SAFE AND ENVIRONMENT FRIENDLY REFRIGERANTS FOR INDUSTRIAL PROCESSES ENERGY RECOVERY

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Abstract: Volatility of energy prices and growing concern over climate change have increased the interest in alternative source of energy to fossil fuels. At the same time, the industry is also facing an ever-increasing pressure to address climate changes by focusing on global warming substances
As part of this strategy, heat waste recovery is being highly considered despite optimization, the major industrial processes (food, chemistry, paper) produce heat waste through for example cooling water, effluent or condensate.
In this paper we focus on industrial heat pumps, an effective heat recovery technology for low to medium grade heat. The use of heat pumps in industrial processes would allowing for recovering heat waste and using the resulting energy to participate again in the process at a higher temperature, thus reducing the need for fossil energy and the use of ground water for industrial output process cooling.
To achieve high efficiency, this technology requires a refrigerant with thermodynamics properties in line with the level of temperature involved in the industrial processes.

This paper introduces AHP1 and AHP2, two promising new low GWP and non flammable refrigerants for industrial heat pumps. Thermodynamics properties of AHP1 and AHP2 are described and their potential application in High Temperature Heat Pumps is discussed. Results show that AHP1 and AHP2 are promising candidates to address the industrial heat pump market needs.

1 INTRODUCTION

Over the previous years the needs for energy savings has become crucial. Cost of fuel and gas increases from day to day and environmental regulations become stricter. Today the major industrial processes (food, chemistry, paper) produce heat wastes through cooling water, effluent, condensate, moisture, and condenser heat from refrigeration plants. A way to reduce energy consumption is to recover these industrial heat wastes and use the resulting energy to participate again in the process.

When the temperature of the process is higher than the temperature of the different waste streams, Heat Pumps have to be used.
Heat Pumps are commonly used in residential market (for heating and hot water production). However relatively few heat pumps are currently installed in industry due to technical issues related to the specific conditions of use. Heat pump for industrial applications needs to produce streams at 80-90°C or 120-130°C with an inlet stream at 30-50°C or 70-80°C. The actual compressors as well as exchangers and working fluids are not designed for being used at a condensing temperature above 70°C. For High Temperature Heat Pumps, the compressor operating conditions are different from residential heat pump operating conditions. There is therefore a need for specific developments to address the market needs. Bobelin et al (2012) have shown the results of a collaborative project using a High Temperature Heat Pump prototype. They experimentally evaluated the performances of the

heat pump prototype for condensing temperatures up to 140C and demonstrated the feasibility of low temperature waste heat recovery.

Widespread use of this technology however requires development of efficient and sustainable working fluids. Originally, CFCs with high critical point temperatures have been used as the working fluid in industrial processes operating under high ambient conditions and at high temperatures. Among the fluids, R-114 has been the most widely used refrigerant in heat pumps applications. The phase-out of chlorine containing refrigerants under the Montreal Protocol and the focus on molecules with high global warming after the Kyoto Protocol has led to active research to find a substitute for R-114 in high temperature applications.

Arkema, as a global supplier of working fluids for refrigeration and air conditioning, has developed AHP1 and AHP2, two refrigerants for High Temperature Heat Pumps.
In this paper, thermodynamics and thermophysical properties of Arkema's AHP1 and AHP2 are presented. Cycle performances of these working fluids have been calculated using vapour compression model.

2 INNOVATIVE WORKING FLUIDS

The heat-pump technology is well-developed for residential applications but its use in industrial processes requires addressing technology and cost barriers (US Department of Energy DOE, 2008)
One of the approaches to expand the potential of low-temperature waste heat recovery is by improvement of the heat pump performance through innovative working fluids.

When considering refrigerant alternatives for the future it is important to select refrigerants with the best balance of:

- direct environnemental concerns (ODP, direct GWP)
- indirect environmental concerns (highest energy efficiency)
- safety for users (flammability and toxicity)

2.1 Physical Properties

Table 1 summarized the properties of AHP fluids and references other refrigerants such as R-245fa and R-114.

Table 1: Physical Properties of AHP molecules and R-114, R-245fa

Substance	Tc (°C)	ODP	GWP (100years)	LFL/UFL (60°C)
AHP1	> 165	0.000	< 13	None
AHP2	> 170	0.000	< 10	None
R-114	146	1.000	10040	None
R-245fa	154	0.000	1030	None

Both AHP fluids have very low GWP, < 13, and negligible ODP. AHP1 and AHP2 did not exhibit flammability limits at 60°C. According to ISO817 and ASHRAE 34, AHP1 and AHP2 shall be assigned to the class 1.

In subcritical compression system applications, the refrigerant critical temperature should be fairly higher than the condensing temperature.

