



**HAL**  
open science

# Inert and Reactive Working Fluids for Closed Power Cycles: Present Knowledge, Applications and Open Researches

Silvia Lasala, Romain Privat, Jean-Noël Jaubert

► **To cite this version:**

Silvia Lasala, Romain Privat, Jean-Noël Jaubert. Inert and Reactive Working Fluids for Closed Power Cycles: Present Knowledge, Applications and Open Researches. Organic Rankine Cycle Technology for Heat Recovery, InTechOpen, 2018, 10.5772/intechopen.79290 . hal-03200214

**HAL Id: hal-03200214**

**<https://hal.univ-lorraine.fr/hal-03200214>**

Submitted on 24 Aug 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

---

# Inert and Reactive Working Fluids for Closed Power Cycles: Present Knowledge, Applications and Open Researches

---

Silvia Lasala, Romain Privat and Jean-Noël Jaubert

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/intechopen.79290>

---

## Abstract

The possibility of selecting the working fluid of a closed power cycle represents one of the most important levers to maximise the efficiency and to optimise the design of this technology. This chapter is intended to provide a description of the present state of knowledge on the effects that fluid thermo-physical properties, such as molecular complexity and molecular mass, have on the design and performance of cycle components. With a view to allow for accounting for multicomponent inert and reactive working fluids along the optimisation process, the chapter then presents the main outstanding scientific barriers which need to be overcome.

**Keywords:** closed thermodynamic cycle, working fluid, inert and reactive mixture, thermodynamic properties, transformations, thermal stability

---

## 1. Introduction

The history of power production systems has been marked by the deployment of two main technologies: the water cycle and the open gas cycle. Both the engines owe their development to the possible exploitation of the traditional high-grade heat sources (i.e. characterised by a high maximum temperature and a huge thermal power), represented by the heat of combustion of fossil fuels. The achievement of a minimum acceptable efficiency level of these technologies requires the availability of a high thermal power, in the case of water cycles, and the achievement of a sufficiently high maximum temperature of the gaseous working fluid, in the case of gas cycles.

Nowadays, the recognised necessity of reducing the environmental impact of power 'production' processes has imposed the exploitation of non-traditional heat sources either recovered from industrial processes or made available by renewable energies (geothermal, biomass and solar thermal energy). These are typically characterised by a lower thermal power and a lower maximum temperature than thermal sources generated by the combustion of fossil fuels.

The efficient and economical recovery of these low-temperature thermal energies is made possible by the use of closed cycles in which the working fluid can be properly selected. Depending on the heat capacities of both the thermal source to be exploited and the cold sink where cycle heat is discharged, the use of different working fluids might be indeed more or less convenient, in terms of both energy conversion efficiency and components design.

Together with the optimisation of the cycle configuration ('process-design' approach), the possibility to define the optimal working fluid for each application ('product-design' approach) represents the greatest degree of flexibility to reduce the irreversibilities of any of these energy conversion processes and, thus, to maximise their efficiency.

Despite the pivotal role represented by the optimal selection of the working fluid, the scientific knowledge level on physicochemical thermodynamic and transport properties, thermal stability and environmental characteristics of fluids do merely allow the reliable utilisation of pure-component fluids.

This chapter aims, firstly, to present a review of the present knowledge level on this topic and, secondly, to highlight the main scientific gaps which currently limit the assessment of the energy potential of closed cycles operating with inert and reactive mixtures as working fluids.

## **2. The state of the art on working fluids for closed power cycles**

Two main criteria exist to differentiate between working fluids, depending on whether they are pure or multicomponent, inert or reactive fluids. According to these classifications, inert fluids may be pure or multicomponent (typically binary) fluids, while reactive fluids may only be multicomponent fluids, as they are mixtures by definition. The advantage represented by the use of optimal inert fluids mainly lies in the possibility of reducing the irreversibilities occurring along the cycle; differently, reactive fluids may allow the substantial increase of the energy 'produced' during fluid expansion, thanks to the conversion of the chemical energy (other than the physical one) of the reactive fluid.

### **2.1. Inert pure fluids**

Nowadays, pure fluids are mainly used as working fluids, among which water represents the pioneer for power cycles. Even now, water is the fluid which is mostly used in a closed thermodynamic cycle, in particular, in the Rankine cycle. The thermodynamic conversion of non-traditional thermal sources (geothermal, biomass, solar thermal and industrial waste heat recovery) is associated to a wide variety of powers, thermal grades and physical states of the

heat sources (liquid, gaseous or two-phase streams) which generally make the use of water cycles unsuitable. The thermodynamic properties of water, in fact, entail the necessity of adopting complex and expensive plant configurations, preventing from their use in low-temperature and low-power applications [1]. In these cases, the design of simple turbines and the occurrence of a single-phase vapour expansion are aspects of primary importance which direct the use of molecules being more complex and heavier than water, currently represented by organic fluids (hydrocarbons, fluorocarbons and siloxanes) [2].

Organic fluids are most conveniently used as subcritical working fluids in power production plants designed to recover heat wasted by industrial processes and many other low-medium-temperature applications. Organic fluids are used up to 400 °C, due to their limited thermal stability. Macchi has presented [2] a 'grey zone' of applications, characterised by a heat source temperature of 300–400 °C and a power output of 8–50 MW, where organic fluids could compete with water cycles.

