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## Short Communication

## Maximum conversion efficiency of hydrogen fuel cells



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## ARTICLE INFO

## Article history:

Received 10 January 2018

Received in revised form

11 March 2018

Accepted 12 March 2018

Available online 7 April 2018

## Keywords:

Maximum efficiency

Hydrogen fuel cell

Entropy generation

Carnot efficiency

## ABSTRACT

Çengel and Boles discuss in their Thermodynamics textbook that the Carnot efficiency bound is not applicable to fuel cells, whereas some researchers have raised objection that maximum conversion efficiency of fuel cells is limited to the Carnot efficiency. We apply the conservation of energy and entropy balance equations to derive expressions for the maximum work of hydrogen-oxygen, hydrogen-air and methane-air fuel cells. We show that the theoretical efficiency of a fuel cell may exceed that of a Carnot engine operating between the same low and high temperatures. Contrary to past studies in that the efficiency of an ideal hydrogen fuel cell is shown to decline with temperature, the maximum efficiency is observed to first decrease with reactants temperature, then remains unaltered and finally rises. The lowest value of the maximum efficiency is found to be 79.3%, 75.7%, and 82.1% for hydrogen-oxygen, hydrogen-air and methane-air fuel cells, respectively. By increasing the stoichiometric coefficient of air, the efficiencies of both hydrogen-air and methane-air fuel cells monotonically increase and they approach the 100% limit at a stoichiometric coefficient of 7.2 and 9.8, respectively. It is shown that a Carnot engine whose heat is supplied by an isothermal combustor proposed in some past studies is not a correct means for comparison of the ideal performance of fuel cells and heat engines.

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## Introduction

Fossil fuel-based power generation and transportation are two major sources of carbon dioxide emissions. The fuel-to-power conversion efficiency of conventional power technologies operating on traditional cycles; e.g., Brayton cycle, Rankine cycle, and Otto cycle, is relatively low due to several losses. On the other hand, hydrogen fuel cells have been regarded as highly efficient devices with limited amount of emissions [1–3], which are expected to play substantial role in automobile and power industries in the coming decades. High temperature fuel cells such as solid oxide fuel cells (SOFC) are

excellent candidate for stationary power generation where the hot reaction products are usually used in a bottoming cycle such as a gas turbine [4–6], steam cycle [7,8], or combined gas/steam cycle [9] to produce additional power.

Understanding the limit of fuel-to-power conversion efficiency is a fundamental step towards enhancing and optimizing the performance of fuel cell-driven power generating systems. There has been a debate in the scientific literature over determination of the maximum conversion efficiency of fuel cells and whether their performance is limited to the Carnot efficiency. Larminie and Dicks [10] compared the efficiencies of an ideal hydrogen fuel cell and a Carnot cycle to show that the efficiency of the former is higher than that of

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the latter depending on the operating temperature. Çengel and Boles [11] argue in their Thermodynamics textbook that the Carnot limit is not applicable to fuel cells. On the other hand, Haynes [12], Lutz et al. [13], and Wright [14] have raised objection arguing that the upper bound of fuel cell efficiency is limited to the Carnot efficiency.

Different expressions have been presented in the literature for maximum work of fuel cell evidently due to the different assumptions employed in some past studies. It appears there is no universally agreed definition of the maximum obtainable work of fuel cells. The maximum work of a fuel cell is often thought to be the change in Gibbs energy [1,13,15–17].

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

where  $\Delta H$  is the difference between the enthalpies of the products and the reactants,  $T$  is the reaction temperature, and  $\Delta S$  denotes the difference between the entropies of the products and the reactants. Both  $\Delta H$  and  $\Delta S$  are determined at temperature  $T$ .

Gaggioli and Dunbar [18] argue that Eq. (1) is not an accurate expression of maximum fuel cell work since it is obtained assuming isothermal operation of the cell whereas a usual cell rather operates adiabatically. Haynes [12] and Linares et al. [19] definition of maximum fuel cell work is that given by Eq. (1) with the reaction temperature  $T$  replaced by the surrounding temperature,  $T_o$ , whereas Wright [14] and Ro and Sohn [20] interpret the change in Gibbs energy at standard conditions as the maximum work. The literature also includes incorrect claims and statements that the conversion efficiency of fuel cells may exceed 100% when the change in the entropy of the reaction is positive [14,21].

