### Lecture # 2

Thermodynamics and Tools to Analyze Conversion Efficiency

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- Conservation laws
- Limits on conversion
- Availability
- Efficiency

Ghoniem, AF Energy Conversion Engineering, Chapter II, Thermodynamics.

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Some Thermodynamics

"Classical Thermodynamics is the only physical theory of universal content which, ... within the framework of its basic notions, will never be toppled." Albert Einstein.

- Energy conversion is governed by conservation principles, and often involves "availability" loss.
- This translates to the all important "efficiency".
- How to maximize conversion efficiency, identify sources of loss and minimize them?

Heat Engine & Fuel Cell, Efficiency?



Ideal thermomechanical vs. electrochemical systems, governing principles and efficiency, and their integration for maximizing the latter

### First Law: Energy Conversion, heat and work transfer, control mass

$$\Delta Q - \Delta W = E_2 - E_1$$

Stored Energy (in terms of state properties, V, u = U / m, Z,  $\zeta$ , ...)

$$E = \underbrace{KE}_{\frac{1}{2}m\mathbf{V}^{2}} + \underbrace{PE}_{mg_{r}Z} + \underbrace{U}_{th} + \underbrace{U}_{ch}_{th} + \underbrace{E_{elas}}_{\frac{1}{2}k_{s}x^{2}} + \underbrace{E_{elect}}_{\varepsilon\varsigma} + E_{mag} + E_{nuc}$$



$$-\delta W_{mech} = \vec{F} \cdot d\vec{x} = -p \, d \forall$$
$$-\delta W_{el} = \mathcal{E} d \varsigma$$
$$-\delta W_{mag} = H \, dM_g$$



## **Control Volume:**

Need mass conservation as well

$$\frac{dm_{CV}}{dt} = \sum_{in} \dot{m}_i - \sum_{out} \dot{m}_i$$
$$\frac{dE}{dt} = \dot{Q} - \dot{W} + \sum_{in} \dot{m}_i (h + ke + pe + ...) - \sum_{out} \dot{m}_i (h + ke + pe + ...)$$
$$E_2 - E_1 = Q - W + \sum_{in} m_i (h + ke + pe + ...) - \sum_{out} m_i (h + ke + pe + ...)$$

# Second Law: Entropy Control mass

$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + (\Delta S)_g \quad \text{or} \quad S_2 - S_1 = \sum_{k=1}^K \frac{\Delta Q_k}{T_k} + (\Delta S)_g$$

Entropy is generated when:

- Heat is transferred across a finite temperature gradient
- Fluid expands across a finite pressure drop
- Mixing of different fluids (or same fluid volumes with different T)
- Chemical reactions causing temperature rise (or drop)

Informally: entropy is generated when a process is performed without work transfer when work could have been obtained (or when it is less than the maximum possible).

One of the original statements: a cyclic machine cannot be used to convert heat into work at 100% efficiency.





Second Law: Entropy



Entropy generation is a quantitative measure of "loss of work"!?

The lost work is measured by the "availability" or "exergy" loss.

### Maximum Work, Availability and limits on energy conversion:

### System (with fixed mass)

"Add" the first and second laws For a system with heat transfer at fixed temperatures

$$W_{use} = Q_H \left( 1 - \frac{T_o}{T_H} \right) + \Xi_1 - \Xi_2 - I_{ir}.$$

system availability is:

$$\Xi = (E - U_o) + p_o (\forall - \forall_o) - T_o (S - S_o).$$

Changes in internal energy, volume or entropy can produce work

 $I_{ir} = T_o (\Delta S)_g \rightarrow \text{internal irreversibility or lost work}$ 



### Examples:

Heat Engine, work produced by heat transfer only: 2 TER\*, high TER fixed at  $T_H$ 

$$W_{\max} = \left(1 - \frac{T_o}{T_H}\right) Q_H = W_{car}$$

\* it is easy to fix  $T_o$ , but not  $T_H$ Can only be realized with:

- Isothermal heat transfer from sources (with zero  $\Delta T$ )
- Ideal expansion/compression

The Carnot cycle is an ideal heat engine (as well as the Stirling and Ericsson cycles)





# Fixed Mass interacting with single TER@ $T_o$ : $W_{\text{max}} = (E_1 - T_o S_1 + p_o \forall_1) - (E_2 - T_o S_2 + p_o \forall_2)$ $= \Xi_1 - \Xi_2$

 $\Xi$ : total exergy or availability difference in case only internal energy is utilized, E = Uwith no change of chemical state,  $U = U_{th}$ .

