2.43 ADVANCED THERMODYNAMICS

Spring Term 2024 LECTURE 10

Room 3-442 Friday, March 8, 11:00am - 1:00pm

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Exergies and first and second law efficiencies

in energy conversion technologies

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Review of basic concepts: Exergy of bulk flow interactions

Exergy associated with an interaction of mass flow in conditions 1



 To obtain the maximum power from the flow in conditions 1, the flow must be taken in a position 'a' in mutual equilibrium with the environment

$$\dot{W}_{rev}^{\rightarrow} = \dot{E}x_1 = \dot{m}[(h_1 - h_a) - T_a(s_1 - s_a)]$$

From the balance of energy and entropy (per unit time) for AM, the optimal equivalent mechanical power of flow in conditions 1 can be determined; which is therefore the exergy per unit time associated with the flow in conditions 1

Review of basic concepts: Exergy of bulk flow interactions

Exergy associated with an interaction of mass flow in conditions 1



 The lowest power that is necessary to use in order to produce the flow conditions in 1 starting from the condition 'a' in mutual equilibrium with the environment

$$\dot{W}_{rev}^{\leftarrow} = \dot{E}x_1 = \dot{m}[(h_1 - h_a) - T_a(s_1 - s_a)]$$

From energy and entropy balances (per unit time) for AM the optimal equivalent mechanical power of flow in conditions 1 can be determined, which is therefore the exergy per unit time associated with the flow in conditions 1

Review of basic concepts: Exergy in heating and cooling bulk flows



Variation of exergy in heating / cooling a flow

Cooling. From energy and entropy balances (per unit time) for AM; the following is found

$$\dot{W}_{\text{rev}}^{\rightarrow} = \dot{E}x_1 - \dot{E}x_2 = \dot{m}[(h_1 - h_2) - T_a(s_1 - s_2)]$$

$$\dot{W}_{\text{rev}}^{\rightarrow} = \dot{E}x_1 - \dot{E}x_2$$
$$= \dot{m}(h_1 - h_2) \left(1 - T_a \frac{s_1 - s_2}{h_1 - h_2}\right)$$

Heating. From the balance of energy and entropy (per unit time) for AM; the following is found:

$$\dot{W}_{rev}^{\leftarrow} = \dot{E}x_2 - \dot{E}x_1 = \dot{m}[(h_2 - h_1) - T_a(s_2 - s_1)]$$

$$\dot{W}_{\text{rev}}^{\leftarrow} = \dot{E}x_2 - \dot{E}x_1 \\ = \dot{m}(h_2 - h_1) \left(1 - T_a \frac{s_2 - s_1}{h_2 - h_1}\right)$$

Review of basic concepts: Exergy in heating and cooling bulk flows



Warning: the use of symbol Q in this case could be misleading, for it is used to represent the energy supplied to the flow, while the interaction is not heat, but a set of continuous heat interactions at temperatures between T_1 and T_2 . The entropy supplied to the flow is equal to

$$\frac{\dot{Q}_A}{T_{\text{lm12}}}$$
 where $T_{\text{lm12}} = \frac{h_2 - h_1}{s_2 - s_1}$

Review of basic concepts: Exergy of an hydraulic jump

Energy balance $0 = \dot{m}(h_1 - h_2) + \dot{m}(w_1^2/2 - w_2^2/2) + \dot{m}(gz_1 - gz_2) - \dot{W}^{\rightarrow}$ $\dot{m}c(T_2 - T_1) = \dot{m}g(z_1 - z_2) - \dot{W}^{\rightarrow}$

If the jump is not exploited (no work)

$$c(T_2 - T_1) = g(z_1 - z_2) \rightarrow \frac{\Delta T}{\Delta z} = \frac{g}{c} = \frac{9.8}{4200} \approx \frac{1}{430} \frac{^{\circ}\text{C}}{\text{m}}$$

