A Review of Kalina Cycle

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ABSTRACT

This paper illustrates a review research of the Kalina Cycle, including an explanation of Kalina Cycle and a simplified Kalina Cycle, a comparison of the Rankine and Kalina Cycles, an overview of the thermodynamics analysis of Kalina Cycle, the different Kalina systems and their various implementations. In addition, various correlations are investigated and explored for the measurement of the thermodynamic properties of NH_3-H_2O mixtures. The concept of low grade heat is discussed. Some technical problems about NH_3-H_2O mixture, i.e. permanence, environmental effects, protection and erosion issues etc. are also addressed. This paper explores the study of various thermodynamic cycles for integrated power plants using low-grade heat sources. The different thermodynamic cycles, using low-grade heat sources for the combined power plant, are reviewed. Comparison of which cycle is best between Kalian and Rankine cycle in converting electrical energy from low temperature sources under different conditions using different research methods has been discussed.

Keywords: Kalina Cycle, Thermodynamic Analysis, Energy–Utilization, Waste heat recovery, Applications.

1. INTRODUCTION:

In today’s world the demand for energy is increasing in line with the growing population, but the resources (fossil fuels) are inadequate and are also declining drastically. It's only a matter of time that we run out of our main source of energy such as oil, gas and coal. In this case, we need to find another source of energy and use that energy to meet our needs. Other forms of energy are solar, geothermal, wind and so on. Of these solar and geothermal forms a source of heat. But one problem is observed here that they are low quality and low heat sources. Again heat itself is a low-quality energy. However, low quality heat means that heat is extracted from low and medium temperature sources whose energy density is low and can't be converted to work. Although there is no integrated specification for low quality temperature range. The main low-grade heat sources, such as solar thermal, geothermal, biomass and industrial thermal waste. Moderate temperature heat from these sources cannot be converted efficiently to electrical power by conventional methods of generation of electricity. Therefore, how to convert these low-grade heat sources into electrical power is of great significance. Organic Rankine Cycle(ORC) which applies the Rankine Steam Cycle principle but uses low boiling point organic working fluids to recover heat from low heat sources. In early 1980s Kalina proposed a new family of thermodynamic power cycles using an ammonia–water mixture as the working fluid and this kind of cycle configuration was named Kalina cycle[1]–[3].It is the thermodynamics process for converting the thermal energy into usable mechanical power. It is a solution of two fluids with different boiling point for its working fluid. As a working fluid, the ammonia-water mixture plays a key role in the Kalina cycle. In various novel thermodynamic cycles, the Kalina cycle has been the most significant improvement in the design of the thermal power plant since the advent of the Rankine cycle in the mid-1800s and has been deemed an ambitious contender to the Organic Rankine Cycle. The "Kalina" technology has been developed over three decades; however, the commercial marketing of the technique began around ten to fourteen years ago. Kalina power cycles work with binary fluid and are uniquely capable of upgrading low-temperature heat to high-efficiency power. The composition of the mixture varies throughout the cycle. High efficiency is due to the close temperature match between the acceptance of the heat cycle and the availability of the heat source as well as the high level of recovery. The process of converting energy from fuel to electrical energy involves the creation of mechanical work. Thermodynamic cycles are being used for successful conversion of heat to mechanical work.

2. DESCRIPTION OF THE KALINA CYCLE AND COMPARISON BETWEEN THE RANKINE AND KALINA CYCLE

2.1. Description of the Kalina cycle

In order to replace the previously used Rankine Cycle as a bottoming cycle for a combined-cycle energy system as well as for generating electricity using low-temperature heat resources, Alexander I. Kalina designed a new power cycle in which ammonia–water is used as a working fluid[2]. The first version of the Kalina cycle is characterized by a second condenser, after the separator, at one intermediate pressure, allowing an additional degree of freedom in the composition of the boiling mixture and allowing the distillation unit to operate at a pressure lower than the maximum one. A further difference concerns the recuperative heat exchanger, which, in the Kalina scheme is placed downstream the turbine. In these situations (medium-low temperatures heat sources application and small power conversion system) the plant layout may be simplified and the cycle has a single main condenser, at the lowest cycle temperature, and the separator is placed after the evaporator[4].

2.2. The thermodynamic concept of the Kalina Power cycle

The Kalina cycle, as shown in Figure 1, consists of six main components: boiler, turbine distiller, absorber, flash tank, and condenser. Except for the absorber and flash tank, these components are the same as those of the Rankine cycle[5].

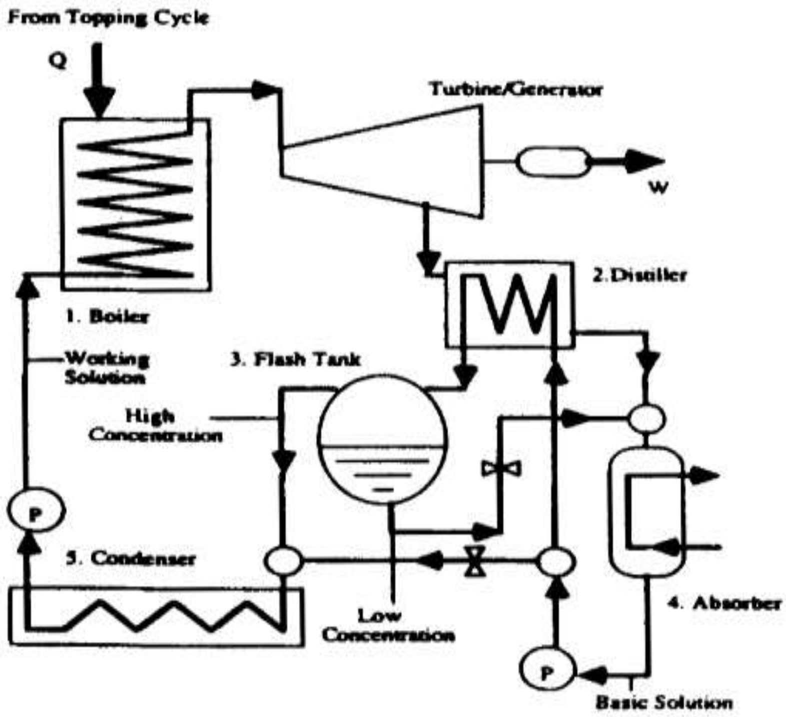


Figure 1: Schematic diagram of the Kalina Cycle[5]

The cycle operates as follows:

The binary mixture, the ammonia/water mixture, boils at a variable temperature. More heat is extracted from the boiler and delivered to the power cycle. The superheated mixture is expanded to the turbine back pressure. The pressure drop through the turbine may be greater than that of the Rankine cycle. The waste heat from the turbine exhaust is used to distil (separate) the low temperature boiling fluid (ammonia) from the high temperature boiling fluid (water), using the significant difference in volatility between the two fluids. The high-concentration (strong solution) and low-concentration (weak solution) fluids are separated in the flash tank. The low-concentration solution is condensed. The high-concentration solution is condensed at a relatively high pressure. This pressure is higher than the turbine back pressure[5].

2.3. A simplified Kalina cycle

A simplified Kalina cycle which has been analyzed by many researchers[6] is adopted in this review to demonstrate concept of the Kalina cycle and its flow diagram is depicted as Figure 2. (The number with square bracket stands for a device in the cycle, while the number without a bracket stands for a state point in the cycle.) As Figure 2 shows, this is a bottoming cycle fed by exhaust gases (1, 2) to the boiler. Superheated ammonia–water vapor (3) is expanded in a turbine to generate work (4). The turbine exhaust (5) is cooled (6, 7, 8), diluted with ammonia-poor liquid (9, 10) and condensed (11) in the absorber by cooling water (12, 13). The saturated liquid leaving the absorber is compressed (14) to an intermediate pressure and heated (15, 16, 17, 18). The saturated mixture is separated into an ammonia-poor liquid (19) which is cooled (20, 21) and depressurized in a throttle and ammonia-rich vapor (22) is cooled (23) and some of the original condensate (24) is added to the nearly pure ammonia vapor to obtain an ammonia concentration of about 70% in the working fluid (25). The mixture is then cooled (26), condensed (27) by cooling water (28, 29), compressed (30), and sent to the boiler via regenerative feed water heater (31).