The AHP1 and AHP2 products have critical temperatures higher than 160°C. These products can therefore be used in subcritical compression systems with a condensing temperature as high as 150°C or more.
Compared to R-114 and R-245fa with critical temperatures of respectively 146 and 154 °C, AHP1 and AHP2 should allow the High Temperature Heat Pump to run at higher condensing temperature and with a higher lift.

2.2 Thermodynamics Properties

Figure 1 presents the saturated pressure curves for AHP1, AHP2, R-114 and R-245fa.

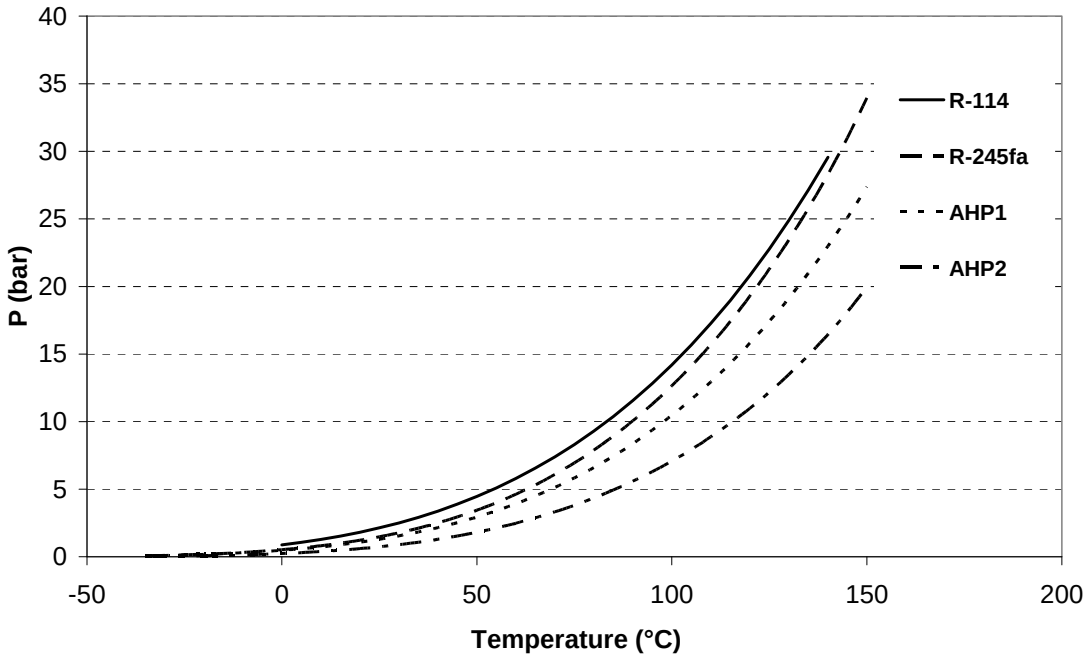


Figure 1: Saturated pressure curves for AHP1, AHP2, R-114 and R-245fa

AHP1 and AHP2 fluids are lower pressure fluids than R-245fa and R-114. At a temperature of 100°C, the saturated pressure of AHP1 and AHP2 is equal or less than 10bars.

3. HEAT PUMP PERFORMANCE

3.1 Introduction

In order to elaborate cycle performance calculations, the RK-Soave equation of state has been used to calculate gas density, enthalpy and entropy data and has been used to predict latent heat of vaporization.
The basic properties required by this equation (critical temperature, critical pressure and vapor pressures versus temperatures) were measured by using a static cell. The acentric factor of each pure product was calculated from measurements of the vapour pressure curves. Ideal gas heat capacity data were also estimated using Benson group contribution method (Poling and al, 2001)
The thermodynamic model using RK-Soave equation is used for cycle properties calculations. These cycles can include heat exchangers (evaporators, condensers…), internal heat exchangers, heater, expansion valves, compressors, liquid pumps and turbines.

The calculated coefficient of performance (COP) is the ratio of the useful energy delivered by the system divided by the energy consumption.

(1) $$COP = \frac{Q_{cond}}{P_{elec}}$$ where $Q_{cond} = calorific\ power\ at\ the\ condenser$, $P_{elec} = Energy\ consumption$

3.2 Cycle performance calculation

The thermodynamic performances of the new low GWP fluids AHP1 and AHP2 have been calculated in vapour compression cycle.

The cycle calculation parameters are presented Table 2

Table 2: Cycle calculation parameters

Condensing Temperature (°C)	135
Evaporating Temperature (°C)	90
Superheat (K)	5
Subcooling (K)	5
Compressor isentropic efficiency	0.70

Results of the calculation for AHP1 and AHP2 are presented Table 3.

