REACHER: the exploration of the use of reactive working fluids for thermodynamic cycles

Silvia Lasala

Thermodynamic cycles are at the basis of the operation of thermal power plants, heat pumps and vapour-compression refrigeration systems. Nowadays, thermodynamic cycles operate with working fluids that are either pure or inert mixtures, such as water, air, organic fluids and helium.

The project REACHER aims to quantify the impact of using reactive working fluids, undergoing rapid and reversible reactions, instead of inert ones (Lasala, 2021). This investigation is divided into four primary work packages (see Figure 1).

Project work packages

WP1 Development of a computational tool for the prediction of thermodynamic properties of reactive fluids.

WP2 Discovery, or design, and full thermophysical and thermochemical characterisation of reactive working fluids suitable for power and heating applications.

WP3 Optimisation of the architecture of thermodynamic cycles operating with reactive working fluids.

WP4 Validation of our calculations on an experimental micro-gas turbine operating on a Brayton cycle.

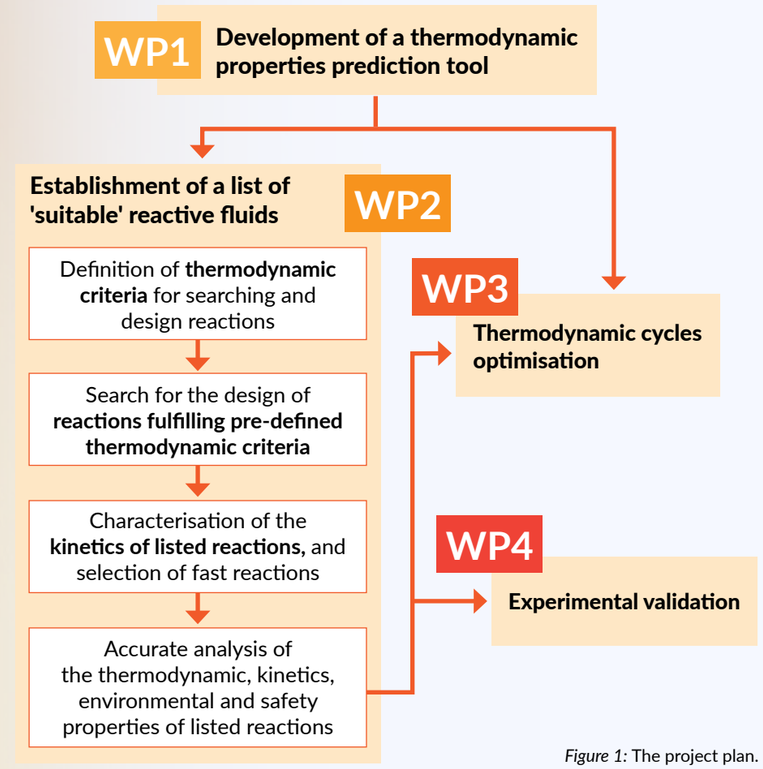

Figure 1: The project plan.

The project spans five years (2022–2027), and we are currently in the middle of the second year. The team comprises six non-permanent members and three members. During the project's first year, we have been working on WP1, WP2 and WP4. In this article, we elaborate on the methodology employed and share some of the results we have obtained. More details will be provided in more specific scientific publications.

The performances of heat pumps operating with fictitious reactive fluids

Building upon work previous to the project, we analysed (Lasala *et al.*, 2021; Barakat *et al.*, 2022) the performance of heat pumps operating on a Brayton and Stirling cycle using fictitious reactive working fluids of the form:

$$A_n = (n/m)\, A_m$$

To this general reaction, we have associated different stoichiometries (n and m) and thermochemistry (enthalpy and entropy of reaction), giving rise to a different set of chemical reactions. We have then assessed the impact of those parameters on the cycle's performance.

The main conclusion of the study is that many reactive fluids exist for which the slight increase of the mass flow rate of the cycle (by 10 per cent, with respect to an inert fluid) can lead to a doubled coefficient of performance (COP) (Barakat *et al.*, 2022), see Figure 2.

