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Development of a multi-level approach to model and optimise the Kalina Split Cycle for marine diesel engines

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Abstract

In the marine sector there is a strong motivation for increasing the propulsion system energy efficiency, mainly because of increasing fuel prices and stricter upcoming emission regulations. The Kalina cycle, based on a mixture of ammonia and water as working fluid, exhibits higher conversion efficiencies than conventional power cycles and could be suitable for this purpose. The Split Cycle technique provides a method to further increase the thermal efficiency, by reducing the thermodynamic losses in the heat recovery system. This is achieved by having two separate streams of different ammonia concentrations entering and leaving a first evaporator stage before being mixed at the inlet of a second evaporator stage. It seems that modelling efforts showing the advantages of the Split Cycle have not been presented in the literature yet. Thus, a thermodynamic model of the Split Cycle is introduced in this work. Modelling and optimisation of the rather complex cycle requires approaching the problem at different system levels. This paper investigates tools and methods suitable for demonstrating the feasibility and advantages of the Split Cycle. The integrated model developed and presented in this paper combines three sub-models all using the NIST REFPROP equations of state: a separator and mixing subsystem model to handle the inherent constraints of the Split Cycle, a component-based model to optimise the heat exchanger operating conditions, and a process model to investigate the complete thermodynamic cycle. Results suggest a 9% net power output increase and 7% higher thermal efficiency compared to the baseline case.

Keywords: Kalina Split Cycle, Multi-Level Modelling, Process Integration, Waste Heat Recovery

1. Introduction

The International Maritime Organisation, under the United Nations organisation, is expected to adopt an energy efficiency design index (EEDI) for ships in 2013. For this reason and because of increasing fuel prices, this sector is in need of technologies that could further improve the efficiency of propulsion systems [1].

In this context, growing attention is paid to waste heat recovery power cycles, with the Kalina Cycle among those. Named from its inventor Alexander Kalina in 1983 [2], this thermodynamic cycle is using a mixture of water and ammonia as working fluid.

It was intended for waste heat recovery in three main fields of application: geothermics at temperatures from 100-200°C [3–10], integrated combustion engine heat recovery mainly at temperatures around 300°C [11–15] and for gas turbines at even higher temperatures [16–20]. A well-documented and tested Kalina cy-
Nomenclature

Acronyms
EEDI Energy Efficiency Design Index
EOS Equation of State
IP Intermediate Pressure
NIST National Institute of Standards and Technologies
SC Split Cycle
TRF Tillner-Roth and Friend

Greek Symbols
$\Delta$ Difference between to states

Symbols
$\dot{m}$ Mass flow rate
$H$ Non-specific enthalpy
$h$ Specific enthalpy
$p$ Pressure
$Q$ Vapour quality
$S$ Mass flow rate splitting fraction

$T$ Temperature
$x$ Ammonia fraction by mass
$y$ Ammonia fraction by mole

Subscripts
b Boiling point
c Composite stream
d Dew point
e Exhaust gas
f Separator feed stream
i Inlet stream
l Lean ammonia concentration
L Liquid fraction
o Outlet stream
r Rich ammonia concentration
V Vapour fraction
w Working fluid

The specific feature of the SC is that two cold streams of different ammonia concentrations run through a preheater and a first evaporator stage. The two streams are then mixed before entering a second evaporator and a superheater.

The higher complexity of this process introduces additional degrees of freedom and unknowns at different system levels. There is therefore a need for a multi-level approach which addresses these modelling and optimisation challenges.

The approach and models developed to evaluate a Kalina SC are presented in the following. The thermodynamic performance of the modified heat recovery system is assessed in comparison with a baseline case, which is a conventional Kalina cycle based on exhaust gases.
at 346°C from marine diesel engines, as documented by Bombarda [25]. The baseline case cycle is a type of Kalina cycle which is common in the literature, among others documented by Leibowitz et al. [21] and Jonsson et al. [19]. The SC model presented in the present work maintains the same constraints and boundary conditions as the baseline case.