Furthermore, the production of high-power outputs is conveniently associated with the use of either water or CO<sub>2</sub> cycles, giving preference to CO<sub>2</sub> for the high-temperature applications represented by solar energy (solar tower technology) and nuclear energy (IV generation of nuclear reactors) [3].

Moreover, it is worth highlighting that, besides the already attested application of high-temperature CO<sub>2</sub> power cycles, this technology may also be considered as a viable solution for the exploitation of medium-temperature heat sources (300–600 °C), competing with organic fluids and water [1].

The optimal choice between fluids for power systems designed to exploit medium-temperature and low-medium heat sources is thus not straightforward. The preferential use of a specific fluid in a particular range of power outputs and source temperatures results, in fact, from the techno-economical optimisation of these technologies, which maximises their efficiency and minimises their costs according to the specific constraints imposed by each application. Thermodynamic properties (in particular, specific molar heat capacities and critical properties) and the molar mass of each fluid influence the performance of the thermodynamic cycle and the design of components.

The nature of a selected pure working fluid does influence the performance of power cycles in the way its thermo-physical properties affect the thermodynamics of the cycle, turbomachines and heat exchanger efficiencies. Subsections 2.1.1 and 2.1.2 briefly introduce the foundations of such a statement.

#### *2.1.1. Effect of fluid molecular complexity and mass on the performance and design of turbomachines*

A preliminary classification of working fluids can be performed according to their molecular weight (first criterion) and to their molecular complexity (second criterion), the latter being related to the degrees of freedom of the molecule and, thus, to their molar heat capacity.

In general, one could erroneously think that more complex molecules are characterised, at all time, by a higher molecular weight. Although this is observable in the majority of cases, such a

conclusion is not universally correct. For example, carbon dioxide is characterised by a higher molecular complexity and a lower molecular weight with respect to krypton. This is shown in **Table 1**. The same table allows another similar comparison, between perfluorohexane and 1-undecanol, the former being heavier and molecularly simpler than the latter.

Molecular complexity influences the design and performance of a thermodynamic cycle, in such a way that complexity affects the degree of freedom of the molecule itself and, thus, the change in the thermodynamic properties of the fluid in response to energy interactions with the environment. In particular, a higher molecular complexity entails a lower adiabatic index,  $\gamma = c_p/c_v$  (see **Table 1**) and, thus, a weaker temperature modification of the fluid, at a given pressure ratio, and a more important pressure change, at a fixed temperature ratio. Along an isentropic compression or expansion of molecules in the ideal gas state, temperature and pressure ratios are related by means of the molecular complexity:

$$T_2/T_1 = (P_2/P_1)^{\frac{\gamma-1}{\gamma}} = (v_2/v_1)^{1-\gamma} \quad (1)$$

By way of example, **Table 1** reports the temperature (or molar volume) and pressure changes, for each considered fluid, resulting from, respectively, pressure and temperature modifications. It can be observed, from **Table 1**, that complex molecules lead to compressions and expansions characterised by high optimal pressure ratios, high molar volume ratios and, thus, poorer turbomachine efficiencies.

Considering the expansion or the compression of different fluids characterised by equal temperature profiles, it is possible to state that turbomachines specific work,  $w$ , results to be proportional to the mass heat capacity of the fluid,  $\bar{c}_p$ , and, thus, to its molecular complexity,  $\gamma$ , and molar weight,  $M$ :

$$w \propto \bar{c}_p = \frac{\gamma}{\gamma-1} \frac{R}{M} \quad (2)$$

The axial size of turbomachines is influenced by the molecular complexity and the molar mass: as the maximum enthalpy change per stage of a turbomachine is limited, the higher the

Fluid	He	Kr	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>6</sub> F <sub>14</sub>	C <sub>11</sub> H <sub>24</sub> O
	Helium	Krypton	Carbon dioxide	Methane	Perfluorohexane	1-Undecanol
M (g/mol)	3.02	83.8	44.01	16.05	338.04	172.31
$c_{v,T=298.15}^{\bullet} \text{ K/R} (-)$	1.500	1.500	3.479	3.291	30.474	31.009
$c_{p,T=298.15}^{\bullet} \text{ K/R} (-)$	2.500	2.500	4.479	4.291	31.474	32.009
$\gamma^{\bullet} = c_p^{\bullet}/c_v^{\bullet}$	1.667	1.667	1.287	1.304	1.033	1.032
$\theta^{\bullet} = (\gamma^{\bullet}-1)/\gamma^{\bullet}$	0.400	0.400	0.223	0.233	0.032	0.031
$T_2/T_1; v_2/v_1$ (with $P_2/P_1 = 4$ )	1.74; 0.44	1.74; 0.44	1.48; 0.37	1.41; 0.35	1.06; 0.26	1.06; 0.26
$P_2/P_1$ (with $T_2/T_1 = 1.25$ )	1.75	1.75	2.72	2.61	1122.28	1264.85

**Table 1.** Main characteristics of working fluids characterised by different molecular weight and molecular complexity.

specific heat capacity resulting from more complex or lighter molecules, the higher the number of stages of the turbomachine.

