



# Chemisorption power generation driven by low grade heat – Theoretical analysis and comparison with pumpless ORC



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## HIGHLIGHTS

- Thermochemical sorption power generation has been theoretically analysed.
- Pumpless ORC has been evaluated and compared with thermochemical sorption cycles.
- Four metallic salts have been used and analysed in sorption cycles.
- Three different working fluid have been used and analysed in pumpless ORC.

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## ABSTRACT

Sorption cycles have been extensively developed for waste heat recovery to deliver cooling, heating, and electricity. Chemisorption cycles using metallic salts as sorbents and ammonia as working fluid have been explored in this work for the maximum potential of pure power generation. In order to get better understanding and more insights, resorption power generation cycle (RPGC) has been theoretically investigated and compared with pumpless organic Rankine cycle (PORC). The PORC operates without a liquid pump in conventional ORC and shares the similar configuration with RPGC. Three different organic fluids (pentane, R123 and R245fa) used in PORCs and four different reactant salts (manganese chloride, strontium chloride, barium chloride and sodium bromide) used in RPGCs have been analysed and evaluated in terms of the power generation capacity, thermal efficiency and energy density under the conditions of heat source temperature from 60 °C to 180 °C and heat sink temperature at 30 °C. The PORCs have higher thermal efficiency of work output for most cases in the studied scenarios, while RPGCs are evidently superior on energy density, at least as twice large as that of the PORCs studied. RPGC and PORC both have intermittent and dynamic operation, and the former one has the potential to have multiple energy productions or perform as energy storage.

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## 1. Introduction

Due to the strengthened awareness of the importance of sustainability, sorption cycles including absorption and adsorption have enjoyed the increasing attention because of their remarkable advantages of benign environmental impact and avoidance of using depletable fossil fuels. These technologies have been extensively developed for air conditioning and refrigeration [1–3], heat pump and heat transform [4,5], desiccant and desalination [6,7], energy storage [8,9], etc. In recent decades, there has been increasing efforts of investigation and promotion on sorption power generation cycles through the integration with turbine/expander [10–13]. Sorption technology will play a major role in the low

carbon future regardless of which kind of energy demand – heating, or cooling, or power [14].

Maloney and Robertson [15] were among the first to study ammonia–water based absorption power generation cycle around 1950s. Later on Kalina cycle was proposed around 1980s [10] and followed by a thriving growth of the family of Kalina Cycle System (KCS) [16–18]. The great potential of efficiency improvement in KCSs justifies further researches and developments on absorption-based power generation, and that implies a promising future of this technology. Goswami cycle was proposed in 1998 to combine an ammonia-based Rankine cycle and an ammonia–water absorption cycle for producing cold and power simultaneously [11]. On the other hand, with regard to solid–gas adsorption power generation, Wang et al. [12] and Bao et al. [13,19] have reported theoretical analysis, numerical simulation and lab-scale prototype demonstration in succession on the cogeneration

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## Nomenclature

|            |                                            |
|------------|--------------------------------------------|
| $c_p$      | specific heat (J/(kg K))                   |
| $h$        | enthalpy (J/kg)                            |
| $\Delta H$ | enthalpy change (J/mol (NH <sub>3</sub> )) |
| $m$        | mass (kg)                                  |
| $N$        | molar number (mol)                         |
| $P$        | pressure (Pa)                              |
| $Q$        | heat (J)                                   |
| $T$        | temperature (°C)                           |
| $u$        | internal energy (J/kg)                     |
| $V$        | volume (m <sup>3</sup> )                   |
| $x$        | vapour quality (–)                         |
| $X$        | global conversion of the reaction (–)      |
| $W$        | mechanical work (J)                        |
| SPC        | specific power capacity (kJ/kg)            |

|        |                        |
|--------|------------------------|
| Greeks |                        |
| $\eta$ | thermal efficiency (–) |

|            |               |
|------------|---------------|
| Subscripts |               |
| c          | condensation  |
| e          | evaporation   |
| l          | large         |
| s          | small         |
| sen        | sensible      |
| W          | work          |
| wf         | working fluid |

performance of the metallic salt–ammonia chemisorption systems. It was concluded that the adsorption-based cogeneration system could have greater potential of cooling production than Goswami cycle [12]. The experimental tests demonstrated the challenges of the integration with the expander and the obstacles was mainly originated from the expander [19].

