

Fuel Cells Versus Heat Engines: A Perspective of Thermodynamic and Production

Efficiencies

Introduction:

Fuel Cells are being developed as a powering method which may be able to provide clean and efficient energy conversion from chemicals to work. An analysis of their real efficiencies and productivity vis. a vis. combustion engines is made in this report. The most common mode of transportation currently used is gasoline or diesel engine powered automobiles. These engines are broadly described as internal combustion engines, in that they develop mechanical work by the burning of fossil fuel derivatives and harnessing the resultant energy by allowing the hot combustion product gases to expand against a cylinder. This arrangement allows for the fuel heat release and the expansion work to be performed in the same location. This is in contrast to external combustion engines, in which the fuel heat release is performed separately from the gas expansion that allows for mechanical work generation (an example of such an engine is steam power, where fuel is used to heat a boiler, and the steam then drives a piston).

The internal combustion engine has proven to be an affordable and effective means of generating mechanical work from a fuel. However, because the majority of these engines are powered by a hydrocarbon fossil fuel, there has been recent concern both about the continued availability of fossil fuels and the environmental effects caused by the combustion of these fuels. There has been much recent publicity regarding an alternate means of generating work; the hydrogen fuel cell. These fuel cells produce

electric potential work through the electrochemical reaction of hydrogen and oxygen, with the reaction product being water.

These fuel cells are seen as advantageous because their operation produces no carbon dioxide. Internal combustion engines produce carbon dioxide as a product of the combustion of a fossil fuel with oxygen, and the release of this carbon dioxide into the atmosphere is thought to contribute to a “greenhouse effect”, which will cause a warming of the earth’s atmosphere, with deleterious effects to the planet’s climate. The fuel cell’s advantage is somewhat meaningless though, if the hydrogen necessary for its operation is produced using a process in which hydrocarbons or coal are burned in order to facilitate hydrogen production. Thus, in order for this to be an advantage for a fuel cell, the hydrogen must be produced by water electrolysis or the thermal decomposition of water, and these methods must be powered by electricity from nuclear power plants or renewable energy sources such as wind, solar, hydro, or biomass power. Our present infrastructure is simply not capable of providing the necessary power without burning hydrocarbons.

Another advantage, assuming the issues of hydrogen fuel supply can be overcome, is the potentially higher efficiency of the hydrogen fuel cell compared to that of an internal combustion engine. This difference in efficiency will be discussed in further detail in this paper.

Internal Combustion Engine Thermodynamics:

An internal combustion engine is a subtype of a broader class of engines known as heat engines. Viewed in an ideal sense, a gasoline internal combustion engine follows

a thermodynamic cycle known as the Otto cycle. This cycle involves four operations in order to complete the cycle, and these operations are

1. Isentropic Compression
2. Constant Volume Heat Addition
3. Isentropic Expansion
4. Constant Volume Heat Rejection

This cycle is illustrated graphically below.

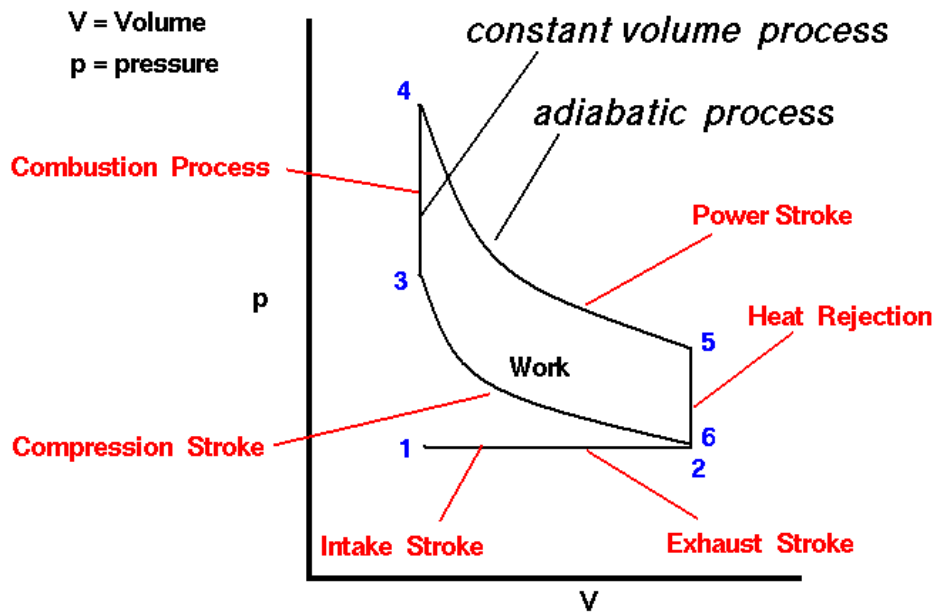


Figure 1:

The Ideal Otto Cycle

The thermal efficiency of such a cycle is the ratio of the work recovered from the cycle to the heat energy input to the cycle. For an ideal heat engine, a simple energy balance suggests that only heat energy is input, and this energy is output from the engine as either mechanical work or waste heat energy. Mathematically, this is expressed as

$$Q_{in} = W_{out} + Q_{out}$$

In this case, Q_{in} is the heat energy input from the fuel combusted in the engine, W_{out} is the mechanical work output from the engine, and Q_{out} is waste heat that is carried out of the engine in the combustion product gases. The efficiency, η_{ideal} is thus

$$\eta_{ideal} = \frac{W_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$$

If we assume that the constant volume heat capacity is constant for air in the engine, then the efficiency can also be stated as

$$\eta_{ideal} = 1 - \frac{T_5 - T_6}{T_4 - T_3}$$

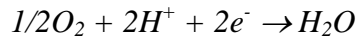
In this equation, the temperatures are taken from the points in the diagram of figure 1, using the ideal gas law to relate temperature to pressure and volume. The consequence of this is that there is a maximum efficiency that can be obtained by an internal combustion engine, even in an idealized sense. For the range of compression ratios (the ratio of minimum and maximum volumes in the engine cylinder as it reciprocates) typical of a gasoline engine, this maximum efficiency is only about 40 to 60 percent. And because this is the ideal efficiency, the actual efficiency will be even lower.

