

High-Temperature Heat Pumps: Thermodynamic, Economic and Experimental Perspectives for Enhanced Integration

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Abstract

Introduction

Belgium, and Flanders in particular, has a strong presence of chemical and petrochemical industries. It is the second largest exporter of chemicals and pharmaceuticals in the European Union [1]. As a result, the chemical and petrochemical industry contributes to almost 40% of the national industrial final energy use [2]. This energy use is mainly due to the demand in heat, which is often driven by the combustion of fossil-fuels. One method of reducing and electrifying primary energy use are industrial high-temperature heat pumps (HTHPs), which recover residual heat and transfer it to process heat at higher temperatures, through the use of electricity.

The Upheat-INES projects (upgraded high-temperature heat integration in energy-intensive sectors), funded by the Flemish government, aim to contribute to the decarbonization of the chemical and petrochemical industry in Flanders. This by supporting the development of industrial-scale vapour compression HTHPs tailored to the industrial processes. In the first phase the focus was on examining chemical and petrochemical processes that could benefit from HTHP integration. For several relevant applications and a large set of generic data, the optimal refrigerants were determined from a thermodynamic and financial viewpoint. In addition, a financial benchmark was made against electric and natural gas boilers and heat transformers. In the second phase, the aim is the design and construction of a proof-of-concept HTHP using a zeotropic mixture. The heat pump is designed to heat thermal oil up to $200 \,^{\circ}$ C.

Methods

Based on the literature and bilateral meetings, several relevant processes in the chemical industry have been identified for HTHP integration. Of particular interest are the production of steam, (pressurized) hot water or thermal oil as a heat transfer medium, while distillation, drying or boiling were amongst others identified as relevant direct applications. HTHPs for steam generation, distillation and drying in the chemical industry are discussed in detail by Vieren et al. [3]. This work, combined with the work of Vieren et al. [4], also includes a high-level comparison of the financial application range of vapour



compression heat pumps and heat transformers compared to electric and natural gas boilers. Furthermore, a thermodynamic model is developed to determine the most suitable refrigerant(s) by optimizing the operating conditions of the heat pump, as described by Vieren et al. [5] and Abedini et al. [6]. The model is able to simulate pure refrigerants in the subcritical, transcritical and supercritical regime and also allows simulating binary mixtures. The COP can be maximized for any set of temperature profiles by a global optimizer which varies the pressure during heat extraction and delivery, the superheat, the subcooling, the use of an internal heat exchanger and the molar fraction in the case of binary mixtures. The methodology also includes working fluid screening and takes technical constraints into account. The approach was further extended so that the levelized cost of heat (LCOH) could be minimized [7]. This was done by implementing costs associated with the heat pump components. For both the thermodynamic as financial optimization several case studies and also a generic set of temperature profiles were analysed. Within the generic set of temperature profiles, the heat source inlet temperature was varied between 80 °C and 120 °C, while the heat sink outlet temperature was varied between 0 K and 30 K while the temperature glide of the heat sink was varied between 0 K and 60 K.

In the follow-up project, a lab-scale vapour compression HTHP is designed. This HTHP uses a zeotropic mixture of water and ammonia. Use of a zeotropic mixture allows better matching to heat sources and sinks with temperature glides. Furthermore, the addition of ammonia offers the advantage of a higher heating capacity, a lower compressor outlet temperature and a lower pressure ratio compared to pure water. Nevertheless, the pressure ratio and compressor outlet temperature are still high for typical applications. This led to the selection of a twin-screw compressor, capable of handling high pressure ratios and two-phase compression. Furthermore, the compressor uses hydrodynamic bearings, enabling oil-free operation, and thus mitigating problems such as oil degradation or loss of lubricity and oil tightness of the oil. The design is made for a thermal oil heat source and heat sink, with temperatures as shown in Table 1, resulting in an average temperature lift of 75 °C. The experimental facility will be designed for a heating capacity of 100 kW_{th}. A simulation of the complete setup has also been constructed within Python. The design is currently being finalized and the components are being selected and ordered.

	Heat source (Thermal oil)	Heat sink (Thermal oil)
Inlet temperature [°C]	120	170
Outlet temperature [°C]	100	200

Table 1: Information on the operational temperature of the experimental set-up.

Results and discussion

The results of the financial and thermodynamic comparison of the vapour compression heat pump (VCHP), heat transformer (HTF), electric boiler (EB) and natural gas boiler (NGB) are discussed in the work of Vieren et al. [3], [4]. Figure 1 gives an overview of which technology has the lowest LCOH as a function of the waste heat availability and the temperature lift. The waste heat availability is described by the waste heat ratio (WHR), which is the ratio of the available residual heat to the heat demand. The temperature lift is characterized by the gross temperature lift (GTL), which is the temperature difference between the heat sink outlet and the heat source outlet. The analysis is performed under two different electricity prices (c_{el}) and electricity to gas price ratios (EGPR).





