

# Carnot Theory: Derivation and Extension\*

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*The present work reports the cycle maximizing the work done per cycle, or, alternatively, the thermal efficiency of a class of reversible heat engines obtained from an optimization analysis. This arrives at and extends the classical Carnot theory of heat engines. The first and second laws of thermodynamics are applied to examine the total work output during a general thermodynamic process. This leads to an extension of the Carnot principles to general thermodynamic processes.*

## SUMMARY OF EDUCATIONAL ASPECTS OF THE PAPER

1. The paper discusses materials for a course in Engineering Thermodynamics.
2. Students in all branches of engineering are taught in this course.
3. Level of the course (year) is Level 2.
4. Mode of presentation is through lectures.
5. The course is presented as a regular course.
6. Hours required to cover the material is one hour.
7. Student homework or revision hours required for the materials is one hour.
8. The first part of the paper provides an alternative approach to introduce the Carnot cycle and two Carnot principles through an optimization analysis. This forms a systematic method for obtaining the Carnot cycle to achieve the optimal performance of cycles, and answers the question whether an engine should operate differently when different performance criteria are used. The second part of the paper applies the first and second laws of thermodynamics to extend two classical Carnot principles to general processes. This forms an answer to the question frequently asked by students what will happen if the process is not a cycle. This also help students in understanding concepts of availability and exergy when they learn second law analysis of engineering systems.
9. The standard text recommended in the course is Y. A. Cengel and M. A. Boles, *Thermodynamics: An Engineering Approach*, 3rd edition, McGraw-Hill (1998), which does not cover this additional material.

## INTRODUCTION

A SYSTEMATIC study of the physical processes governing steam engines was undertaken first by

Sadi Carnot, a French engineer, resulting in his remarkable paper *Réflexions sur la puissance motrice du feu et sur les machines propres a developper cette puissance* (On the Motive Power of Heat) published in 1824 [1]. In his work, Carnot constructed an ideal cycle, which is now well known as the Carnot cycle, and analyzed its thermal efficiency. Carnot showed that:

1. Any engine, using heat from a hot reservoir at temperature  $T_h$  to do work, has to transfer some heat to a reservoir at lower temperature  $T_l$ .
2. The thermal efficiency of the Carnot cycle was working medium-independent.
3. No engine could convert into work more of heat taken in at  $T_h$  than the fraction  $\eta_c = 1 - T_l/T_h$  known as the Carnot efficiency.

Later, a systematic proof of the Carnot theory was carried out by Rudolf Clausius based on the second law of thermodynamics, which is now known as the Carnot principles [2]. Since then, however, no significant development was made on the Carnot theory. Indeed, the theory is still largely taught today along lines which follow closely those set out by Carnot and Clausius.

Several questions arise from the re-examination of the Carnot theory. Among them is the systematic method for obtaining the process paths to achieve the optimal process values. Indeed, classical Carnot theory contains no technique for deriving Carnot cycle to achieve maximum efficiency. Another question is concerned with whether the engine should operate differently when different performance indices such as work and efficiency are maximized. Furthermore, the Carnot principles are only for the cyclic devices (heat engines), stating that:

1. The efficiency of an irreversible heat engine is always less than the efficiency of a reversible one operating between the same two reservoirs;
2. The efficiencies of all reversible heat engines operating between the same two reservoirs are the same.

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The questions regarding the performances of a general thermodynamic process have been left unanswered.

The motivation for the present work comes from the desire of deriving the Carnot theory in a systematic and rigorous way and extending the Carnot theory to answer questions mentioned above. This yields a systematic technique to find the optimal cycle and an extension of the Carnot principles to the general thermodynamic processes. The present work is believed to be of both pedagogical and academic importance by noting that the classical Carnot theory is only on analyzing the performances of the Carnot cycle with known process paths rather than deriving the cycle to achieve the optimal performances.

### DERIVATION AND EXTENSION: CYCLES

Heat engines may be conveniently classified by the type of cycle undergone by the working fluid. For the engines considered in this work, such cycles are made up of totally reversible processes in which working fluid undergoes reversible transformations (internal reversibility) and is coupled to the environment through reversible processes (external reversibility) [2, 3]. They are reversible engines discussed in thermodynamic textbooks.

For a cycle,

$$\Delta S = \oint dS = 0 \quad (1)$$

Here  $\Delta S$  is the change of the working fluid in entropy. In the present work we choose entropy as the independent variable and temperature as the dependent variable. Then the property of the working fluid is represented by the function relation  $T = T(S)$ .

Let  $T_h$  and  $T_l$  be the temperature of the hottest and coldest thermal reservoirs, then the function  $T = T(S)$  must satisfy:

$$T_l \leq T \leq T_h \quad (2)$$

Furthermore, we require:

$$S_i \leq S \leq S_m \quad (3)$$

where  $S_i$  and  $S_m$  are the minimum and maximum values of entropy permitted during the cycle, respectively.