2. Kalina Split cycle

Ammonia-water is a zeotropic mixture, which means that vapour and liquid phases at equilibrium never have both identical temperatures and compositions. During evaporation and condensation processes, the liquid and vapour compositions of zeotropic mixtures will continually change, and the saturation temperatures of these two phases will vary in consequence. It is thus possible to affect the thermophysical properties of the Kalina working fluid either by changing the operating pressure or by varying the ammonia concentration of the mixture.

Ammonia, being more volatile than water, is the first component to evaporate. The ammonia concentration in the liquid phase progressively decreases, causing a continual rise of the boiling temperature. The existence of this temperature glide may lead to a better match between the temperature profiles of the heat source and the working fluid, reducing the internal irreversibilities of the heat recovery process.

In an attempt to further reduce them, Dr. Kalina proposed in his patent petitions an alternative arrangement of this power cycle, referred to as the Split Cycle [24]. Other work of the same author [26] suggested that this configuration could reach a 2nd law efficiency of 75-80% for various heat sources.

The idea of the SC is to use two separate streams of ammonia-water, with different concentrations, running through a first evaporator. An important constraint proposed by Kalina is to have the ammonia-rich stream exit the first evaporator as saturated vapour (dew point) while the ammonia-lean stream exits as saturated liquid (bubble point). This proposed constraint is important for minimising thermodynamic losses and is therefore adopted in this work, leaving an investigation of the consequences of this assumption for future work. The constraint makes it harder to set initial parameters and to optimise the cycle and is thus providing motivation for developing the presented methodology. The two streams are then mixed into a composite stream and the newly formed two-phase mixture is evaporated and superheated before running through the turbine.

The modified Kalina SC is illustrated in Figure 1. The main differences from the conventional configuration are the use of additional mixers, splitters, pumps and recuperators between the separator and the turbine. In the simple Kalina cycle, the ammonia-rich vapour at the top outlet of the separator flows through a recuperator first and then a mixer before being condensed, while the ammonia-lean liquid at the bottom flows through another recuperator before being throttled.

In the SC, the very ammonia-rich vapour is first split into two sub-streams (19 and 26). Both are partly diluted in different proportions with fractions of the very ammonia-lean liquid flow and pass a succession of two recuperators where they are cooled down. The richer of these two streams (22) is then condensed (23) and pumped (24), before it is preheated (25) and flows through the heat recovery system. The leaner stream (29) is pumped (30) and preheated (31) before running through the first evaporator. These two streams are then mixed at the same temperature (1) before entering the second evaporator (2) and the superheater (3).

The very ammonia-lean liquid from the bottom of the separator is split into three sub-streams. Two (16 and 17) are used to adjust the concentration and mass flow rate of the
two rich vapour sub-streams from the top of the separator. The latter (13) runs through a recuperator where it is cooled down (14) before being throttled (15) and mixed with the ammonia-rich solution out of the turbine system.

Theoretical studies showed that, compared to the conventional configuration, the SC induces a lower entropy generation because of the better match between the temperature profiles of the two cold streams and the heat source [26]. The gradient of the evaporation temperature curve can to some degree be adjusted to the temperature profile of the heat source by selecting the optimal composition of each of the two streams, as illustrated in Figure 2. The line from (25,31) to the point \( T_{rb} \) represent the preheating stage. From here to point (1), (2) and (3) the fully drawn line shows the heat transfer in the SC case. The upper dashed line show how the heat transfer would be if the stream were not split but instead the composite stream was used. The point \( T_b \) shows the boiling point of the composite stream, and it is clear that the pinch point temperature difference is much smaller and possibly violated in this case. The lower dashed line from \( T_{rbub} \) to (2), shows how the heat transfer would happen if only the rich stream concentration was used. Evaporation would occur at lower temperatures and thus likely causing a lower thermal efficiency.

3. Methodology

Given the constraint of having identical temperatures and pressures of the rich and lean streams exiting the first evaporator, whilst also requiring the rich stream to be saturated vapour and the lean stream saturated liquid, initial parameter estimation and subsequent optimisation at full process level are not feasible. The choice was made to build two sub-models which could accurately predict the op-
timum performance of the full process and subsequently obtain full process validation. In the next sub-sections, three modelling levels are considered and presented: thermodynamic property level, governing subsystems at component level and full process level.