The evident efficiency advantage that characterizes the Kalina cycle is realized from the heat exchange process of the heat acquisition in the evaporator and the heat rejection in the condenser. The Recuperator Exchangers achieve additional efficiency. These gains are made possible by the unique variable boiling and condensing characteristics of the NH_3-H_2O mixture of working fluid. The varying temperature during heat transfer processes reduces the thermodynamic irreversibility of the heat exchange and the effect of the thermal pinch on the boiler.

When the NH_3-H_2O mixture is heated the more volatile NH_3 tends to vaporize over pure water first. As the NH_3 concentration of the remaining liquid decreases, the saturation temperature of a pure substance (water / steam) increases, providing a better match to a hot gas heat source such as a gas turbine exhaust. The working fluid is divided into streams with different concentrations, providing a great deal of flexibility to optimize heat recovery and allow condensation at greater than atmospheric pressure.

2.4. Comparison between the Kalina & Rankine/ORC cycle

The Carnot cycle has been described in thermodynamics as the most efficient thermal cycle possible, in which there are no heat losses and consists of four reversible processes, two isothermal and two adiabatic. It was also represented as an expansion and compression cycle of a reversible heat engine that does work without heat loss. In addition, huge volumes of renewable energy sources such as solar, thermal, geothermal, biomass, and industrial waste heat are now visible. By conventional methods of generating power, the moderate temperature heat from these sources cannot be converted efficiently to electrical power. So how to convert these low-grade heat sources into electrical power is of high significance. Comparison of different cycles therefore helps in combating and finding a suitable cycle for conversion.

The Kalina cycle is principally a ‘‘modified’’ Rankine cycle. The modifications that complete the transformation of the cycle from Rankine to Kalina consist of proprietary system designs that specifically exploit the virtues of the ammonia–water working fluid. These special designs, either applied individually or integrated together in a number of different combinations, comprise a family of unique Kalina Cycle Systems. This is somewhat analogous to the Rankine cycle which, in fact, has many design options such as reheat, regenerative heating, supercritical pressure, dual

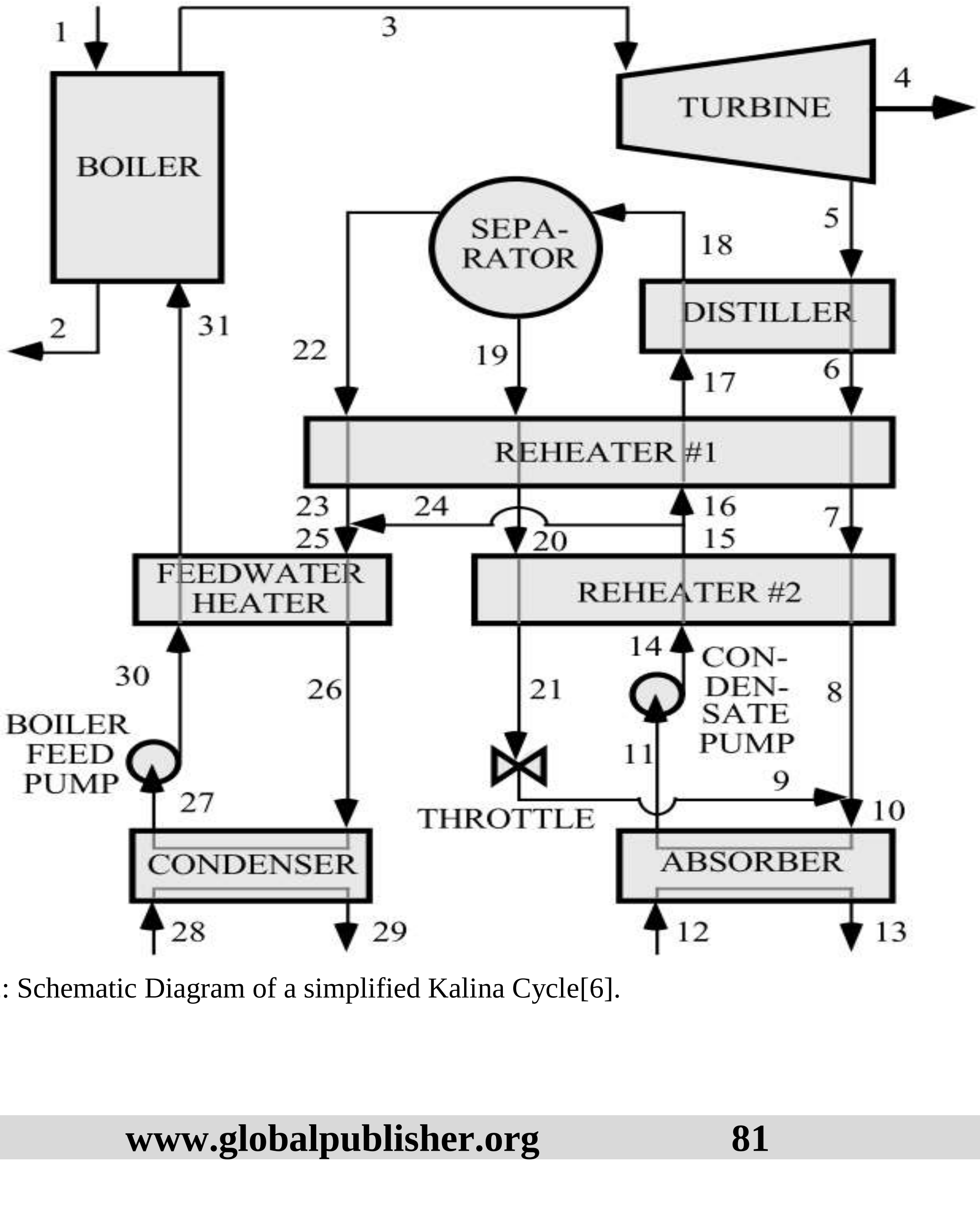


Figure 2: Schematic Diagram of a simplified Kalina Cycle[6].

pressure, etc. all of which can be applied in a number of different combinations in a particular plant[7], [8].

In theory, the Kalina cycle can help convert approximately 45% of a direct-fired system's heat input to electricity and up to 52% for a combined-cycle plant (a gas turbine produces exhaust, which enables a steam turbine to produce electricity). This compares with about 35% and 44%, respectively, for the steam cycle[9]. Moreover, the Kalina cycle cycles can give up to 32% more power in the industrial waste heat application compared to a conventional Rankine steam cycle. However, the Kalina cycle in small direct-fired biomass-fueled cogeneration plants do not show better performance than a conventional Rankine steam cycle[10]. When both cycles are used as a ‘‘bottoming’’ cycle with the same thermal boundary conditions, it can be found when the heat source is below 1100 1F (537 1C), the Kalina cycle may show 10 to 20% higher second law efficiencies than the simple Rankine cycle[11].

Jonsson[12] in her doctorial thesis investigated the Kalina cycles as bottoming processes for natural gas–fired gas and gas– diesel engines. It was shown that the Kalina cycle has a better thermodynamic performance than the steam Rankine cycle for this application. All simulated Kalina cycle configurations generated more power than the steam cycles, except for one simple Kalina cycle configuration compared with a dual-pressure steam cycle. The best Kalina bottoming cycle could generate 40–50% more power than a single-pressure steam cycle and 20–24% more power than a dual-pressure steam cycle. A Kalina bottoming cycle could add 6–8 percentage points in efficiency to the gas engines, while a single- pressure steam bottoming cycle could add about 5 percentage points. For the gas–diesel engines, the efficiency augmentation was 4–7 percentage points for the Kalina bottoming cycles, 4–5 percentage points for a single-pressure steam cycle and 4–6 percentage points for a dual-pressure steam cycle.