Moreover, it is possible to show that the radial dimensions of turbomachines depend only on the molecular complexity, the pressure and the temperature of the fluid. In particular, and contrary to axial extension, cross-sectional areas are minimised by the use of complex molecules that would reduce the volumetric flow of the stream.

To reduce the design complexity of turbomachines and to increase their efficiency (limiting the number of stages, the variation of volumetric flow and avoiding the occurrence of supersonic conditions), it is thus preferable to adopt **simple and heavy fluids**. The higher radial dimensions of turbomachines that would result from the use of simple molecules could be reduced by an increasing fluid pressure.

It is worth highlighting that the molecular complexity determines, in particular, the inclination of saturation vapour curve in the T-s diagram: the increase in temperature or in pressure results, respectively, in an increase or a decrease in saturated-vapour entropy. Depending on whether the influence of temperature or that of pressure overrides, the saturated-vapour curve slopes positively or negatively in the T-s plane (**Figure 2(a)** and **(c)**). In the case of (c), which concerns complex molecules, the expansion of saturated-vapour fluids in saturated Rankine cycles favourably occurs in the superheated vapour phase (the so-called 'dry' expansion), avoiding the inefficient expansion of the fluid in the two-phase region. Herein, a simple approach to allow for distinguishing between these two families of fluids is presented.

Assuming, for simplicity, that the vapour behaves as a perfect gas, it is possible to write that

$$ds_{gas}^{sat} = c_p^{\bullet} \frac{dT}{T} - R \frac{dP^{sat}}{P^{sat}} \quad (3)$$

Considering the Antoine equation for saturation pressure,  $\ln(P^{sat}) = A - B/T$ , and its differential form:

$$\frac{dP^{sat}}{P^{sat}} = \frac{B}{T^2} dT \quad (4)$$

and substituting it into Eq. (3), it is possible to deduce

$$\frac{ds_{gas}^{sat}}{dT} = \frac{1}{T} \left( c_p^{\bullet} - R \frac{B}{T} \right) \quad (5)$$

or, defining  $B^* = B/T_r$ ,

$$\frac{ds_{gas}^{sat}}{dT} = \frac{1}{T} \left( c_p^{\bullet} - R \frac{B^*}{T_r} \right) \quad (6)$$

Equation (6) shows that when the combination of  $c_p^{\bullet}$  and of  $T_r$  of the fluid is such that  $c_p^{\bullet} = R \cdot B^*/T_r$ , the saturation vapour curve is vertical in the plane T-s. Practically, it is possible to observe the existence of an average value for  $B^*$  common to most of fluids. Considering Antoine equation in the reduced variables,  $\ln(P_r^{sat}) = A^* - B^*/T_r$ , and letting it pass through the



critical point ( $P_r = 1$ ,  $T_r = 1$ ), it follows that  $A^* = B^*$ ; optimising  $B^*$  for different fluids in the reduced temperature domain  $T_r \in (0.75; 1)$ , it is possible to observe that, for most common fluids,  $B^* \sim 7$  (see **Figure 1**).

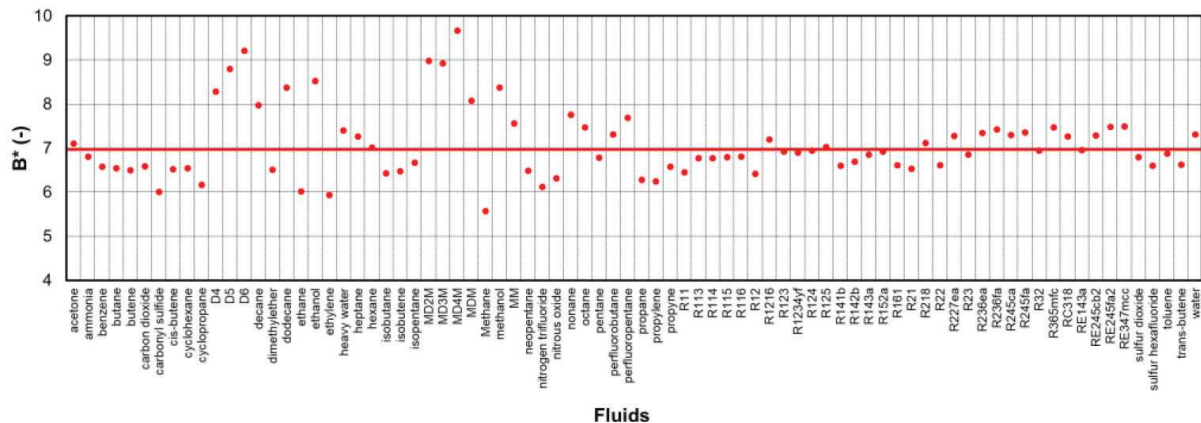
A very rough criterion to distinguish between fluids characterised by positively or negatively sloped saturation vapour curves consists in considering the saturation vapour curve in the temperature range identified by  $T_r \in [0.65; 0.85]$  and comparing the perfect gas heat capacity of the fluid,  $c_p^*$ , calculated at the intermediate temperature defined by  $0.75 \cdot T_c$ , with the two limits  $R \cdot B^*/T_r = 70$  J/mol/K (with  $B^* = 7$  and  $T_r = 0.85$ ) and  $R \cdot B^*/T_r = 90$  J/mol/K (with  $B^* = 7$  and  $T_r = 0.65$ ): fluids having a  $c_p^*(T_r = 0.75) > 90$  J/mol/K are typically characterised by a retrograde saturation vapour curve, while fluids having  $c_p^*(T_r = 0.75) < 70$  J/mol/K most likely have a non-retrograde saturation vapour curve. Fluids with  $c_p^*(T_r = 0.75) \in [70$  J/mol/K;  $90$  J/mol/K] have, in general, quasi-isentropic saturation vapour curves (**Figure 2(b)**).