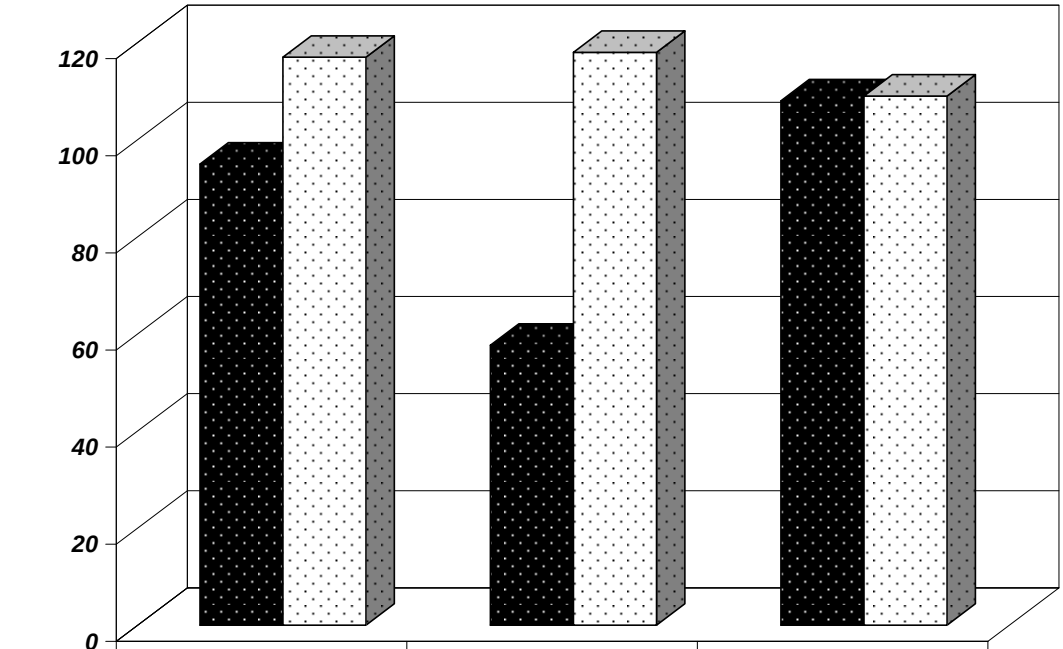
Table 3: Cycle performances calculations using AHP1 and AHP2

Fluid	Evaporator Pressure (kPa)	Condenser Pressure (kPa)	Compression ratio (p/p)	Discharge Temperature (°C)	Volumetric capacity, CAP (kJ/m^3)	COP
AHP1	837	2098	2.51	140	5299	5.06
AHP2	558	1500	2.69	135	3708	5.07

Compared to AHP2, AHP1 exhibited similar COP, a significantly higher volumetric capacity and a lower compression ratio. However the discharge temperature was 5°C higher than that of AHP2.

In an attempt to examine the potential of substituting for R-114 in High Temperature Heat Pumps, all results for AHP1 and AHP2 were also expressed as a percentage of the values of R-114 obtained in the same cycle conditions (Figure 2). R-245fa was added as reference.

As shown in Figure 2, both AHP1 and AHP2 show better performance than R-114. The COP average increase is about 17%. However volumetric capacities of both low GWP products are lower. For AHP1 the deficit is about 5% whereas AHP2 shows a loss of about 40%.



	AHP1	AHP2	245fa
%CAP	95	58	108
%COP	117	118	109

Figure 2: Capacity (CAP) and Coefficient of performance (COP) of AHP1, AHP2 and R-245fa relative to R-114

3.3 Influence of temperature lift

The maximum theoretical efficiency of a vapour compression system is defined by the Carnot theorem.

(2) $$COP_{Carnot} = \frac{T_{cond}}{T_{cond} - T_{evap}} \text{ where } \begin{matrix} T_{cond} = condensation\ temperature \\ T_{evap} = evaporation\ temperature \end{matrix}$$

The efficiency of a vapour compression system is therefore directly related to the difference between the evaporator and condenser temperatures, known as temperature lift.

Regardless the nature of the working fluid, the efficiency will decrease with the increase of the temperature lift. However, the rate of decrease of the COP will depend on the thermodynamics properties of the fluid and more specifically on the slope of the saturation curve.

Figure 4 presents the COP of AHP1 for the condensation temperature of 130°C and different evaporation temperatures. Also represented is the comparison of the COP of AHP1 versus the COP of R-114 under the same conditions and expressed as a percentage difference versus R-114.