Fuel Cell Thermodynamics:

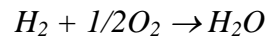
A fuel cell works by generating electric power via an electrochemical reaction. Because this is not a heat engine, it does not suffer from the same limitations as a heat engine. The most common type of fuel cell envisioned for replacing the internal combustion engine is the hydrogen fuel cell. This fuel cell operates using hydrogen gas as a feedstock, which is oxidized at the anode of the cell in the reaction



At the cell cathode, oxygen reacts with the protons generated at the anode to form water in the reaction



The overall reaction of the cell is simply the two reactions combined, which is



This is shown schematically in figure 2.

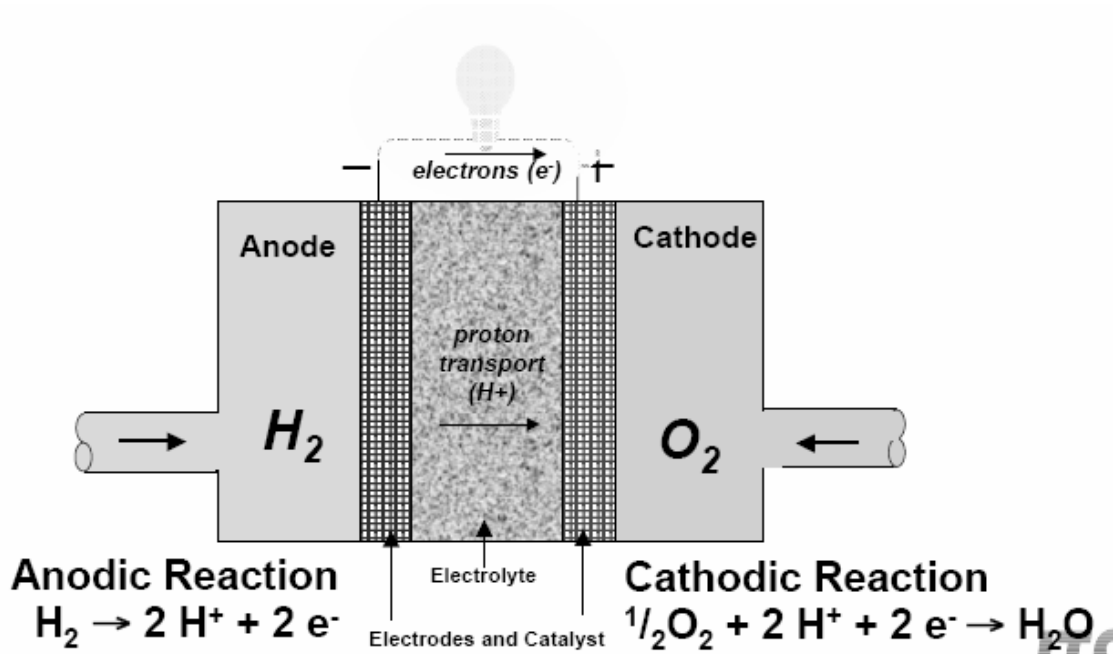


Figure 2: Schematic of Fuel Cell

The reaction creates an electric potential across the cell. Different types of fuel cells use different fuels, such as methanol, or different reactions that involve different ion transport mechanisms, but the method of operation is similar for all fuel cells. The voltage generated by the reaction is a function of the free energy change for the reaction, and this relationship is the Nernst Equation, stated below.

$$\Delta G = -nFE$$

In the Nernst equation, n is the number of electrons exchanged during the reaction (both of the half cell reactions, which are the individual reactions taking place at the anode and cathode, involve 2 electrons, so $n = 2$). F is the faraday constant, which is the electric charge of one mole of electrons, 96,485 coulombs per mole. E is the potential for each reaction. For the overall reaction, at room temperature, the free energy change of the reaction, producing water vapor, is 228.6 kJ/mol. This gives a potential of 1.25V.

In order to find the ideal efficiency of the fuel cell, it is necessary to compare the maximum available work from the reaction to the energy contained within the fuel. The maximum available work is simply the free energy change mentioned above, 228.6 kJ/mol. The energy content of the fuel is the enthalpy change for the reaction, which in this case is 241.8 kJ/mol. The efficiency is the ratio of the maximum available work from the reaction to the enthalpy change of the reaction, or

$$\eta_{ideal} = \frac{\Delta G}{\Delta H}$$

For the reaction of the fuel cell, this ideal efficiency is approximately 94%. This much higher theoretical efficiency is what makes fuel cells attractive.

Roadblocks to Fuel Cell Adoption:

While fuel cells offer a much higher ideal thermodynamic efficiency of around 94% compared to a maximum of about 60% for internal combustion engines, there are other issues involved which hinder the use of fuel cells on a large scale basis. These issues include

- Lack of infrastructure for hydrogen fuel manufacture, transport, and storage

- Need to make hydrogen by electrolysis or reforming, which can erase any efficiency advantage of the fuel cell if the power to manufacture hydrogen is generated using another combustion process, such as coal power plants
- Expense of making fuel cells, owing in large part to the need for expensive catalysts to speed the reaction
- Kinetic issues of the fuel cell

Issues related to infrastructure and manufacture of hydrogen are important and would require significant investment to overcome, but solutions exist. Using renewable energy or nuclear energy to electrolyze water into hydrogen and oxygen can bypass combustion energy. Transport and storage solutions, including both pressure storage and chemical storage solutions, are currently under development. Fuel cell manufacture costs can be brought down significantly with further advances in catalysts, manufacturing techniques, and with the increase in manufacturing volume. However, as kinetic issues are a function of the nature of electrochemical reactions, these issues are more difficult to deal with.

One kinetic issue is the rate at which reactants can be brought to the electrodes. Because the reaction takes place at the electrode surface, instead of within a volume, a fuel cell is designed to maximize the possible electrode surface area. This design necessarily makes for smaller pathways for transit of the reactants, and so rather than bulk transit mechanisms, diffusion mechanisms control the speed at which reactants can be brought to the system. This helps to limit the rate at which fuel cells operate.