Beside the positive effect that the use of complex molecules has on dry expansions, they also entail the convenient similar gradient of vapour and liquid isobars, in the T-s plane (see **Figure 2**). Complex fluids are thus particularly suitable to exploit variable temperature heat sources.

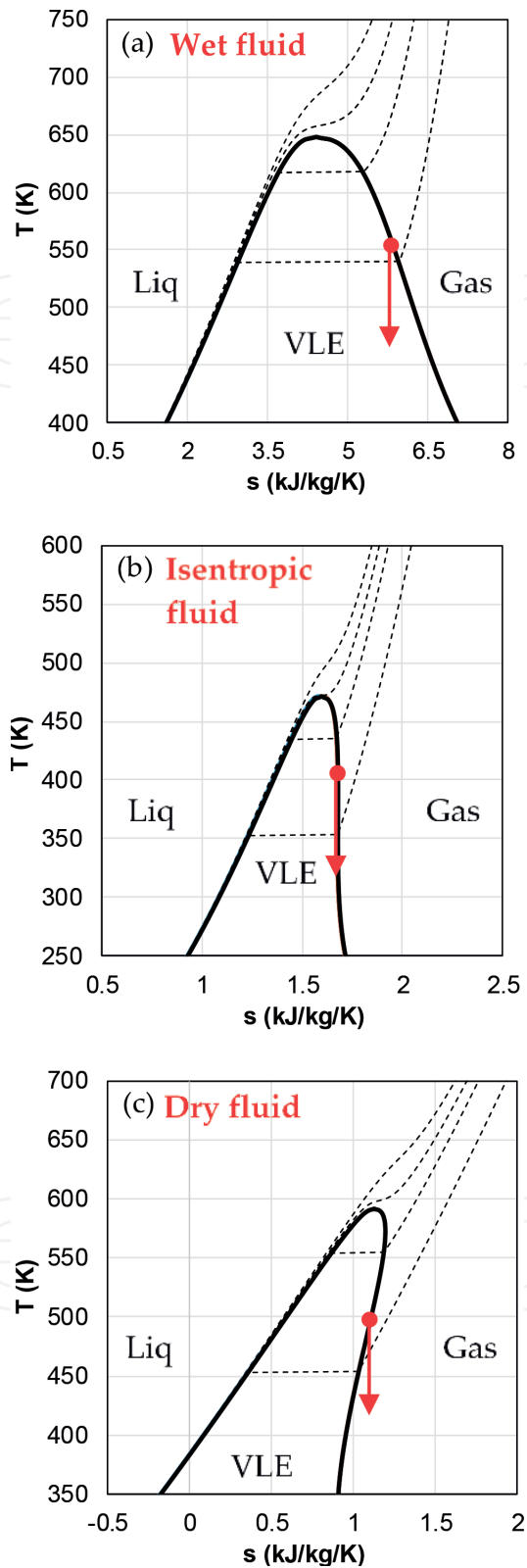
### 2.1.2. Effect of fluid molecular complexity and mass on the performance and design of heat exchangers

The nature of the working fluid also affects the design of heat exchangers. Two aspects have to be considered in sizing heat exchangers: the capacity of the adopted fluid to exchange heat and the mechanical power consumed by compressors to enable the fluid flowing through the heat exchanger.

It is possible to show [4] that the most important parameter of an optimal heat transfer fluid is the molar mass, which should preferably be low (**light molecule**) to allow the maximisation of heat exchange coefficients. Heavy molecules would instead entail the adoption of heavy and expensive heat exchangers.



**Figure 1.** Parameter  $B^*$  which minimises, for 90 considered fluids, the objective function  $\sum_i (P_r^{sat}(T_i) - \exp(B^* - B^*/T_{r,i}))^2$ . Critical properties and saturation pressures,  $P_r^{sat}(T_i)$ , have been extracted from the NIST standard reference database 23, Refprop 9.1.



**Figure 2.** T-s diagrams of water (a) with isobars 5–35 MPa, R11, (b) and toluene (c) with isobars 0.5–6.5 MPa. For the sake of completeness, the red arrows indicate an isentropic expansion for the three considered fluids, from their saturated-vapour state.



Moreover, the low optimal compression ratios resulting from the use of **simple molecules** allow the reduction of the pressure levels of the fluid crossing the heat exchangers and, thus, of their sizes and investment costs.

### 2.1.3. Further considerations

As mentioned in Section 2.1.1, usually complex fluids are heavy fluids and, vice versa, simple fluids are light fluids. It is thus not straightforward to select an optimal fluid even considering only guidelines reported in Sections 2.1.1.