3.1. Thermodynamic property level

Tillner-Roth and Friend (TRF) presented their model of the ammonia-water system in 1998 [27]. Their motivation was the rising interest in modelling the Kalina cycle and thus the arising need for an accurate model for this working fluid mixture over a wide range of concentrations, temperatures and pressures. At the time, there was seemingly no model covering both the liquid, two-phase and vapour domains with satisfying accuracy [27]. Based on a thorough survey [28] of the publicly available experimentally obtained properties for the system, a fundamental equation of state (EOS) which is claimed to be accurate up to 40 MPa was derived.

Thorin et al. [29] compared in 1999 the Tillner-Roth and Friend model with both experimental data and two other EOS derived for the ammonia-water system (Stecco-Desideri and Ibrahim and Klein). Analysis showed that the TRF EOS is generally more accurate than the two other EOS because of an additional correction factor. Additionally the TRF EOS is valid up to higher pressures than the two others which are valid up to 11.5 and 20 MPa respectively. Thorin also compared the thermal efficiency of a Kalina cycle using boiler pressures between 10-18 MPa and found that the choice of EOS does influence the efficiency up to 1.5% points at high pressures.

For the above mentioned reasons and since the TRF EOS is included as a property model in Aspen and in Matlab with NIST REFPROP, this EOS was chosen for the sub- and full process models. A disadvantage of using this property model is its complexity. Except when the phase is specified, the model needs first to determine if the fluid is in the liquid, vapour or two-phase domain. As experienced by the authors and as also confirmed by personal communication with Eric Lemmon (NIST), the TRF model in REFPROP has occasional non-convergence issues (at certain random points in the thermodynamic domain). In Aspen Plus it is possible to specify phase and thereby to increase the convergence efficiency. When compared to the Peng-Robinson EOS, the TRF EOS seems to be significantly more accurate for the Kalina cycle. Consequently, the baseline model in the present work has minor deviations in the thermodynamic properties at some points in the process, compared to the model in the work of Bombarda (which is used as baseline) [25]. An advantage of the Peng-
Robinson EOS is that it is simpler and converges easily, a benefit traded in this work in order to obtain better accuracy.

3.2. Subsystem Level

A subsystem is here regarded as a system of components which is an integrated part of the whole process. In the following, two subsystems are discussed: firstly, the heat exchangers system described earlier, and secondly, the separation and mixing system. The motivation for making the models of these subsystems is to ease initial parameter estimations and optimisation of the process. Both subsystems were validated using corresponding subsystem models in Aspen Plus.

3.2.1. Heat exchanger system

The composite working fluid mass flow rate exiting the boiler can be used as a measure proportional to the process work output, since the thermodynamics state at the boiler outlet is held constant. The aim of the following methodology is thus to uncover the relation between the maximum possible mass flow rate and the composition of the two split streams.

Rich and lean streams entering and exiting the first evaporator should have identical temperatures and pressures, and leave as saturated vapour and liquid respectively. Any chosen composition of the rich stream \(x_r\) results therefore in only one possible composition of the lean one and only one ratio between the rich and lean mass flow rates.

Thus the final optimisation is based on the rich stream composition versus boiler mass flow.

Composition of the lean mass flow \(x_l\) is calculated from the rich stream composition by solving the following equation system:

\[
\begin{align*}
T_{r,d} &= T(p = p_w, Q = 1, x = x_r) \\
T_{l,b} &= T(p = p_w, Q = 0, x = x_l) \\
T_{r,d} - T_{l,b} &= 0
\end{align*}
\]

where \(T_{r,d}\) is the dew point temperature of the rich stream, \(T_{l,b}\) is the bubble point temperature of the lean stream, \(p_w\) is the working fluid pressure and \(Q\) is vapour quality. Then, the mass flow ratio between the rich and lean streams are found by solving the following mass balance equations (note that the actual mass flow of the composite stream \(\dot{m}_c\) is not known at this stage):