The primary task of this article is to establish an accurate expression for the maximum work of hydrogen fuel cells by correctly applying the conservation of energy and entropy balance equations, and to address inaccurate statements about the fuel-to-power conversion systems; in particular fuel cells. The key assumptions employed in the analysis include the ideal gas behavior of all gases which take part in cell reaction and negligible pressure drop within the fuel cell.

## Ideal hydrogen fuel cell

Consider a hydrogen fuel cell (Fig. 1) in which oxygen and hydrogen are fed to the cathode and anode, respectively. The operation of the fuel cell is assumed to be steady-state, adiabatic and isobaric. The reactants enter the fuel cell at temperature  $T_R$  and pressure  $p_o$ . The reaction product (water) leaving the cell at temperature  $T_P$  is dumped to the

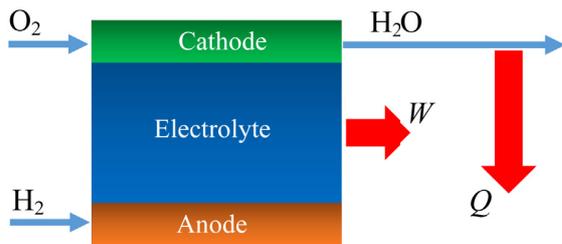


Fig. 1 – Schematic of a hydrogen fuel cell.

surrounding assumed to be at temperature  $T_o$  and pressure  $p_o$ . The net reaction between the hydrogen and oxygen is



Denoting the electrical work production of the fuel cell per unit mole of hydrogen by  $W$ , and applying the conservation of energy to the fuel cell, we have

$$h_{\text{H}_2}(T_R) + 0.5h_{\text{O}_2}(T_R) = W + h_{\text{H}_2\text{O}}(T_P) \quad (3)$$

Note that  $h$  accounts for both enthalpy of formation and sensible enthalpy.

$$h = h_f + \int_{T_{\text{ref}}}^T c_p dT \quad (4)$$

where  $h_f$  denotes the molar enthalpy of formation,  $T_{\text{ref}}$  is a reference temperature, and  $c_p$  is the molar specific heat at constant pressure.

We now determine the entropy generation due to the operation of the fuel cell of Fig. 1.

$$S_{g,\text{fuel cell}} = s_{\text{H}_2\text{O}}(T_P, p_o) - s_{\text{H}_2}(T_R, p_o) - 0.5s_{\text{O}_2}(T_R, p_o) \quad (5)$$

Consistent with the arguments of Bejan [22,23] and Haseli [24,25], we need to also account for an additional source of entropy generation due to the cooling process of the reaction product that is discharged to the surrounding. Thus, the total entropy generation (per mole of hydrogen) is

$$\begin{aligned} S_{g,\text{tot}} &= S_{g,\text{fuel cell}} + S_{g,\text{cooling}} \\ &= [s_{\text{H}_2\text{O}}(T_P, p_o) - s_{\text{H}_2}(T_R, p_o) - 0.5s_{\text{O}_2}(T_R, p_o)] \\ &\quad + \left[ \frac{Q}{T_o} + s_{\text{H}_2\text{O}}(T_o, p_o) - s_{\text{H}_2\text{O}}(T_P, p_o) \right] \\ &= \frac{Q}{T_o} + [s_{\text{H}_2\text{O}}(T_o, p_o) - s_{\text{H}_2}(T_R, p_o) - 0.5s_{\text{O}_2}(T_R, p_o)] \end{aligned} \quad (6)$$

where

$$Q = h_{\text{H}_2\text{O}}(T_P) - h_{\text{H}_2\text{O}}(T_o) \quad (7)$$

A combination of Eqs. (3), (6) and (7) to eliminate  $Q$  and  $h_{\text{H}_2\text{O}}(T_P)$  yields

$$T_o S_{g,\text{tot}} + W = E + T_o [s_{\text{H}_2\text{O}}(T_o, p_o) - s_{\text{H}_2}(T_R, p_o) - 0.5s_{\text{O}_2}(T_R, p_o)] \quad (8)$$

