

# **SIMULATION OF A THERMODYNAMIC CYCLE WITH ORGANIC ABSORBENTS AND CO<sub>2</sub> AS WORKING FLUID**

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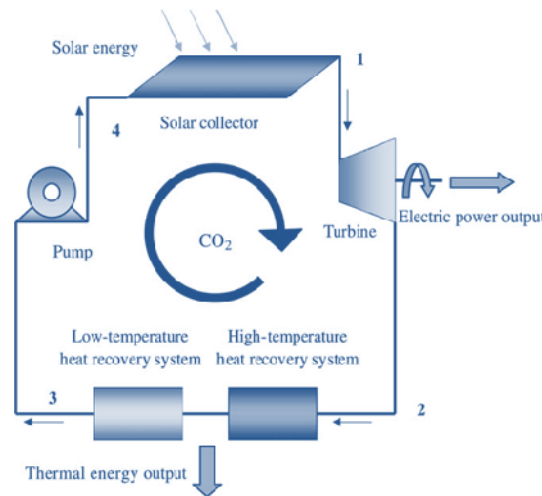
## **ABSTRACT**

This paper presents a performance simulation of the Goswami cycle with carbon dioxide-amyl acetate as binary working fluids for power generation with a moderate temperature heat source. The study of the optimized cycle performance was carried out for different heat source temperature supplements. The simulation results of the thermodynamic process show that the cycle can produce power and has a potential in the application of a solar power plant.

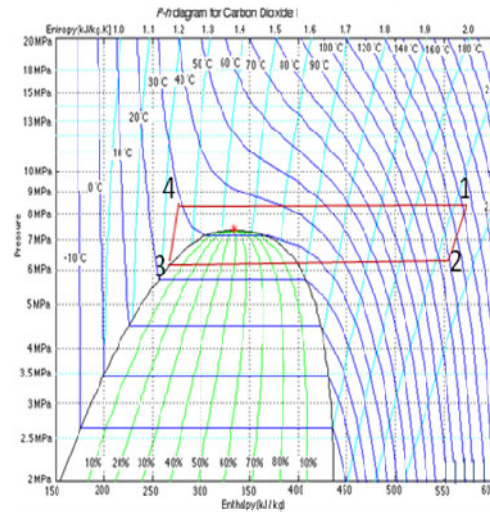
## **INTRODUCTION**

Carbon dioxide (CO<sub>2</sub>, R744) is a non-toxic, non-combustible, non-corrosive refrigerant which has been widely used [1]. The critical pressure and temperature of carbon dioxide are 73.8 bars and 31.1°C, respectively. Because of this low critical temperature, supercritical carbon dioxide can be used in thermodynamic cycles with moderate temperature heat sources [2]. The research on supercritical carbon dioxide Rankine power cycle has caught the attention of researchers during the last few years [3-9]. Current studies on pure carbon dioxide-based Rankine cycle are mainly for application in solar thermal power systems. A schematic diagram of the carbon dioxide-based Rankine cycle using solar energy directly as a heat source is shown in Fig.1, which is also shown in a carbon dioxide P-H diagram [9]. The drawback of the cycle is that the cycle low pressure must be higher than 6Mpa to condense CO<sub>2</sub> at a temperature higher than the ambient temperature of 20°C or higher (process 2→3). The high pressure of the cycle also needs to be over 73.1 bars due to the fact that the boiler pressure has to exceed the critical pressure of the working fluid. The pressure ratio of this cycle is around 1.3.

In this paper we have conducted a performance simulation of a Goswami power cycle with CO<sub>2</sub>-Amyl Acetate as the binary working fluids. Detailed information about the Goswami cycle can be found in [10-11]. Compared to pure carbon dioxide-based Rankine cycle described above, instead of being cooled down to liquid, carbon dioxide is absorbed by an organic fluid in the absorber, which allows the turbine outlet pressure go much lower.



