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Energy and exergy analysis of the Kalina cycle for use in concentrated solar power plants with direct steam generation

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Abstract

In concentrated solar power plants using direct steam generation, the usage of a thermal storage unit based only on sensible heat may lead to large exergetic losses during charging and discharging, due to a poor matching of the temperature profiles. By the use of the Kalina cycle, in which evaporation and condensation takes place over a temperature range, the efficiency of the heat exchange processes can be improved, possibly resulting also in improved overall performance of the system. This paper is aimed at evaluating the prospect of using the Kalina cycle for concentrated solar power plants with direct steam generation. The following two scenarios were addressed using energy and exergy analysis: generating power using heat from only the receiver and using only stored heat. For each of these scenarios comparisons were made for mixture concentrations ranging from 0.1 mole fraction of ammonia to 0.9, and compared to the conventional Rankine cycle. This comparison was then also carried out for various turbine inlet pressures (100 bar to critical pressures). The results suggest that there would be no benefit from using a Kalina cycle instead of a Rankine cycle when generating power from heat taken directly from the solar receiver. Compared to a baseline Rankine cycle, the efficiency of the Kalina cycle was about around 5% lower for this scenario. When using heat from the storage unit, however, the Kalina cycle achieved efficiencies up to 20% higher than what was achieved using the Rankine cycle. Overall, when based on an average assumed 18 hours cycle, consisting of 12 hours using heat from the receiver and 6 hours using heat from the storage, the Kalina cycle and Rankine cycle achieved almost equal efficiencies. A Kalina cycle operating with an ammonia mole fraction of about 0.7 returned an averaged efficiency of about 30.7% compared to 30.3% for the Rankine cycle.

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1. Introduction

Concentrated solar power (CSP) is expected to play an important part in future energy infrastructure. The International Energy Agency projects that with proper support, CSP could provide 11.3% of the total world electricity production by 2050 [1]. At present, most CSP projects still rely on subsidies, but with improvements to system and component design future CSP plants may be able to compete with fossil fuel based energy sources [2].

Most commonly, CSP plants operate by heating a heat transfer (HT) fluid such as thermal oil or molten salt in the solar receiver(s). The heat is then transferred to the power block by heat exchange between the HT fluid and the working fluid. Consequently, the properties of the HT fluid impose limitations on the operation parameters of the power block. In particular, the maximum temperature at which the HT fluid remains chemically stable limits the maximum temperature which the working fluid may reach. For thermal oils the maximum operating temperature is around 400 °C, and for molten salts around 500-550 °C [3]. While molten salts have a higher maximum temperature they also have the disadvantage of a relatively high melting point (120-200 °C) [3]. A high melting point increases the risk of solidification in the receiver(s). To avoid this, heat must be expended to keep the salt warm during periods with insufficient or no solar irradiation. Heat which could otherwise be used for power generation.

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**Nomenclature**

- $c_p$: Specific heat capacity [J/kg-K]
- CSP: Concentrated solar power
- DSG: Direct steam generation
- $\dot{E}$: Exergy flow rate [kW]
- $\dot{H}$: Enthalpy rate [kW]
- HP: High pressure
- HT: Heat transfer
- LP: Low pressure
- $P_{cr}$: Critical pressure [bar]
- $\dot{Q}$: Heat transfer rate [kW]
- $S$: Entropy rate [kW/K]
- $S_{gen}$: Rate of entropy generation [kW/K]
- $T$: Temperature [K]
- TES: Thermal energy storage
- $\dot{W}_{net}$: Net power output [kW]

**Subscripts**

- 0: Dead state
- dest: Destroyed
Direct steam generation (DSG), in which the working fluid is heated in the solar receiver(s) and then sent directly to the power block, is not limited by usage of a HT fluid (Figure 1). This means that higher temperatures may be reached, resulting in better thermal efficiencies. However, it is more complicated to integrate DSG with thermal energy storage (TES) [4]. In a typical TES based on sensible heat storage, the constant evaporation and condensation temperature of water/steam results in large exergy losses during heat transfer to and from the storage. The problem can be circumvented by for instance dividing the storage into three parts and using a phase changing material to store the latent heat [4]. However, such a system is more complex and expensive than the sensible heat only alternative. While not necessary, TES is often considered an integral part of modern CSP systems as it improves the reliability, flexibility and profitability of the plant [5].

