## AN ENVIRONMENTAL AND THERMODYNAMIC ATTEMPT TO REPLACE R-134 A FROM MARINE REFRIGERATION SYSTEMS

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## ABSTRACT

When talking about the need to preserve the environment, the evaluation of a refrigerant is associated also with its Global Warming Impact (GWP), together with its Ozone Depletion Potential (ODP). R-134a is one of the most used refrigerants in marine refrigeration, but this refrigerant, like all others belonging to HFC family, presents a high GWP. International concern over global warming directed researches in marine refrigeration towards finding more environment friendly substitutes of R-134a.

In this respect, the present article deals with the environmental and physical properties comparison and also with a thermodynamic assessment of R-134a and one of its possible substitute - the mixture between propane (R-290) and isobutane (R-600a), in different rates. These refrigerants present a null Ozone Depletion Potential and a neglectible Global Warming Impact, resulting that their mixture is benign for the environment. Also, the thermodynamic analysis will reveal the acceptance of the mixture (R-290 - R-600a) instead of R-134a, since the volumetric cooling capacity and the Coefficient of Performance present close values.

Keywords: refrigeration, global warming, mixture.

## 1. INTRODUCTION

In the last years, Global Warming Potential (GWP) is considered as important as Ozone Depletion Potential (ODP), when it is about assessing a refrigerant. CFCs have been widely spread as refrigerants, but they became regulated because of their chlorine content (CFCs consumption was banned in 1996).

Thus, the investigation on their substitutes started. HFCs are chlorine free, but they still have a high value for GWP.

This is the reason for growing interest in developing natural refrigerants, in particular Hydrocarbons (HC), for new applications in refrigeration and air-conditioning systems.

Generally speaking, when choosing a refrigerant, it should have required thermo-physical properties, should be compatible with available lubricants and other materials from the refrigerating system, should not require operation at extreme pressures, should be nontoxic, non-flammable, benign to the environment, completely stable inside the system, easy to be produced, handled, detected, recycled or destroyed and cheap.

R-134a (or HFC-134a) belongs to HFC family; this refrigerant is widely used in marine refrigeration, but increasing concern over its GWP and its effect on the environment has led specialists to focus on other options.

These alternatives must act in the refrigerating system similar to R-134a and also the substitution should be economically feasible and profitable from an environmental point of view.

This paper presents a thermodynamic discussion regarding the possibility to replace R-134a with a mixture of two natural refrigerants: propane (R-290) and isobutane (R-600a), both of them belonging to Hydrocarbon family.

This option is based on the fact that Hydrocarbons have good physical and thermodynamic properties,

present material compatibility, are low cost, safe in operation and more environmentally safe than R-134a (null ODP - as R-134a, but lower GWP). Some properties of the three refrigerants mentioned up to now are given in Table 1.

Table 1. Thermo-physical properties of R-134a, R-290, R-600a

| Refrigerant                                   | R-134a                           | R-290   | R-600a  |
|---|----------------------------------|---|---|
| Chemical<br>formula                           | CH <sub>2</sub> FCF <sub>3</sub> | CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> | CH(CH <sub>3</sub> ) <sub>2</sub> CH <sub>3</sub> |
| Class   | HFC                              | HC  | HC  |
| Molecular<br>Mass (g/mol)                     | 102,03                           | 44,10   | 58,12   |
| Critical<br>Temperature<br>(°C)               | 101,1                            | 96,7  | 134,7   |
| Critical<br>Pressure<br>(MPa)                 | 4,06                             | 4,25  | 3,64  |
| Boiling Point<br>(°C)                         | -26,1                            | -42,20  | -11,7   |
| Lower<br>Flammability<br>(% Volume in<br>Air) | Non<br>flammable                 | 2,10  | 1,70  |
| Autoignition<br>Temperature                   | 770                              | 470   | 460   |

| (°C)                               |      |    |    |
|------------------------------------|------|----|----|
| ODP                                | 0    | 0  | 0  |
| GWP                                | 1300 | 20 | 20 |
| Atmospheric<br>lifetime<br>(years) | 16   | <1 | <1 |

The mixtures on which we focus are (55% R-290 – 45% R-600a) and (50% R-290 – 50% R-600a).