According to conclusions of Sections 2.1.1 and 2.1.2, it is always convenient to use simple molecules, from the point of view of the design and performance of both turbomachines and heat exchangers. However, the opposite effect that the molar mass of the fluid has on heat exchangers and turbomachines implies the necessity of solving a techno-economical optimisation problem.

## 2.2. Inert mixtures

There exist applications (an ensemble of hot and cold thermal sources and thermodynamic cycles) in which restricting the search for a working fluid in the range of available pure fluids highly limits the efficiency of the energy system. It is for this reason that, with the increasing interest to exploit a wider variety of thermal sources (other than combustion sources), in the 1990s, researchers started envisaging the possibility of using inert mixtures as working fluids, considering the selection of their composition as the most effective lever for the optimal design of closed thermodynamic cycles. The following two cases of closed power cycles represent blatant examples of the importance of utilising mixtures instead of pure working fluids to better optimise the heat exchange between working fluid and hot source and to reduce the power required for fluid compression.

### 2.2.1. Organic Rankine cycles

Cycles based on organic components, also called ORC (organic Rankine cycles), are mostly operated in subcritical modes (Rankine cycles). In such configurations, the isothermal evaporation and condensation of a pure fluid is the most efficient solution when the heat source and the cold sink present an isothermal profile. However, heat sources and/or sinks are usually available to these cycles with a variable temperature profile: typical heat sources are flue gases discharged by internal combustion power cycles (i.e. Brayton, Diesel and Otto engines), gaseous biomass combustion products, geothermal fluids and liquid solar fluids; variable temperature sinks are usually represented by liquid water heated for cogeneration purposes and/or cooling air used in the condenser.

In the case of variable temperature heat sources, the flexible adjustment of the composition of a zeotropic working fluid could allow the thermodynamically optimal matching between the variable temperature profile of the working fluid, characterised by a temperature glide, and the one of the thermal sources.

### 2.2.2. $\text{CO}_2$ condensation cycles

To exploit high-temperature heat sources (e.g. solar, nuclear and coal power plants) in the presence of low-temperature cooling sinks at less than 15–20 °C, carbon dioxide is usually proposed as an optimal working fluid in transcritical power cycles because of its critical properties, natural availability, corrosion-neutral properties and simpler turbomachinery design compared to helium Brayton cycles and water Rankine cycles.

However, when the available cooling source is, for example, air at ambient temperature (e.g. concentrated-solar-power technologies located in desert areas),  $\text{CO}_2$  transcritical cycles cannot be used since the low critical temperature of pure  $\text{CO}_2$ , 31 °C, prevents  $\text{CO}_2$  from condensation when air temperature is higher than 30 °C. To benefit from the use of transcritical cycles, instead of the more compression power consumer Brayton ones, it is useful to increase the critical temperature of pure  $\text{CO}_2$  to 40–50 °C by adding a small quantity of a properly selected second component (inorganic compounds such as  $\text{TiCl}_4$ ,  $\text{TiBr}_4$ ,  $\text{SnCl}_4$ ,  $\text{SnBr}_4$ ,  $\text{VCl}_4$ ,  $\text{VBr}_4$ ,  $\text{GeCl}_4$ , fluorocarbons such as  $\text{C}_6\text{F}_{14}$ , etc.) to carbon dioxide [5–7]. In [5], it is shown how the critical temperature of the system may be increased by adding a small molar amount of  $\text{C}_6\text{F}_{14}$  or  $\text{TiCl}_4$  to  $\text{CO}_2$ .

Similarly, the increase of the critical point of fluids allowed by the use of mixtures could also enable the more efficient use of condensing cycles instead of supercritical ones in very low-temperature applications. A typical example is represented by power cycles which reject their thermal heat into a stream of liquefied natural gas (cool source of the cycle), in order to convert it from liquid to vapour phase, from ambient temperature to –150 °C [8]. Currently, the use of particularly efficient pure fluids (e.g. nitrogen, argon, oxygen), which are fluids which critical temperature is lower than the minimum temperature achieved by the cycle, has been mainly proposed. Mixing one of these low critical temperature components with a small amount of a high critical temperature one (e.g. krypton) could allow the improvement of an increase of the critical temperature of the fluid and thus the lower-power consuming compression of a liquid instead of a gas.

### 2.2.3. Major scientific obstacles

Nowadays, the scale of the deployment of mixtures does not yet reflect the numerousness of studies undertaken to evaluate the potential of using multicomponent working fluids.

Despite the resources allocated in this research domain over the past years, this research topic still encounters some major scientific obstacles, described in the following sections 2.2.3.1–2.2.3.3, which feed the uncertainty surrounding the results of these studies and which limit the reliable use of multicomponent working fluids.

#### 2.2.3.1. Thermodynamics of mixtures

The design of multicomponent working fluids requires mixing pure fluids characterised by some very different thermodynamic properties, which are typically critical coordinates or triple points and saturation properties.