For parabolic troughs, small-scale test plants have successfully used DSG at pressures up to 100 bar [6]. For higher pressures solar power towers are probably a more suitable solution due to the more compact receiver and lack of moving parts.

1.1. The Kalina cycle

The Kalina cycle is a variation of the Rankine cycle in which the working fluid is a mixture of ammonia and water. Ammonia and water forms a zeotropic mixture where evaporation and condensation take place over a temperature range rather than at a constant temperature. When using DSG, the varying evaporation temperature of the Kalina cycle can improve the match between the temperature profile of the working fluid and a TES based on sensible heat storage, both during charging and discharging. Ideally, this should result in a more efficient system design.

For the power block, using stored heat as the heat source results in a situation similar to that of a bottoming cycle in a combined cycle design. Kalina cycles used as the bottoming cycle in combined cycles have been shown to produce upwards of 40% more power than a single pressure Rankine cycle [7] and to achieve a 10-20% higher second law efficiency [8]. However, Dejfors et al. [9] showed that for a direct fired biomass cogeneration plant, which is a situation similar to DSG in the receiver, the Kalina cycle did not offer any improvements over the Rankine cycle.

This paper is aimed at evaluating whether there is a benefit to using the Kalina cycle for CSP plants with DSG compared to the conventional Rankine cycle. Different mixture compositions are compared in an effort to investigate how the ammonia mole fraction affects the first law efficiency of the cycle and the rate of exergy destruction in the various components. Comparisons are made both for heating the mixture directly in the solar receiver and by heat exchange with the TES.

Section 2 presents the Kalina cycle design and the connection with the rest of the CSP system. Section 3 offers a more detailed description of the methodology and assumptions used to generate the results which are then presented and analysed in section 4. A discussion of the findings is given in section 5.
A second paper by the same authors [10] presents a similar cycle in a CSP plant with a turbine inlet temperature of 450 °C, but considers a situation where the cycle is always run at the design point and with a constant heat input. To achieve this, the storage included an external heater which was used when necessary to maintain a constant turbine inlet temperature. This simplified the operation of the cycle, but also imposed a different set of design conditions.

2. System description

For the solar receiver, the outlet temperature was set at 550 °C. This temperature is achievable in solar tower setups as well as in modern parabolic troughs [6]. In the investigation, emphasis was placed on the design of the power block, and the efficiency of the solar collector/receiver subsystem was not taken into consideration.

Ammonia at high temperatures (+400 °C) may cause issues with nitridation. It is unclear how this issue affects the Kalina cycle as it has not been possible to find any specific data in the literature concerning the issue of nitridation when using ammonia-water mixtures at the temperatures and pressures considered in this work. However, the Canoga park test plant performed tests using ammonia-water mixtures up to temperatures of 515 °C and pressures of 115 bar [11]. Under these conditions the effect of nitridation was found to be insignificant as water inhibits the process. A 2002 patent by Alexander Kalina [12] further claims that additives added to the working fluid may increase stability of the mixture and prevent issues with nitridation up to temperatures of 2000 °F (1090 °C) and pressures up to 10,000 Psi (690 bar).

The molten salt Hitec XL was chosen as the storage medium. Hitec XL has a usable temperature range of 120-500 °C [3]. In the model this was limited to 130-490 °C to ensure that the salt did not exceed its usable range. The system was also constrained to utilise the full temperature range of the storage medium in order to minimise the physical size of the storage.

The chosen layout for the Kalina cycle is a simplified version of the one used in the Canoga park test.