The ideal reaction potential of the fuel cell is dependent on the free energy change of the reaction used in the cell, but this potential is reduced by a number of losses in the system. The electron pathways in the fuel cell are not without electrical resistance, and

so this causes a voltage drop equal to the path resistance multiplied by the electric current in the cell, as per Ohm's law. There must also be a driving force to bring electrons and protons to their respective electrode. This causes not only a voltage drop that affects the efficiency of the reaction, but it also puts a limit on the rate of reaction that can be reached because of diffusion rates. The rate of reaction in the fuel cell is equivalent to the rate of electron flow in the cell, which is simply an electric current. This electric current is given using the Butler-Volmer equation in electrochemistry, which gives the electric current as a function of cell potential. This equation is given as

$$i = F \left[k_f c_o e^{(-\beta VF / RT)} - k_r c_r e^{((1-\beta)VF / RT)} \right]$$

In the Butler-Volmer equation, I is the current in the electrochemical cell, F is the Faraday constant, k_f is the forward reaction rate constant, k_r is the backward reaction rate constant, β is a parameter expressing the symmetry of the reactions, C_o and C_r are the concentrations of oxidized and reduced species, R is the gas constant, and T is the absolute temperature. With all other parameters held constant, it can be seen that by manipulating the cell voltage, the current in the cell can be manipulated. By increasing the voltage in the cell, the current is increased. The problem with this is that this increased cell voltage acts as an energy loss for the cell, and the cell is essentially trading voltage for current. The power of an electrochemical cell is the product of the current and the voltage, or $P = IV$. There is therefore a power of 0 at 0 voltage or 0 current, and so there will be a maximum power that is achieved by the cell. This is shown graphically in figure 3.

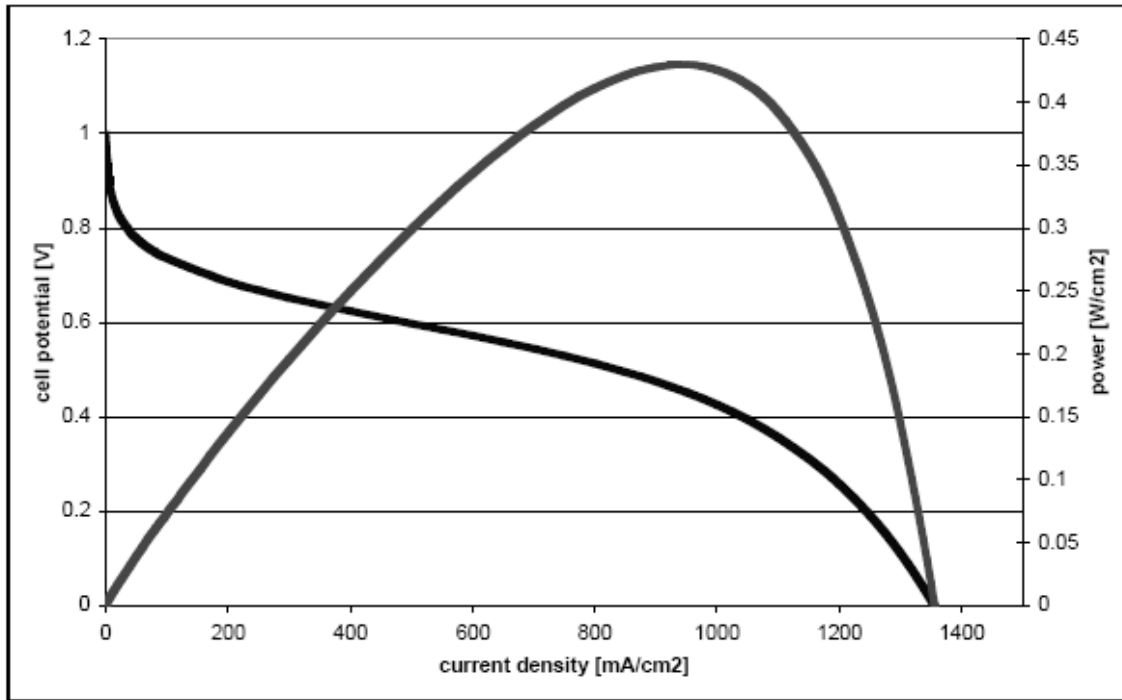


Figure 3: Fuel Cell Power with Varying Current and Cell Potential

This limited rate of power generation for a fuel cell contrasts with combustion processes, where the kinetics of burning fuel are very fast. Whereas the rate of energy delivery by a combustion engine is largely limited by mechanical limitations on how fast reciprocating engines can operate, fuel cells are inherently limited by their method of energy conversion. This limit causes fuel cell stacks to be larger and heavier than a comparable power output combustion engine, and increased weight and size work against efficiency in transportation applications.

II. FUEL CELL EFFICIENCY

Fuel cells are electrochemical energy conversion systems that merely convert chemical energy into electric energy, basically through a constant temperature process. A sketch of fuel system is shown in figure 4. Recently, a number of publications have label fuel cells

as “Non-Carnot limited” energy conversion devices. For instance, Çengel and Boles^[1] have indicated that “Fuel cells are not heat engines, and thus their efficiencies are not limited by the Carnot efficiency.” However, this statement should be carefully interpreted. Fuel cells are “non-Carnot limited” only because their performance efficiency does not depend on the reservoirs’ temperature, and consequently one should not be tempted to conclude that an ideal fuel cell can be consider as a better energy converter device than the ideal Carnot cycle.^[2] The fuel cell efficiency according to the second law of thermodynamics derived in this paper follows basic thermodynamics principles found in Holman^[3] and Lutz et al.^[4]

By definition, the thermal efficiency for a work producing device is the fraction of heat supplied that is converted to net work.

$$\eta = \frac{W_{out}}{Q_{in}} \quad (1)$$

The first law states that for a particular device the change of the internal energy is generated by the heat transfer to or from the system and work done by or produced over the system, i.e. $dU = dQ - dW$. In the specific case of a fuel cell, since it operates under an open system we must consider the presence of flow work ($p dV$) and electrical work generated, thus the first law becomes $dU = dQ - p dV - dW_{elec}$.