Figure 1: Technology with the lowest LCOH as a function of the WHR and GTL, for two different electricity prices and EGPRs.

The results of the thermodynamic model are described by Abedini et al. [6] and Vieren et al. [5]. Abedini et al. [6] focused specifically on the comparison between pure working fluids and binary mixtures. For the case studies considered, they found that binary mixtures were the most promising refrigerants, being either zeotropic or azeotropic depending on the application. It was found that, next to the potential COP increase due to temperature matching, mixtures may lead to a trade-off in thermophysical properties. Vieren et al. [5] focused specifically on comparing transcritical cycles to the classical subcritical cycles for applications with large heat sink temperature glides. They found that transcritical cycles show higher COPs for temperature glides of 60 K and above. Nevertheless, for lower temperature glides, transcritical cycles could also be an option as they show much higher volumetric heating capacities and lower pressure ratios and compressor outlet temperatures. The main limitation is their high gas cooler pressure. A general comparison, incorporating both pure working fluids operating in the subcritical, transcritical and supercritical regimes as binary mixtures, is also made for a generic set of temperature profiles, discussed in the method section. The results of the analysis are summarized in Table 2 [8].



 Table 2: Generalization of the fluids, and corresponding operational modes, with the highest COP for each type of boundary condition [8].

		Heat Source		
		Latent	Sensible	
Sink	Latent	Subcritical pure fluid • Flammable: hydrocarbons • Non-flammable: water (near-) azeotropic mixtures • Flammable: water/acetone (azeotrope) • Non-flammable: x	 <u>Zeotropic mixtures and pure fluid</u> <i>Flammable</i>: water/acetone <i>Non-flammable</i>: water 	
Heat	Sensible	Zeotropic mixtures and pure fluid (Medium ΔT _{sink}) • Flammable: mixtures of HCs • Non-flammable: water Transcritical cycles (Large ΔT _{sink}) • R1336Mzz(Z) or R1234ze(Z)	 <u>Zeotropic mixtures</u> <i>Flammable</i>: acetone/toluene and acetone/water Non-flammable: water/ammonia 	

The same table as depicted above is also made for a minimum LCOH, rather than a maximum COP. The corresponding results are shown in Table 3 [7].

 Table 3: Generalization of the fluids, and corresponding operational modes, with the lowest LCOH for each type of boundary condition [7].

		Heat Source		
		Latent	Sensible	
t Sink	Latent	Subcritical pure fluid Flammable • Acetone, methanol, ethanol (always) • Cyclobutene (low T _{source} and T _{sink}) • Non- or mildly flammable • Water (high T _{source}) • HFOs and HCFOs (low T _{source} and T _{sink})	Subcritical pure fluid Flammable • Cyclobutene, Cyclopentane, Cis-2-Butene (low T _{sink}) • Acetone, Methanol, Ethanol (high T _{sink}) Non- or mildly flammable • Water (high T _{sink} and T _{source}) • HFOs and HCFOs (low T _{sink} and T _{source})	
		(near-) azeotropic mixtures Flammable Mixtures of hydrocarbons (always) Mixtures of water and hydrocarbons (medium T _{source}) Non- or mildly flammable None	Zeotropic mixtures Flammable • Mixtures of hydrocarbons and mixtures of hydrocarbons and ammonia (always) • Mixtures of water and hydrocarbons (medium T _{source}) Non- or mildly flammable • Water/ammonia (high T _{source})	
Hes	Sensible	Subcritical and transcritical pure fluids Flammable • Cyclobutene and Cis-2-Butene (low and medium T _{sink}) • Non- or mildly flammable • HFOs and HCFOs (low and medium T _{sink}) • Water (high T _{source} and T _{sink}) • (near-) azeotropic mixtures Flammable • Mixtures of hydrocarbons (high T _{sink}) • Mixtures of hydrocarbons with water or ammonia (high T _{source} and high T _{sink}) • Mon- or mildly flammable • None	 <u>Zeotropic mixtures</u> Flammable Mixtures of hydrocarbons and mixtures of hydrocarbons and ammonia (always) Mixtures of water and hydrocarbons (medium T_{source}) Non- or mildly flammable Water/ammonia (medium T_{source}) 	



The design of the HTHP is being finalized and no results can be presented yet. Instead, a timeline is shown in Figure 2.



Conclusion

The Flemish chemical and petrochemical industry can significantly reduce its fossil-fuel use by employing high-temperature heat pump technology. Upheat-INES examines where high-temperature heat pumps can be integrated in the chemical and petrochemical industry. It also explores the refrigerant options for vapour compression high-temperature heat pumps up to 200 °C for a wide range of case studies and generic temperature profiles. This is done from both a thermodynamic and a financial viewpoint. The results show that the optimum refrigerant responds to the temperature profiles of the case study. Within the follow-up project, a design is made for a high-temperature heat pump, using a zeotropic water and ammonia mixture to provide heat up to 200 °C. The aim is to start the experimental campaign in the second half of 2024.

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