Figure 2. Schematic diagram of the modelled Kalina cycle
plant [11]. A schematic diagram is given in Figure 2. Temperature, pressure and ammonia mole fraction are specified at the turbine inlet (1). Heat from the turbine outlet stream (2) is used to preheat stream (12) up to a temperature which is determined by the pinch point. Additional heat is then recovered from stream (3) to heat stream (14). Stream (4) is then mixed with a lean ammonia solution from the separator (18) to form the basic solution (5). This solution is then condensed (6), pumped to an intermediate pressure (7) and separated into two streams (8) and (14). The split fraction is determined by the model such that the temperature in (4) is as low as possible. Stream (14) is sent to the vaporiser where it is partially evaporated using the heat from stream (3). The vapour fraction after the vaporiser (15) is determined by the pinch point. Stream (15) then enters the separator which separates the stream into an ammonia rich vapour (19) and a lean liquid (16). Heat from stream (16) is used to preheat stream (11). Stream (16) is then throttled and mixed with stream (4). The rich vapour (19) is mixed with the basic solution in stream (8) to again form the working solution and is then condensed in the HP condenser. The state after the HP condenser is saturated liquid and combined with the pinch point and cooling water temperature constraints, the HP condenser determines the intermediate pressure, as the LP condenser determines the turbine outlet pressure. After the HP condenser (10) the working solution is pumped to the specified turbine inlet pressure and sent through the preheaters (13). When using the receiver stream, stream (13) is simply heated to the specified temperature of 550 °C (1), whereas when using salt from the storage unit the heat exchange follows a counterflow arrangement and the temperature is dictated by the salt. Depending on the pressure and ammonia mole fraction, the temperature at point (13) may exceed the required outlet temperature of the salt. In this case the temperature in (13) is no longer governed by the pinch point in the second preheater, but is instead determined by the salt heat exchanger.

3. Methodology

3.1. Exergy analysis

Exergy, unlike energy, represents the quality of a stream of energy rather than the quantity. As such the analysis of exergy flows and their destruction offers a better baseline for the performance of the cycle and its components. In this work the exergy analysis method follows the approach presented by Kotas [13] and centres around the entropy balance for a control volume:

$$\dot{S}_{\text{gen}} = \frac{dS}{dt} + \sum \dot{S}_{\text{out}} - \sum \dot{S}_{\text{in}} - \sum \frac{Q}{T_i} \geq 0$$

(1)

Here, $\dot{S}_{\text{gen}}$ represents the generated entropy in the control volume, $dS/dt$ the accumulation of entropy inside the control volume, $\sum \dot{S}_{\text{in}}$ and $\sum \dot{S}_{\text{out}}$ the flow of entropy in and out of the control volume respectively and $\sum Q/T_i$ is the entropy generation associated with heat transfer. Combining an exergy balance with the entropy balance for a control volume results in the Gouy-Stodola theorem [13]:

$$\dot{E}_{\text{dest}} = T_0 \dot{S}_{\text{gen}}$$

(2)

The Gouy-Stodola theorem offers a relatively simple approach to calculate the rate of exergy destruction, $\dot{E}_{\text{dest}}$, in various components based solely on the dead state temperature $T_0$ and the entropy generation. Furthermore, this approach also accounts for changes in chemical exergy associated with the change in chemical potential when changing the mixture composition, which is important in the mixing and separation processes. The dead state was set at 25 °C and 1.013 bar.
3.2. Modelling

Modelling was carried out in Aspen Plus v7.2 [14] and all models were steady-state models. The thermodynamic properties of the ammonia-water mixture were calculated using the Peng-Robinson equation of state with an extension by Boston and Mathias [15].

The properties of Hitec XL are not readily available in Aspen Plus. The Solar advisor model's reference manual provides a correlation which may be used to approximate the $c_p$ value of Hitec XL [16]. However, when compared to an assumption of a constant $c_p$ value, the maximum error obtained in the temperature range 130-490 °C was 3.4 °C. The error reached its maximum value in the evaporation section of the heat exchanger which reduced the impact of the error since the temperature difference here was already greater than the pinch point. Thus, for simplicity a constant $c_p$ value was assumed.