The adoption of the Kalina cycle to a certain heat source and a certain cooling fluid sink has one degree of freedom more than the ORC cycle, as the ammonia–water composition can be adjusted as well as the system high and low pressure levels[13]. In a particular case in the Republic of Croatia, the geothermal source has a higher temperature(175 1C), therefore, ORC in which isopentane is used as the working fluid has better both the thermal efficiency (the First Law efficiency) and the exergetic efficiency (the Second Law efficiency): 14.1% vs. 10.6% and 52% vs. 44% [14]. The performance of trilateral power cycle (TLC) and compared it with ORC and the Kalina cycle, from the viewpoints of thermodynamics and thermo-economics[15]. An integrated system of ammonia– water Kalina–Rankine cycle (AWKRC) for power generation and heating & studied the performances of the AWKRC system in different seasons with corresponding cycle loops[16].

3. THERMODYNAMIC ANALYSIS

The Kalina cycle is a novel thermodynamic cycle, as compared to the Rankine cycle. Correspondingly, the conclusion drawn on the Kalina cycle from both the energy and exergy analysis is essential for its further real implementation.

3.1. Energy analysis based on the first law of thermodynamics

The Kalina cycle has identical devices in cycle design, compared to the Rankine cycle. But the Kalina cycle has one degree of freedom more than the Rankine cycle, which is the ammonia – water mixture fraction. Therefore the thermodynamic efficiency of the Kalina cycle would be greatly influenced by the fraction of ammonia – water mixture and the parameters of devices in the loop. With respect to the fraction of ammonia – water mixture, design studies of the Kalina cycle for low to moderate temperature geothermal resources indicate different compositions of ammonia – water mixtures, commonly around 70 wt% NH_3[6], [13], [17]–[19].

Marston [20] holds the similar opinion in his research on a three- stage Kalina cycle and concluded the Kalina cycle models have frequently used a boiler working fluid of 70 wt% ammonia; however, the optimum composition is a function of many design parameters. Nag and Gupta [21], in their exergy-based study, determined that the most effective ammonia fraction is about 73 wt%. A similar exergy-based analysis by Borgert and Velasquez [22] put the optimum ammonia fraction at about 58 wt%. Nasruddin [23] et al. performed an energy and exergy analysis on KCS34 with mass fraction ammonia–water mixture variation. The result of their study shows that the maximum efficiency and power output are achieved at 78 wt% ammonia–water mixture. Arslan [24] performed an exergoeconomic evaluation assuming KCS 34 was used for generating electricity from Simav geothermal field and found that for the case with 80 wt% ammonia fraction, the maximum energetic efficiency is 14.9%. The only available application of KCS34 is in Husavik, Iceland, with an installed capacity of 2 MW and a working fluid of 82 wt% ammonia[25]. When the Kalina cycle is matched with the Rankine cycle to establish a combined cycle, the optimum fraction of ammonia water mixture was found to be 89 wt% [26].

With respect to the first law efficiency, among all devices in the Kalina cycle, the key parameters which can influence the cycle performance are: separator temperature[20], [21], [26]–[29], turbine inlet pressure[30]–[34] , turbine inlet temperature [21], [29], [33], [34], and turbine output pressure [23], [34]. Turbine inlet condition (temperature and composition) and separator temperature can effect both the first and the second law efficiencies of the Kalina cycle [21].

For a given turbine – inlet mass fraction, as the separator temperature rises, the cycle efficiency increases up to a limit and then begins to decline. For a given turbine – inlet mass fraction and separator temperature, the cycle efficiency will be increased by reducing the separator pressure. The temperature of the separator at constant turbine inlet temperature decreases with the increase in the concentration of the turbine inlet[29]. Moreover, the cycle efficiency will be enhanced for a given separator temperature by minimizing the separator pressure[28]. By enhancing the temperature and pressure at the inlet Turbine and the dropping of turbine back pressure will definitely increase the cycle thermal efficiency[34]. Its efficiency depends on the turbine inlet pressure (Bottoming cycle) for a Rankine – Kalina Combined (RKC) cycle.

Maximum output is gained in the RKC cycle at a turbine inlet pressure of 41.70 bar[31]. Furthermore, research shows that an optimum ammonia fraction can also be found for a given turbine inlet pressure that yields the maximum cycle efficiency[30].

If the outlet pressure from turbine is constant, by expanding the ammonia mass fraction will increase system efficiency. If the mass fraction is constant it will increase the device efficiency by reducing the exit pressure from the turbine[23]. According to Rogdakis [35] study, the efficiency of the Kalina cycle can be measured with regard to the two pressures p_M (medium pressure) and p_L (low pressure) as

$$\eta = \frac{A}{pL} + Bp_L + C \qquad (1)$$

Where,

$$A = -0.94470085\, p^2_M + 8.8705682\, p_M - 22.047349 \qquad (2)$$

$$B = -0.38132389\, p^2_M + 4{:}0481463\, p_M - 11.702681 \qquad (3)$$

$$C = 1.2152930\, p^2_M + 13.127963 p_M + 81.367228 \qquad (4)$$

Lolos and Rogdakis[36] calculated the efficiency η for a great number of combinations of the minimum temperature T_L (12 to 22 1C) and low pressure p_L (1 to 4 bar) and derived the following correlations linking the efficiency with independent variables of the cycle(T_L, the minimum temperature; p_L, the low pressure, t_H, the maximum temperature of the cycle).

$$\eta = a_2 + b_2\, T_H + c_2\, T^2_H \qquad (5)$$

Where,

$$a_2 = -0.049 - 0.0022 T_L \qquad (6)$$

$$b_2 = 0.0035 \times 0.92^{1/p_L} \qquad (7)$$

$$c_2 = -2.36 \times 10^{-6} - 2.19 \times 10^{-6}\, p_L + 3.14 \times 10^{-7}\, p^2_L \qquad (8)$$

3.2. Exergy analysis based on the second law of thermodynamics

Energy-Utilization Diagrams (EUD) is an important engineering tool to improve exergy efficiency of energy conversion systems[37], [38]. The exergy losses of the system are shown by a graphical presentation which gives a useful overall description of the process. The use of mixtures as working fluids has opened new possibilities to improve the efficiency of power and refrigeration cycles with less costly equipment. Mixtures may be an important substitute for CFC refrigerants, thus, decreasing environmental problems[6].

3.2.1. Energy Utilization Diagrams

In the present method, it is assumed that a system is composed of a number of subsystems containing energy-donating and energy-accepting processes. Let us consider the processes in a subsystem. The first law of thermodynamics states that the total energy is conserved, i.e.[6]:

$\sum \Delta H_k = 0 \; (k = 1, \ldots, k\hat{})$, (1)

Where kˆ is the number of processes in the subsystem. Classified into energy donors and energy acceptors, the above equation becomes

$\sum \Delta H_k^{ed} + \sum \Delta H_k^{ea} = 0$, (2)

where the superscript ed and ea mean energy donor and energy acceptor, respectively. The second law of thermodynamics states that the total entropy is increased:

$\sum \Delta S_k = \sum \Delta S_k^{ed} + \sum \Delta S_k^{ea} \geq 0$. (3)

Then exergy is lost in the process system:

$\sum \Delta E_k = \sum \Delta H_k - T_0 \sum \Delta S_k = - T_0 \sum \Delta S_k \leq 0$. (4)

If we introduce the availability factor A[39],

$A = \Delta E / \Delta H$, (5)

Equation 4 may be converted to:

$- \sum \Delta E_k = \sum \Delta H^{ea}{}_k \, (A^{ed}{}_k - A^{ea}{}_k)$. (6)

When kˆ goes to infinity the relation becomes:

$- \int dE = \int (A^{ed} - A^{ea}) \, dH^{ea}$. (7)

Hence, by plotting A^{ed} and A^{ea} against H^{ea}, the exergy loss in the subsystem is represented by the area between Aed and Aea. This we call Energy-Utilization Diagrams[6].