For our ideal fuel cell lets assume that it also operates under an isobaric process, and introducing the enthalpy definition, $H = U + pV$, into the first law equation we have $dH = dQ - dW_{elec}$. In order to maintain a constant temperature process in our ideal reversible fuel cell, the heat transfer must be defined using the entropy concept $dQ = T dS$. Inserting this equation in our previous first law equation we have

$dH - TdS = -dW_{elec}$. The left-hand side of this equation represents the variation in Gibbs free energy ($G = H - TS$) for an isothermal process. Therefore, the net work output is given by $W_{out} = -\Delta G_R$, where $\Delta G_R = G_{(T,Pr od.)} - G_{(T,Re act.)}$. This expression points out the fact that the maximum work that can be obtained from the fuel cell chemical reaction is equal to the difference in Gibbs free energy of the reaction.

In the particular case of a fuel cell, the heat input is heating value of the fuel, which is also defined as the enthalpy of combustion or reaction, that is $Q_{in} = -\Delta H_R$. Inserting the net work output and heat input into equation (1),

$$\eta_{FC} = \frac{\Delta G_R}{\Delta H_R} \quad (2)$$

Equation (2) points out that the thermal efficiency of an ideal fuel is defined as the ratio of variations in Gibbs free energy and enthalpy of reaction computed at the specific pressure and temperature of reactants and products. This statement has been accepted by several authors^[3,4,5]. However, Hassanzadeh, and Mansouri^[6] have drawn our attention to a basic concept missed in the previous efficiency definition. Since we are assuming an ideal fuel cell, the work produced by such a device must be reversible. By definition the maximum work, which is the total reversible work of our electrochemical device, can be only reached when the system final state is in equilibrium with the surroundings, at their standard pressure and temperature (T_0, P_0) .

$$W_{max} = W_{elec,rev}(T_0, P_0)$$

$$W_{max} = -\sum_{P-R} N_i (h_0 - T_0 S_0)_i = \sum_{P-R} N_i g_i(T_0, P_0)$$

$$W_{max} = -G_{prod.}(T_0, P_0) + G_{reac.}(T_0, P_0) = -G_R(T_0, P_0)$$

Inserting the latter expression in equation (1) we obtain the thermal efficiency of an ideal fuel cell at reference temperature and pressure.

$$\eta_{FC} = \frac{W_{\max}}{Q_{in}} = \frac{-\Delta G_R(T_0, P_0)}{-\Delta H_R(T_0, P_0)} \quad (3)$$

Nevertheless, both thermal efficiency expressions have something in common. And it is that for an exothermic reaction where ΔH_R is negative, efficiencies greater than 100% can be computed in the case where ΔS_R is positive,^[7] to be precise,

$$\eta_{FC} = \frac{\Delta H_R - T\Delta S_R}{\Delta H_R} = 1 - T \left(\frac{\Delta S_R}{\Delta H_R} \right)$$

Thus, the current fuel cell efficiency equation violates the Kelvin-Planck statement of the second law of thermodynamics which states^[1]:

“It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work, i.e. No heat engine can have a thermal efficiency of 100 percent.”

Obviously, the above second law statement is referring to devices that produce or consume work such as heat engines and refrigerators, respectively. However, because of the global application of the second law of thermodynamics over all realizable processes, the above statement has been reformulated and presented by Hassanzadeh, and Mansouri^[6] using the stable equilibrium state of a system defined by Hatsopoulos and Keenan^[8] as follows:

“A system having specified allowed states and an upper bound in volume can reach from any given state a stable state and leave no net effect on the environment.”

With this generalized second law statement in mind and due to the significant influence of the ΔS_R sign on the efficiency equation, a redefined expression has been proposed by Jacob and Jain^[9] depending on whether ΔS_R is positive or negative. The new equation takes into consideration the heat absorbed or released by the fuel cell, and it is denoted as η_{FC}^r ,

$$\eta_{FC}^r = \frac{\Delta G_R}{\Delta H_R + q} \quad (4)$$

Where q represents the heat exchanged by the fuel cell with the environment, that under reversible conditions is $q_{rev} = -T_{cell}\Delta S$. Lutz et al.^[4] and Hassanzadeh, and Mansouri^[6] have suggested similar expressions to equation (4) for the case $\Delta S_R > 0$, and when heat transfer from the surroundings is included in Q_{in} , respectively

$$\eta_{FC} = \frac{-\Delta G_R}{-\Delta H_R + T\Delta S_R} = \frac{\Delta H_R - T\Delta S_R}{\Delta H_R - T\Delta S_R} = 1, \text{ and}$$

$$\eta_{FC} = \frac{W_{max}}{Q_{in}} = \frac{-\Delta G_R(T_0, P_0)}{-\Delta H_R + T_0\Delta S_R} = \frac{-\Delta G_R(T_0, P_0)}{-\Delta G_R(T_0, P_0)} = 1$$

These expressions provide a fairer yardstick to compare fuel cells and heat engines thermal efficiencies, since both devices will be constrained to the same second law of thermodynamic limit, and neither one will be able to break this law.^[4] Furthermore, from the above equations we may conclude that the main advantages of the fuel cell systems are the possibility to obtain a 100 per cent conversion of the Gibbs free energy and straight conversion of chemical energy into electrical energy.^[6]

III. THE HEAT ENGINE EFFICIENCY

Heat engine is any device that converts heat into mechanical work operating under a cycle limited by two temperature sinks. A sketch of Carnot heat engine is shown in figure 5. For the purpose of simplification in our comparison, we will only consider internal combustion engines (ICE) and external combustion engines (ECE). In order to derive the thermal efficiency expression for a Carnot heat engine let us use equation (1). For a device that produces work and exchanges heat with two thermal energy reservoirs, we know from the first law of thermodynamics that: $W_{net,out} = Q_H - Q_L$. Where Q_H and Q_L represent the heat received from a high temperature sink (T_H) and the heat rejected to a low temperature sink (T_L), correspondingly. Inserting the $W_{net,out}$ in our eq.(1) we have,

$$\eta = 1 - \frac{Q_L}{Q_H} \quad (5)$$

The latter equation tells us that the thermal efficiency of heat engine solely depends on the rate of heat transfer to and from the device. Since all heat engines operate under a cycle, eq. (5) can be further simplified by applying the Clausius inequality that states that the cyclic integral of $\delta Q/T$ is always less than zero for irreversible processes and equal to zero for reversible processes. In other words, $\oint \frac{\delta Q}{T} \leq 0$; for the reversible heat engine

becomes $\oint \frac{\delta Q}{T} = 0$. Evaluating the integral we have,

$$\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0, \text{ or } \frac{Q_L}{Q_H} = \frac{T_L}{T_H} \quad (6)$$

