



# Ammonia/ionic liquid based double-effect vapor absorption refrigeration cycles driven by waste heat for cooling in fishing vessels

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## ABSTRACT

To use high-temperature waste heat generated by diesel engines for onboard refrigeration of fishing vessels, an ammonia-based double-effect vapor absorption refrigeration cycle is proposed. Non-volatile ionic liquids are applied as absorbents in the double-effect absorption system. In comparison to systems using ammonia/water fluid, the complexity of the system can be reduced by preventing the use of rectification sections. In this study, a multi-scale method is implemented to study the proposed system, including molecular simulations (the Monte Carlo method) for computing vapor-liquid equilibrium properties at high temperatures and pressures, thermodynamic modeling of the double-effect absorption cycles, and system evaluations by considering practical integration. The Monte Carlo simulations provide reasonable vapor-liquid equilibrium predictions. 1-butyl-3-methylimidazolium tetrafluoroborate is found to be the best performing candidate among the investigated commercialized ionic liquids. In the proposed cycle, the best working fluid achieves a coefficient of performance of 1.1 at a cooling temperature of  $-5^{\circ}\text{C}$ , which is slightly higher than that obtained with generator-absorber cycles. Integrated with the exhaust gas from diesel engines, the cooling capacity of the system is sufficient to operate two refrigeration seawater plants for most of the engine operating modes in high-latitude areas. Thereby, the carbon emission of onboard refrigeration of the considered fishing vessel could be reduced by 1633.5 tons per year compared to the current practice. Diagrams of vapor pressures and enthalpies of the studied working fluids are provided as appendices.

## 1. Introduction

Global warming is one of the critical issues of the society in this age. According to the International Maritime Organization [1], maritime transport emits around 1000 million tons of carbon dioxide ( $\text{CO}_2$ ) annually and is responsible for about 2.5% of global greenhouse gas emissions along with 15% and 13% of global  $\text{NO}_x$  and  $\text{SO}_x$  emissions. Fishery is one of the major parts of the maritime transport sector. Vessels for pelagic seas usually demand refrigeration plants, which consume fuel or electricity onboard [2]. The refrigeration plant is one of the largest electricity consumers onboard of fishing vessels, typically using 50% of the total power [3]. Diesel engines are normally used for propulsion and on-board electricity generation in trawlers. The engines also produce a significant amount of waste heat [4]. A study [5] shows that a large 2-stroke marine diesel engine may waste 50% of total fuel energy and 25.5% of the total energy is wasted through the exhaust gas ( $250\text{--}500^{\circ}\text{C}$ ) [2].

Heat activated vapor absorption refrigeration (VAR) systems provide opportunities to recover waste heat and to use it to cool down fish

and onboard space. Fernández-Seara et al. [6] designed, modeled, and analysed a gas-to-thermal fluid waste heat recovery system based on an ammonia/water ( $\text{NH}_3/\text{H}_2\text{O}$ ) cycle for onboard cooling applications. Cao et al. [7] carried out a study on a water/lithium bromide ( $\text{H}_2\text{O}/\text{LiBr}$ ) VAR system powered by waste heat for space cooling in a cargo ship. In their study, the cooling  $COP$  is 0.6 and an electricity-based coefficient of performance ( $COP$ ) could be up to 9.4. Thereby, fuel consumption and  $\text{CO}_2$  emission for the cooling system are reduced by 62%. Recently, Salmi et al. [4] modeled both an  $\text{H}_2\text{O}/\text{LiBr}$  single-effect (SE) VAR cycle and an  $\text{NH}_3/\text{H}_2\text{O}$  refined cycle for cooling on a bulk carrier ship with waste heat recovered from exhaust gases, jacket water and scavenge air cooler. The VAR system has a theoretical potential to save 70% of electricity in comparison to a compression air-conditioning system. They also pointed out that the  $\text{H}_2\text{O}/\text{LiBr}$  cycle is more efficient ( $COP$  of 0.75–0.85) and  $\text{NH}_3/\text{H}_2\text{O}$  is more suitable for below-freezing-point cooling ( $COP$  of 0.5).

Exhaust gases seem to be the best source of waste heat onboard to drive absorption chillers, even though they cannot be cooled down below  $167^{\circ}\text{C}$  because of a risk of sulfur corrosion [4]. At temperatures above

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**Nomenclature**

|              |   |
|--------------|---|
| <i>COP</i>   | coefficient of performance [–]                            |
| $c_p$        | specific heat capacity [kJ/(kg K)]                        |
| <i>DR</i>    | distribution ratio [–]                                    |
| <i>f</i>     | circulation ratio [–]                                     |
| $h/\Delta h$ | specific enthalpy (difference) [kJ/kg]                    |
| <i>k</i>     | scaling parameter [–]                                     |
| <i>M</i>     | a notation of densities or heat capacities in Eq. (2) [–] |
| <i>Mw</i>    | molecular weight [kg/kmol]                                |
| $\dot{m}$    | mass flow rate [kg/s]                                     |
| <i>P</i>     | pressure [bar]  |
| $\dot{Q}$    | heat load [kW]  |
| <i>q</i>     | quality [–]   |
| <i>R</i>     | ideal gas constant [8.314472 J/(mol K)]                   |
| <i>T</i>     | temperature [°C or K]                                     |
| $\dot{W}$    | power [kW]  |
| <i>w</i>     | mass fraction [–]   |
| <i>x</i>     | mole fraction [–]   |
| <i>Z</i>     | compressibility [–]                                       |