3.2.2. Kalina Cycle

For the thermodynamic properties of the ammonia-water mixture used in the Kalina cycle, a basic model is assumed. In the gas phase, above water T_{sw} is the saturation temperature, it is believed that the overheated mixture serves as an ideal solution of superheated ammonia and water vapor (Figure 3). In the gas phase, when the temperature is between the pure water saturation temperature T_{sw} and the mixture dew point T_d, the water portion is assumed at the considered pressure to be in a meta-stable vapor state. Similarly in the liquid region, we assume a meta-stable liquid state for ammonia between the saturation temperature of pure ammonia T_{sa} and the bubble point of the mixture T_b. We have a saturated steam mixture with ammonia mass fraction X_g and a saturated liquid mixture with ammonia mass fraction X_f in the wet vapor mixture area $T_d > T > T_b$. In the liquid region below the bubble point of the T_b mixture, a Gibbs excess function is assumed for moving away from ideal-solution conduct[40].

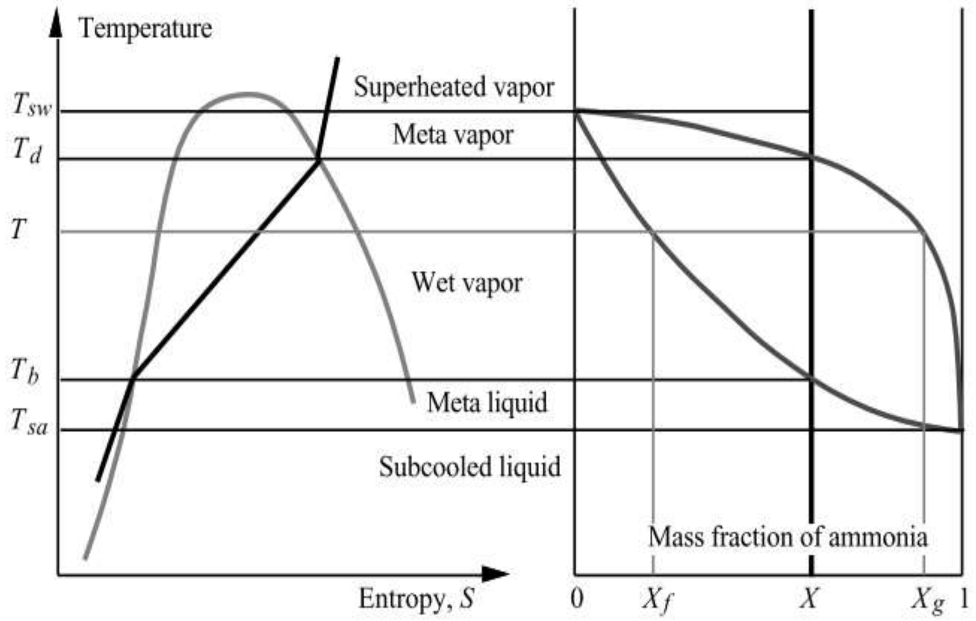


Figure 3: The various states on T-S and T-X diagrams[6].

3.2.3. Energy–Utilization Diagram of the Kalina cycle

Figure 3 illustrates the Energy-Utilization Diagram for the Kalina cycle presented above. This diagram shows the scheme of energy transformations by plotting the amount of energy transformed on the abscissa (i.e., coordinate for the first law of thermodynamics) and the energy levels of the donor process (A^{ed}) and the acceptor process (A^{ea}) on the ordinate (i.e., coordinate for the second law). It is found that there are pinches at several points. Hence, it is not so easy to operate the system and much attention should be paid especially to these pinches. However, when this is solved, the uniform distribution of exergy loss shows that this system is well-optimized. The diagram is divided into different parts related to the components of the Kalina cycle in Figure 2. This figure clearly shows whether the quality of the energy, i.e., exergy, supplied is sufficient and the level of excess. The total exergy loss in each subsystem is shown as the area between the energy donating and energy accepting lines. (The shadowed area.) In the boiler exergy from the exhaust gases, the energy donating line is curved downwards, is transferred to the ammonia-water mixture, where we can see the portion indicating variable temperature boiling in the middle of the energy accepting line. For the turbine gas expansion is the energy donor and its energy level becomes greater than unity, while a work sink with A = 1 is the energy acceptor. The area between these two energy levels gives the exergy loss in the turbine and the work generated is obtained as the width of ΔH^{ea}.

The remaining part of the diagram shows the heat exchange in the remaining subsystems indicating a very well optimized system[6].

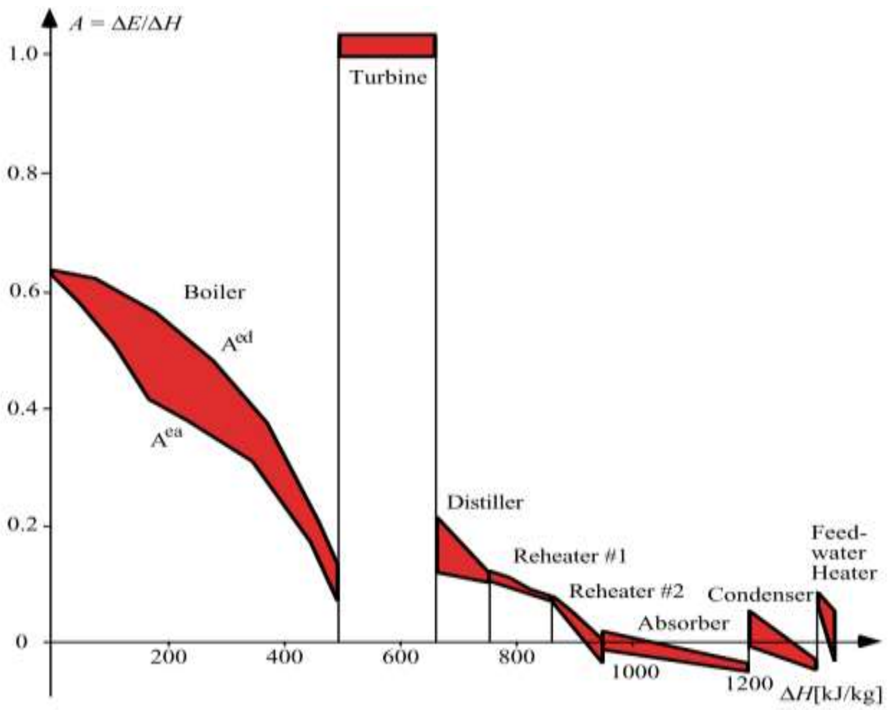


Figure 4: Energy-Utilization Diagram for the Kalina cycle[6].

Among all devices in the Kalina cycle, the boiler (heat recovery vapor generator) has the maximum exergy degradation. The second and third biggest exergy destruction occurs, respectively in turbine and condenser. The exergy destruction in high temperature recuperator and that in low temperature recuperator account for the other main exergy destruction[5], [6], [31], [41], [42]. Therefore, the boiler can greatly increase the cycle efficiency by reducing the exergy losses of these components. In addition, as a critical component for a Kalina high-pressure cycle, turbine must either be multi-stage or rotate at very high rotational speed to ensure isentropic performance satisfactory[4].

4. SELECTION OF WORKING FLUID

Power generation has recently sparked and gained fame. However, conventional energy is not always economically viable because of its capital costs and high cost of fuel. In this case, the use of non-conventional cycles becomes an important factor for working towards fulfilling energy needs. The efficiency of non-conventional cycles is greatly dependent on fluid selection. The study of various authors on fluid selection for the ORC and Kalina cycle is concluded. The lifeblood of the Kalina cycle is a mixture of ammonia – water as a Functional stream. Ammonia – water mixtures have some essential features unlike that of either pure water or pure ammonia. A fusion of the two fluids works like a completely fresh substance. There are four key variations[8]:

First, a mixture of ammonia – water requires a varying temperature to boil and condense. In comparison, pure water and pure ammonia both have steady or constant temperatures of boiling and condensing.

Second, the thermophysical properties of an ammonia–water mixture can be altered by changing the ammonia concentration. The thermophysical properties of water and ammonia are fixed.

Third, ammonia–water has thermophysical property that causes mixed fluid temperatures to increase or decrease without a change in the heat content. The temperature of water or ammonia does not change without a change in energy.