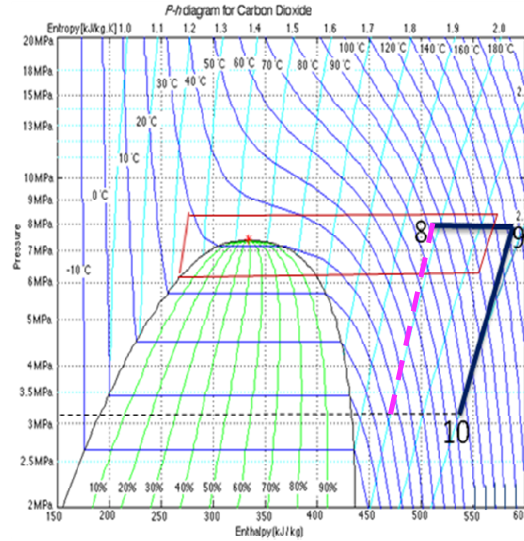
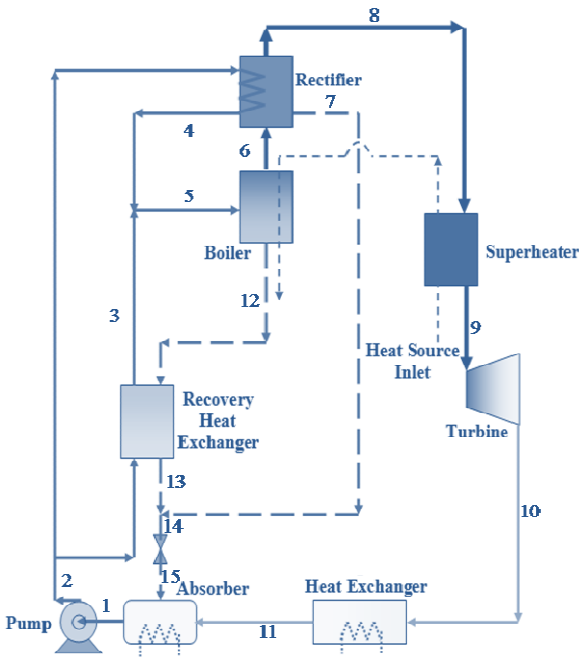
(a) A schematic diagram of the Rankine cycle



(b) Process of the cycle in a CO<sub>2</sub> P-H diagram

Fig.1 A CO<sub>2</sub> based Rankine cycle powered by solar energy [11]

A basic configuration of the cycle under simulation is shown in Fig.2. The thermodynamic cycle with CO<sub>2</sub> and amyl acetate as the binary working fluid can be described below. A mixture of CO<sub>2</sub> and the organic absorbent (amyl acetate) is pumped to a high pressure. This stream is preheated by the returning weak solution from the boiler and pumped to the boiler, where it is partially boiled. The vapor generated is rich in CO<sub>2</sub>. A “rectifier” is used to increase the concentration of CO<sub>2</sub> in the vapor by condensing some of the organic absorbent out. The rectified vapor is superheated and expanded through the turbine, which produces power through a generator. The pressure ratio can be as high as 2.5. Yet it must be mentioned that only a part of the carbon dioxide can be vaporized from the absorbent in the boiler. The process with carbon dioxide vapor is shown in a P-H diagram (Fig.2 (b)), which is 8→9→10, and the quadrilateral is the process for pure carbon dioxide cycle for comparison. The dotted line from point 8 shows the process without superheating which is explained later in the report. Please note that the complete cycle cannot be shown on a thermodynamic chart because such a chart with binary fluids is not available.



(a) A schematic diagram of the Goswami cycle      (b) Process of the cycle in a CO<sub>2</sub> P-H diagram

Fig.2 A CO<sub>2</sub> + organic absorbent-based binary-fluid Goswami cycle

## SIMULATION PROGRAM

The simulation program code was written in FORTRAN. Two major subroutines were used to predict the properties of the fluids, and to control and optimize of process. The following described the details.