For max $|W_{\text{max}}|$ , final state (2) must be in equilibrium with environment (restricted dead state),  $T_2 = T_o$ ,  $p_2 = p_o$ 

## For a control volume

$$\dot{W}_{cv} = \sum_{TERs} \left( 1 - \frac{T_o}{T_i} \right) \dot{Q}_i - \left( \frac{d\Xi_{cv}}{dt} - p_o \dot{\forall}_{cv} \right) \\ + \sum_{in} \dot{m}_i \xi_i - \sum_{out} \dot{m}_i \xi_i - \dot{I}_{ir} \\ \xi = \left( \tilde{h} - h_o \right) - T_o \left( s - s_o \right) \\ \text{(flow exergy/availability per unit mass)} \\ \tilde{h} = h + ke + pe$$

for an ideal gas, fixed  $c_p$  $\Delta h = c_p \left( T_2 - T_1 \right),$   $\Delta s = c_p \ell n \left( \frac{T_2}{T_1} \right) - \Re \ell n \left( \frac{p_2}{p_1} \right)$  For steady operation of a CV interacting with 2 TER and stream:

$$\dot{W}_{cv} = \underbrace{\left(1 - \frac{T_o}{T_H}\right)}_{\text{Carnot Engine}} \dot{Q}_H + \underbrace{\dot{m}(\xi_{in} - \xi_{out})}_{\text{flow stream}} - \dot{I}_{ir} \qquad \xi = (\tilde{h} - h_o) - T_o(s - s_o)$$

For maximum work:

- zero irreversibility,  $I_{ir} = 0$
- equilibrium with environment,  $\xi_{out} = \xi_{env}$

For steady operation of a CV interacting with a stream only:  $\dot{Q}_H = 0$ 

Entropy and exergy analysis serve the same purpose, they are interchangable Either can be used to determine the source of inefficiency in a complex system **Example 2.8.** (subcooled) Water at 200 kPa and 100°C is expanded in an adiabatic throttle valve to a final pressure of 20 kPa. The process does not involve any work transfer. An inventor claims to have designed a device that generates work of 10 kJ/kg of water while maintaining the same inlet and outlet conditions of the throttle and exchanging heat with the environment at 25°C. Is this claim feasible?



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assume steady operation, neglect changes in the kinetic and potential energies. At 200 kPa and 100 °C,  $h_1 = h_{f@100^{\circ}C} = 419.17 \text{ kJ/kg}$  and  $s_1 = s_{f@100^{\circ}C} = 1.3072 \text{ kJ/kg-K}$ . energy balance across an adiabatic throttle is:  $h_2 = h_1 = 419.17 \text{ kJ/kg}$ . The final state is determined by knowing the final pressure,  $p_2$ , and the final enthalpy,  $h_2$ . Since the enthalpy falls between the saturated liquid and the saturated vapor values at 20 kPa,  $h_{f@20kPa} = 251.42 \text{ kJ/kg}$  and  $h_{g@20kPa} = 2608.9 \text{ kJ/kg}$ , the quality of the mixture is  $x_2 = (h_2 - h_f)/h_{fg} = 0.0712$ , and the entropy is  $s_2 = s_f + x_2 s_{fg} = 0.8320 + 0.0712 \times 7.9073 = 1.3354 \text{ kJ/kg-K}$ .

maximum work is the difference between the availability between initial and final states:  $w_{\text{max}} = (h_1 - T_o s_1) - (h_2 - T_o s_2) = T_o (s_2 - s_1) = 8.417$  kJ / kg

work output claimed by the inventor is higher than maximum value, not possible.

# Using exergy analysis to determine the performance of a system and how to improve it

A closed-cycle gas turbine power plant, shown in the following figure, operates with air as a working fluid. Conditions are shown in figure. Analyze the losses and propose improvements

State	<i>T</i> (K)	p (atm)	h (kJ/kg.K)	$\xi$ (kJ/kg)
1	300	1	0	0
2	808.3	20	510.4	469.8
3	1600	20	1305.2	1058.9
4	816.4	1	519.4	217.5



Energy (and availability) are added (from outside) in process 2-3 only. For maximum work all availability added should be used as work How much is lost in each component and with the exit stream? To determine performance

of individual components:

For a flow process:

 $Q - W = \Delta h$ 

Maximum work

= change in availability

$$(W_{\max})_{turbine} = \xi_4 - \xi_3, \ (W_{\max})_{compr} = \xi_2 - \xi_1,$$
$$(W_{\max})_{exitstream} = \xi_4 - \xi_1,$$

state 1 taken as reference

to find maximum work by system

$$W_{sys} = \left(1 - \frac{T_o}{T_i}\right)Q_i + \xi_1 - \xi_4 - I_{ir}$$

for max work,  $\xi_4$  should be equal to  $\xi_1$ 

and  $I_{ir} = 0$ .  $W_{sys,max} = \left(1 - \frac{T_o}{T_i}\right)Q_i$ 

to determine the RHS, apply the same to HX, with  $I_{ir} = 0$ :

 $0 = \left(1 - \frac{T_o}{T_i}\right)Q_i + \xi_2 - \xi_3, \text{ and substitute: } W_{sys,max} = \xi_3 - \xi_2$ 

	Enthalpy change (kJ/kg)	Availability change (kJ/kg)
Heat Exchanger	$h_3 - h_2 = 794.8$	$\xi_3 - \xi_2 = 589.1$
Compressor Turbine	$W_c = 510.4$ $W_t = 785.8$	-469.8 841.4
Net Work	$(h_3 - h_4) - (h_2 - h_1) = 275.4$	
Air out at 4	$h_4 - h_1 = 519.4$	217.5

First law efficiency is 275.4/794.8 =34.6%

Second law efficiency is 275.4/589.1=46.7% Compressor irreversibility  $\frac{\dot{I}}{\dot{m}} = -\frac{\dot{W}}{\dot{m}} + \xi_1 - \xi_2 = 40.6 \text{ kJ/kg}$ Turbine irreversibility  $\frac{\dot{I}}{\dot{m}} = -\frac{\dot{W}}{\dot{m}} + \xi_3 - \xi_4 = 55.6 \text{ kJ/kg}$ 

losses with exit stream = 217.5 kJ/kg

### Many Heat Engines since ...















Gas turbine engines and turbo jet engine



GEnx Engine 53,000-75,000 pounds thrust



Benjamin Thompson/Lord Rumford established the equivalency of heat and work, worked on cannons, invented the modern fireplace, drip coffee maker, etc., his bust in Rohde Island (and a historical society named after him)



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#### Rumford birthplace (1753) and museum, Elm St, Woburn MA



Image courtesy of Mass.gov.

Benjamin Thompson born 1753 in Woburn, MA, educated in Harvard, married Sarah Rolfe from Concord NH, then called Rumford. Worked on boring cannons, helped the British during the revolutionary war, and ran to England, where became Lord Rumford, eventually moved to Munich and contributed much to physics and thermodynamics.

The inverse of a heat engine is refrigerators and air conditioners, arguably the most important invention of engineering in the 20<sup>th</sup> century.

### **Power Plant Efficiency** Do we have an Energy or an Entropy Crisis?







Fuel Cell Handbook, 7th Ed., by EG&G Technical Services, U.D. DOE, Office of Fossil Energy, NETL, Morgantown, W Va, Nov 2004, p. 8-91.

What have engineers been doing over the past 200 yeas?



The best **heat engine** (thermal to mechanical) is a Carnot engine operating between two fixed temperatures:

the (thermo-mechanical) converison efficiency of the engine is

$$\eta_{I} = \frac{W_{net}}{Q_{H}} = 1 - \frac{Q_{o}}{Q_{H}}, \text{ also called the first law efficiency}$$
$$\eta_{car} = 1 - \frac{T_{o}}{T_{H}}$$

temperatures are in absolute, e.g., in K=273+C  $T_o \sim 300$  K,

maximum fuel combustion temperature ~ 1800-2400 K

 $T_H / T_o = 6 - 8$ ,  $\eta_{car} = 84 - 88\%$ 

the efficiency depends critically on T of the heat source! also on the cold side T



A heat engine operating between a continuous stream starting at a high temperature and the environment has a lower efficiency.

If the stream pressure is fixed:

$$W_{\max} = \int_{T_o}^{T_H} \left( 1 - \frac{T_o}{T} \right) dQ = \int_{T_o}^{T_H} \left( 1 - \frac{T_o}{T} \right) C dT$$
$$= C \left[ \left( T_H - T_o \right) - T_o \ell n \frac{T_H}{T_o} \right]$$

OR (since streams at same  $p_o$ )

$$W_{\max} = \xi_H - \xi_o = (H_H - H_o) - T_o (S_H - S_o)$$

$$\eta_{car}^* = 1 - \ell n \left( \frac{T_H}{T_o} \right) / \left( \frac{T_H}{T_o} - 1 \right)$$

$$T_H / T_L = 6 - 8, \ \eta_{car}^* = 70\%$$





- 1. Geothermal heat @  $T_H \sim 100-150$  C
- 2. Solar concentrators produce heat @  $T_H \sim 300 600 C$
- 3. Nuclear reactors  $T_H \sim 300-600$  C
- 4. Combustion, only limited by material,  $T_H \sim 1400$  2100 C.