Setting  $S_{g,\text{tot}}$  equal to zero leads to an expression for the maximum work.

$$W_{\text{max}} = E + T_o [s_{\text{H}_2\text{O}}(T_o, p_o) - s_{\text{H}_2}(T_R, p_o) - 0.5s_{\text{O}_2}(T_R, p_o)] \quad (9)$$

where

$$E = h_{\text{H}_2}(T_R) + 0.5h_{\text{O}_2}(T_R) - h_{\text{H}_2\text{O}}(T_o) \quad (10)$$

It can be inferred from Eq. (9) that the total amount of heat dissipated to the surrounding at maximum work is

$$Q = -T_o [s_{\text{H}_2\text{O}}(T_o, p_o) - s_{\text{H}_2}(T_R, p_o) - 0.5s_{\text{O}_2}(T_R, p_o)] \quad (11)$$

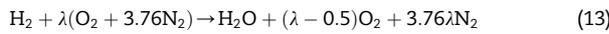
So, the maximum efficiency of the fuel cell is

$$\eta_{\text{max}} = \frac{W_{\text{max}}}{E} = 1 + T_o \left[ \frac{s_{\text{H}_2\text{O}}(T_o, p_o) - s_{\text{H}_2}(T_R, p_o) - 0.5s_{\text{O}_2}(T_R, p_o)}{E} \right] \quad (12)$$

The expression that we found for the maximum fuel cell work, Eq. (9), is neither the Gibbs energy at reaction temperature nor that at standard conditions. However, if we assume the reactants enter the fuel cell at the surrounding temperature; i.e.  $T_R = T_o$ , the maximum work, Eq. (9), and maximum efficiency, Eq. (12), will be the same as those reported by Ro and Sohn [20].

## Hydrogen-air fuel cell

A more realistic analysis needs to account for the fact that oxygen is not freely available in the nature. We consider a hydrogen fuel cell which uses air as the oxidizer. Thus, the overall cell reaction between the hydrogen and air is



where  $\lambda$  is a stoichiometric coefficient equal to or greater than 0.5.

The derivation procedure for the maximum work is the same as that described in the previous section. The following expression is obtained for  $W_{max}$ .

$$W_{max} = H_R - H_{P,o} + T_o(S_{P,o} - S_R) \quad (14)$$

where

$$H_R = [h_{\text{H}_2} + \lambda(h_{\text{O}_2} + 3.76h_{\text{N}_2})]_R \quad (15)$$

$$S_R = [s_{\text{H}_2} + \lambda(s_{\text{O}_2} + 3.76s_{\text{N}_2})]_R \quad (16)$$

$$H_{P,o} = [n_v h_{\text{H}_2\text{O}(v)} + (\lambda - 0.5)h_{\text{O}_2} + 3.76\lambda h_{\text{N}_2}]_{P,o} + (1 - n_v)[h_{\text{H}_2\text{O}(l)}]_{P,o} \quad (17)$$

$$S_{P,o} = [n_v s_{\text{H}_2\text{O}(v)} + (\lambda - 0.5)s_{\text{O}_2} + 3.76\lambda s_{\text{N}_2}]_{P,o} + (1 - n_v)[s_{\text{H}_2\text{O}(l)}]_{P,o} \quad (18)$$

where  $n_v$  is the number of moles of water vapor which depends on its partial pressure in the reaction products [11]. As the products cool down to the surrounding temperature a portion of water vapor may condense and the rest is left as vapor in the products mixture.

The difference between the enthalpy of the reactants at the cell entrance and the enthalpy of the products at the conditions of surrounding is the net energy supplied to the system. On the other hand, the amount of waste energy discharged to the surrounding at maximum work is  $T_o(S_{P,o} - S_R)$ , where with the aid of Eqs. (16) and (18), we find

$$\begin{aligned} S_{P,o} - S_R = & \lambda \left[ (s_{\text{O}_2})_{P,o} - (s_{\text{O}_2})_R \right] + 3.76\lambda \left[ (s_{\text{N}_2})_{P,o} - (s_{\text{N}_2})_R \right] \\ & + n_v \left( s_{\text{H}_2\text{O}(v)} \right)_{P,o} - 0.5(s_{\text{O}_2})_{P,o} - (s_{\text{H}_2})_R \\ & + (1 - n_v) \left( s_{\text{H}_2\text{O}(l)} \right)_{P,o} \end{aligned} \quad (19)$$

The standard entropies of hydrogen, oxygen, nitrogen and water at 298.15 K and 1 bar are taken from the NIST database [26].