The integration with turbomachinery opens up enormous possibilities of new advanced and versatile cycles based on solid–gas sorption, and it also expands the spectrum of technologies on low grade heat recovery. Doubtlessly, new challenges come along with new technologies. It is well-known that a typical single-effect ammonia-based chemisorption refrigeration cycle (termed as conventional adsorption cycle in the context) consists of one solid sorbent-contained reactor, one condenser and/or one evaporator. Another type of chemisorption cycles substitutes one secondary reactor containing a secondary sorbent for the condenser/evaporator in the conventional adsorption cycle, which is termed as resorption cycle in many articles [20–22]. In most cases, a resorption cycle can be at comparatively lower working pressure than a conventional adsorption cycle when with a given primary sorbent, depending on the used secondary sorbent. The downsides of operating at lower pressure is that the condensing temperature for the adsorption heat dissipation has to be lower than it is necessary in conventional adsorption cycle; additionally, it is unfavourable with respect to mass transfer issue especially during the low-pressure process of cold generation [23]. Nevertheless, when it comes to the integrated system for power generation, resorption cycle can take advantage of the lower equilibrium pressure of the secondary sorbent so that the pressure difference between upstream and downstream of the expander is amplified when with the given primary sorbent. In this instance, the improvement in integrated resorption systems for pure power generation is worthwhile exploring. There has been massive works on pure refrigeration/heat pump performance but a handful of works on cogeneration performance of chemisorption cycles. The present work will for the first time reveal the potential of pure power generation based on resorption cycle (resorption power generation cycle, RPGC), i.e. mechanical energy production in both half cycles.

Amidst various technologies to recover low grade heat for power generation, ORC has been widely recognised as promising and feasible [24]. Recently, a concept of pumpless ORC (PORC) has been proposed to eliminate the working fluid pump for a more compact and efficient arrangement, because the pump tends to cause the most critical decline in the net cycle efficiency in small scale systems [25,26]. The omitting of the liquid pump turns the ORC to a batched operation, as similar with the RPGCs, instead of the working fluid circulating through each system component

one after another. An evaporator, one expander and one condenser are connected in sequence with valves controlling, the manipulation of which can exchange the role of evaporator and condenser. The external thermal constraints swap periodically between two vessels (the evaporator and the condenser) to create the thermodynamic state swing of the working fluid so that the working fluid flows back and forth through the expander for power generation.

The present work has conducted theoretical thermodynamic evaluations in terms of thermodynamic states, thermal efficiency of work output, energy density and specific power capacity to explore the maximum potential of RPGCs and also compare it to PORC since these two power generation cycles have similar configuration and operating manner. The RPGCs using different pairs of working sorbent salts have been investigated, and four metallic salts were used to group different pairs. They are manganese chloride (MnCl<sub>2</sub>), strontium chloride (SrCl<sub>2</sub>), barium chloride (BaCl<sub>2</sub>) and sodium bromide (NaBr) as they represent different thermodynamic equilibrium. It should be noted that the resorption system with a pair of two same salts has not been reported elsewhere. Meanwhile, three different organic working fluids, pentane, R123 and R245fa, have been evaluated for PORC.

## 2. Thermodynamic cycles and analysis methods

### 2.1. Adsorption power generation cycle

The conventional adsorption power generation cycle (APGC), RPGC and PORC can employ the same configuration as depicted in Fig. 1. In an APGC system, one of the vessels is adsorption/desorption reactor that contains compressed solid composite sorbent of metallic salts and porous substances (like expanded graphite, activated carbon and vermiculite), while the other vessel serving as condenser/evaporator is filled with the working fluid. An expander is mounted in between these two vessels, and the pipeline is arranged to allow the working fluid to pass through the expander in either direction for two half-cycle power generation.

Fig. 2 exemplifies an ideal thermodynamic cycle based on BaCl<sub>2</sub> (0–8NH<sub>3</sub>) reaction in P–T diagram and T–S diagram. The <sup>1</sup>red line in Fig. 2(a) is the equilibrium line of BaCl<sub>2</sub> ammoniate while the red line in Fig. 2(b) represents the states of the desorbed ammonia from BaCl<sub>2</sub> ammoniate at different desorption temperatures. At the beginning of APGC, there is a pre-expansion period where all valves are closed, while the adsorbent reactor is heated to a higher equilibrium

<sup>1</sup> For interpretation of color in Fig. 2, the reader is referred to the web version of this article.

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