Inserting expression (6) into equation (5) yields,

$$\eta_{th,Carnot} = 1 - \frac{T_L}{T_H} \quad (7)$$

Equation (7) shows that there are two possible approaches to maximize the thermal efficiency of the Carnot heat engine; either increasing the temperature at which heat is supplied to the engine or reducing the temperature at which heat is rejected from the engine. This statement is also applicable to real heat engines. Furthermore, the efficiency tends towards one only when $T_H \rightarrow \infty$ or $T_L \rightarrow 0$. For actual heat engines, the unity efficiency limit is impossible to reach due to the fact that T_H must remain finite, besides that, it can not be considerably increased because of metallurgic restrictions, and T_L is always fixed by the environment conditions.

IV. COMPARISON OF THERMODYNAMIC EFFICIENCY

In order to establish a thermodynamic comparison of reversible fuel cell and reversible heat engines, Haynes^[2] conducted a brief exergy analysis over both devices assumed as “reversible thermodynamic black boxes.” As shown in the figure 6, both systems are fed

energy flows with equivalent exergy ‘A’, then $Exergy_A = \sum (\dot{n}_i a_i)_{inlet,FC} = \left[1 - \frac{T_0}{T_H} \right] \dot{Q}_H$

Haynes concluded that due to the fact that the maximum work is a point function, i.e. only depends on the specified initial and final states, both system will produce the same reversible work. Otherwise, presuming better fuel cell efficiency means that its reversible work is path dependent, which is a violation of thermodynamic laws. He also emphasized that any valid comparison between both energy conversion systems should be made utilizing an external reversible heat engine instead of the conventional heat engine which typically has many irreversibilities, inherently linked to its combustion process. A similar approach from the point of view of the exergy perspective is proposed by Wright^[10], who states that heat engines and fuel cells are restricted to the same second law constraint

regardless of material property requirement. He also proposed the ‘exergetic’ or second law efficiency to evaluate the actual performance of heat engine and fuel cells under exothermic or endothermic reactions. Such proposal is additionally supported by Rao et al.,^[7] who claim that in this manner the maximum efficiency will always be bounded by 100% independently of a positive or negative entropy reaction. Despite the fact that the previous arguments seem to be reasonable, Jacob and Jain^[9] claim that under normal circumstances the availability of the energy flows at the exit of an ideal fuel cell and an externally reversible heat engine is non-depreciable and thus the efficiency will be different, although both systems are reversible. They also argued that the exergetic approach is more suitable for comparing the efficiency of dissimilar devices for energy conversion.

An analytical similarity between the thermal efficiency of an ideal fuel cell and the Carnot heat engine was performed by Lutz et al.,^[4] who substituted the high temperature reservoir of the heat engine with a combustion reactor as shown in figure 7. To compute the maximum efficiency of the modified Carnot cycle, Lutz et al. introduced a ‘combustion’ temperature as $T_c = \Delta H_R / \Delta S_R$; then they deduced that the heat supplied by the reactor becomes $Q_H = \Delta H_R(T_c)$, while the heat rejected yields $Q_L = T_L \Delta S_R(T_c)$.

Inserting these expressions into equation (5) they have,

$$\eta_{Carnot} = \frac{\Delta H_R(T_c) - T_L \Delta S_R(T_c)}{\Delta H_R(T_c)}$$

According to Lutz et al.^[4] the previous expression provides an equivalent yardstick to compare fuel cell and a Carnot heat engine operating with an isothermal reactor, additionally it shows that both systems are restricted to the same maximum efficiency. As

an example, utilizing the reaction between pure hydrogen and oxygen, they computed that the thermal efficiency for a fuel cell stated by eq. (2) at 300 K is 93.5%; while for the modified Carnot cycle using a combustion temperature of 3802 K the thermal efficiency is 92.1%. Conversely, Jacob and Jain^[9] have found two relevant issues regarding the Lutz et al. approach. First, the combustion temperature (T_c) defined at $\Delta G = 0$ can lead us to negative temperature values, which is impossible to achieve for absolute thermodynamic temperatures; and second the specified temperature ($T_c = 3802K$) needed in the chemical reactor of the modified heat engine to nearly match the efficiency of the ideal fuel cell is well beyond today's metallurgic limits. Precisely, this second issue is the main reason why Jacob and Jain argue that fuel cells are more likely to produce electricity with unmatched thermodynamic efficiency; besides the fact that for a fuel cell reaction with $\Delta S > 0$, the cell generates electric energy from two sources: the electrochemical fuel oxidation and the heat absorbed from the environment.

V. ENTROPY PRODUCTION IN FUEL CELLS

In the first section, the efficiency equations (2) and (3) for ideal fuel cells were derived. However, those equations only provide an estimation of the system performance under hypothetical conditions. It turns out that the actual efficiency of real fuel cells is significantly reduced because of the irreversibilities associated with the process. The main sources of irreversible losses in real fuel cells can be grouped in:^[11]

- Activation-related losses, caused by activation energy of the electrochemical reaction.
- Ohmic losses, generated by ionic resistance in the electrolyte and electrodes.
- Mass transport losses, caused by finite mass transport limitation rates of the reactants.
- Mixing entropy

