivity” 3

“None or Slight hazard for health” and “Slight or Moderate flammability” and “None or Slight reactivity” 4

“None or Slight hazard for health” and “None or Slight flammability” and “None or Slight reactivity” 5

The working fluid melting temperature is a critical parameter for the LHP startup. If it is above +40°C, potential problems with the LHP startup and reliability issues are expected. Preliminarily it is preferable to select a working fluid with a lower melting point. The desirable melting temperature $T_{melt}$ is < -40°C, and the following grading was used.

| Evaluation                                      | $\Pi_{T_{melt}}$ score |
|------------------------------------------------|------------------------|
| $T_{melt}$ >+40°C                              | 0 (fluid rejected)     |
| $T_{melt}$ is not in the literature or not well defined | 1                     |
| $T_{melt}$ <+20°C                              | 2                     |
| $T_{melt}$ <1°C                                | 3                     |
| $T_{melt}$ <20°C                               | 4                     |
| $T_{melt}$ <40°C                               | 5                     |

The working fluid critical temperature must be higher than maximal operational temperature to assure the LHP proper performance. Usually, the fluid properties that are important for LHP operation are degraded close to the critical point. Thus, the minimal critical temperature was set as $T_{cr}$ = +220°C, and the following grading was used.

| Evaluation                                                | $\Pi_{T_{cr}}$ score |
|----------------------------------------------------------|----------------------|
| $T_{cr}$ <+220°C                                         | 0 (fluid rejected)   |
| $T_{cr}$ is not in the literature or/and not well defined | 1                    |
| +220°C < $T_{cr}$ < +250°C                               | 2                    |
| $T_{cr}$ cannot be found in the literature but can be estimated and the value is above 250°C | 3                    |
| $T_{cr}$ > +250°C                                         | 4                    |
| $T_{cr}$ > +300°C                                         | 5                    |

The figures of merit (FOM) are some of the main features to be assessed during the working fluid selection. They represent a combination of the fluid physical properties, e.g. latent heat of vapourisation, surface tension, vapour and liquid densities and vapour and liquid viscosities. FOMs make it possible to compare heat-transfer characteristics of LHP, such as maximum transmitted power $Q_{max}$ and conductivity $C$ when switching from one working fluid to another.

The maximum transmitted power is defined from the LHP capillary-hydrodynamic limit [9] and is characterised by the following criteria (1) and (2).

$$Fm_l = \frac{\rho_l \Delta H_v \sigma}{\eta_l} \quad \text{liquid-based criteria} \quad (1)$$

$$Fm_v = \rho_v \cdot \Delta H_v \cdot \sigma \quad \text{vapour-based criteria} \quad (2)$$

where:
- $\rho_l$ and $\rho_v$ are the liquid and vapour densities respectively, kg/m$^3$;
- $\Delta H_v$ - the latent heat of vapourisation, J/kg;
- $\sigma$ - the surface tension, N/m;
- $\eta_l$ - the liquid dynamic viscosity, Pa·sec.
The criterion (3) characterises the LHP conductivity at maximum transmitted power.

\[
Fm_c = \frac{\rho c \Delta T}{\sigma}
\]  

(3)

It is possible to estimate the LHP conductivity by multiplying (3) by (1) for the liquid phase and (3) by (2) for the vapour phase. As a result,

\[
Fm_{c,l} = Fm_c \cdot Fm_l = \frac{\rho c \rho_v \Delta H_v^2}{\eta_l}
\]  

(4)

\[
Fm_{c,v} = Fm_c \cdot Fm_v = \rho_v^2 \cdot \Delta H_v^3
\]  

(5)

The general rule for FOMs can be formulated as follows: the higher these parameters are the better working fluid for the two-heat transport device is. The \( Fm_{c,l}, Fm_v \) and \( Fm_{c,v} \) values calculated for \( T=+180^\circ C \) were used for working fluids grading in line with approach presented graphically below.