\[
\begin{align*}
\dot{m}_c - \dot{m}_r + \dot{m}_l &= 0 \\
x_c\dot{m}_c - x_r\dot{m}_r - x_l\dot{m}_l &= 0
\end{align*}
\]

where \(\dot{m}_r\) and \(\dot{m}_l\) are the mass flow rates of the rich and lean streams and \(x_c\) is the composite stream composition, i.e. the stream exiting the boiler. Using an energy balance over the entire boiler, the mass flow of the (composite) working fluid, can be found. The hot source mass flow, pressure and temperature at the outlet and inlet are known parameters. Also known is the superheater approach, the pressure of the working fluid as well as the inlet states (pressure, temperature and composition) of the working fluid streams:

\[
\dot{m}_c = \dot{m}_c - \frac{h_{e,i} - h_{e,o}}{h_{w,o} - \frac{\dot{m}_r}{\dot{m}_r + \dot{m}_l}h_{r,i} - \frac{\dot{m}_l}{\dot{m}_r + \dot{m}_l}h_{l,i}}
\]

where \(\dot{m}_c, h_{e,i}\) and \(h_{e,o}\) are the mass flow rate and enthalpies in and out of the boiler respectively. \(h_{w,o}, h_{r,i}\) and \(h_{l,i}\) are the enthalpies of the working fluid exiting the boiler and the rich and lean stream entering. All enthalpies in the above equation are found using \(h = h(T, p, x)\). Upon finding the mass flow of the composite stream, the rich and lean mass flows can be calculated. In order to estimate the minimum temperature difference in the boiler, both heat exchangers are divided into a number of steps \(n\). The first evaporator (including preheater) is modelled by dividing the temperature between outlet and inlet into steps \(\Delta T_s\) and assuming temperature equilibrium between the
lean and rich streams in each division. Hereby
the enthalpy in each step is found:

$$\Delta T_s = \frac{(T_{l,b} - T_{w,i})}{n}$$ (7)

$$T_{r,i} = T_{l,i} = T_{w,i} + (i-1)\Delta T_s$$ (8)

$$\Delta H_{s,j} = \dot{m}_r (h_{r,j} - h_{r,1}) + \dot{m}_l (h_{l,j} - h_{l,1})$$ (9)

where \( i = [2, 3, \ldots, (n+1)] \) and \( j = [2, 3, \ldots, n] \),
\( T_{w,i} \) is the working fluid temperature, \( \Delta H_s \)
the difference in enthalpy between two steps
with \( i \) and \( j \) representing the step number.
Since the enthalpy increase numerically in
each step is the same for working fluid and
heat source, the temperature of the hot source
at each step is thus found from the enthalpies,

\[ T_r = T(h, p, x) \]

The minimum temperature
difference can now be found and a similar
approach is used for the second evaporator.
By varying \( x_r \) the maximum working fluid
mass flow rate is found, but still the question
remains whether the mixing system can deliver
the corresponding rich and lean streams.

### 3.2.2. Mixing system

Desired outputs from the mixing system
model are the mass flow fractions of the three
splitters (\( S_1, S_2 \) and \( S_3 \) respectively), as shown
in figure 1, and the mass flow feeding the separator (\( \dot{m}_f \)).
Inputs are the mass flow rates and compositions found in the heat exchanger sub-
model. Being fed by the separator, the
mixing subsystem model includes this com-
ponent beginning from the inlet of the separator,
a stream which composition (\( x_f \)) is chosen to
be the same as the baseline case for comparison reasons. Other inputs to the model are
\( p_w, x_c \) and \( \dot{m}_c \). Assuming an isothermal adi-
abatic process, the single stage separator can
be modelled with the use of the EOS and an ammonia mass balance. The equilibrium
concentrations of the liquid and vapour phases (\( x_l \)
and \( x_v \)) are found using a REFPROP function,
provided an assumed temperature and pressure
\( (T_f \) and \( p_f \)) similar to the baseline case (from
the Bombarda article [25]):

\[ [x_L, x_V] = X(T = T_f, p = p_f, x = x_f) \] (10)

where \( x_{18} = x_V \) and \( x_{11} = x_L \) (figure 1).
Solving the following equation system of mass
balances, provides the liquid and vapour mass flows from the separator:

\[ \dot{m}_{11} = \dot{m}_f - \dot{m}_{18} \] (11)

\[ x_f \dot{m}_f - x_{18} \dot{m}_{18} - x_{11} \dot{m}_{11} = 0 \] (12)