These losses are translated into exergy destruction or entropy production that negatively impact the fuel cell performance, and therefore are accountable for the major lost of fuel cell's power potential. For this reason, the entropy production analysis has become a significant parameter in the design of fuel cells. In general, entropy production rates (\dot{S}_p) are computed by multiplying local transport fluxes with correspondent driving force^[12] In other words,

$$\dot{S}_p = \frac{1}{T} \dot{R}[\text{driving_force}(s)] \quad (8)$$

In the previous equation, T represents the absolute temperature, while \dot{R} is the process rate. Lior^[12] also states that the rate of useful energy destruction, \dot{A}_d , is directly related to the entropy production rate as follows,

$$\dot{A}_d = T_0 \dot{S}_p \quad (9)$$

In his Ph.D. dissertation, de Groot^[13] discussed a well detailed and extensive assessment of the exergy losses in high temperature molten carbonate fuel cell (MCFC) and solid oxide fuel cells (SOFC). He considered the temperature and pressure gradient, as well as difference in concentration, chemical potential and electrical potential as the main driving forces responsible for the entropy generation. Heat rejection was presented as the most significant irreversible loss, responsible for 50% of the total exergy destruction as shown in figure 8. Furthermore, de Groot links exergy loss in chemical reaction to heat transfer for a chemical reaction in which the reaction enthalpy is greater than the reaction exergy. More importantly, he identified the temperature at which the electrochemical reactions occurs as the most crucial parameter that affects the efficiency of the fuel cells.

A complete evaluation of the exergy losses in a Proton Exchange Membranes Fuel Cells (PEMFC) was performed by Kabelac and Sieme^[14]. They presented the local entropy production rate expressed as the total sum of the 'independent fluxes' and 'thermodynamic forces'. The independent fluxes considered were; heat flux, electric current density, water flux, hydrogen flux and oxygen flux. According to them, these fluxes are generated by the driving forces of temperature gradients, chemical potential and electric potential. Their analysis showed that the ohmic losses are the principal source of irreversibilities in the membrane. However, heat transfer was found to have a moderate influence in the entropy production due to the fact that the temperature gradient was small in the membrane and more importantly, an isothermal behavior was assumed. Naterer et al.^[15] confirmed that for PEMFCs and SOFCs the higher entropy production rate was triggered by higher ohmic losses that occurred while operating at low temperatures.

van den Oosterkamp et al.^[16] conducted an exergy analysis over a 25 KW phosphoric acid fuel cell integrated with a hydrogen manufacturing unit, concluding that the entropy production attributable to heat transfer accounts for 30% of the electric energy generated. The previous conclusions are also supported by Woudstra et al.^[17] who recommended four general guidelines in order to optimize the heat transfer process in fuel cell and consequently reduce the exergy losses.

VI. ENTROPY PRODUCTION IN HEAT ENGINES

As in fuel cells, the efficiency equation (7) derived for heat engines provide a theoretical performance of the device. However, under real conditions the efficiency of the heat

engine will be substantially reduced due to irreversibilities. The main sources of irreversibilities and entropy productions that can be found in actual heat engines are:^[10]

- Incomplete combustion,
- Material restrictions on T_H because of corrosion,
- Irreversible heat transfer and mixing process,
- Products rejected at $T > T_0$,
- Heat rejection at $T > T_0$,

Under these circumstances, a new efficiency equation for Carnot heat engines operating at maximum power with heat transfer irreversibilities was defined by Curzon and Ahlborn^[18] as,

$$\eta = 1 - \left(\frac{T_L}{T_H} \right)^{\frac{1}{2}} \quad (10)$$

The difference between the ideal Carnot efficiency and the actual heat engine efficiency is showed by Winterbone^[19] in figure 9. Additionally, it is important to mention that for irreversible heat engines with the previous equation efficiency model, the maximum power and the minimum entropy production rate are two different operating conditions as stated by Salamon et al.^[20]

VII. COMPARISON OF PRODUCTION EFFICIENCY

The comparison of production efficiency for fuel cells and heat engines will be briefly addressed in light of the exergy losses associated with the regular combustion process inherent to heat engines and the fuel cell reactions. According to Hassanzadeh and Mansouri^[6] the primary difference between these processes is that the chemical reaction executed in a combustion process involves heat transfer, while in a fuel cell it takes place

in a charge transfer. In charge a transfer, the existing energy of the electrons can be completed added. On the other hand, the actual combustion produces an oxidation of the fuel through a highly irreversible heat transfer process in which 20-30% of the fuel exergy is wasted and almost 80% of the combustion irreversibility happens during the internal thermal energy exchange process.^[21]

Comparing the exergy issues between the conventional combustion and the fuel cell reaction, Lior^[12] presented the following expression to determine the useful power consumption when fuel is burned with air,

$$\dot{A}_d = T_0 \dot{S}_p = \frac{T_0}{T} \dot{R}_f \lambda = \frac{T_0}{T} \dot{R}_f (\mu_{fuel} + \mu_{oxygen} - \mu_{products})$$

where \dot{R}_f is the rate of fuel and λ is the chemical affinity, which is consider the driving force for the reaction and equivalent to the difference between the chemical potentials (μ) of the reactants and products. Applying the later equation to a solid oxide fuel cell, Lior states that the energy destruction will be lower in this device due to the fact the chemical potential of the oxygen is reduced by passing the oxygen trough the solid electrolyte before the fuel oxidation.

VIII. SUMMARY

Conclusions:

The much higher theoretical efficiency of fuel cells when compared to internal combustion engines have creates much interest in them as fuel supplies become more expensive to develop and exploit. The mechanism by which they operate does restrict somewhat their advantages, as there is a trade off between the rate at which power can be extracted from the cell and the efficiency at which that extraction can occur. In order to

be competitive with internal combustion engines, the fuel cell must not only extract power in an efficient way, but it must do so at a rate useful for its intended purposes and in a package that also makes sense for its application. Time will tell how achievable such a system will be.

The thermodynamic and production efficiencies of fuel cells and heat engine were explored. Two expressions to compute the thermodynamic efficiency of fuel cells depending on whether the reaction is exothermic or endothermic, were derived and examined. The thermodynamic efficiency was found to be the major source of controversy among different authors due to the fact that efficiencies greater than one are computed when ΔS_R is positive. Regarding this issue, it was found that most of the authors suggested an exergy or second law efficiency in order to obtain a consistent yardstick on the fuel cell performance. The Carnot heat engine efficiency equation was derived and compared with the ideal fuel cell equation following the guidelines of one author. The entropy generation in fuel cells was studied from the perspective of several experimental results obtained by different researchers. Most authors confirmed that the major source of irreversibilities in fuel cells is the ohmic heating, which produces significant heat transfer losses that negatively impact the performance and power production of fuel cells. Finally, the production efficiency of fuel cells and heat engines was briefly explored from the perspectives of the irreversibilities inherent to the combustion process.