The condenser used cooling water, which was assumed to have an inlet temperature of 30 °C and a temperature rise of 15 °C. The cooling water is supplied to the two condensers in serial, i.e. first to the HP condenser and then to the LP condenser or vice versa. The order in which the condensers receive the cooling water affected the efficiency of the system. The optimal configuration further depends on the mixture composition. The cycle was optimised such that the order of water supply to the condensers which resulted in the highest cycle efficiency, for a given ammonia mole fraction, was used.

Further assumptions related to the modelling of the cycle were:
- Pressure drops and heat losses in components and piping were neglected.
- The turbine was assumed to have an isentropic efficiency of 0.80 and a mechanical efficiency of 0.98.
- The pumps were assumed to have an efficiency of 0.90.
- All heat exchangers were constrained to a pinch point temperature difference of at least 10 °C.
- The upper limit for the pressure into the turbine was set at the critical pressure. Critical pressures were interpolated from the experimental data of Sassen et al. [17].

In the case of pure water the cycle is replaced with a simple Rankine cycle consisting of a turbine, condenser, pump and receiver/salt heat exchanger. The Rankine cycle was constrained to the same set of boundary conditions and component constraints as were applied to the Kalina cycle.

4. Results

4.1. Heat input from solar receiver

When using only heat from the solar receiver, the simple Rankine cycle is preferable to the Kalina cycle (Figure 3.a). At constant pressure, increasing the ammonia fraction of the mixture decreases both the bubble and dew point temperatures. Compared to the constant evaporation temperature of pure water this increases the exergetic losses in the receiver (Figure 4). Normally this is offset by the Kalina cycle being able to achieve a higher pressure than the Rankine cycle. However, in the case of heat input from solar radiation there is no pinch point constraint on the pressure in either of the cycles. This is due to the solar radiation not having a distinct temperature profile. Simultaneously the exergy destruction in the turbine decreases with increasing ammonia mole fraction.

The Kalina cycle also offers a better match with the cooling water temperature leading to a smaller exergy destruction in the condenser. Although not enough to offset the increased exergetic losses in the receiver, the matche between the temperature profiles in the condensers reaches an optimum for a working solution with ammonia mole fraction of around 0.6-0.8, which helps explain the peak in performance of the Kalina cycle around this ammonia mole fraction.
4.2. Heat from storage

When power is generated using only heat from the storage unit, the temperature profile of the molten salt influences the maximum allowable pressure level in the cycle due to the pinch point constraint. In Figure 3.b only those points which correspond to allowable pressure levels are shown. At mole fractions of 0.3 and below the maximum allowable pressure is below the previously plotted minimum of 100 bar.
and as such only the point corresponding to the maximum allowable pressure for each specific mole fractions is plotted (Table 1). At mole fractions above 0.4 the tendency is similar to that of the scenario where only heat from the receiver was used. An ammonia mole fraction of 0.6-0.8 once again corresponds to the composition which offers the best fit with the cooling water. However in this scenario the curves are more flat around the optimum as the salt also limits the allowable temperature after the first preheater for mole fractions above 0.7 in order to satisfy the pinch point constraint.

Table 1. Maximum pressures for the simple Rankine cycle and lean ammonia working solutions when using the storage

<table>
<thead>
<tr>
<th>Mole fraction of ammonia [-]</th>
<th>Maximum pressure [bar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure water</td>
<td>12</td>
</tr>
<tr>
<td>0.1</td>
<td>29</td>
</tr>
<tr>
<td>0.2</td>
<td>51</td>
</tr>
<tr>
<td>0.3</td>
<td>92</td>
</tr>
</tbody>
</table>

5. Discussion

The defining feature of the Kalina cycle, the temperature glide during phase change, is primarily beneficial when utilising a sensible heat source such as waste heat [7,18,19] or in this case, molten salt. However, when not utilising a sensible heat source the temperature glide is only beneficial in the condensers. In their study of a direct fired biomass cogeneration plant, Dejfors et al. [9] were able to achieve very similar efficiencies for the Kalina cycle and a Rankine cycle with steam extraction and reheat, while in this work the Kalina cycle was inferior to even the simple Rankine cycle when using the receiver. Dejfors et al. [9] operated with a temperature difference from heat sink inlet to outlet of 40-60K as well as the Kalina cycle being allowed to operate at a higher pressure than the Rankine cycle. Both
these aspects favours the Kalina cycle, but in general when given the same pressure, the results presented in this paper suggest that the Kalina cycle would not be able to outperform the (steam) Rankine cycle.