The following equations are common for the
three splitters, here splitter 1:

\[ x_{26} = x_{18} \] (13)

\[ x_{19} = x_{18} \] (14)

\[ \dot{m}_{26} + \dot{m}_{19} = \dot{m}_{18} \] (15)

\[ \dot{m}_{26} = S_1 \dot{m}_{18} \] (16)

Where \( S_1 \) is the ratio to be found and used
in the full process model. The mixers are de-
scribed by both a mass balance and an ammo-
nia mass balance:

\[ \dot{m}_{27} = \dot{m}_{16} + \dot{m}_{26} \] (17)

\[ x_{27} \dot{m}_{27} = x_{16} \dot{m}_{16} + x_{26} \dot{m}_{26} \] (18)

This equation system is solved iteratively
and returns the separator feed mass flow and
the splitter fractions, thereby producing the
desired rich and lean streams characteristics
(\( \dot{m}, x \)). Coupling of the two sub models de-
scribed here provides an accurate tool needed
to optimise the full process of the Kalina Split
cycle within the boundary conditions given.

### 3.3. Process modelling

#### 3.3.1. Available models

Aspen Plus is a widely used commercial pro-
cess simulation software, which is based on sev-
eral methods and packages for estimations of
3.3.2. General modelling assumptions

The simulations of the simple Kalina cycle and of the Split Cycle were both based on the following assumptions and data, adopted from the baseline case, which is based on work presented by Bombarda [25]. The chemical compounds considered in the simulations are: N₂, O₂, H₂O, CO₂, Ar and NH₃. The heat source considered in this study are exhaust gases from two marine diesel engines, with the following molar composition 74.6% N₂, 11.7% O₂, 6.7% H₂O, 5.9% CO₂ and 1.1% Ar and a total mass flow rate of 35 kg/s. The ammonia-water mixture enters the heat recovery system at a temperature of 83.5°C and has the following mass composition at the inlet of the turbine 77.2% NH₃, 22.8% H₂O. Assumptions on the process design are listed below:

- Exhaust gas pressure and temperature: 2 bar and 346°C
- Stack temperature: 127.7°C
- Minimum allowable pinch point temperature difference in boiler: 21.9°C
- Super heater approach: 16°C
- Minimum allowable pinch point temperature difference in low and intermediate pressure (IP) recuperators: 4.5°C
- Minimum allowable pinch point temperature difference in high pressure recuperator: 16.5°C
- Pressure levels: 5.94, 10, 100 bar
- Separator temperature: 100°C
- Cooling water temperature: 20°C
- Adiabatic separator
- Homogeneous fluid flow and temperatures
- Turbine mechanical and isentropic efficiency: 96% and 75%
- Pumps driver efficiency and isentropic efficiency: 95% and 70%
- Ammonia concentration in composite stream, y₃: 78.6%
- Heat to the environment and pressure losses in heat exchangers are neglected

3.3.3. Specific modelling assumptions

Specific assumptions related to the design of the Kalina process without Split Cycle are listed below:

- IP condensation temperature: 33°C
- IP recuperator: 2 streams

Specific assumptions related to the design of the Kalina process with Split Cycle are listed below:

- Additional pumps have the same efficiency
- Additional mixers and splitters are adiabatic
- IP condensation temperature: 26°C
• IP recuperator: 4 streams

One of the main differences between the conventional Kalina process and the Split Cycle is the ammonia concentration of the rich mixture at the inlet of the heat recovery system. In the first case, the ammonia content is between 70-75 wt%, which corresponds to a condensing temperature of about 33°C at a pressure of 10 bar. In the second case, the ammonia content of the rich stream is 10 percentage points higher, which corresponds to a condensing temperature of 26°C.