The final difference is not really a change in a basic feature, but rather an important change in a fluid property. This is the freeze temperature. Water freezes at a relatively high temperature of 0 1C, while pure ammonia freezes at −78°C. Solutions of ammonia–water have very low freezing temperatures. The use of ammonia in the mixture allows for successful use of waste heat sources, causing ammonia – water work fluid to boil at lower temperatures. Using a binary fluid allows the composition of the working fluid to be varied by distillation, providing a richer concentration in the heat-acquisition stage heat vapor recovery generator (HRVG) and leaner composition in the low-pressure condenser. Since ammonia's molecular weight is similar to that of water, a standard back pressure, multi-stage turbine-generator is used.

For many reasons, a combination of ammonia and water is used as a working fluid[32], [43], [44]:

First, the use of a lighter component (ammonia), allows efficient use of the waste heat stream at a higher pressure by causing boiling to start at lower temperature.

Second, the use of a mixture allows the composition to be varied by the use of distillation, resulting in a richer composition for the boiler, and a leaner composition in the condenser with low pressure. Ammonia – water's variable temperature boiling process decreases losses in heat transfer processes in the power plant, thereby improving performance. Third, because of the similar molecular weights of ammonia and water (17.03 vs. 18.015) the ammonia–water vapor behaves virtually the same as steam, which allows the use of standard steam turbine components. Fourth, standard materials can be used. Carbon steel and high-temperature standard alloys are suitable for the ammonia handling. In the ammonia service, the use of copper and copper alloys is prohibited only. Fifth, ammonia is readily available, and is relatively cheap. Sixth, the ammonia is not environmentally hazardous. Seventh, there are proven safety protocols for the storage and use of ammonia in applications in industrial plants.

By comparison, the previously dominant hydrocarbons in this application are flammable and can pose a threat to explosions. Organic fluids are also known as contributors to photochemical smogs, depletion of the ozone layer. Organic fluids can pose a threat to local ecosystems in the event of an accidental spill. Thermodynamic performance analysis of the Kalina cycle needs data on thermophysical properties for ammonia – water mixtures for which composition (expressed as ammonia mass fraction in mixtures) represents a third independent variable. With the introduction and development of the Kalina cycle technology, Exergy Inc. which was founded by A. I. Kalina began to perform the research on ammonia–water properties. In 1998, Exergy Inc. completed its first set of ammonia–water properties by combining the experimental data of numerous researchers with a theoretical approach by Kalina, Tribus and others.

This work is embodied in a computer program called ‘‘WATAM’’ which Exergy Inc. utilizes in the design of all its Kalina Cycle power plant designs[45]. Compare WATAM with Peng–Robinson(PR) Equation of State (EOS) in modeling the high-pressure ammonia–water system for the Kalina cycle study, it can be found although the PR EOS provided a reasonable fit of the vapor liquid equilibrium(VLE), it tended to overestimate the ammonia concentration in the near-critical vapor phase. The PR EOS also overestimated mixture critical pressures. WATAM provided a slightly more accurate description of the VLE, especially in the near-critical region. WATAM also yielded a much better correlation of saturated liquid densities for the ammonia–water mixture than the PR EOS [46].

Over 30 correlations formed by the various researchers in Literature lists, the thermodynamic properties of ammonia – water mixtures[21], [46]–[66]. The theoretical background and basis of these correlations can be divided into nine groups: cubic equations of state[46], [57], [60]–[66], virial equations of state[47]. Gibbs excess energy[21], [46], [56], [64], [66], [48]–[55], corresponding states method[58], [59], perturbation theory[55], [56], [58], [59], [67], group contribution theory[47], [48], [58], [59], [65]–[69], [49]–[56], Leung-Griffiths model[69], Helmoltz free energy[70] and polynomial functions[71], [72].

Most of the correlations available today for the thermodynamic properties of ammonia – water mixtures were designed for lower temperatures and lower pressures than is typical in power cycles. When used in simulations of a simple Kalina cycle, those correlations previously used in simulations of the ammonia-water power cycle, give cycle efficiencies with a differences which is not exceeding 3%.

However, the variations in saturation properties between the correlations at high pressures, high temperatures and high ammonia mass fractions are considered. While the current correlation seems more theoretically rational than the older correlations commonly used in power cycle simulations, there are still minor variations in the final results of the thermal efficiency cycle simulations. Therefore it should be fair to draw conclusions from earlier research using the older correlations. It should be noted, however, that no, or very few, experimental data are available in the critical and super-critical region of ammonia – water mixtures, and that the behavior of the mixture in this area is uncertain[73], [74].

5. DIFFERENT KALINA STRUCTURES AND THEIR VARIOUS IMPLEMENTATIONS

Kalina cycle system was suggested in the early 1980's[1]–[3]. The cycle was published in 1984[2] was later designated as Kalina Cycle System 1(KCS 1). A new improved version, which offers a 10 percent improvement of efficiency over the original KCS 1, has been developed and labeled KCS 6 in order to achieve a significant improve on the matching of the working fluid and the heat source heat-temperature curves in the boiler. For smaller units (less than 20 MW of total output; around 8 MW bottoming cycle) KCS 1 would be preferable; for large units the more complicated KCS 6 would be preferable[75]. In general, each Kalina Cycle framework in the design family has a particular application and is recognized by a unique system number. Table 1[76] lists the Kalina cycle developmental status up to the end of 1980s.The developmental status of the Kalina cycle up to the end of 1980s is lists in Table 1[76].

KCS 6, intended for the gas turbine-based bottoming cycle, the combined cycle provides the optimum efficiency of all the Kalina cycles[8], [76]. In the case of fired direct (fuel) plants, KCS 5 is particularly applicable[8]. KCS 5n is identical to KCS 5, except for elimination of the water loop. Since the input gasses are not as high as in a combustion system, the high end of the system does not have as much heat. As with KSC 5, the hot gases are mostly used to superheat rather than to boil[76]. KCDCS has proved to have substantial advantages over Initial NBC (KCS-11) as regards thermodynamic period Low Pressure Efficiency. Hence, it can be suggested as a feasible and warranted alternative to Initial NBC (KCS-11), for up to 70 bar pressure[77]. One of the most significant implementations of the Kalina cycle is power generation from low temperature geothermal[19], [23]–[25], [78]–[80]. Using Organic Rankine Cycle (ORC) technology, Kalina cycle geothermal plants deliver major performance, cost, protection and environmental benefits over geothermal binary power plants. A plant of Kalina produces 30% to 50% more power than an ORC plant. For geothermal applications there are several different designs of the Kalina system Figure 5 displays three of the more basic Kalina Cycle Systems (KCS) designs for low temperature geothermal. KCS 11 relates most to geothermal temperatures from about 250 to 400˚F [121 to 204 ˚C]. Temperatures below 250˚F [121 ˚C] are ideal for KCS 34 and KCS 34 g.

The KCS 34 is more suitable for combined power generation and downstream district heating applications for these lower temperature systems, whereas the KCS 34 g is suited for smaller plants[81]. If the heat source had a maximum temperature of 240˚F (116˚C) only, the process of ammonia – water vaporization will end at a point where liquid is still present in the process stream. This is the reason it displays separators in Figure 5 for KCS 34 and KCS 34 g systems used in geothermal applications with low temperatures. The separator ensures that the vapor is directed towards the turbine. The KCS 11 and 34 designs have pre-condenser recuperators in the turbine exhaust stream[81].