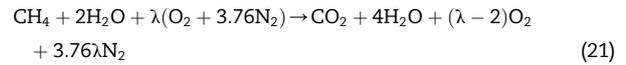
## Fuel cell operating on methane and air

Since hydrogen, the same as oxygen, is not freely available in the nature, we suppose now that methane is used as the main

fuel. It is first reformed with water to produce carbon dioxide and hydrogen. The net (reforming plus water-gas shift) reaction is



The hydrogen is then fed to the anode to electrochemically react with the oxygen of the air that is supplied to the cathode. Thus, the system takes in methane, water and air through three different streams (all at ambient conditions), and exhausts a mixture of carbon dioxide, steam, oxygen and nitrogen to the environment. The overall chemical reaction can therefore be represented as



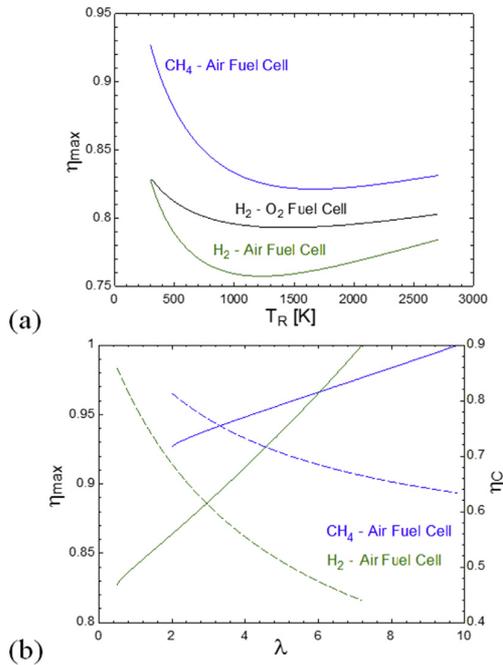
## Maximum efficiency comparison

The maximum conversion efficiencies of the hydrogen-oxygen, hydrogen-air, and methane-air fuel cells are compared in Fig. 2. The trend of the maximum efficiency varying with the reactants temperature (Fig. 2a) for all three fuel cells is very much similar. The maximum conversion efficiency takes place at the reactants temperature of 298.15 K. However, by increasing the reactants temperature, the efficiency first decreases, then remains unaltered over a temperature range, and finally begins to rise. The efficiency-plateau for the hydrogen-oxygen, hydrogen-air, and methane-air takes place at 1350–1540 K, 1170–1300 K, and 1590–1730 K, respectively. At a given reactants temperature, the maximum efficiency of the methane-air fuel cell is the highest, whereas that of the hydrogen-air fuel cell is the lowest, and that of the hydrogen-oxygen fuel cell in between. The lowest value of the maximum efficiency is 82.1%, 75.7%, and 79.3%, respectively, for CH<sub>4</sub>-air fuel cell, H<sub>2</sub>-O<sub>2</sub> fuel cell, and H<sub>2</sub>-air fuel cell and the corresponding highest maximum efficiency is 92.7%, 82.7% and 82.7%.

A further comparison is shown in Fig. 2b where the effect of  $\lambda$  is examined on the maximum efficiencies of the hydrogen-air and methane-air fuel cells, where in the former  $\lambda \geq 0.5$ , and in the latter  $\lambda \geq 2$ . In both devices, the maximum efficiency increases linearly with the stoichiometric coefficient of air with the slope of  $\eta_{max} - \lambda$  for the hydrogen-air fuel cell being greater than that of the methane-air fuel cell. As seen in Fig. 2b, the maximum efficiency of 100% is achieved at  $\lambda = 7.2$  and  $\lambda = 9.8$  in hydrogen-air and methane-air fuel cells, respectively. An efficiency of 100% corresponds to a case where the entire energy supplied to the fuel cell is converted into electrical energy, and the entropy difference between the products at the ambient conditions and reactants at the inlet of the fuel cell is zero.