5.1. Combined Generation

Fig. 6 shows a simplified calculated weighted average efficiency, based on an assumed daily operation pattern of 12 hours of using heat from the receiver followed by 6 hours of storage based generation. When possible the same pressure was used in both instances. When this was not possible, e.g. when the pressure violated the pinch point constraint in the storage scenario, the maximum pressure which satisfied all constraints was used instead. The results shown in Fig. 6 do not take part load performance into account, but are simplified by assuming that the cycle would always operate in its corresponding design state.

The results suggest only a minor difference in the expected efficiency when comparing the Kalina cycle with the simple Rankine cycle. The poor performance of the Rankine cycle when using stored heat was offset by improved efficiency when using the receiver, and vice versa for the Kalina cycle. Thus, the more storage based generation, the larger the benefit of using the Kalina cycle.

In a real plant the physical dimensions of components remain constant which means that part load performance of these components would have to be considered when the cycle switches from one operating state to another. Again, unlike the Rankine cycle, the Kalina cycle is able to operate at the same pressure level in both scenarios. Similarly, by properly choosing the discharge rate of the stored heat it would also be possible to maintain roughly the same mass flow in the system, reducing the difference between the two operating states to the turbine inlet temperature. While this difference would still affect the rest of the cycle, such as pinch points in the various heat exchangers, the impact is expected to be less than that of the Rankine cycle. However further work would be necessary to fully quantify these effects.

The primary disadvantage of the Kalina cycle lies in the increased complexity of the system and the increased cost of the larger number of components. The higher condensation pressure of the Kalina cycle will help offset some of these costs by reducing the size of the LP condenser and LP turbine stages. The better performance of the Kalina cycle when using the storage would also decrease the size and cost of the storage tank. Additional improvements could also be made to the Rankine cycle to increase the efficiency, such as adding regenerative preheating by steam extraction and a second pressure level. The latter would be particularly beneficial, since this would also increase the cycle efficiency when using stored heat which

Fig. 6. Simple weighted average cycle efficiency. Results are based on an assumed daily operation pattern of 12 hours of heating the working fluid directly in the receiver followed by 6 hours of generation based on stored heat.
is otherwise the primary downside of the Rankine cycle.

One of the constraints imposed on the storage is that the entire temperature range of the salt must be utilised. By relaxing this constraint it is possible to increase the efficiency of the power block at the cost of reducing the energy density of the storage. Decreasing the energy density would increase the capital cost of the storage. This potential trade-off is primarily relevant for the Rankine cycle, as the Kalina cycle is already able to utilise pressures all the way up to the pressure limit (which is the critical pressure).

6. Conclusion

In the present study a Kalina cycle for use in CSP plant based on DSG was modelled. The results suggest that in a system without TES there was nothing to gain by using a Kalina cycle instead of the conventional Rankine cycle. Compared to the Kalina cycle, the Rankine cycle achieved about 5% better efficiency for this scenario. However, when discharging the storage, the Kalina cycle was able to achieve an efficiency about 20% higher than that of the Rankine cycle.

The results suggest that averaged over the course of a working day (12 hours of using heat from the receiver and 6 hours of using the storage) the Kalina cycle and the Rankine cycle would achieve about equal efficiencies. The results also indicate that a mixture with an ammonia mole fraction of 0.60-0.70 resulted in the highest efficiency, which was 0.4 percentage point higher than that of the Rankine cycle.

References