Temperature of the heat source (preheater and clinker the cooler exhaust streams) for the typical cement plant are in the range from 200°C to 400°C. Both heat sources are listed as medium to low temperature heat for the production of electrical power. These heat sources are well adapted for the use of the Kalina cycle process for waste heat recovery (WHR) to generate the electricity[43], [44]. The Kalina cycle can use waste heat from the cement production process to produce electrical energy without additional fuel consumption and reduce the cost of electrical energy for cement production. Kalina Cycle System (KCS) 1–2 is used for waste heat recovery power plant for a cement factory[43]. Its typical process schematic is shown in Figure 6[41] Used single-flash steam cycle, dual-pressure steam cycle, Organic Rankine Cycle (ORC) and Kalina co-

Table 1[76]

Kalina cycle developmental status

System	Application	Cycle efficiency ratio (Kalina/Rankine)	Net plant output ratio (Kalina/Rankine)	Development status
KCS1	Bottoming cycle small plants	(32.0/26.6)=1.2[82]	(49.5/46.0)=1.07[a]	Design completed for Canoga Park Demonstration Design
KCS 2	Low temperature geothermal	(20.5/13.1)=1.56	(17.6/10.3)=1.71[b,c]	Design completed
KCS 3	High temperature geothermal and industrial waste			Under development
KCS 4	Cogeneration			Planned
KCS 5	Direct-fired for coal and other solid fuels	(48.6/42.2)=1.15[83]	(40.9/34.6)=1.18[d]	Design completed
KCS 5n	High temperature gas-cooled nuclear reactor	(46.0/36.0)=1.28[82]	(46.0/36.0)=1.28[84]	Design completed
KCS 6	Bottoming for utility combined cycle	(37.8/28.7)=1.32[83]	(56.4/51.0)=1.11[a]	Design completed
KCS 7	Direct fired, split cycle	(50.0/42.2)=1.19[83]	(42.4/34.6)=1.22[d]	Under development
KCS 8	Bottoming cycle, split cycle	(39.0/28.7)=1.36 [83]	(56.67/51.0)=1.11[a]	Under development
KCS 9	Retrofit subsystem for existing plant	N/A	(40.4/34.6)=1.17[d]	Under development

KCS 12	Low temperature geothermal	(19.2/13.1)=1.47[84]	(16.5/10.3)=1.6[b,c]	Design completed
KCS34	cascade utilization of low-grade waste heat[85]	N/A	N/A	Design completed
KCDCS	Biomass chp plants[77]	N/A	N/A	Design completed
KCS-11	Bagasse-fired cogeneration plant of sugar industry[86]	N/A	N/A	Under development

[a] For entire combined cycle. [c] Includes losses due to reinjection pumps and other auxiliaries.

[b] Compared to Heber Plant binary cycle. [d] Includes losses from fuel handling and plant auxiliaries.

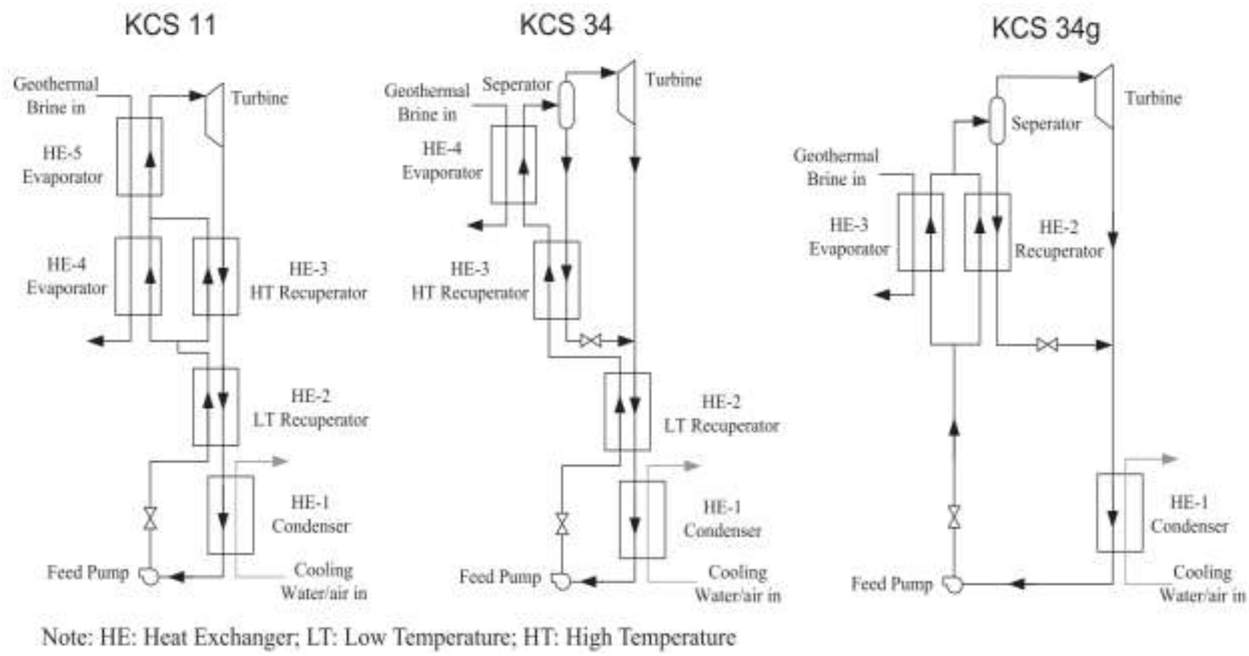
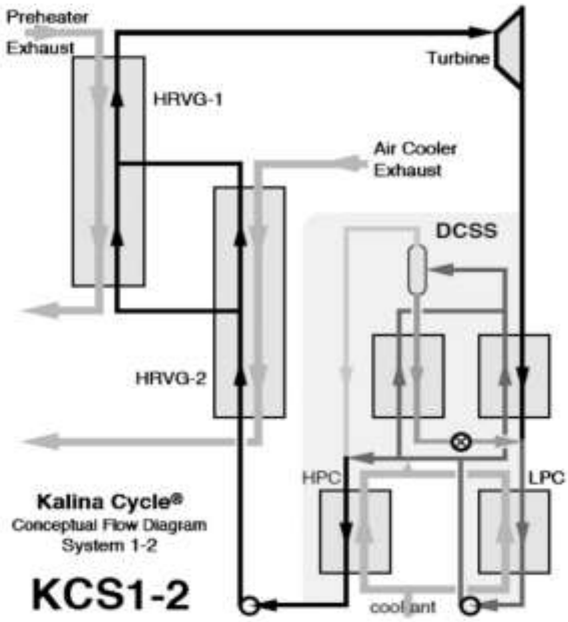


Figure 5: Kalina Cycle Systems for Low Temperature Geothermal[29].



Note: HRVG: Heat Recovery Vapor Generator; LPC: Low Pressure Condenser; HPC: High Pressure Condenser; DCSS: Distillation and Condensation Sub System.

Figure 6: Kalina Cycle for a Cement Klin.

-generation cycle to recover waste heat from pre-heat exhaust and clinker cooler exhaust gasses in cement plant. Compared to other methods, the Kalina cycle will achieve the best value from the point of view of exergy efficiency. The ORC has the lowest exergy efficiency under the same condition, while the single flash steam cycle and the dual-pressure steam cycle have improved performance in the recovery of waste heat of the cement factory. It is inferred that the ORC, which is superior in the recovery of low-grade waste heat, may not be appropriate for waste heat recovery in the cement plant due to the relatively high temperature of the waste heat source. With this temperature range, the Kalina cycle is 20% to 40% more efficient than the Rankine cycle[43]. Figure 7 displays the flow diagram of concentrating photovoltaic/Kalina cycle combined system; consists mainly of two main components, namely the concentrated photovoltaic subsystem and the Kalina cycle subsystem (with an absorption chiller)[87].