#### Example 2.10

An industrial plant requires high temperature heat, which it generates by burning kerosene. After extracting the "useful" high temperature heat from the combustion products, the plant discharges gases at 950 K and 1 atm. The flow rate of combustion gases is 2.0 kg/s. A waste heat-recovery system (WHRS) is proposed for the utilization of the energy in the hot exhausted gases. It consists of a steam generator, the heat recovery steam generator (HRSG) and a steam turbine. The isentropic efficiency of the turbine is 94%, and steam exits the turbine at 40 °C. Assume the pinch point temperature difference of 10 °C. Atmospheric conditions are at 1 atm. and 300 K. Assume the hot combustion products as an ideal gas with the same properties as air, specific heat is  $c_{p,GAS} = 1.048$  kJ/kg-K. Calculate the exergy losses in this system.





Green, gas Red, steam

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Maximum work from the stream is obtained using the availability of the hot gases:

Maximum Work 
$$= \dot{\Xi}_{GASES} = \dot{\Xi}_{1g} = \dot{m}_{1g} [(h_{1g} - h_{0g}) - T_0(s_{1g} - s_{0g})] = 638.1 \text{ kW}$$

Now we calculate the mass flow rate of turbine water (do not yet know exit conditions of steam): energy balance between the two streams from the cold side of HRSG to pinch point (PP),

 $\dot{m}_{1g}(h_{2'g} - h_{2g}) = \dot{m}_{w}(h_{1'c} - h_{1})$ 

from tables, specific enthalpy of saturated water at 100 atm:  $h_{1'c} = 1413.0 \text{ kJ/kg}$ . Looking at enthalpy of water at T = 300 K and p=101325 kPa:  $h_1 = 121.8 \text{ kJ/kg}$ . From the steam tables, the saturation temperature  $T_{1'c}$  at 10132.5 kPa is <u>585.2 K</u>.

Pinch point temperature difference is 10 K.  $T_{2'g} = T_{1'c} + 10 = 595.2$  K

Therefore, mass flow of water is:

$$\dot{m}_{w} = \frac{\dot{m}_{1g}C_{P,GAS}(T_{2'g} - T_{2g})}{(h_{1'c} - h_{1})} = \frac{2.01.048(595.2 - 310)}{(1413 - 121.8)} = 0.4629 \text{ kg/s}$$

After knowing mass flow rate of water, we apply energy equation for the entire HRSG

$$\dot{m}_{1g}(h_{1g} - h_{2g}) = \dot{m}_w(h_2 - h_1)$$

This gives  $h_2 = 3020 \text{ kJ/kg}$ .

With  $h_2 = 3020 \text{ kJ/K}$  and  $p_2 = 100 \text{ atm}$ , from steam tables, we get  $\underline{T_2} = 650.7 \text{ K}$ .

Loss of work/irreversibility in HRSG:

$$0 = \sum \left( 1 - \frac{T_0}{T_j} \right) \dot{Q}_j - \dot{W}_{CV} + \dot{\Xi}_{1g} - \dot{\Xi}_{2g} + \dot{\Xi}_1 - \dot{\Xi}_2 - \dot{\Xi}_{DESTRUCTION}$$

First two terms are zeros Irreversibility =  $\dot{\Xi}_{DESTRUCTION} = 637.7 - 549.8 = 87.48 \, kW$ 

For the turbine, exit temperature T = 273+40=313 K (we know it is 2 phase), from tables, saturation pressure is 7.323 kPa.

 $T_2 = 650.7$  K,  $p_2 = 10132.5$  kPa,  $h_2 = 3020$  kJ/kg and  $s_2 = 6.091$  kJ/kg-K Isentropic conditions of steam exiting turbine are:  $p_3 = 7.323$  KPa,  $s_{3s} = s_2 = 6.091$  kJ/kg-K. From steam tables, isentropic enthalpy is  $h_{3s} = 1895$  kJ/kg. The actual conditions (enthalpy) of steam exiting turbine can be found from

$$\eta_T = \frac{(h_2 - h_3)}{(h_2 - h_{3s})} \Longrightarrow 0.94 = \frac{(3020 - h_3)}{(3020 - 1895)}$$

 $T_{\rm rest} = \frac{1}{100} = \frac{1$ 

This gives  $h_3 = 1962 \text{ kJ/kg}$ . Using  $h_3$  and  $p_3$  and  $T_3 = 313 \text{ K}$ , from steam tables:  $s_3=6.307 \text{ kJ/kg-K}$  (less than  $s_{3\text{sat steam}}$ , verifying it is a two-phase flow mixture).