## Fundamental misconceptions

Two misconceptions surrounding the operation of fuel cells reported in some past studies need to be carefully addressed. The first issue is the incorrect claim(s) about the possibility of fuel cell efficiency being greater than 100%; e.g. Refs. [14,15],



**Fig. 2 – Comparison of the maximum efficiencies, (a) the effect of reactant temperature with  $\lambda = 0.5$  for H<sub>2</sub>-air fuel cell, and  $\lambda = 2$  for CH<sub>4</sub>-air fuel cell; (b) the effect of  $\lambda$  with  $T_R = 298.15$  K and the respected Carnot efficiency (dashed lines).**

when the entropy of the reaction products is greater than that of the reactants. This misconception has been addressed to some extent by Lutz et al. [13] and Li [16]. The second misconception is with respect to inaccurate calculations which has led to a claim that the upper bound of fuel cell efficiency is limited to the Carnot efficiency.

To resolve the first issue, one must first realize that an efficiency of greater than 100% in any fuel-to-power conversion system is in violation of the first law or conservation of energy. For further elaboration, let us reconsider Fig. 2b. As discussed previously, the maximum efficiency monotonically increases with  $\lambda$  and reaches the 100% limit at a certain value of  $\lambda$ . The results shown in Fig. 2b for maximum efficiency are calculated at the regime of fully reversible; i.e. when the total entropy generation is zero.

It is mathematically correct that a further increase in  $\lambda$  beyond the 100% efficiency limit (e.g.  $\lambda = 7.2$  in hydrogen-air fuel cell) would yield a maximum work output higher than the total input energy provided we continue to assume that the system still operates at the reversible limit. However, since an efficiency of greater than 100% violates the first law, we conclude that the reversible operation would no longer be possible and the generation of entropy would be unavoidable. For instance, it is impossible for the hydrogen-air fuel cell to operate at fully reversible limit for any value of  $\lambda$  greater than 7.2 (see Fig. 2b) so the maximum efficiency would be 100% despite the system would generate entropy.

Shown in Fig. 2b is also the efficiency of a Carnot engine that operates between the same low temperature ( $T_R = 298.15$  K) and high temperature ( $T_H$ ) of each fuel cell. It is obvious that for each mole of hydrogen consumed in the cell and fixed reactants temperature, an increase in the air amount supplied to the cell would lower the temperature of the reaction products, hence the corresponding Carnot efficiency would also decrease.

Fig. 2b clearly shows that under identical operating conditions, the efficiency of a fuel cell can be greater than the Carnot efficiency. In the comparison of the performance of fuel cells to heat engines, Lutz et al. [13] proposed a Carnot engine whose input heat is supplied by an isothermal combustion reactor; see Fig. 3a. By introducing a “combustion temperature” defined as the ratio of the net change in enthalpy to the net change in entropy of reaction, they derived a relationship for the Carnot efficiency as the ratio of Gibbs energy to the net enthalpy change, whereby concluding that the maximum efficiency of fuel cells is limited to the Carnot efficiency. The derivation is followed by a numerical example which compares a hydrogen-oxygen fuel cell operating at 300 K with a Carnot engine whose highest temperature is the “combustion temperature”. The values obtained for the efficiency of fuel cell and Carnot engine are 93.5% and 92.1%, respectively. For the following reasons this method of performance comparison between a fuel cell and a heat engine is incorrect.

First, when comparing the thermodynamic efficiency of a given heat engine, such as a gas turbine engine operating on Brayton cycle, with that of a Carnot cycle, it is common to take the lowest and the highest real temperatures of the engine and calculate the efficiency of the Carnot engine operating between the same low and high-temperatures. In the case of a gas turbine cycle, as an example, which takes in air from the atmosphere and the source of heat is the combustion of fuel, the lowest temperature ( $T_L$ ) is the ambient temperature and the highest temperature ( $T_H$ ) of the cycle is the turbine inlet temperature.