# 2. ON VAPOR COMPRESSION REFRIGERATION MACHINES

Refrigeration is a process aiming at temperature decrease in a space or its contents under the one of the surroundings. Refrigeration is used in the carriage of some liquefied gases and bulk chemicals, in air conditioning systems, to cool bulk  $CO_2$  for fire fighting systems and to preserve perishable foodstuff during their transport on sea.

Refrigeration plants on board the ship may be small domestic refrigeration unit types (for provisions) up to large plants (for reefer vessels).

A simple vapour compression refrigeration system is given in Figure 1. It consists of four main components: compressor, condenser, expansion valve and evaporator.



Figure 1 Schematic representation of simple vapor compression refrigeration system

The working principle is described below.

Low pressure and temperature vapor refrigerant (state 4) is compressed by the compressor and reaches high pressure and temperature (state 1).

This vapor is condensed at constant pressure and temperature  $(p_c, T_c)$  in the heat exchanger called condenser, by rejecting heat, resulting refrigerant in liquid state (2).

The decrease of the pressure of the refrigerant (from  $p_c$  to  $p_0$ ) is done by the help of the expansion valve. Low pressure liquid refrigerant (at state 3) is led to the evaporator. Here, the refrigerant absorbs heat from the circulating fluid, which is cooled.

The transition from liquid state to vapor state takes place at constant pressure and temperature  $(p_0, T_0)$ . Vapors of refrigerant (state 4) result and the cycle is repeated.

Regarding energy, the following are to be stated:

- the compressor requires work; this work is supplied to the refrigeration system from the surroundings;
- changes in state take place in the evaporator and condenser from liquid to gas (the energy required being named *heat of vaporization*) and from gas to liquid (the energy released being named *heat of condensation*);
- in the expansion valve there is no heat exchange since throttling process is isenthalpic (it proceeds without any change in enthalpy).

### 3. THERMODYNAMIC EQUATIONS

• The volumetric cooling capacity (VCC) is a measure of the compressor size for needed operating conditions; it represent the effect of cooling obtained per  $1 \text{ m}^3$  of refrigerant entering in the compressor (Almeida et al, 2010):

$$VCC = \frac{(h_{00} - h_{i0}) \cdot \eta_{vol,ideal}}{v_{ic}}$$
(1)

where:

 $\label{eq:hi0} \begin{array}{l} h_{i0} \ /h_{00} - \mbox{ specific enthalpies inlet/outlet evaporator,} \\ [kJ/kg], \end{array}$ 

 $v_{ic}$  – specific volume at compressor inlet, [m<sup>3</sup>/kg]

• The pressure ratio ( $\beta$ ) is the ratio between the condensation pressure ( $p_c$ ) and the evaporation pressure ( $\beta$ ):

$$\beta = \frac{p_c}{p_0} \tag{2}$$

• The Coefficient of Performance (COP) is the rate between the heat extracted at low temperature and the work supplied; COP is essentially a measure of the plants operating efficiency:

$$COP = \frac{Q_0}{P_c}$$
(3)

• The cooling capacity, or the refrigerating effect,  $Q_0$ , and the power needed to drive the compressor ( $P_c$ ) are found as:

$$Q_0 = m_{ref} (h_{00} - h_{i0})$$
(4)

$$P_{c} = m_{ref} \left( h_{0c} - h_{ic} \right)$$
(5)

where:

m<sub>ref</sub> - mass flow of the refrigerant, [kg/h],

 $\label{eq:hic} \begin{array}{l} h_{ic} \, / \, h_{0c} - \text{specific enthalpies inlet/outlet compressor,} \\ [kJ/kg] \end{array}$ 