Cascata delle Marmore, Italy, 165 m

Entropy balance

$$0 = \dot{m}(s_1 - s_2) + \dot{S}_{irr}$$

$$\dot{S}_{irr} = \dot{m}c \ln \frac{T_2}{T_1} = \dot{m}c \ln \left(1 + \frac{T_2 - T_1}{T_1}\right) \approx \dot{m}c \frac{T_2 - T_1}{T_1} = \frac{\dot{m}g(z_1 - z_2) - \dot{W}^{\rightarrow}}{T_1}$$

If the jump is exploited in best way (maximum work)

$$\dot{W}_{\text{max}} = \dot{m}g(z_1 - z_2) \rightarrow \frac{\dot{W}_{\text{max}} / \dot{m}}{z_1 - z_2} = g = 9.8 \frac{\text{m}}{\text{s}^2} = 9.8 \frac{\text{kJ/ton}}{\text{m}} = \frac{42 \text{ MJ/ton}}{4300 \text{ m}}$$



Review of basic concepts: Exergy in heating and cooling bulk flows



Cooling of a fluid using heat at a temperature different from the environment (refrigeration or absorption machine)

$$\dot{Q}_A = \dot{m}(h_1 - h_2)$$

$$\eta_{\rm I} = \frac{\dot{m}(h_1 - h_2)}{\dot{Q}} = \frac{\dot{Q}_A}{\dot{Q}}$$

$$\eta_{\text{II}} = \frac{\dot{m}[(h_1 - h_2) - T_o(s_1 - s_2)]}{\dot{Q}\left(1 - \frac{T_o}{T_Q}\right)} = \frac{\dot{Q}_A \left[1 - T_o \frac{s_1 - s_2}{h_1 - h_2}\right]}{\dot{Q}\left(1 - \frac{T_o}{T_Q}\right)}$$

Review of basic concepts: Exergy in heating and cooling bulk flows



$$\dot{W}^{\rightarrow} = \dot{m}(h_1 - h_2) \left(1 - T_a \frac{s_1 - s_2}{h_1 - h_2} \right) + \dot{Q} \left(1 - \frac{T_a}{T_Q} \right) - T_a \dot{S}_{irr}$$

$$\dot{W}_{rev 12}^{\rightarrow} = \dot{E}x_1 - \dot{E}x_2$$

$$\dot{W}_{rev \dot{Q}}^{\rightarrow} = \dot{E}x_{\dot{Q}}$$
exergy reduction of
the flow between
inlet and outlet by the heat
interaction interaction interaction

Review of basic concepts: Temperature of the equivalent heat interaction in heating / cooling for a liquid flow

The ratio between exergy and the energy content in heating / cooling of a liquid flow

$$\begin{split} \dot{E}x_1 &= \dot{m}[(h_1 - h_a) - T_a(s_1 - s_a)] & \dot{m} & \downarrow & \downarrow \\ \dot{E}x_2 &= \dot{m}[(h_2 - h_a) - T_a(s_2 - s_a)] & \dot{m} & \downarrow & \downarrow \\ \dot{E}x_{12} &= \dot{E}x_2 - \dot{E}x_1 = \dot{m}[(h_2 - h_1) - T_a(s_2 - s_1)] & \dot{Q} \\ &= \dot{m}[c(T_2 - T_1) + (p_2 - p_1)/\rho - T_a c \ln(T_2/T_1)] \\ &= \dot{m}c(T_2 - T_1) \left[1 - \frac{T_a \ln(T_2/T_1)}{T_2 - T_1}\right] - \frac{\dot{m}}{\rho} (p_1 - p_2) \\ \Delta \dot{E}x_{12} \approx \dot{Q} \left[1 - \frac{T_a \ln(T_2/T_1)}{T_2 - T_1}\right] & \downarrow \\ \dot{Q} \left[1 - \frac{T_a}{T_Q}\right] & \text{Exergy loss due to pressure drop in the duct. It is equal to the minimum number of the distribution of$$

where

$$T_Q = T_{\text{lm12}} = \frac{(T_2 - T_1)}{\ln(T_2/T_1)}$$

Exergy loss due to pressure drop in the duct. It is equal to the minimum pumping work. It is generally negligible with respect to thermal term.