### Property Data

Physical properties of the working fluid are of key importance in the simulation of the cycle. Temperature, pressure, specific volume, enthalpy, and entropy are needed at all the state points. However, the experimental data is limited. An equation of state (EOS) is necessary to calculate the state and the property at each point in the cycle. Peng-Robinson equation of state is a widely used method in industries for the calculation of vapor-liquid mixtures. The expression for a modified Peng-Robinson model (PPR78) is shown below [12]:

$$P = \frac{RT}{v - b_1} - \frac{a_1(T)}{v(v + b_1) + b_1(v - b_1)} \quad (1)$$

with,

$$R = 8.314472 \text{ J mol}^{-1}\text{K}^{-1}$$

$$b_1 = 0.0777960739 \frac{RT_{c,d}}{P_{c,d}}$$

$$a_1 = 0.457235529 \frac{R^2 T_{c,d}^2}{P_{c,d}} \left[ 1 + m_1 \left( 1 - \sqrt{\frac{T}{T_{c,d}}} \right) \right]^2 \quad (2)$$

$$\text{if } \omega_1 \leq 0.491 \quad m_1 = 0.37464 + 1.54226\omega_1 - 0.26992\omega_1^2$$

$$\text{if } \omega_1 > 0.491 \quad m_1 = 0.37462 + 1.48503\omega_1 - 0.164423\omega_1^2 + 0.01666\omega_1^3$$

where P is the pressure, R is the ideal gas constant, T is the temperature, a and b are the EOS parameters, v the molar volume,  $T_c$  the critical temperature,  $P_c$  the critical pressure, and  $\omega$  the acentric factor.

### Process Control and Optimization

In order to optimize the performance of the system and control the system to be working in a reasonable range, a control and optimization program is needed. The controlling and optimization of the thermodynamic cycle is a non linear programming (NLP) problem, which is handled by a search method called Generalized Reduced Gradient (GRG) method in this project. GRG is one of the most popular NLP method in use today.

The target functions for this program are the efficiencies of the cycle. The efficiencies studied are thermal efficiency, second law efficiency and the resource utilization efficiency (RUE). Thermal efficiency of a cycle is the ratio of net work output to the heat supplied, that is

$$\eta_1 = \frac{(W_{net} + E_c)}{Q_h} \quad (3)$$

where  $W_{net}$  is the net work output,  $Q_h$  is the total heat input.

The second law of efficiency, also known as exergy efficiency, is a measure of the performance of a device relative to its performance under reversible conditions. An expression of the second law efficiency corresponding to the cycle under investigation is,

$$\eta_{II} = \frac{W_{net}}{\dot{m}_{hs} \left[ h_{hs,in} - h_{hs,out} - T_o (s_{hs,in} - s_{hs,out}) \right]} \quad (4)$$

where  $\eta_{II}$  is the second law efficiency,  $W_{net}$  is the net work output,  $\dot{m}_{hs}$  is the mass flow rate of the heat source,  $T_o$  is the ground state temperature,  $h$  and  $s$  are enthalpy

and entropy respectively, and the subscript “*hs,in*” means heat source in, “*hs,out*” means heat source out.

The resource utilization efficiency (RUE) considers all of the available energy in the resource even though all of it is not used up in the process. The resource utilization efficiency is the recommended choice in evaluating resources that are “discarded” after use in the cycle, such as a geothermal resource, where, the heating fluid is re-injected into the ground after extraction of energy from it in the power plant. The RUE is also applied to other applications, such as a coal power plant. To sum up, optimization of the resource utilization efficiency (RUE) is a good choice to ensure that maximum use is made of the energy source or fuel. An expression for RUE of the cycle under investigation is,

$$\eta_R = \frac{W_{net}}{\dot{m}_{hs} [h_{hs,in} - h_o - T_o (s_{hs,in} - s_o)]} \quad (5)$$

where  $\eta_R$  is the resource utilization efficiency,  $h_o$  and  $s_o$  are the enthalpy and entropy at the ground level.

## Main Program

The main program sets the thermodynamic equations for each state point, as well as the boundaries of the variables, variable relations, and target function. Limits of the variable values have to be specified in constrained optimization. The purpose of specifying limits is to ensure that the values at the optimum conditions are achievable, meaningful, and desirable in practice.