Following analyses are to find function  $T = T(S)$  which makes the work done, thermal efficiency or whatever else we choose as an objective functional an extreme. In this paper, we investigate the optimal operation of engines in terms of maximum work and maximum efficiency as follows.

### Maximum work

By applying the first law of thermodynamics to the cycle, the work done per cycle may be written as:

$$W = \oint T(S) dS \quad (4)$$

Therefore we should maximize  $W$  subject to the constraint (1), i.e., we maximize:

$$L = W - \lambda \Delta S = \oint (T(S) - \lambda) dS \quad (5)$$

by varying  $T(S)$ .

In order to take account of constraints (2) and (3), we replace  $T$  and  $S$  by two new variational parameters  $\theta$  and  $\phi$  such that

$$T = \frac{1}{2}(T_h + T_l) + \frac{1}{2}(T_h - T_l) \tanh \theta \quad (6)$$

$$S = \frac{1}{2}(S_m + S_i) + \frac{1}{2}(S_m - S_i) \tanh \phi \quad (7)$$

where  $\theta$  and  $\phi$  are unconstrained. It is now a simple matter to maximize  $L$  by applying Euler-Lagrange equation as:

$$\frac{1}{4}(T_h - T_l)(S_m - S_i) \operatorname{sech}^2 \theta \operatorname{sech}^2 \phi = 0 \quad (8)$$

This leads to:

$$\theta = \pm \infty \quad (9)$$

or

$$\phi = \pm \infty \quad (10)$$

which mean that:

$$T = T_h \text{ or } T_l \quad (11)$$

and

$$S = S_i \text{ or } S_m \quad (12)$$

Therefore, optimal trajectory is made up of four branches:

$$T(S) = T_h \quad (13)$$

$$T(S) = T_l \quad (14)$$

$$S = S_i \quad (15)$$

$$S = S_m \quad (16)$$

It is a simple matter to prove that the Legendre's necessary condition [4] is also satisfied along each of these branches. The resultant optimal cycle is shown in Fig. 1. At corners 1-4, it is simple to show that both first and second Weierstrass-Erdmaun corner conditions [4] are satisfied.

In order to show that this is the true maximum, it is usually to consider second variation of  $L$ . If the second variation is less than zero for all admissible functions in a particular one-parameter family, the result is regarded as the true maximum. However, this is fallacious as pointed out in [4]. It is only the necessary condition for the maximum

that the first variation is zero and second variation is less than zero. Readers are referred to [4] for this. In the best knowledge of the author, the general sufficient conditions have not been established in the calculus of variations. An *ad hoc* proof is usually produced for some problems. Fortunately, the second law of thermodynamics concludes that the solution obtained is really a maximum for our problem.

Under optimal trajectory, the maximum work is:

$$W_{\max} = (T_h - T_l)(S_m - S_i) \quad (17)$$

and the efficiency is:

$$\eta = W_{\max}/Q_1 = 1 - T_l/T_h \quad (18)$$

Here

$$Q_1 = \oint T(S)\psi(dS) dS \quad (19)$$

is the input energy with  $\psi(dS)$  as the Heaviside step function [ $\psi(x) = 1$  if  $x > 0$ ,  $\psi(x) = 0$  if  $x < 0$ ]. It is worth noting that  $\eta$  is constant once  $T_l$  and  $T_h$  are fixed. However,  $W_{\max}$  increases proportionally with  $(S_m - S_i)$ .

The cycle derived above is the Carnot cycle operating between  $T_h$  and  $T_l$ . It is worth to note that the fact that we need only the hottest and coldest reservoirs and that we do not need any other reservoirs is not a trivial result. Also, the derivation does not depend on the working medium.

#### Maximum efficiency

It is often useful to run an engine at maximum efficiency rather than some other operating goal such as we did above. The efficiency is, as usual, defined by:

$$\eta = W/Q_1 \quad (20)$$

where  $W$  and  $Q_1$  are defined by equations (4) and (19), respectively.

This is a quotient of two integrals. There are two ways to obtain its optimal trajectory. One is to maximize  $\eta$  for a fixed input energy  $Q_1$ . If the resulted maximum value of  $\eta$  is dependent on  $Q_1$ , the optimization of  $\eta$  with respect to  $Q_1$  is followed to achieve the final result. The other is to maximize  $\eta$  directly based on the following theorem.