Mixing different pure fluids (which generally involves two species) may result in a multicomponent system which thermodynamic properties highly deviate from those of each

pure component that forms the mixture. Such a deviation quantifies the level of non-ideality of the mixture (i.e. the importance of molecular interactions) and, thus, the difficulty in modelling its thermodynamic properties. An extreme typical example is represented by binary mixtures of type III (according to the classification of van Konynenburg and Scott) which present a specific composition range for which critical pressure achieves infinitely high values [5, 9].

The main issue affecting applied thermodynamics concerns the absence of a universal model (equation of state) which enables the reliable prediction of thermodynamic properties of mixtures characterised by a more or less pronounced level of non-ideality, without relying on experimental data. Still today, in fact, all the available equations of state contain parameters which need to be calibrated or, at least, validated over experimental data [10, 11].

However, the level of empiricism of thermodynamic models (mostly cubic and molecular-based equations of state) is decreasing over the years, meaning that parameters, which account for the incapability of the thermodynamic theory to model the reality, are more and more representative of physical quantities. For example, the modelisation of mixture properties by means of cubic equations of state requires the use of mixing rules to account for molecular interactions.

The application of more theoretically grounded mixing rules (e.g. the latest excess Helmholtz energy-based mixing rules instead of quadratic van der Waals mixing rules) enables the more accurate and reliable calculation of thermodynamic properties of mixtures [12, 13]. The same consideration also applies to molecular-based models [14, 15].

A typically recognised problem is the unreliable calculation of the critical region and two-phase thermodynamic properties of multicomponent working fluids intended for closed power cycles, by currently available thermodynamic models and, also, simulation tools based on inappropriate available algorithms.

Furthermore, the uncertainty of measurement of some thermodynamic properties (e.g. specific heat capacities or vapour-liquid equilibrium properties of highly non-ideal mixtures) is still too high to enable their reliable use for calibrating and validating models.

#### 2.2.3.2. *Transport properties of mixtures in two phase*

The available scientific results on forced convection vaporisation or condensation of zeotropic mixtures are very limited. Many studies have analysed the performance of heat exchangers crossed by zeotropic fluids, without providing information on the local conditions in the evaporating streams [16].

The lack of information on transport properties actually feeds the overall uncertainty affecting heat exchangers sizing, on the one hand, and pressure drops evaluation, on the other.

#### 2.2.3.3. *Thermal stability of mixtures*

The thermal stability of a working fluid or a mixture represents its capability to preserve all its main physical properties unchanged because of the heating. This is a key parameter for the selected working fluid in a power plant, since even a partial decomposition may cause loss of

power or, even worse, the occurrence of serious faults in fundamental components, such as turbines or heat exchangers. Moreover, as a general rule, the greater the thermal stability, the greater the maximum temperature at which the fluid can be used and the better the performance of the power plant.

Different approaches have been proposed so far to assess the thermal stability of pure fluids [17]. However, all experimental laboratories that investigate the thermal stability of fluids only focus on pure fluids, and, at present, an experimental technology being able to test the thermal stability of mixtures is still absent according to authors' knowledge.

### 2.3. Reactive fluids

Researches undertaken during the last years on working fluids have ignored the promising results published by a dozen scientists in the years 1960–1990 which reversibly proposed reactive working fluids for mainly military, spatial and power production applications.

Over that period, four reactive systems ( $P_4 \rightleftharpoons 2P_2$ ,  $Al_2Cl_6 \rightleftharpoons 2AlCl_3$ ,  $2NOCl \rightleftharpoons 2NO + Cl_2$ ,  $N_2O_4 \rightleftharpoons 2NO_2 \rightleftharpoons 2NO + O_2$ ) and two generalised reacting schemes ( $A_2 \rightleftharpoons 2A$ ;  $2A \rightleftharpoons 2B + C$ ) have been considered. Preliminary results obtained in these studies have shown that the utilisation of certain reactive fluids ( $N_2O_4$ ,  $NOCl$ ) rather than pure fluids and inert mixtures can lead to the increase of the conversion efficiency of power cycles of more than 10 percentage points [18–20].

In particular, it has been observed [18, 19, 21–24] that such an improvement follows from the specific evolution of the equilibrium composition of the reactive fluid and from the involvement of the energy of reaction; more precisely, authors attested that the presence of a proper chemical reaction leads to the increase of the power output, resulting from the augmented (1) energy released by the fluid during expansion and (2) energy exchanged in heat exchangers, thanks to the increased heat capacity and coefficients of heat exchange of reactive fluids.

It can be easily shown that the adoption of reactive fluids characterised by an exothermic reaction ( $\Delta_R H^\circ < 0$ ) along fluid expansion leads to an increased production of produced work ( $\delta w$ ):

$$\delta w^{\leftarrow} \stackrel{\text{Adiab.}}{=} dh = \underset{\substack{\text{Perfect} \\ \text{gas}}}{c_p} dT + \left( \frac{\partial h}{\partial P} \right)_{T,n} dP + \Delta_R H^\circ \frac{d\xi}{\dot{m}}$$

$$= \underset{\substack{<0 \\ \text{along} \\ \text{fluid} \\ \text{expansion}}}{c_p} dT + \Delta_R H^\circ \frac{d\xi}{\dot{m}} \quad (7)$$

Despite the promising results revealed by these studies on reactive fluids, nonetheless obtained under simplification assumptions of perfect gas mixtures, researches on reactive working fluids have been abandoned at their preliminary stage of development. Many scientific obstacles, in fact, limited and still limit the applicative study of reactive working fluids.