## SIMULATION RESULTS AND DISCUSSION

Simulation of this cycle was carried out and the outputs were optimized at different heat source temperatures. Based the simulations, the maximum first law efficiency, second law efficiency, and RUE (Energy utilization efficiency) are 6%, 25%, and 21% respectively. The pressure ratio is 2.2-2.5, which is much higher than the one with pure carbon dioxide Rankine cycle (1.3). The high pressure and low pressure requirements of the cycle are 75-85bars and 34.48 bars for maximum output. The function of a superheater is to superheat the CO<sub>2</sub> before it goes to the turbine to get maximum work output (see Fig.2). However, when the heat source temperature is 390K or below, the temperature difference between the boiler and the superheater is 5K or below, which makes the superheater inefficient and impractical. Therefore, with a heat source temperature lower than 390K, the simulation was undertaken with no superheater (see the dotted line in Fig.2). It is not practical to use a heat source with a temperature lower than 370K for this cycle with the present working fluid pair. The following is a detailed discussion about the results.

## Efficiencies at Different Heat Source Temperature Supply

Influence of the heat source temperature on the optimized efficiencies is shown in Fig.3. The curves are disconnected at 390K, because there is no superheater when the temperature is lower than that. The following discussion is based on the system with superheater, i.e., when the temperature is higher than 390K.

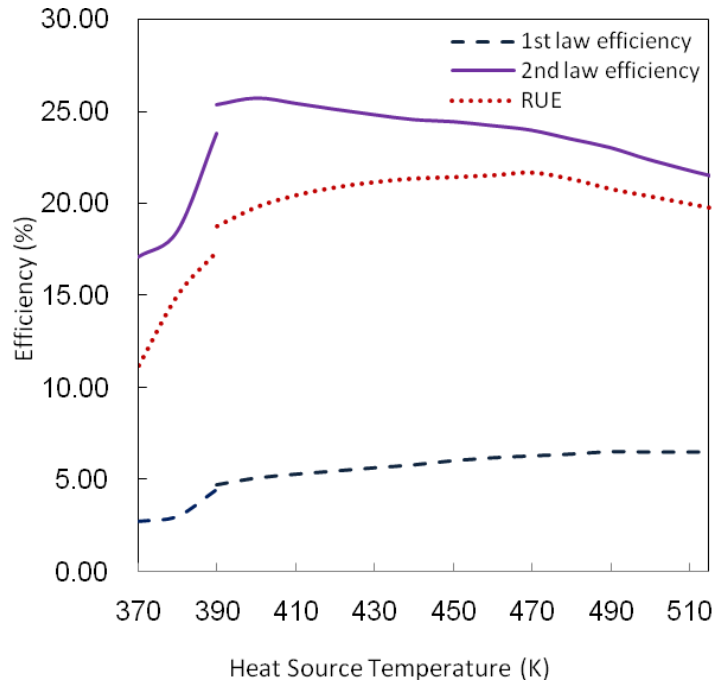


Fig. 3 Optimized cycle efficiencies with different heat source temperature supplement

From Fig.3, the first law efficiency (thermal efficiency) shows a rise from 4.70% to 6.53% with the increase of the heat source temperature from 390K to 515K. However, the second law efficiency and the RUE are higher at lower temperatures. Figure 4 and 5 are the net work output vs. heat source temperature and the heat source flow rate needed vs. heat source temperature. From Fig.4 we can see that net work output is much lower in the low temperature range. The reason is that when the heat source temperature is lower, the impact of the superheater is less. Also, Fig.5 shows that with lower temperature heat source, larger heat source flow is needed.