**Theorem 1.** The function yielding the extreme of the quotient of two functionals  $J_1$  and  $J_2$  should satisfy the Euler-Lagrange equation for the intermediate functional:

$$H = J_1 - \lambda_0 J_2 \quad (21)$$

The constant  $\lambda_0$  is determined from the condition:

$$\lambda_0 = J_1(y_e)/J_2(y_e) \quad (22)$$

where  $y = y_e$  yields the extreme of the functional:

$$J_3 = J_1/J_2 \quad (23)$$

*Proof.* Since:  $J_3 = J_1/J_2$ , then:

$$\delta J_3 = (J_2 \delta J_1 - J_1 \delta J_2)/J_2^2$$

Suppose that  $y = y_e(x)$  yields the extreme of the functional  $J_3$ . Then  $\delta J_3 = 0$ , and therefore (if  $J_2 \neq 0$ ):

$$J_2(y_e)\delta J_1 - J_1(y_e)\delta J_2 = 0$$

Using the notation  $\lambda_0 = J_1(y_e)/J_2(y_e)$ , we obtain:

$$\delta J_1 - \lambda_0 \delta J_2 = \delta(J_1 - \lambda_0 J_2)$$

and we arrive at the theorem above.

For our problem, two methods lead to the same result. Shown in this paper is the second method. Applying Theorem 1 to our problem, maximizing  $\eta$  in equation (20) under constraint (1), is the same as maximizing:

$$L = W - \lambda \Delta S - \lambda_0 Q_1 \quad (24)$$

It is simple to show that we again obtain the Carnot cycle as shown in Fig. 1 with:

$$\eta_{\max} = 1 - T_l/T_h \quad (25)$$

and

$$W = (T_h - T_l)(S_m - S_i) \quad (26)$$

These are the same as those in equations (17) and (18).

Once again, the Legendre's necessary condition and both first and second Weierstrass-Erdmaun corner conditions are satisfied by the solution. Also the second law of thermodynamics concludes that this is a true maximum. The optimal process paths can also be regarded as the representation of the property of the optimal working fluid. This shifts the focus from the process to the working fluid. The optimal path 2-3 in Fig. 1, for example, may be realized not only through an isothermal process but also through any working fluid with the property of entropy-independent temperature. Boiling water under the constant pressure has this property. Then the boiling water may be used to realize this path under the constant pressure.

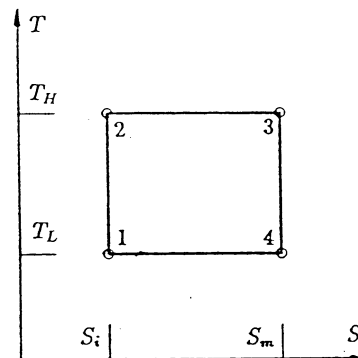


Fig. 1. Optimal cycle of reversible heat engines.

**EXTENSION: PROCESSES**

Consider a mass system  $A$  undergoing a process from state 1 to state 2 in Fig. 2. The work directly delivered by the system is termed the internal work  $W_i^{12}$ . The work produced by auxiliary cyclic devices is called external work  $W_e^{12}$  ( $= \sum_{i=1}^n W_{ei}^{12}$ ). Such auxiliary cyclic devices are required to ensure external reversibility [2, 3] in any heat exchanges between the system and its environment for a general process 1–2. The sum of  $W_i^{12}$  and  $W_e^{12}$  is termed total work  $W_t^{12}$ . Note that the process in the auxiliary devices is cyclic. The change in the total energy of the combined system  $A^+$ , comprising  $A$  and the auxiliary cyclic devices, is thus equal to that for the system  $A$  alone. The  $W_t^{12}$  and  $Q_0^{12}$  ( $= \sum_{i=1}^n Q_{0i}^{12}$ ) are the work and heat interactions between the system  $A^+$  and its surroundings, respectively. A striking feature of  $W_t^{12}$  can be revealed by applying both first and second laws of thermodynamics to the system  $A^+$ , and is summarized as the following theorem which can be regarded as an extension of the Carnot principles to the general processes.

*Theorem 2.* For a system exchanging heat with a single thermal reservoir (the environment at temperature  $T_0$  for example), the total work output is the same for all totally reversible processes between the same specified end states 1 and 2, which is termed the maximum total work symbolized with  $W_{iR}^{12}$ . During any irreversible process between these same specified end states, the total work output  $W_{iI}^{12}$  is always less than  $W_{iR}^{12}$ .

*Proof.* To prove this theorem, consider two processes  $R$  and  $I$  between 1 and 2, as shown in Fig. 3(a). One process ( $R$ ) is totally reversible, and the other ( $I$ ) is irreversible. The amount of total work produced during the totally reversible process  $R$  is  $W_{iR}^{12}$ , and the amount produced during the irreversible one is  $W_{iI}^{12}$ . The heat exchanged with the environment during the totally reversible process  $R$  is  $Q_{0R}^{12}$ , and the heat to the environment during the irreversible one  $I$  is  $Q_{0I}^{12}$ .