• The specific enthalpy of superheated vapors at the end of the irreversible isentropic compression is given by:

$$h_{irrc} = h_{ic} + \frac{h_{revc} - h_{ic}}{\eta_{iz,c}}$$
(6)

where:

 $h_{rev\ c}$  – specific enthalpy of superheated vapors at the end of the reversible isentropic compression, [kJ/kg],

 $\eta_{iz.c}$  – isentropic efficiency of the compressor

The refrigerant mass flow is calculated with:

$$\mathbf{n}_{\rm ref} = \frac{\mathbf{Q}_0}{\mathbf{q}_0} \tag{7}$$

where:

 $Q_0$  – cooling capacity, [kW],

q0 - specific cooling effect, [kJ/kg]

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## 4. CASE STUDY

In the following a comparison of cycles working with R-134a is made and two mixtures between propane and isobutane.

Input data are: condensation temperature  $t_c = 55^{\circ}C$ , evaporation temperature  $t_0 = -20^{\circ}C$ , cooling capacity  $Q_0 = 140$  W.

In Table 2 results of the comparative analysis are given.

Table 2. Comparison between refrigeration cycles

| Refrigerant  | R-134a | R-290/<br>R-600a<br>(55/45) | R-290/<br>R-600a<br>(50/50) |
|--|--------|-----------------------------|-----------------------------|
| Volumetric<br>cooling Capacity<br>VCC (kJ/m <sup>3</sup> )                     | 744    | 785,33                      | 750,21                      |
| Coeficient of<br>Performance COP   | 2,05   | 2,10                        | 2,13                        |
| Temperature at compressor outlet $t_{0c}$ (°C)                                 | 141    | 128,4                       | 127,3                       |
| Specific volume at<br>compressor inlet<br>v <sub>ic</sub> (m <sup>3</sup> /kg) | 0,213  | 0,375                       | 0,401                       |

One of the considered mixtures might replace R-134a if it presents similar values for VCC and COP, because similar VCC means that it is not needed to modify the compressor size, while at least same COP means that the performance of the refrigeration system will not decrease.

Founded values show that R-290 / R-600a mixture (50/50) presents similar VCC as R-134a and a slightly higher COP.

Also, refrigerant vapors leave the compressor at a lower temperature than R-134a vapors, meaning that a better chemical stability of the refrigerant and of the lubricant oil is assured.

### 5. CONCLUSIONS

Marine refrigeration systems remove heat from spaces, objects or materials on board the ship and move it to another location, maintaining them at the temperature below that of the sourrounding atmosphere. Vapor compression cycles with reciprocating compressors are most often met on board the ship.

Commonly used refrigerants CFCs (Chlorofluorocarbons) and HCFCs (Hydrochlorofluorocarbons) were replaced because of their chlorine content.

Substitutes of these refrigerants are HFCs (Hydrofluorocarbons), among them the most spread being R-134a (HFC-134a). But R-134a is only non-ozone-depleting. International concern over relatively

high global warming potential of R-134a has directed efforts towards identification of potential substitutes.

This paper presents a comparison between the behaviour in a vapor compression refrigeration system of R-134a and two mixtures resulted from propane (R-290) and isobutane (R-600a), 55 / 45% and 50 / 50%.

The refrigerant given by the propane-isobutane mixture presents null ODP (like R-134a), but much lower GWP.

The mixture (50/50%) presents similar VCC values as R-134a, thus a possible substitution would not need a change in compressor size (VCC related to the mixture:  $750,21 \text{ kJ/m}^3$ ; VCC related to R-134a: 744 kJ/m<sup>3</sup>).

The mixture (50/50%) presents a slightly higher COP value than R-134a, meaning that the performance of the refrigeration system is somewhat improved (COP related to the mixture: 2,13; Cop related to R-134a: 2,05).

The mixture (50/50%) presents a lower value for the compressor's discharge temperature, thus a longer use of the compressor being possible.

## 6. **REFERENCES**

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