| Evaluation | \( \pi_{psat} \) score |
|------------|----------------------|
| \( p_{sat} < 0.1 \text{ bar} \) | 0 (fluid rejected) |
| \( p_{sat} \) not in the literature or not well defined | 1 |
| \( p_{sat} > 20 \text{ bar} \) | 2 |
| 0.1 bar < \( p_{sat} < 1 \) bar | 3 |
| 10 bar < \( p_{sat} < 20 \) bar | 4 |
| 1 bar < \( p_{sat} < 10 \) bar | 5 |

Maximum operating pressure directly impacts the LHP weight, reliability, mechanical and integration properties. Generally, it is preferable to have saturated vapour pressure below 10 bar at \( T=+180^\circ C \) because the higher pressure would reinforce the design of the LHP components and, as a result, increase the LHP size and weight. Minimum pressure for LHP operation depends on the wick average porous size and nature of the liquid. It was selected as \( p_{sat} = 0.1 \) bar. The saturated vapour grading criteria are the following.

The working fluid compatibility with common LHP materials used for wicks, envelopes, containers and transport lines is critically important for the LHP long-term operation and reliability. The most common materials used in LHP are stainless steel (baseline material for this study), titanium, copper, nickel and aluminium. To grade the working fluids under analysis, the data from the literature [10] were investigated. In case of absence or contradictory information for a specific combination of the material and fluid, the pair was considered partially compatible. The compatibility grading criteria are the following.
The working fluid availability in a high-purity state is important for the purposes of this study while keeping in mind the real-life applications of the novel LHP product. The grading criteria for available purity levels are the following.

| Evaluation                                      | \( \Pi_{purity} \) score |
|------------------------------------------------|--------------------------|
| The maximum available purity level is < 98%    | 0 (fluid rejected)       |
| The maximum available purity level is > 98%    | 1                        |
| The maximum available purity level is > 99%    | 2                        |
| The maximum available purity level is > 99.5%  | 3                        |
| The maximum available purity level is > 99.8%  | 4                        |
| The maximum available purity level is > 99.9%  | 5                        |

Other aspects such as physical and chemical stability at high temperatures (+180°C), price and delivery time were also considered. The data were collected from leading EU suppliers of chemicals and refrigerants to investigate these aspects, and the following grading criteria were formulated.

| Evaluation                                      | \( \Pi_{avail} \) score |
|------------------------------------------------|-------------------------|
| Fluid is not thermally stable @ \( T=+180^\circ C \) | 0 (fluid rejected)      |
| Fluid is partially thermally stable @ \( T=+180^\circ C \) (no data in literature or inconsistent data); high price (>1000 Euro per 100 g) and/or high delivery time (>3 months) | 1                        |
| Fluid is partially thermally stable @ \( T=+180^\circ C \) (no data in literature or inconsistent data); has reasonable price (<1000 Euro per 100 g) and delivery time (<1 month) | 2                        |
| Fluid is thermally stable @ \( T=+180^\circ C \); has high price (>1000 Euro per 100 g) and delivery time (<1 month) | 3                        |
| Fluid is thermally stable @ \( T=+180^\circ C \); has reasonable price (<1000 Euro per 100 g) or delivery time (<1 month) | 4                        |
| Fluid is thermally stable @ \( T=+180^\circ C \); has both reasonable price (<1000 Euro per 100 g) and delivery time (<1 month) | 5                        |

As a result, the initial working list was decreased down to 22 substances. The total score was calculated as the sum of specific marks. The result with the total scores \( \Pi_{total} \) is presented in Figure 1.

\[
\Pi_{total} = \Pi_{f_{m,v}} + \Pi_{f_{m,v'}} + \Pi_{f\text{-}mc,L} + \Pi_{haza} + \Pi_{T\text{-}melt} + \Pi_{T\text{-}cr} + \Pi_{psat} + \Pi_{comp} + \Pi_{purity} + \Pi_{avail}
\]

Among these 22 working fluids, six ones have the maximal score \( \Pi_{total} \) and worth to be further studied. Methanol, ethanol and isopropanol belong to the alcohol class. However, methanol has the simplest molecule among alcohols and, therefore, it is the most stable of them. Thus, ethanol and isopropanol were rejected, and four candidate working fluids (methanol, toluene, acetone, and 1,2-dichlorobenzene) were kept for further investigations.
2.3 Stage 3: Study of chemical compatibility of the working fluids and LHP wick material(s)