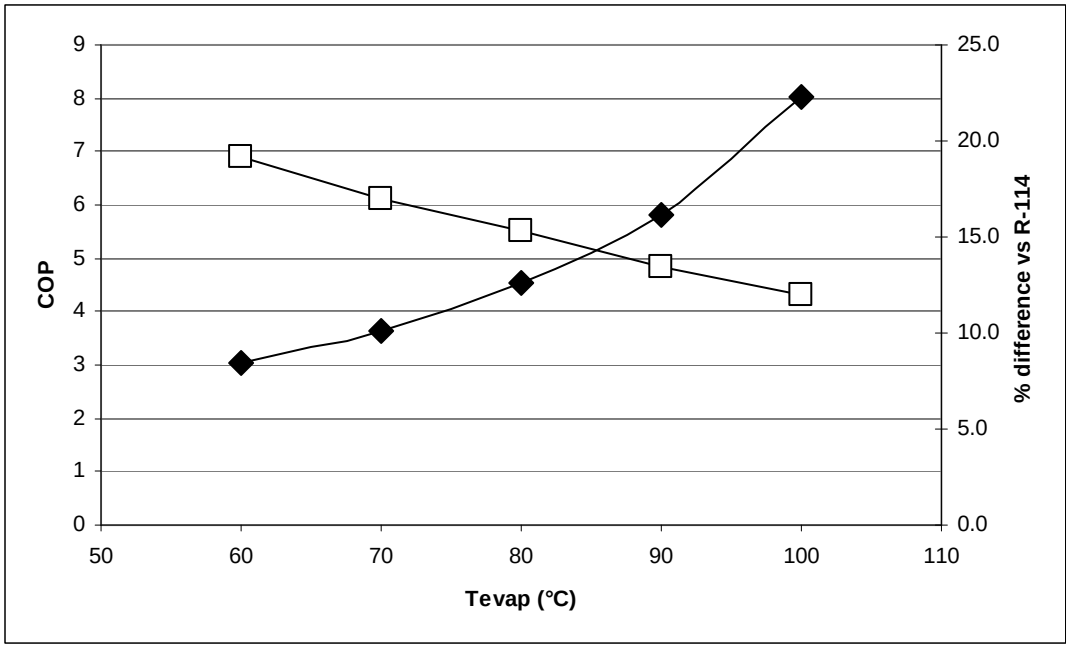


Figure 3. Absolute values of COP of AHP1 (♦) and percentage difference versus COP of R-114 (□) for condensation temperature of 130°C

For all tests conditions, temperature lift values between 70 and 30°C, AHP1 shows higher COP than R-114. It can be noted than the highest difference can be found for at the biggest temperature lift, with an improvement of the COP of R-114 of about 20%.
Compared to R-114, AHP1 will lead to High Temperature Heat Pump with higher efficiency.

4 CASE STUDY

Many case studies can be found in the industry where the use of a heat pump could increase the temperature of a waste-heat source to a temperature where the waste heat becomes useful (Wang et al, 2010).

Examples can be found in the chemical industry. The following description of a real application helps illustrate how heat pumps can be integrated into process operations.

As part of the production of an organic chemical, reactants enter a process reactor at 110°C. Due to the particular properties of the chemical reactions involved, the outlet temperature of the fluid is 90°C.
The characteristics of this flux are presented Table 4.

Table 4: Process characteristics

Flow rate (m3/s)	Cp of organic chemicals (kJ/kg)
16.10^{-3}	1.63

Today, the heat of this flow is not used and can be considered as lost. As there is no direct need for this heat to be reused in the process, a heat pump could be used to produce low-pressure stream (134°C and 3 bar) that is needed for distillation column boilers.

Estimated vapor production can be calculated by considering a heat pump using AHP1, with an evaporating temperature of 90°C, a condensing temperature of 140°C, an internal heat exchanger and superheating equal to 5°C.

Table 5: Estimated savings when using a High Temperature Heat Pump with AHP1

COP	Heating capacity (kW)	Vapor produced (kg/h)	Compression Energy (kW)	Cost savings[1] (k€/year)
4.1	862	1436	210	308

[1] assuming that the cost of vapor = 30€/tons and the cost of electricity is 55€/MWh

5 CONCLUSION

High Temperature Heat Pump is a promising technology for energy recovery when conventional passive-heat recovery is not possible. The potential benefit of low-grade waste heat recovery is significant as demonstrated by the simple industrial case study presented in this paper.

But before this technology can be significantly used, technological and cost barriers have to be addressed. One of these is the need for innovative and sustainable fluids that would allow the High Temperature Heat Pumps to run with higher efficiency.
AHP1 and AHP2, two new low GWP and non-flammable fluids, have been presented. Cycle calculations results showed improved efficiency for a High Temperature Heat Pump running with AHP1 or AHP2.
Therefore, AHP1 and AHP2 have to be seen as potential refrigerant for these applications.

6 REFERENCES

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