From thermodynamic viewpoint,  $T_H$  is in fact the adiabatic flame temperature if the combustor is assumed to operate adiabatically. The undergraduate Thermodynamics textbooks compare the performance of an irreversible engine to that of the Carnot engine in this manner. In other words, for the purpose of efficiency comparison between a Brayton cycle and a Carnot cycle operating between the same low and high temperatures, we do not determine a “hypothetical” temperature as the ratio of the change in enthalpy to the change in entropy of combustion reaction. The numerical example presented in Ref. [13] assumes that the Carnot engine operates between 300 K and 3802 K whereas the operating temperature of the fuel cell is 300 K; which would give a zero Carnot efficiency if the comparison had been made correctly; see Ref. [10].

The model of Fig. 3 is very much similar to the power plant model of Bejan [27] with a difference that the combustor in Fig. 3a is isothermal whereas the one presented by Bejan is adiabatic. To reversibly transfer heat from the combustor to the engine dictates  $T_H = T_C$ , and because  $T_H > T_L$  we conclude that the combustion product (water) leaves the combustor at

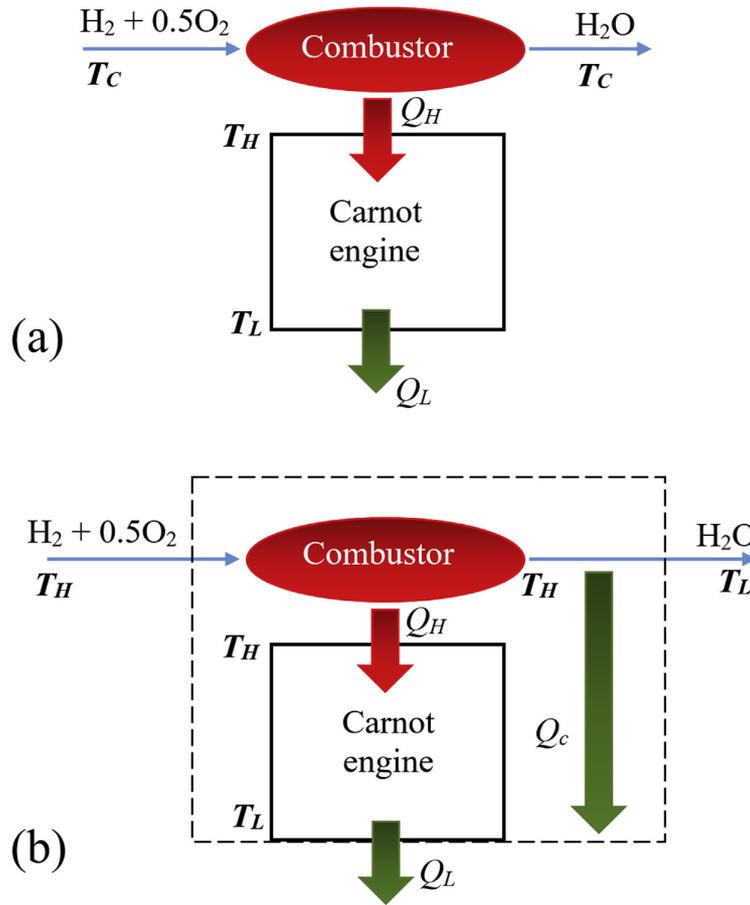


Fig. 3 – Combined Carnot engine and isothermal combustor, (a) the schematic of a system where 1 mol of hydrogen is oxidized with half mole of oxygen, (b) calculation of the total entropy generation associated with operation of the system in accordance with Bejan's work [27].