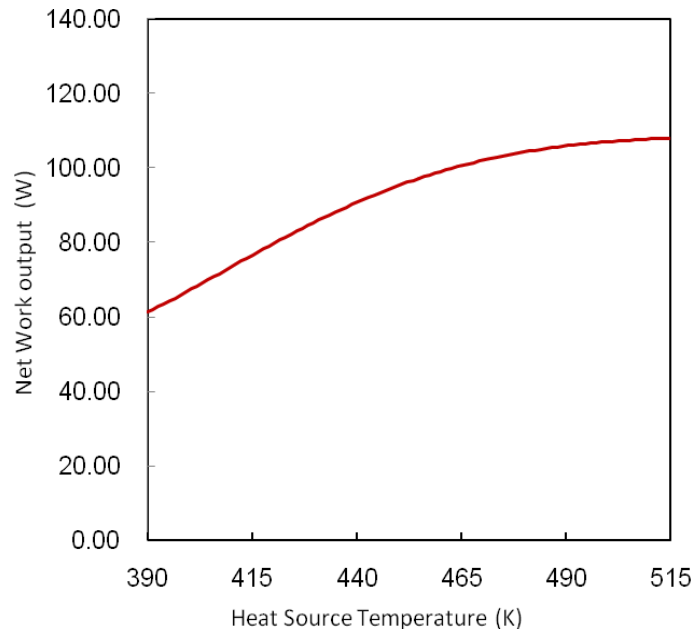


Fig.4 Net work output vs. heat source temperature

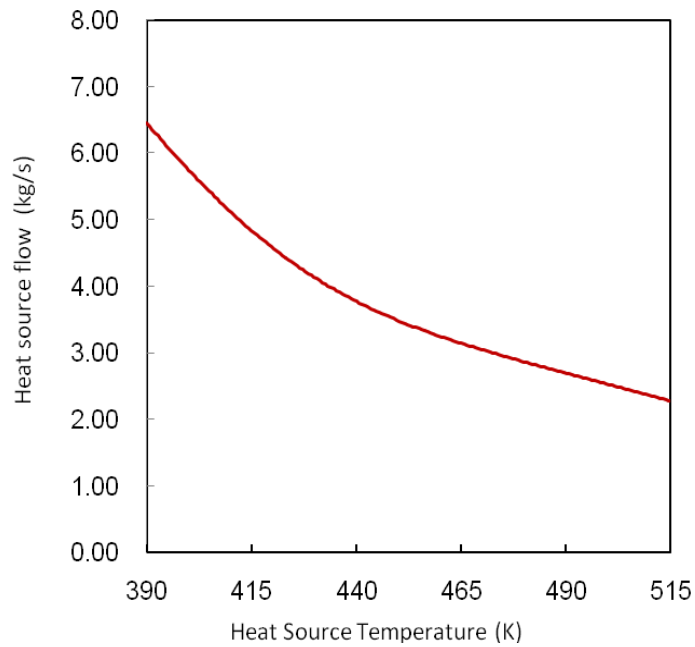


Fig.5 Heat source flow rate needed vs. heat source temperature

### Influence of the cycle high pressure

It has been mentioned that the high pressure (pressure in the boiler) of the cycle working in the supercritical state is 75-85bars. A question comes as to why it should not go higher to

increase the pressure ratio. The answer lies in the fraction of the carbon dioxide being vaporized in the boiler which is highly influenced by the pressure in it. Fig.6 is the graph of the fraction of carbon dioxide that has been vaporized vs. the corresponding pressure. Curves of three temperatures in the boiler are plotted. With a boiler pressure of 115 bars, the fractions of carbon dioxide vaporized are only 3%, 29% and 41% for boiler temperature of 390K, 420K and 450K respectively. This would require very high flow rates which would be a major reason of inefficiency. Therefore, a higher pressure does not necessarily lead to a better output. In regard to the cycle under investigation, a cycle high pressure of 75-85 bars is a favorable range.