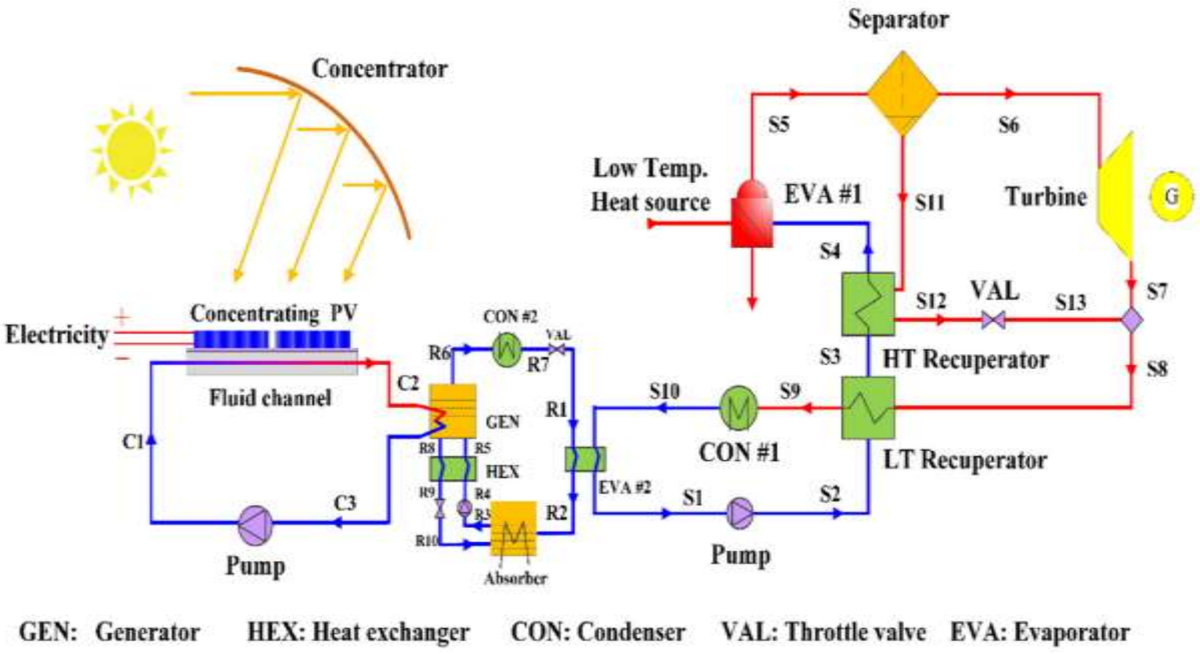
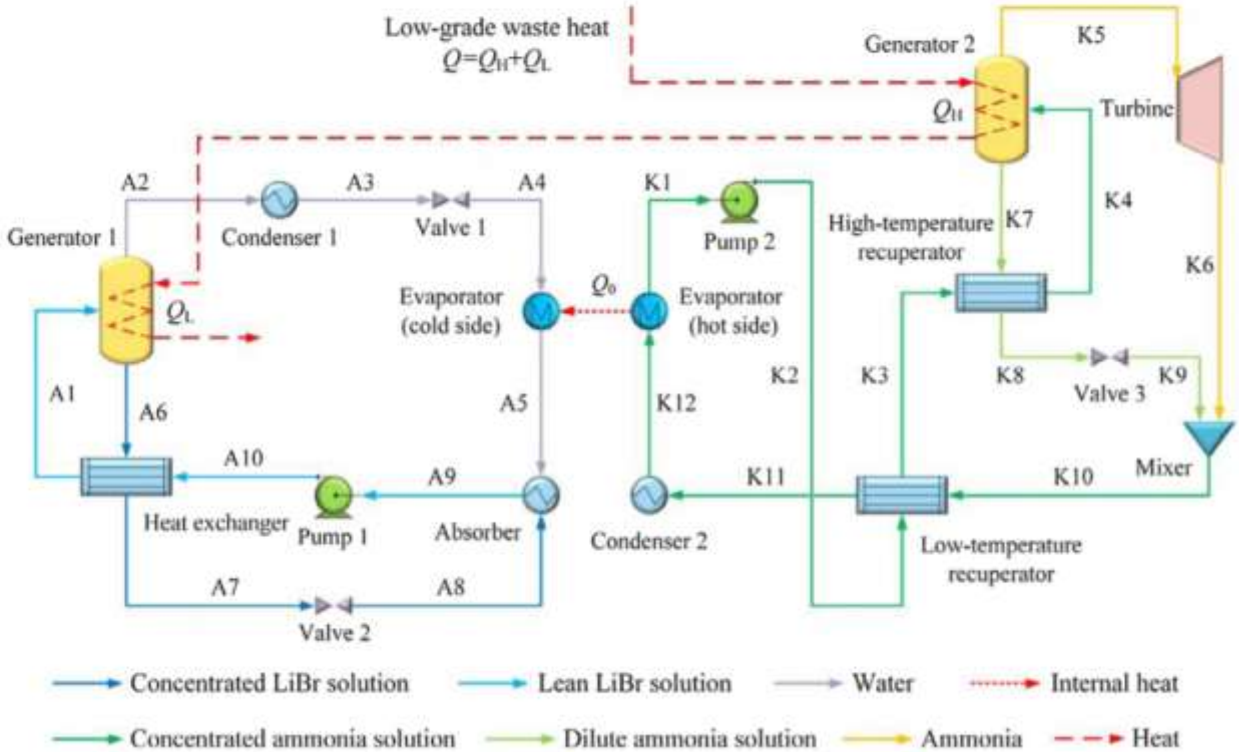


Figure 7: Flow diagram of concentrating photovoltaic/thermal and Kalina cycle combined system

The key findings of the analysis are summarized as follows[87]:

a) By using an absorption chiller, turbine outlet pressure is reduced, and more mechanical power is generated.
b) The overall solar energy efficiency is about 24% in the combined system, increased by 19.8% compared to that (4.2%) of the CPV without cooling while integrating M-Si.
c) The contribution of waste heat from M-Si in the overall solar energy efficiency is about 10%.
d) In comparison with typical photovoltaics, the relative enhancement of high-grade solar energy conversion results in more mechanical power ranges from 10% to 60%.
e) Differentiating from the direct use of photovoltaic waste heat to drive a thermal cycle, photovoltaics can operate in low-temperature conditions.
f) The efficiency of Kalina cycle has a potential increase among 2–3% in comparison with the stand-alone Kalina cycle.
g) The integrated device is capable of handling the fluctuation of irradiation by using the Kalina cycle instead of an expensive storage tank.

This combined system offers a new pathway to mechanical power by using thermal cycle not appropriate low-temperature waste heat of photovoltaics. In addition, the Kalina cycle's mechanical power output can be increased by using the cooling energy produced to further reduce the turbine-outlet pressure[87]. The coupled system consists of two cycles: an absorption chiller utilizing LiBr/H2O solution as the working pair and a Kalina cycle of KCS-34 using ammonia-water solution as the working medium. These two cycles are integrated through a heat transfer process in an evaporator, namely employing the LiBr/H2O absorption chiller as an auxiliary cooling source for enhancing the system operation of the Kalina power generation cycle. Both cycles are driven by a specific low-grade waste heat source. The heat source is artificially divided into two parts: the high-temperature part and low-temperature part. The part with a higher temperature of the thermal energy is introduced into the Kalina cycle for electrical power generation and the lower temperature part is suitable for the absorption chiller to produce cold load to cool down the exhaust stream of the Kalina cycle. Thus, the given low-grade waste heat is recovered by the coupled cycle through the thermal energy cascade utilization[85]. Figure 8 shows the schematic diagram of the coupled LiBr/H2O absorption chiller/Kalina cycle. Net power output decreases obviously with higher turbine backpressure while rises with increasing ammonia concentration. At refrigeration temperature of 2 ℃, the coupled system produces the maximum electricity generation because the system



can reach to a lower turbine outlet pressure. The optimal thermal efficiency is 0.1678 in all studied cases. After being integrated with the LiBr/H2O absorption chiller, the net power output of the Kalina cycle is improved by nearly 45%[85].

Figure 8: Schematic diagram of the coupled LiBr/H2O absorption chiller/Kalina cycle[85].

The component diagram depicting the sugar production and power generation processes in a 3500 TCD sugar factory located in India is shown in Figure 8. The power and heat required for operating

the sugar production related machinery is supplied by the cogeneration plant of the factory[86].