### 2.3.1. Major scientific obstacles

Knowledge gaps listed in Section 2.2.3, which regard the thermodynamics, transport properties and thermal stability of mixtures, clearly represent barriers for the deployment of reversible reactive working fluids too, as they are, by definition, mixtures. Moreover, the extensive analysis of the potentiality offered by the specific use of these fluids would also require addressing the specific lacks briefly described subsequently.

#### 2.3.1.1. Thermodynamics of adiabatic expanding and compressing fluids, which undergo reversible and instantaneous reactions

So far, thermodynamic transformations of fluids in expanders and compressors have only been studied under the assumption of inert fluid. The preliminary researches on reactive fluids do not report any indication about the thermodynamic treatment of the expansion/compression of a reactive fluid.

Different from inert (iso-composition) gaseous adiabatic expansions, which are isentropic in the case of zero thermodynamic losses, reactive expanding fluids need to be modelled as a series of infinitesimal expansions, of pressure variation  $dP$ , each one subdivided into two transformations: (1) iso-composition adiabatic expansion, from pressure  $P$  to pressure  $P + dP$ ; and (2) adiabatic isobar reaction, at the pressure  $P + dP$ .

No one theoretical reference has been found in the study that analyses this thermodynamic transformation.

#### 2.3.1.2. Theoretical comprehension of the dependence of cycle performance and design on the type of chemical reaction

There exist many types of chemical reactions which, in the direction of their spontaneous evolution, may be characterised by a fast or a slow kinetics, by an increasing or a decreasing number of moles and which may be exothermic or endothermic. The effect of the occurrence of a reaction during fluid expansion or compression, fluid heating or cooling depends on its characteristics, which can beneficiate or disadvantage the efficiency of the energy conversion process.

With the aim of expanding the research of optimal working fluids to reactive mixtures, it is necessary to preliminarily address these points.

## 3. Conclusion

This chapter aims to boost researches devoted to the comprehension of the impact on power cycles of the characteristics of their working fluid. To this end, the chapter presents the state of the art on pure and multicomponent inert and reactive working fluids, highlighting the major scientific obstacles that nowadays primarily need to be overcome in order to allow a thorough research of the best working fluid for each application of closed power cycles:

- definition of a predictive and universal thermodynamic model for mixtures;
- experimental and theoretical investigation of the transport properties of mixtures;
- experimental and theoretical assessment of mixture thermal stability;
- comprehension of the effects that reactive fluid characteristics have on cycle performance and design.

## Acknowledgements

The authors wish to thank ASME IGTI ORC Power Systems—KCORC for funding the publication of this chapter.

## Nomenclature

### Symbols

$T$	temperature
$P$	pressure
$h$	molar enthalpy
$s$	molar entropy
$\Delta_R H^\circ$	enthalpy of reaction
$\dot{\xi}$	rate of extent of reaction
$\dot{m}$	mass flow rate
$M$	molar weight
$c_p, c_v$	molar heat capacity at constant pressure and constant volume
$v$	molar volume
$A, B, A^*, B^*$	parameters
$w$	specific work
$R$	universal gas constant

### Subscripts

$c$	critical property
$r$	reduced property



### Superscripts

- perfect gas property
- sat* saturation property

### Accents

- specific mass property

### Author details

Silvia Lasala\*, Romain Privat and Jean-Noël Jaubert

Address all correspondence to: [silvia.lasala@univ-lorraine.fr](mailto:silvia.lasala@univ-lorraine.fr)

Ecole Nationale Supérieure des Industries Chimiques, Laboratoire Réactions et Génie des Procédés, Université de Lorraine, Nancy, France

### References

- [1] Astolfi M, Alfani D, Lasala S, Macchi E. Comparison between ORC and CO<sub>2</sub> power systems for the exploitation of low-medium temperature heat sources. *Energy*. 2018
- [2] Macchi E. 1 – Theoretical basis of the organic Rankine cycle. In: *Organic Rankine Cycle (ORC) Power Systems*. 2017. pp. 3-24. Available from: <https://doi.org/10.1016/B978-0-08-100510-1.00001-6>
- [3] Dostal V, Hejzlar P, Driscoll MJ. The supercritical carbon dioxide power cycle: Comparison to other advanced power cycles. *Nuclear Technology*. 2006;**154**(3):283-301. Available from: <https://doi.org/10.13182/NT06-A3734>
- [4] El-Wakil MM. *Nuclear Power Engineering*. New York, USA: Mc Graw-Hill; 1962. 556 p.
- [5] Lasala S, Bonalumi D, Macchi E, Privat R, Jaubert JN. The design of CO<sub>2</sub>-based working fluids for high-temperature heat source power cycles. In: *Energy Procedia*. 2017. pp. 947-954. Available from: <https://doi.org/10.1016/j.egypro.2017.09.125>
- [6] Lasala S, Invernizzi C, Iora P, Chiesa P, Macchi E. Thermal stability analysis of Perfluorohexane. *Energy Procedia*. 2015;**75**. Available from: <https://doi.org/10.1016/j.egypro.2017.09.125>
- [7] Bonalumi D, Macchi E, Lasala S. Miscela a base di anidride carbonica come fluido di lavoro in cicli termodinamici. 2017