In violation of the theorem, we assume that

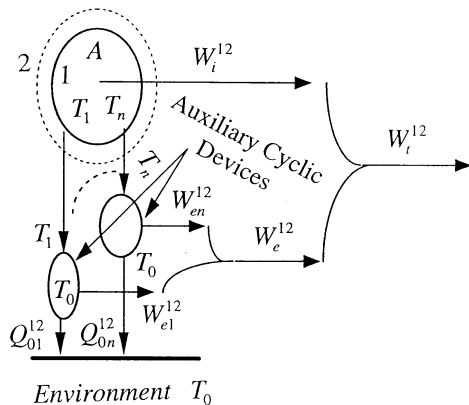


Fig. 2. Total work and totally reversible process.

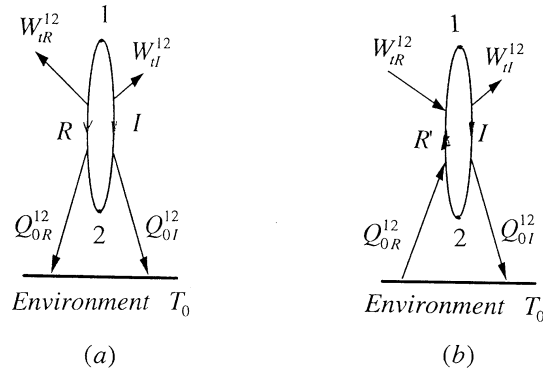


Fig. 3. Proof of theorem 2.

$W_{iI}^{12} > W_{iR}^{12}$  and thus  $Q_{0I}^{12} < Q_{0R}^{12}$  by the first law of thermodynamics. Now let the reversible process be reversed as a process  $R'$  from 2 to 1. This process will receive a work input  $W_{iR'}^{12}$  from the surroundings and a heat input  $Q_{0R'}^{12}$  from the environment.

Now considering the  $R'$  and  $I$  together as a cycle (Fig. 3(b)), we have an engine that produces a net work in the amount of  $W_{iI}^{12} - W_{iR'}^{12}$  while exchanging heat with a single reservoir in the amount of  $Q_{0R'}^{12} - Q_{0I}^{12}$ , which is a violation of the Kelvin-Planck statement of the second law of thermodynamics. Therefore we conclude that:

$$W_{iI}^{12} \leq W_{iR}^{12} \tag{27}$$

However, if the equality holds in equation (27), the process  $I$  must be reversible as the process  $R'$  could then also act as the erasing process of  $I$ . This is certainly against the initial assumption. Consequently, we have:

$$W_{iI}^{12} < W_{iR}^{12} \tag{28}$$

Since both processes  $R$  and  $I$  are arbitrarily chosen as the totally reversible and irreversible respectively, this is the proof that the total work output during an irreversible process is always less than that during a totally reversible process.

Now we replace  $I$  and  $R$  by two arbitrarily chosen totally reversible processes  $R_1$  and  $R_2$  respectively. Equation (27) leads to  $W_{iR_1}^{12} \leq W_{iR_2}^{12}$ . Similarly, if  $I$  and  $R$  are replaced by  $R_2$  and  $R_1$  respectively, equation (27) yields  $W_{iR_2}^{12} \leq W_{iR_1}^{12}$ . As both expressions are true, to satisfy them simultaneously, we must have:

$$W_{iR_1}^{12} = W_{iR_2}^{12}$$

However,  $R_1$  and  $R_2$  are any two totally reversible processes between the specified end states 1 and 2, so that we conclude:

$$W_{iR_1}^{12} = W_{iR_2}^{12} \equiv W_{iR}^{12} \tag{29}$$

This and equation (28) together establish the above-stated theorem. While work is generally dependent on the characteristics of process,  $W_{iR}^{12}$  is uniquely-valued for all totally reversible

processes between two specified end states 1 and 2. Therefore, it must represent the change of a state property.

It should be noted that the theorem is not valid for the internal work output as, with variable temperature of the system  $A$ , we cannot find a single thermal reservoir to ensure the reversible heat transfer.

### CONCLUSIONS

The optimization theory is used to derive and extend the classical Carnot theory. Two performance indices, work done per cycle and thermal efficiency, are used in the process of optimization. Same results are obtained for these two performance indices. This shows that the operation of the

engines considered in this work should remain unchanged when different performance indices are optimized.

The optimization analysis for reversible heat engines arrives at the Carnot theory of heat engines. Unlike the classical thermodynamics, the new approach provides methods for deriving the Carnot cycle to achieve maximum work or efficiency.

The first and second laws of thermodynamics are employed to show that: (1) the total work output during any irreversible process is always less than that during a totally reversible one between the same specified end states, and (2) the total work output is the same for all totally reversible processes between the same specified end states. This may be regarded as the extension of the Carnot principles to the general processes.

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