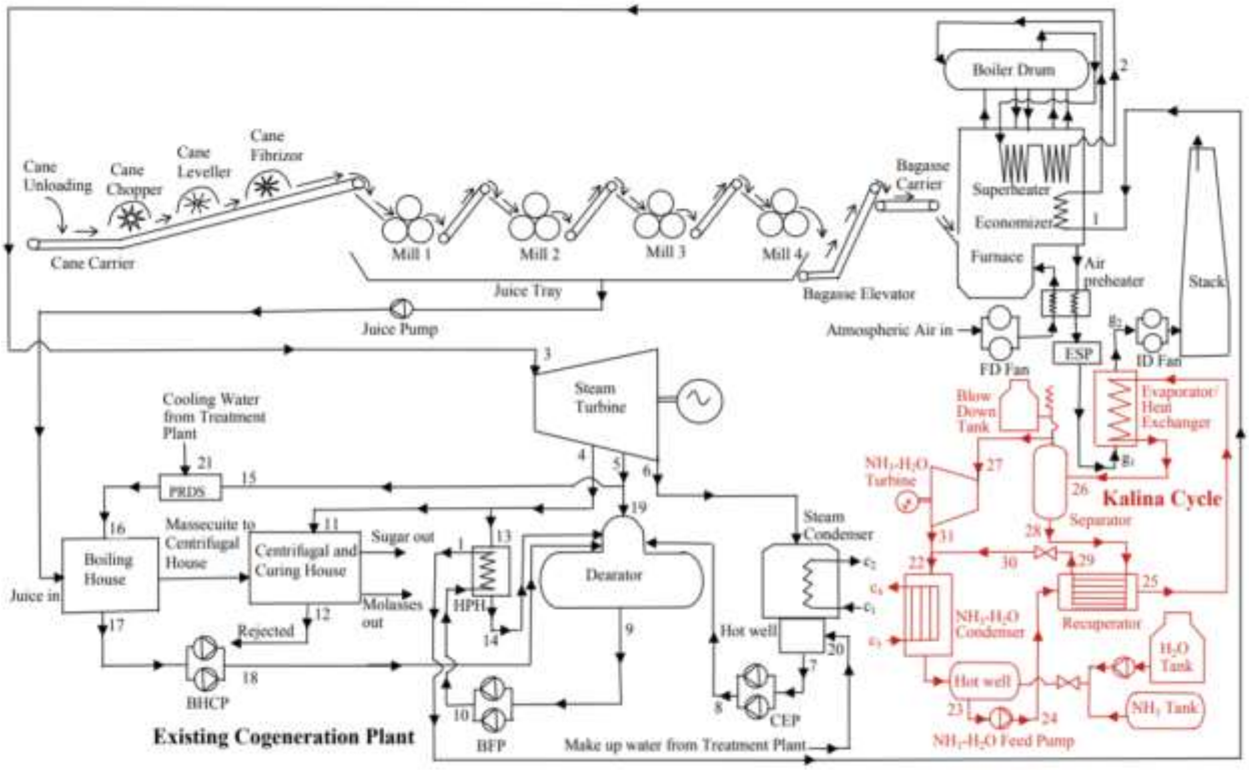


Figure 8: Kalina Cycle System 11 (KCS-11) integrated with the cogeneration plant of the considered 3500 TCD sugar factory[86].

The exergy analysis of the aforesaid cogeneration plant had revealed that 6.34% of the fuel energy input and 5.20% of the fuel exergy is lost to the environment through exhaust gases. In order to exploit the waste exhaust heat for conversion into power, Kalina cycle system (KCS11) was theoretically integrated with the existing cogeneration plant and the performance of the combined system was studied. A reasonable pressure of 4000 kPa at turbine inlet and an optimum ammonia mass fraction of 0.8 in the NH3-H2O mixture were chosen for the Kalina cycle[86]. It was determined on the basis of the acid due points calculations Using exhaust gas heat up to a temperature of just 105 ° C. Results indicated that with the values of ammonia, When exhaust heat is used to reduce the gas temperature from existing 160–105 ° C, an additional net power of 375,2135 kW is produced by the Kalina cycle, which increases the overall cogeneration efficiency of the plant by 0.3819% and the overall cogeneration efficiency by 0.315%. The condenser and evaporator exergy destruction rates (109,9811 kW) and (100,2637 kW) were the largest[86].

In addition to the applications in the geothermal and cement industries and the application presented at the start of this section, other application of the Kalina cycle was also developed for the conversion of ocean thermal energy (OTEC)[33], diesel engine based combined cycle[4], [88] coal-fired [8] and also nuclear.

6. LOW GRADE HEAT

Energy is required in multiple forms in several energy applications. Usually, these sources of energy provide a mixture of heating, cooling, mechanical energy and electrical power. These types of energy are often provided by a heat engine. According to the second law of thermodynamics, a heat engine can never have complete efficiency; thus, a heat engine can always produce a surplus of low-temperature heat. This is widely known as low-grade heat. Renewable energy sources, such as solar thermal, geothermal and significant volumes of industrial waste heat or low-grade heat, are potentially promising energy sources capable, in part, of meeting world demand for electricity. The temperature of the low-grade heat stream is the most important parameter, since the efficient use of residual heat or the efficiency of energy recovery from low-grade heat sources will depend mainly on the difference in temperature between the source and the appropriate sink. The Kalina cycle and the Organic Rankine Cycle (ORC) are the main cycles that have been developed to transform low-grade heat into electricity.

Table 2

Temperature range of various types of low-grade sources.

Sources of low-grade heat	Temperature Range
Solar thermal	70˚C-800˚C
Geothermal	149˚C-370˚C
Industrial waste thermal	80˚C-400˚C

7. TECHNICAL ISSUES FOR THE ENGINEERING IMPLEMENTATION OF THE KALINA CYCLE

The main concern for the engineering implementation of the Kalina cycle focuses on the environmental and safety aspects of the ammonia-water mixture. Whereas someone may believe in a strong smell and discomfort the properties of ammonia are a nuisance, which are actually beneficial. First, they’re self-alarming. Second, these properties will ensure that the operator maintains a healthy, tight plant.

Ammonia is formed as a decomposing by-product of nature. It is natural and thus does not lead to environmental emissions or global warming. Ammonia has also been documented to help the atmosphere by neutralizing acidic contaminants in the air. The chances of fire and explosion due to ammonia are very low. Ammonia will not allow combustion after the ignition source has been removed. And eventually at atmospheric pressure ammonia is gaseous. It's much lighter than air, which makes it easier to fly.

Another issue is the chemical stability of ammonia – water mixture and the possible problems caused by ammonia – water corrosion of the component.

Tests were performed to determine the effect of an ammonia – water system on conventional plant materials' life expectancy. Over the past 20 years, work has been carried out both in the laboratory and at the demonstration plant at Canoga Park. The test results indicate that traditional building materials for power plants which operate up to turbine throttle temperatures of 1000˚F are reasonable[45]. However, it is not advisable to use ammonia-water mixture at more than 400˚C, because NH3 becomes unstable at higher temperatures, leading to nitride corrosion[31]. In a Kalina cycle plant the ammonia – water working fluid poses different material issues than in a steam plant. The oxidation of plant components during the power cycle is less likely due to exceptionally low levels of oxygen within the working fluid. However, nitridation of high temperature components is a concern which should be considered when selecting superheater, reheater and high temperature turbine parts[89]. Except for the turbines and the superheaters, the temperatures are low enough for the use of carbon steels[7]. As far as the design of the turbine is concerned, copper-based alloys are prone to corrosion in the presence of ammonia, so that some material replacement might be required[27].

In 2009, Whittaker[90] performed a comprehensive analysis of corrosion problems at the Kalina Cycle Geothermal Power Plant in Husavik, Iceland. The investigation claims that mild steel and aluminum tend to be unsafe materials for Kalina Cycle Systems, but that some stainless steels (304, 316, nitronic 60 and duplex) and 6Al–4V titanium do not seem to have corrosion.

8. CONCLUSION

Research on the kalian cycle has been reviewed in this review article. In this review article, the Kalina and Rankine cycles were compared in order to find the best cycle for transforming various low-temperature heat sources into electrical power under different conditions using different research methodologies. The Kalina cycle was designed to replace the previously used Rankine Cycle as a bottoming cycle for the combined-cycle energy system as well as for the generation of electricity using low-temperature heat resources. In general, the Kalina cycle has better thermodynamic performance than the Rankine cycle and the organic Rankine cycle, both in terms of thermodynamic first & second law efficiency. The Kalina cycle has a family of configurations that are used in various fields. At present geothermal power generation has become an effective implementation of Kalina cycle. NH_3-H_2O combination is environmentally friendly and safe enough for engineering purposes.

Acknowledgement

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