In order to fully condense the ammonia-rich stream in the Split Cycle, the operating temperature of the condenser should be decreased from 33°C to 26°C (effectuated by larger cooling water flow rate). As a consequence, the operating parameters of the cooling system and of the condenser are slightly different compared to the baseline case.

3.3.4. Optimisation

Optimisation of the Split Cycle is conducted by changing the pressure level to reach the same pinch point temperature difference in the heat recovery system (21.9°C) while keeping the same temperature inlet and outlet conditions, and an identical ammonia concentration at the boiler outlet (point 3 Figure 1).

4. Results and discussion

By varying the rich (and lean) stream compositions, the temperatures of the working fluid in the first evaporator changes and thus also the pinch point. This variation is shown in Figure 3 at pressures from 100 to 140 bar. The constraint of pinch point temperature difference of 21.9°C is not respected at any concentration at 140 bar pressure and above and the maximum net work output without any violation is found at 138 bar and an $x_{rich}$ of 0.90. It is also shown in the figure how the pinch point temperature difference is larger than the baseline case of 21.9°C, when using SC at baseline pressures and high rich stream concentrations.

Changing the rich and lean streams compositions does not enable significant changes in the maximum mass flow rate and consequently the turbine work output. The maximum obtainable turbine work output at various concentrations and pressures is shown in Figure 4. The maximum output is, in most cases, found at rich stream compositions of about 0.90.
recovery system, as seen from the hot source side, is shown. Looking at the SC case at 100 bar, it is seen that the alignment of temperatures of the hot and cold streams, is deteriorated compared to the baseline case. Despite that, the turbine work output is slightly higher because the early evaporation of the rich stream enables a higher mass flow rate, a parameter limited by the pinch point temperature difference. Compared to the baseline case, the optimised case at 138 bar shows a visibly closer alignment of temperatures of the hot and cold streams, while the pinch point temperature difference is not changed from that of the baseline case. The average temperature in the heat uptake is clearly higher in this case. Although the Split Cycle streams are only separated in the first evaporator, the improved match continues through the second evaporator.

Using the SC configuration is thus seen to enable an increased maximum pressure in the cycle without violating the pinch point temperature difference constraint. Reversely, the baseline case does not allow higher pressures without a pinch point temperature difference violation, indicating that the baseline cycle parameters are indeed optimised. Figure 6 shows how the turbine work, cycle net work and thermal efficiency increase with higher boiler pressure. The shown cases were optimised in terms of concentrations and mass flows of the rich and lean streams, aiming at maximum power. Even more power could be obtained with a smaller pinch point temperature difference. Temperature and vapour quality at the turbine outlet decrease slightly as the inlet pressure increases without affecting the rest of the process markedly. The vapour quality at 138 bar is 96% compared to 99% in the baseline case.

As should be expected, the relative increases in thermal efficiency of the cycle and the net work output are identical and in the baseline case the thermal efficiency is 20.1% while at 138 bar in the optimised SC case 21.5% is achieved. States of all the points in the optimised Split Cycle are shown in the appendix.

5. Conclusion

A thermodynamic model of the Kalina Split Cycle and a methodology for optimising the cycle was presented. The methodology, consisting of two subsystem models, has made it possible to optimise the entire cycle effectively. It has been shown that the concept of using two different streams instead of one running through the evaporator does bring some advantages. The temperature development of the working fluid can be altered by changing the composition and mass flow rates of the two streams, in order to obtain a better alignment
of temperatures of the hot and cold streams in the heat exchanger.

Since the richer stream evaporates first and thus results in a larger pinch point temperature difference, higher boiler pressures and work outputs are enabled without violating the pinch point temperature difference limitation.

Results suggest a turbine power output increase of about 9% can be achieved resulting in an increase in thermal efficiency of 7%, or an increase from 20.1 to 21.5% thermal efficiency for the cycle.

Acknowledgements

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References

[22] Zervos NG, Leibowitz HM, Robinson K.


### Appendix A. States in the Kalina Split Cycle referring to Figure 1

<table>
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<th>Point</th>
<th>$p$, bar</th>
<th>$T$, °C</th>
<th>$x$</th>
<th>$\dot{m}, \text{kg s}^{-1}$</th>
<th>$Q$</th>
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