- [8] Invernizzi CM, Iora P. The exploitation of the physical exergy of liquid natural gas by closed power thermodynamic cycles. An overview. *Energy*. 2016;**105**:2-15. Available from: <https://doi.org/10.1016/j.energy.2015.09.020>
- [9] Privat R, Jaubert J-N. Classification of global fluid-phase equilibrium behaviors in binary systems. *Chemical Engineering Research and Design*. 2013;**91**(10):1807-1839. Available from: <https://doi.org/10.1016/j.cherd.2013.06.026>
- [10] Lasala S, Chiesa P, Privat R, Jaubert J-N. Optimizing thermodynamic models: The relevance of molar fraction uncertainties. *Journal of Chemical & Engineering Data*. 2017 Feb 9; **62**(2):825-832. Available from: <http://doi.org/10.1021/acs.jced.6b00853>
- [11] Lasala S, Chiesa P, Privat R, Jaubert J-N. Modeling the thermodynamics of fluids treated by CO<sub>2</sub> capture processes with Peng-Robinson + residual Helmholtz energy-based mixing rules. *Industrial and Engineering Chemistry Research*. 2017;**56**(8). Available from: <http://doi.org/10.1021/acs.iecr.6b04190>
- [12] Lasala S, Chiesa P, Privat R, Jaubert J-N. VLE properties of CO<sub>2</sub>-based binary systems containing N<sub>2</sub>, O<sub>2</sub> and Ar: Experimental measurements and modelling results with advanced cubic equations of state. *Fluid Phase Equilibria*. 2016;**428**:18-31. Available from: <https://doi.org/10.1016/j.fluid.2016.05.015>
- [13] Lasala S. *Advanced Cubic Equations of State for Accurate Modelling of Fluid Mixtures. Application to CO<sub>2</sub> Capture Systems*. Italy: Politecnico di Milano; 2016
- [14] Economou IG. Statistical associating fluid theory: A successful model for the calculation of thermodynamic and phase equilibrium properties of complex fluid mixtures. *Industrial and Engineering Chemistry Research*. 2002;**41**(5):953-962. Available from: <http://doi.org/10.1021/ie0102201>
- [15] Tan SP, Adidharma H, Radosz M. Recent advances and applications of statistical associating fluid theory. *Industrial and Engineering Chemistry Research*. 2008;**47**(21):8063-8082. Available from: <http://doi.org/10.1021/ie8008764>
- [16] Incropera FP, DeWitt DP, Bergman TL, Lavine AS. *Fundamentals of Heat and Mass Transfer*. Vol. 6, Water. 2007. 997 p. ISBN: 978-0471457282
- [17] Invernizzi CM, Bonalumi D. 05 – Thermal stability of organic fluids for organic Rankine cycle systems. In: *Organic Rankine Cycle (ORC) Power Systems*. 2017. pp. 121-151. Available from: <http://doi.org/10.1016/B978-0-08-100510-1.00005-3>
- [18] Stochl RJ. Potential Performance Improvement Using a Reacting Gas (Nitrogen Tetroxide) as the Working Fluid in a Closed Brayton Cycle - NASA TM-79322; 1979
- [19] Angelino G. Performance of N<sub>2</sub>O<sub>4</sub> gas cycles for solar power applications. *Proc Inst Mech Eng 1847-1982 (vols 1-196)*. 1979;**193**:313-320. Available from: [https://doi.org/10.1243/PIME\\_PROC\\_1979\\_193\\_033\\_02](https://doi.org/10.1243/PIME_PROC_1979_193_033_02)
- [20] Huang HM, Govind R. Use of dissociating gases in Brayton cycle space power systems. *Industrial and Engineering Chemistry Research*. 1988;**27**:803-810. Available from: <https://doi.org/10.1021/ie00077a015>

- [21] Huang SH, Radosz M. Equation of state for small, large, polydisperse and associating molecules. *Industrial and Engineering Chemistry Research*. 1990;**29**:2284-2294. Available from: <http://doi.org/10.1021/ie00107a014>
- [22] Cheung H. Dissociating gas as a working fluid for space plant. *Energy Convers*. 1968;**8**: 125-128. Available from: [https://doi.org/10.1016/0013-7480\(68\)90114-9](https://doi.org/10.1016/0013-7480(68)90114-9)
- [23] Hasah MZ, Martin RC. Use of dissociating gases as primary coolants and working fluids in power cycles for fusion reactors. *IASMiRT*; 1989. Available from: [https://repository.lib.ncsu.edu/bitstream/handle/1840.20/29799/DC\\_250636.pdf?sequence=1&isAllowed=y](https://repository.lib.ncsu.edu/bitstream/handle/1840.20/29799/DC_250636.pdf?sequence=1&isAllowed=y)
- [24] Jacobs TA, Lloyd JR. The influence of the equilibrium dissociation of a diatomic gas on Brayton-cycle performance. *Journal of Applied Mechanics*. 1963:288-290. Available from: <https://doi.org/10.1115/1.3636527>

IntechOpen