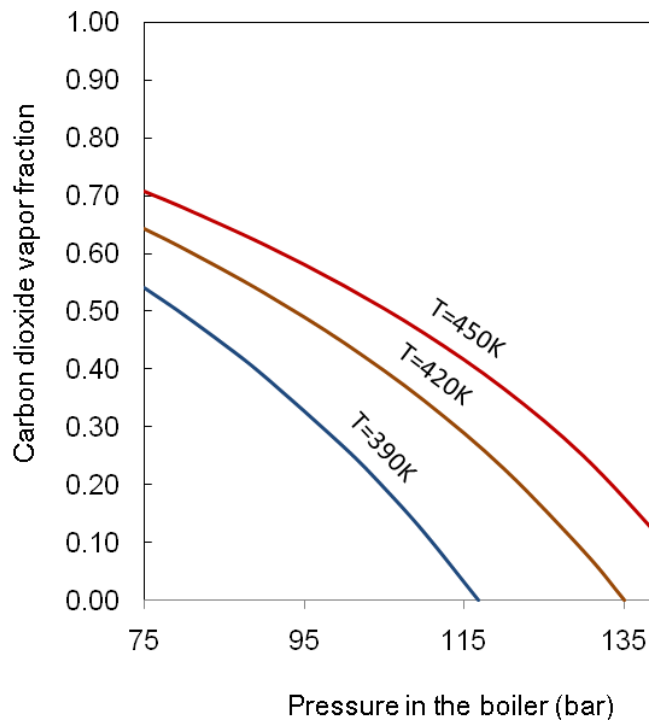
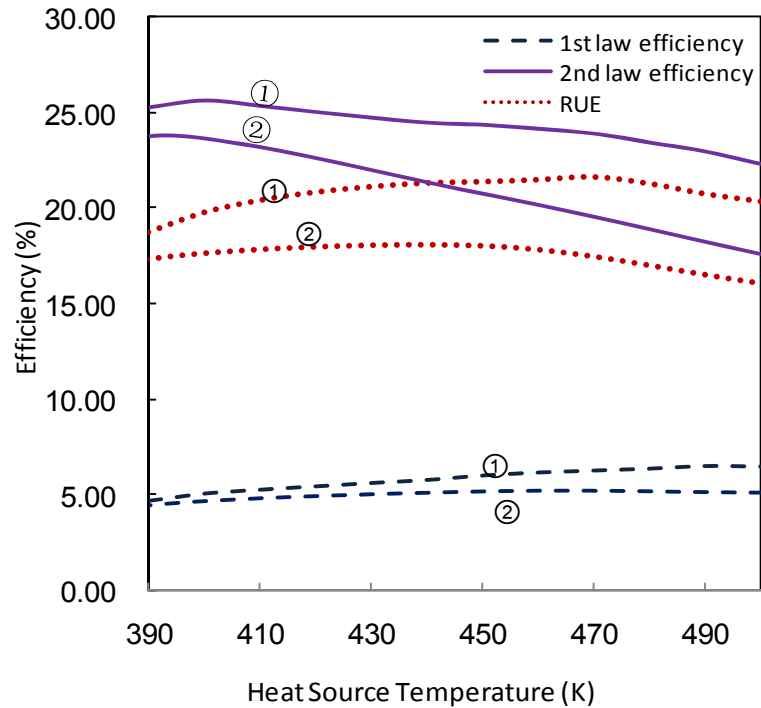


Fig.6 Fraction of CO<sub>2</sub> that can be vaporized vs. the corresponding pressure

### **Influence of the superheater at heat source temperatures higher than 390K**

It has been mentioned that a superheater is not recommended at a heat source temperature lower than 390K. The following is to discuss the influence of superheating for a heat source temperature higher than 390K, with results shown in Fig.7. It is easy to notice that the efficiencies of the system with superheating are higher than those without superheating. Therefore, a superheater could be used to improve the system efficiencies when the heat source temperature is higher than 390K.





Note: ○: System with superheater; □: System with no superheater

Fig.7 Influence of superheating when the heat source temperature is higher than 390K

## Conclusions

This work studied the performance of Goswami thermodynamic power cycle with CO<sub>2</sub> and Amyl Acetate as the working fluids. The cycle was simulated by a FORTRAN program. The simulation results showed that the cycle can obtain reasonable efficiencies. The drawback of the process is that it needs very high pressures to run the cycle, which may lead to material problems. Since only a part of the carbon dioxide can be vaporized from the absorbent in the boiler, the cycle requires high flow rates.

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