$T_C$  that is higher than the ambient temperature  $T_L$ . Since the reaction product is discharged to the atmosphere, as in most real engines, we need to account for the entropy generation due to the cooling process of the combustion product from  $T_C$  to  $T_L$ , as argued by Bejan [27]. Thus, the model of Fig. 3a is not fully reversible. The entropy generation sources that should be included in the calculation of the total entropy generation are illustrated in Fig. 3b. Hence,

$$S_g = \frac{Q_L}{T_L} + \frac{Q_C}{T_L} + [s_{H_2O}(T_L) - s_{H_2}(T_H) - 0.5s_{O_2}(T_H)] \quad (22)$$

For a fixed value of  $T_L$ , Eq. (22) is a function of  $T_H$  only so that there exists an optimum  $T_H$  at which  $S_g$  is minimum. For instance, at  $T_L = 298.15$  K, the minimum entropy generation takes place at  $T_H = 1430$  K at which  $S_{g,min} = 238.8$  J/K per unit mole of hydrogen burnt; see Fig. 4.

The thermal efficiency of the system of Fig. 3 is

$$\eta_{th} = \frac{W}{Q_{in}} \quad (23)$$

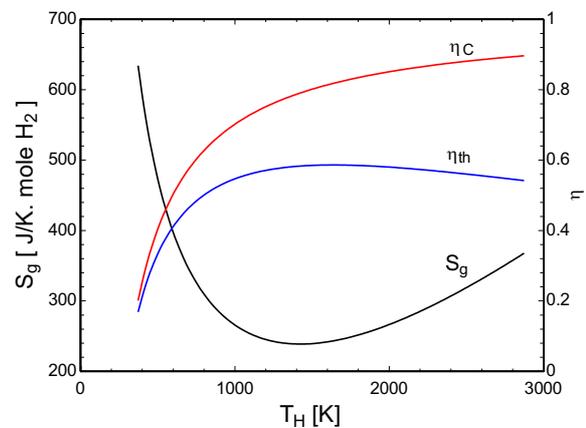


Fig. 4 – Entropy generation and thermal efficiency of the system of Fig. 3, and the efficiency of the reversible compartment (Carnot engine) varying with  $T_H$ .

where  $W = Q_H \eta_c = -\Delta h_R \left(1 - \frac{T_L}{T_H}\right)$ ,  $Q_m = W + Q_L + Q_c$ , and  $-\Delta h_R$  is the reaction heat evaluated at  $T_H$  that is supplied to the Carnot engine.

The thermal efficiency and the efficiency of the reversible compartment in Fig. 3 (Carnot engine) varying with  $T_H$  are depicted in Fig. 4. It is evident that the thermal efficiency of the model of Fig. 3 is less than the corresponding Carnot efficiency over the temperature range shown in Fig. 4. The efficiency of the Carnot engine monotonically increases with  $T_H$ . On the other hand, the thermal efficiency attains its maxima at the same optimum  $T_H$  which minimizes the total entropy generation per unit mole of hydrogen. Haseli [28,29] has shown that to maximize thermal efficiency in a combustion-driven power generating system (e.g., gas turbine cycle) is equivalent to minimize the total entropy generation rate per unit flowrate of fuel referred to as *specific entropy generation* (SEG).

Comparing the efficiency of the hydrogen-oxygen fuel cell shown in Fig. 2 with that of the Carnot engine (Fig. 4), it can be readily deduced that limiting the fuel cell efficiency to the Carnot efficiency operating between the same low and high temperature is incorrect from thermodynamic perspective. It must be noted that an ideal fuel cell having an efficiency greater than the Carnot efficiency is not in violation of the second law that prohibits complete conversion of *heat* to mechanical work.

## Conclusion

The maximum work production of three different hydrogen fuel cells is examined through a combination of the energy conservation and entropy balance equations. It is shown that there exists a reactants temperature at which the maximum conversion efficiency attains a minimum value, and as the reactants temperature further increases, it begins to rise. The lowest value of the maximum efficiency is found to be 79.3%, 75.7%, and 82.1% for hydrogen-oxygen, hydrogen-air and methane-air fuel cells, respectively. The efficiencies of the last two fuel cells monotonically increase with the stoichiometric coefficient of the air and reach 100% at  $\lambda = 7.2$  in the hydrogen-air fuel cell and at  $\lambda = 9.8$  in the methane-air fuel cell. The results reveal that the maximum efficiency of a fuel cell can exceed that of a Carnot engine operating between the same low and high temperatures.

## Acknowledgment

The research fund provided by Central Michigan University is gratefully acknowledged.

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