Turbine Work rate is 489.5 kW.  
But 
$$0 = -\dot{W}_{turbine} + \dot{\Xi}_{in} - \dot{\Xi}_{out} - \dot{I}$$
  
Change of Availability in the turbine is:  
 $\Delta \dot{\Xi} = \dot{m}_{w} \left[ (h_{2} - h_{3}) - T_{o} (s_{2}s_{3}) \right] =$   
 $0.4629 \left[ (3020 - 1962) - 300 (6.091 - 6.307) \right] = 519.4 \, kW$ 

Exergy loss is the difference between change and work, **29.88 kW** This is much less that exergy destroyed in HRSG.

### Thermodynamic Efficiencies

Conversion Efficiency or first law efficiency  $\eta_I = \frac{\text{All what you get}}{\text{All what you pay}}$ 

heat engines 
$$\eta_I = \frac{\text{net work out}}{\text{Heat in}}$$

Electrochemical Efficiency for battery or fuel cell 
$$\rightarrow \frac{\text{Work (Electrical Energy) out}}{\text{Chemical Energy in/used}}$$

electrochemical efficiency for charging battery or electrolyzer 
$$\rightarrow \frac{\text{Chemical Energy stored}}{\text{electrical Energy in}}$$

Co-generation efficiency(bad definition but it is used) 
$$\rightarrow \frac{\text{Work} + \text{Heat}}{\text{Chemical Energy}}$$
  
a better definiton is  $\rightarrow \frac{\text{Work} + (1 - \frac{T_o}{T_H})Q_H}{\text{Chemical Energy}}$ 

### **Thermodynamic Efficiencies**

Conversion Efficiency or first law efficiency  $\eta_I = \frac{\text{Work/Energy/Heat OUT}}{\text{Heat/Energy/Work IN}}$ 

Thermomechanical Efficiency of a Heat Engine  $\rightarrow \frac{\text{Work (Mechanical)}}{\text{Heat}}$ 

Combustion Efficiency  $\rightarrow \frac{\text{Thermal Energy}}{\text{Chemical Energy}}$ 

Reforming Efficiency  $\rightarrow \frac{\text{Chemical Energy Out}}{\text{Chemical Energy In}}$ 

Fuel Utilization Efficiency of a combustion engine  $\rightarrow \frac{\text{Power (Mechanical)}}{\text{Rate of Chemical Energy in}}$ 

In heating and cooling equipment, we define: The Coefficient of Performance (can be larger than 1)



# In combustion we use the stored chemical energy to define efficiencies:









In direct conversion between chemical and electrical energy (fuel cells and electrolysis), we use the stored chemical energy of the fuel to define efficiencies:



converting a unit mass of hydrogen to water

# WTW or LCA requires knowledge of process efficiency and overall integration of processes and systems ...



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Bossel, Towards a Sustainable Energy Future, Oct 2004

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Effectiveness, or Second Law Efficiency= $\frac{\text{actual efficiency}}{\text{maximum efficiency}} = \frac{\text{work}}{\text{maximum work}}$ 

System interacting with 2 TER only: 
$$\eta_{II} = \frac{W_{net}}{W_{max}} = \frac{W_{net}/Q_H}{1 - T_L/T_H}$$

System processing a stream: 
$$\eta_{II} = \frac{W_{net}}{W_{max}} = \frac{W_{net}}{\Delta \Xi} \rightarrow \text{ work producing cycle (system)}$$

Device expanding a stream:  $\eta_{II} = \frac{w_{net}}{w_{max}} = \frac{w_{net}}{\Delta \xi} \rightarrow$  work producing cycle

In an isothermal process with an ideal gas:

$$\hat{w}_{\max} = \Delta \hat{\xi} = \Delta \hat{h} - T_o \Delta \hat{s} = \Re T_o \ell n \left(\frac{p}{p_o}\right)$$



other important efficiencies (related to the second law) turbine isentropic efficiency  $\eta_T = \frac{W}{W_{\text{max}}} = \frac{W}{W_{is}}$ 

note that for an adiabatic turbine,

$$W_{\max} = \xi_1 - \xi_2 = (h_1 - h_2) - T_o((s_1 - s_2)) = (h_1 - h_2)$$
  
compressor isentropic efficiency  $\eta_T = \frac{W_{\min}}{W} = \frac{W_{is}}{W}$ 



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