All organic fluids are subject to thermal decomposition due to the tendency to isomerise and convert into smaller molecules. In heat transfer devices this effect is known as non-condensable gas (NCG) formation and can lead to the device operation failure. Generally, long-term stability of thermal fluids is linked to the difference between the fluid critical temperature and heat transfer device maximum operational or non-operational temperature. The smaller the difference, the more likely is the high rate of working fluid decomposition. Moreover, the heat transfer device materials can serve as decomposition catalysts or can directly react with the working fluid. LHPs, which have a very large surface area of the wick, are especially sensitive to NCG presence, thus the working fluid long term thermal stability and compatibility with the wick and envelope materials should be analysed.

In theory, all candidate working fluids are compatible with AISI 316 stainless steel [6, 7]). However, to the best of our knowledge, there is no systematic data regarding the compatibility of selected fluids for temperatures above 130-150°C. The only one toluene-stainless steel compatibility study performed at 280°C was found [8], but it was performed for heat pipe with sufficiently less wick surface area.

Thus, to mitigate potential risks associated with NCG generation inside of LHP and to evaluate lifetime expectations for the whole thermal management system all candidate working fluids were subjected to chemical compatibility tests following an approach earlier used by authors for lower temperatures (up to 130°C) [11].

For this purpose, a special test bench was developed. A basic element of the test bench – a test block for one fluid – is presented in Figure 2. The test block consisted of two thermosyphons charged by the same fluid and a common heater. Each thermosyphon had a stainless-steel envelope and a wick inside the evaporator zone. Two thermocouples were installed on the bottom and top parts of the thermosyphon. An increase of difference between the lower and upper thermocouple indicates the NCG formation. It should be noted that the heater temperature was controlled at +300°C. However, the temperatures in the condenser zone varied for different thermosyphon pairs (230°C for toluene and
200°C for 1,2-dichlorobenzene (Dowtherm E)) due to the different thermophysical properties of the working fluids.

In total, five test blocks were used in experimental studies: (1) 3 times distilled toluene, (2) undistilled toluene, (3) 3 times distilled acetone, (4) 3 times distilled methanol, and (5) high purity (>99.9%) 1,2-dichlorobenzene (Dowtherm E).

The results of the tests can be summarised as follows:

- **Toluene**: At the moment of this article preparation, the tests run 3561 hours for distilled toluene and 1926 hours for undistilled toluene. The tests showed steady performance of the thermosyphons charged with toluene; the temperature difference is within acceptable limits.

- **Acetone**: The test showed performance degradation in the first thermosyphon after 190 hours of continuous operation. The second thermosyphon started failing after 351 hours. The test was stopped.

- **1,2-dichlorobenzene (Dowtherm E)**: Overall, 1,2-dichlorobenzene has been performing steadily since the beginning of the test campaign. But after pinching off the charging valve, a partial leak of the working fluid was discovered. The test was stopped after 351 hours.

- **Methanol**: There were several attempts to perform the tests, but in any case, methanol degraded and formed NCG within 72 hours, thus deemed not worth further investigations.

3. Conclusions

The objective of this study was (a) to perform the analysis of available working fluids and select those one(s) that would be able to comply with the technical requirements for heat dissipation in a harsh environment and (b) to analyse the chosen working fluids long term stability and compatibility with the LHP’s wick and envelope materials.

The results of the study show that two working fluids (toluene and 1,2-dichlorobenzene) are capable of continuous operation within LHP for the temperature range (from +100°C to +200 °C). Both fluids showed high performances and chemical compatibility with stainless-steel wick. However, toluene is selected as a primary working fluid because the global efficiency mark (36) is higher than for 1,2-dichlorobenzene (30).

Applying toluene as a working fluid, a demonstrator of passive cooling system based on a LHP technology will be created to control the sensible part of the UHBR aircraft engine bleed system valve below 200 °C in harsh environment (heat sink temperature up to 100°C; air temperature around the
valves up to 300°C; temperature of air passing through the valves up to 750°C). It will help to reduce power consumptions for cooling needs and will contribute to integration of fuel-efficient propulsion concepts for the next generation short and medium range aircraft.

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