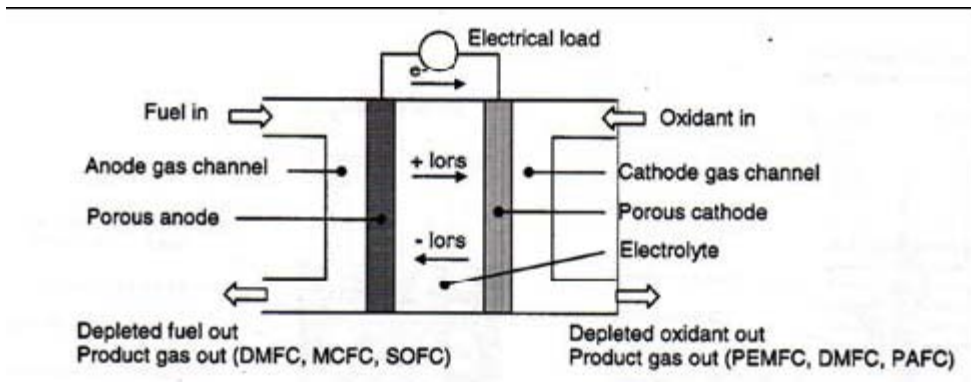


Figure 4. Fuel cell basis.^[22]

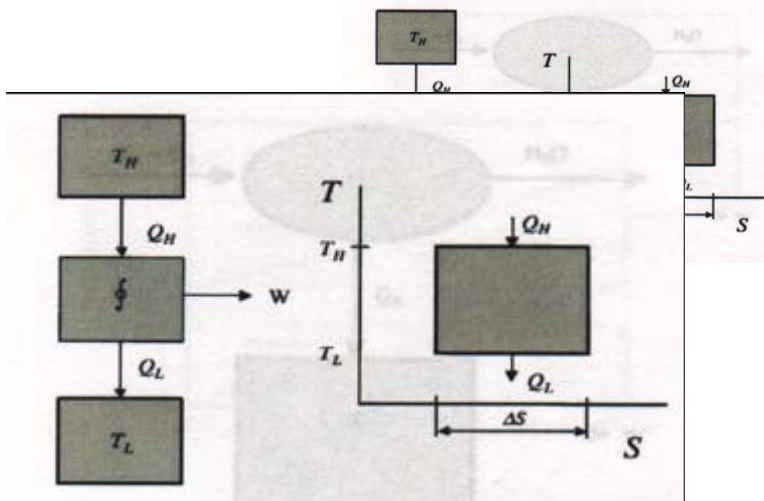
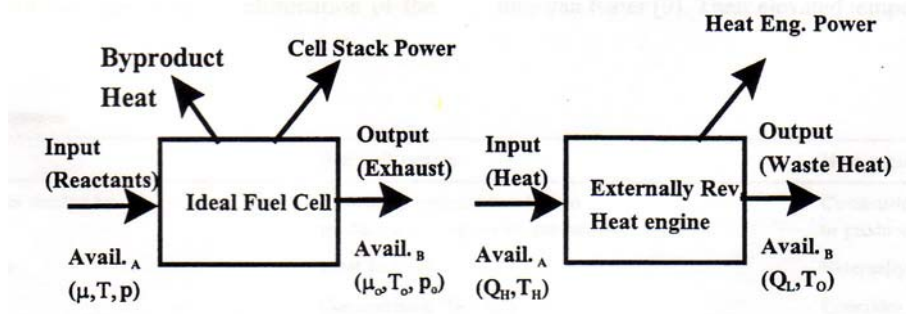


Figure 5. Sketch of a Carnot heat engine and temperature-entropy diagram (right).^[4]



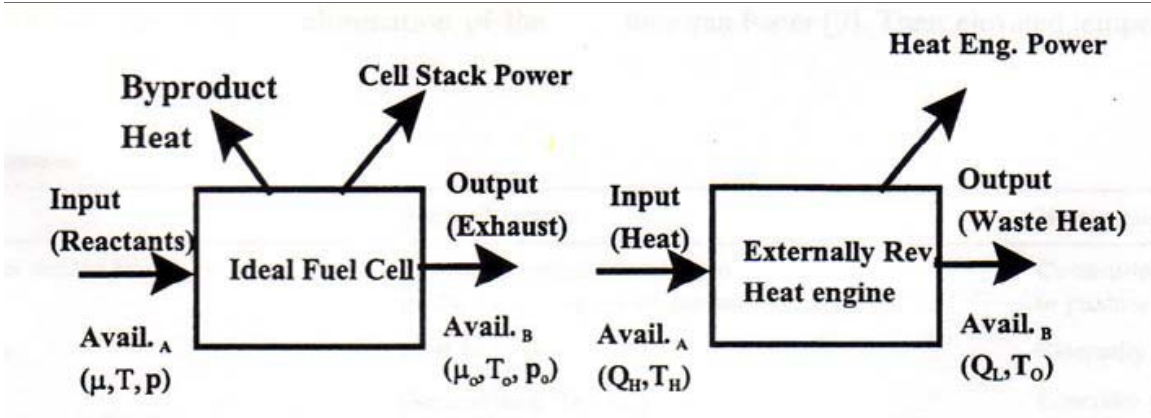


Figure 6. Reversible fuel cell and heat engine.^[2]