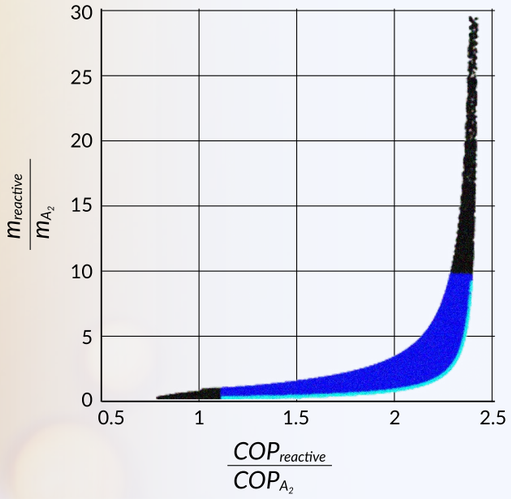

Figure 2: The ratio of the COP of a heat pump operating with a reactive working fluid and the COP of a heat pump using inert working fluids as a function of the ratio between the mass flow rate of the reactive fluid heat pump with respect to the inert one. In both cases (inert or reactive fluid), the thermal power output of the heat pump is the same. Each black point of the cycle represents a different fictitious fluid.

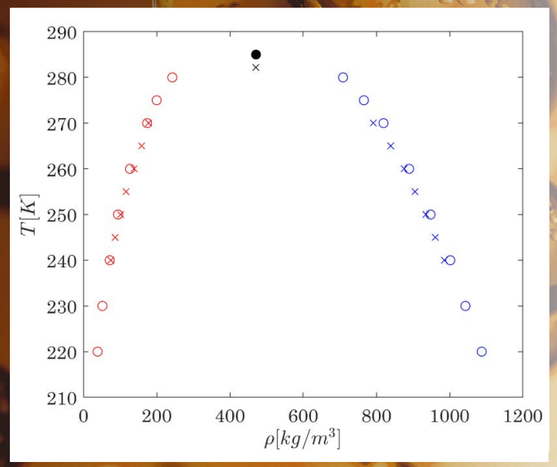

Figure 3: Monte Carlo simulations for the system NO_2 – saturation density-temperature curve.

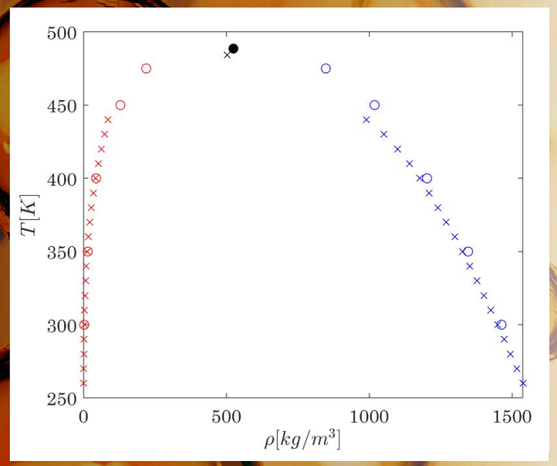

Figure 4: Monte Carlo simulations for the system N_2O_4 – saturation density-temperature curve.

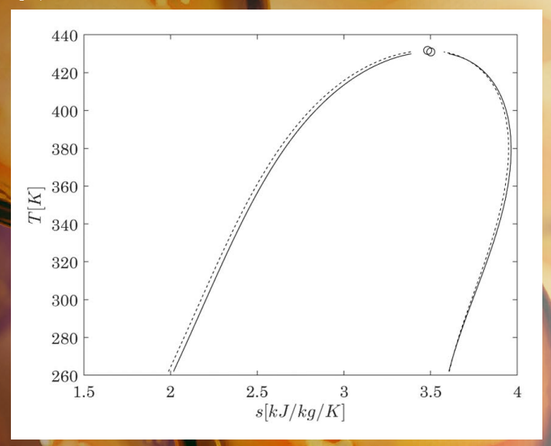

Figure 5: Temperature-entropy diagram of the reactive mixture N_2O_4 = $2NO_2$. The two curves make reference to the same calculation done with different sets of input critical properties for the equation of state.

The characterisation of the thermodynamic properties

Assessing the performance of thermodynamic cycles requires the calculation of the thermodynamic properties of reactive working fluids (enthalpy, entropy, density, composition of the fluid, etc., in one-phase or two-phase conditions). Those properties can be determined thanks to the methodological approach we describe in a paper under submission (for more details, visit www.univ-lorraine.fr/erc-reacher). This methodology integrates quantum mechanics calculations needed to determine thermochemical properties (standard enthalpy of formation, entropy, and the heat capacity of ideal gas) and force field-based Monte Carlo simulations to enable the determination of the non-measurable temperature and pressure of the critical points of inert NO_2 and N_2O_4 (see Figures 3 and 4).