**Greek symbols**

|            |                                    |
|------------|------------------------------------|
| $\alpha$   | parameter in the NRTL model [–]    |
| $\epsilon$ | Lennard-Jones energy parameter [–] |
| $\eta$     | efficiency [–]                     |
| $\rho$     | density [kg/m <sup>3</sup> ]       |
| $\tau$     | parameter in NRTL model [–]        |

**Subscript and superscript**

|         |  |
|---------|--|
| 1, 2... | state point                            |
| abs     | absorption                             |
| c       | critical point                         |
| con     | condensation/low pressure condensation |
| eva     | evaporation                            |
| ex      | exhaust gas                            |
| gen     | generation                             |
| hpg     | high pressure generation               |
| i       | inlet                                  |
| ig      | ideal gas properties                   |
| IL      | ionic liquid component                 |
| lc      | low pressure condenser                 |
| lg      | low pressure generator                 |

|                 |                                    |
|-----------------|------------------------------------|
| mix             | mixing properties                  |
| NH <sub>3</sub> | NH <sub>3</sub> component          |
| o               | outlet                             |
| onset           | onset                              |
| p               | pump                               |
| sat             | properties of a saturated system   |
| sol             | solution                           |
| sub             | properties of a supercooled system |
| whr             | recovered waste heat               |
| V               | vapor                              |

**Abbreviation**

|                           |   |
|---------------------------|---|
| ABS                       | absorber  |
| CON                       | condenser   |
| CWP                       | chilled water plant   |
| DE                        | double-effect   |
| EVA                       | evaporator  |
| EXP                       | experimental (data)   |
| FP                        | freezing plant  |
| GAX                       | generator-absorber heat exchange                                |
| GEN                       | generator   |
| HC                        | high pressure condenser   |
| HG                        | high pressure generator   |
| HX                        | heat exchanger  |
| iHX                       | intermediate heat exchanger                                     |
| IL                        | ionic liquid  |
| LG                        | low pressure generator  |
| MC                        | Monte Carlo   |
| NRTL                      | non-random two-liquid activity coefficient model                |
| REC                       | rectifier   |
| RSW                       | refrigeration seawater (plant)                                  |
| SE                        | single-effect   |
| SHX                       | solution heat exchanger   |
| SIM                       | simulated (data)  |
| VAR                       | vapor absorption refrigeration                                  |
| VLE                       | vapor-liquid equilibrium/vapor-liquid equilibria                |
| WHR                       | waste heat recovery   |
| [bmim][BF <sub>4</sub> ]  | 1-butyl-3-methylimidazolium tetrafluoroborate                   |
| [emim][Tf <sub>2</sub> N] | 1-ethyl-3-methylimidazolium bis(tri-fluoromethylsulfonyl) imide |
| [emim][SCN]               | 1-ethyl-3-methylimidazolium thiocyanate                         |

150 °C, double-effect vapor absorption refrigeration (DE-VAR) cycles, in which the refrigerant is generated twice, are able to achieve higher thermal efficiencies by taking advantage of the higher temperature of the heat sources [8]. However, these cycles usually utilize the working fluid H<sub>2</sub>O/LiBr, which cannot meet the demand of below-freezing-point cooling. With NH<sub>3</sub>/H<sub>2</sub>O, the DE-VAR is not feasible because of the need of rectifiers which introduce a higher complexity.

To use higher temperature exhaust gases for below-freezing-point cooling onboard, NH<sub>3</sub> with ionic liquids (ILs) working fluids is proposed to be used in DE-VAR systems. ILs, a family of room-temperature molten salts, have been intensively studied due to their potential in replacing the absorbents in conventional absorption refrigeration and heat pump technology [9]. ILs show strengths such as high boiling points, strong affinities with refrigerants and high chemical and thermal stabilities [9]. Moreover, NH<sub>3</sub> based absorption systems have strengths such as below-freezing-point cooling, free of air infiltration and low impact on the environment (zero for both ozone depletion and global warming potentials).

NH<sub>3</sub>/ILs working fluids in absorption cycles have received significant attentions in the past decade. Yokozeki and Shiflett [10]

reported the first vapor-liquid equilibrium (VLE) data of four NH<sub>3</sub>/ILs working pairs. By including measurements and correlations of the other four NH<sub>3</sub>/ILs pairs, the performance of the eight NH<sub>3</sub>/ILs fluids in an SE absorption cycle was compared in Ref. [11]. Most of their studied imidazolium ILs are currently well commercialized. Functional ILs with NH<sub>3</sub> in SE absorption cycles were also investigated. For instance, Chen et al. [12] investigated the VLE property of NH<sub>3</sub> with a metal ion-containing imidazolium IL. A thermodynamic performance of a VAR cycle using the studied fluids was conducted in a sequential work by the same authors [13]. Ruiz et al. [14] studied some ammonium ILs. Cera-Manjarres [15] explored six other ILs including imidazolium and ammonium ILs with a hydroxyl group (-OH). By applying more reliable mixing enthalpies and experimental heat capacities, Wang and Infante Ferreira [16] explored the performance of nine NH<sub>3</sub>/ILs fluids in SE absorption cycles for heat pump systems. The authors identified promising absorbents which work with NH<sub>3</sub> in absorption cycles under 130 °C heating.

Nevertheless, the above studies were all applied at temperature and pressure ranges available for SE-VAR cycles. The DE-VAR cycle requires

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