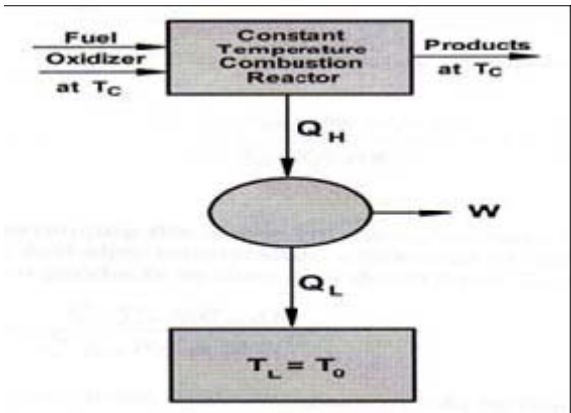
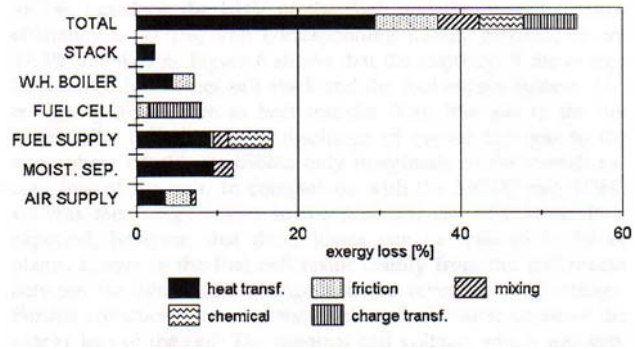


Figure 7. Modified Carnot heat engine with a combustion reactor.^[6]



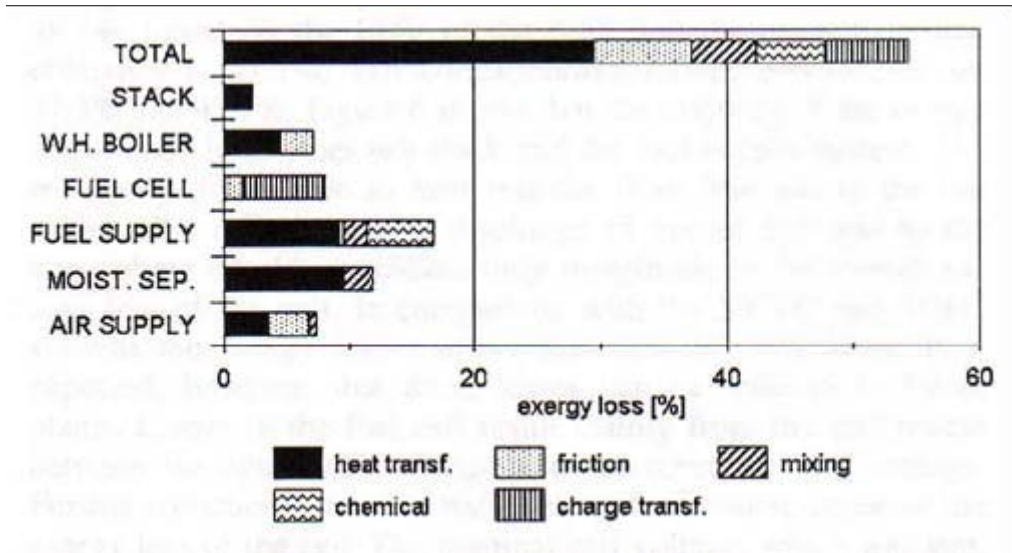


Figure 8. Causes of exergy loss in a MCFC system with external reforming.^[13]

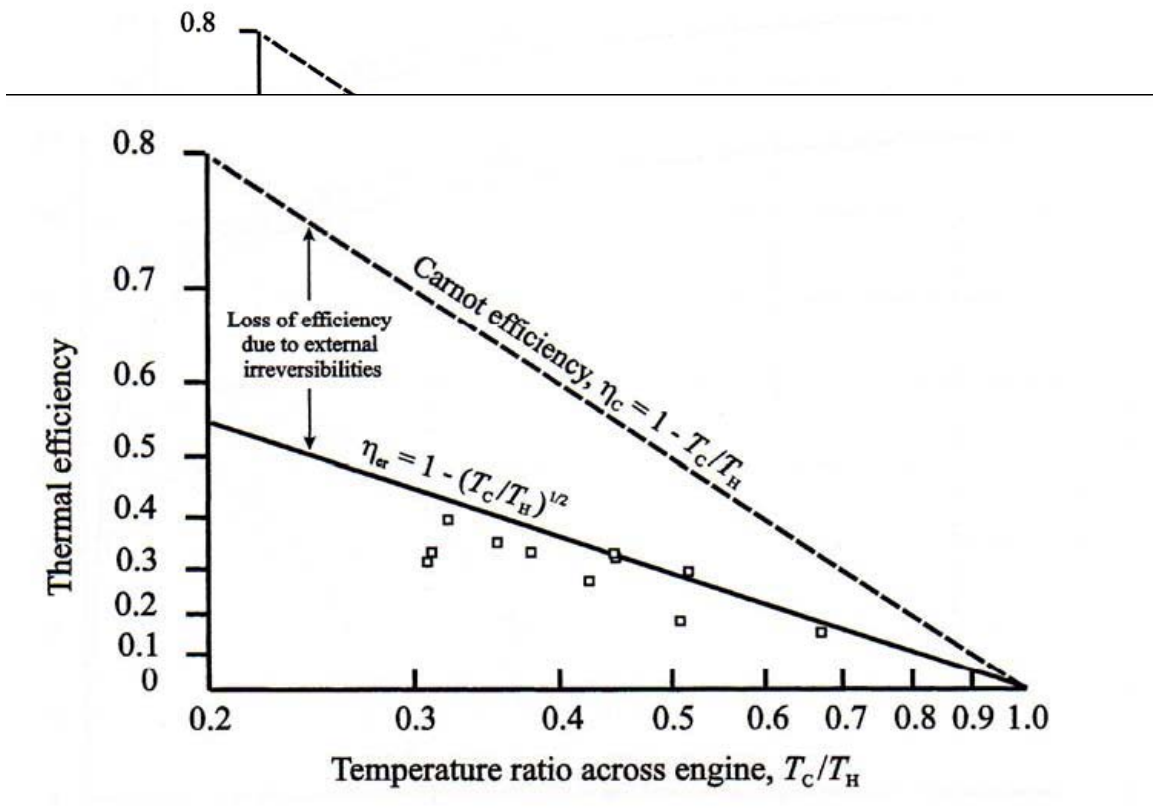


Figure 9. Thermal efficiency of power plant compared with that of endo-reversible cycle. Each square depicts data from actual plant.^[19]

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