The code produced to perform these calculations integrates algorithms for the computation of reactional and, if more than one phase is coexisting, phase equilibrium. Two codes are being realised, one for determining those properties as a function of specified independent variables and a second to plot phase equilibrium diagrams for all the studied fluids. Figure 5 shows a temperature-entropy diagram of the reactive mixture N_2O_4 = $2NO_2$. This code is scheduled to be released as open-source in 2024.

The reaction design

In the project, we developed an algorithm and computational code capable of designing thousands of dimerisation reactions. Next, we'll employ quantum mechanics simulations their enthalpy and entropy of reaction. These properties collectively establish the equilibrium constant, governing the reaction's behaviour under temperature and pressure variations. Subsequently, we'll conduct an initial screening based on these properties.

The pilot

The pilot was designed (Figure 6) and is currently under construction. It is equipped with four operating units: a 3.5 kW turbine, a shell and tube heat exchanger, a 15 kW compressor, and an electric heater. The first successful test consisted of running the turbine at the highest speed, separated from the circuit operating as a motor. The second test consists of operating the pilot in an open circuit: ambient air is taken from the inlet of the compressor and is rejected into the atmosphere after the cooler. Then, during the third test, the engine will be run in a closed circuit with N_2. During the last test, a mixture of N_2 and a reactive working fluid will be tested in the same closed circuit. The performance will be assessed and compared to the calculated values.

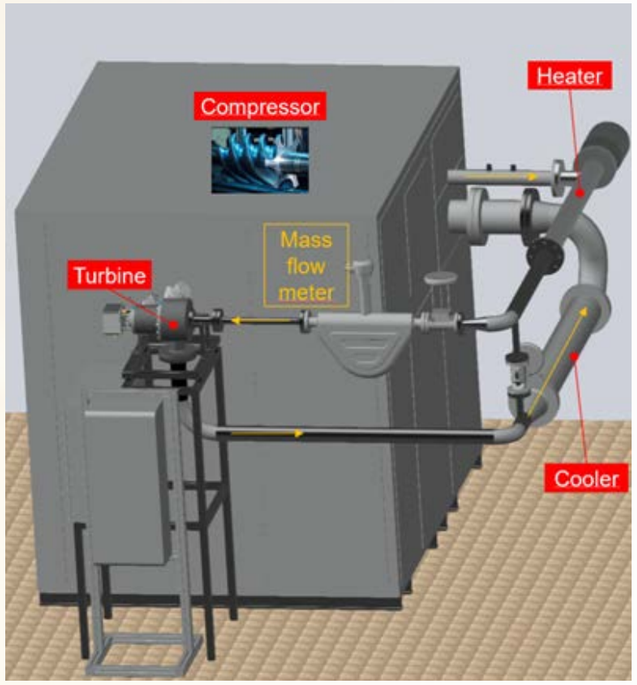

Figure 6: Pilot under realisation.

Moreover, among the measurements performed on the pilot, Raman spectroscopy measurements will be obtained before and after each pilot unit to validate the expected evolution of the chemical reaction. A preliminary experimental activity, already under development, consists of analysing the Raman spectra of some reactive fluids and calibrating the probes.

Next challenges

We will continue to improve the thermodynamic model based on our calculations, the thermodynamic code and the authomatisation of the final characterisation of each designed reactive fluid. To conclude, we are beginning with the optimisation of the cycle architecture.

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REACHER
REACTIVE FLUIDS FOR ENERGY

PROJECT SUMMARY

With the aim to effectively increase the performances of power plants, refrigeration systems and heat pumps, this project proposes the use of equilibrated reactive working fluids instead of inert ones. It applies an original methodology that integrates thermodynamic and kinetic predictive tools to discover and characterise suitable reactive fluids, allowing for the quantification of the effects of reaction features on system performance and optimal architecture.

PROJECT LEAD PROFILE

Silvia Lasala, principal investigator in REACHER, is currently assistant professor at the University of Lorraine, ENSIC-LRGP (France). In 2016, she got her PhD at Politecnico di Milano (Italy) with a thesis aiming at improving the thermodynamic modelling of CO_2-based streams in CO_2-capture-and-storage systems. During her PhD, she also worked in designing and characterising inert working fluids for thermodynamic cycles. Then, she carried out a postdoc at LRGP (France), investigating the kinetics and thermodynamics of liquefying hydrogen and researching the possible use of inert and novel reactive working fluids in power and trigeneration plants.

PROJECT CONTACTS

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