Review of basic concepts: Temperature of the equivalent heat interaction in heating / cooling for an ideal gas flow

The ratio between exergy and the energy content in heating / cooling of a liquid flow

Review of basic concepts: Temperature of the equivalent heat interaction in heating / cooling for a boiling or condensing flow

The ratio between exergy and the energy content in heating / cooling of a liquid flow

$$\begin{split} \dot{E}x_1 &= \dot{m}[(h_1 - h_a) - T_a(s_1 - s_a)] & \dot{m} \\ \dot{E}x_2 &= \dot{m}[(h_2 - h_a) - T_a(s_2 - s_a)] \\ \Delta \dot{E}x_{12} &= \dot{E}x_2 - \dot{E}x_1 = \dot{m}[(h_2 - h_1) - T_a(s_2 - s_1)] \\ &= \dot{m}[h_{\mathrm{fg}}(x_2 - x_1) - T_a s_{\mathrm{fg}}(x_2 - x_1)] \\ &= \dot{m}h_{\mathrm{fg}}(x_2 - x_1) \left[1 - \frac{T_a s_{\mathrm{fg}}}{h_{\mathrm{fg}}}\right] \\ \Delta \dot{E}x_{12} &\approx \dot{Q} \left[1 - \frac{T_a s_{\mathrm{fg}}}{h_{\mathrm{fg}}}\right] \\ \dot{Q} \left[1 - \frac{T_a}{T_Q}\right] & \text{Here we assumed negligible pressure drop.} \end{split}$$

$$T_Q = \frac{h_{\rm fg}}{s_{\rm fg}}$$

Review of basic concepts: Minimum exergy for low temperature heating a liquid or ideal-gas flow

Ratio between exergy and energy content for a liquid flow:

For example, for the heating of pressurized water from 60°C to 120°C (in an environment at 300 K)

$$\frac{\Delta \dot{E} x_{12}}{\dot{Q}} = 1 - \frac{T_a \ln(T_2/T_1)}{T_2 - T_1} = 1 - \frac{300 \ln(393/333)}{60} = 0.172$$

For the heating of water from 20°C to 60°C (in an environment at 300 K)

$$\frac{\Delta \dot{E} x_{12}}{\dot{Q}} = 1 - \frac{T_a \ln(T_2/T_1)}{T_2 - T_1} = 1 - \frac{300 \ln(333/293)}{40} = 0.040$$

Review of basic concepts: Exergy associated with a fossil fuel (definition)



 T_o and p_o standard: 25°C and 1 atm

Review of basic concepts: Exergy associated with a fossil fuel (in practice)

In the **second part of the course** we will prove that the exergy of a hydrocarbon $C_k H_\ell$ or coal, prior to its combustion, is within ±2.5% of the LHV of the fuel

 $\dot{E}x_{fuel} \approx -\dot{m}(\Delta h^o - T_o \Delta s^o)$ $\dot{Q}_{fuel} \approx -\dot{m}\Delta h^o = \dot{m}$ LHV

Where

 Δh^o The enthalpy of combustion T_o and p_o Δs^o The entropy of combustion T_o and p_o $LHV = -\Delta h^o$ lower heating value HHV is the higher heating value of the fuel For all hydrocarbons:

 $|T_o \Delta s^o / \Delta h^o| \le 0.025$

Therefore, in practice, we can use the approximation:

$$\dot{E}x_{\text{fuel}} \approx \dot{Q}_{\text{fuel}} \approx \dot{m} \text{ LHV}$$

HHV = LHV + $\ell h_{\text{fg,water}}(T_o)$ for example for methane LHV = $50.06 \frac{\text{MJ}}{\text{kg}}$ and HHV = $55.54 \frac{\text{MJ}}{\text{kg}}$ ℓ is the number of hydrogens in the C_kH_{\ell} molecule

for the details see chapter 31 of G&B, Thermodynamics, Dover 2005, Tab.31.7

Review of basic concepts: Lower heating values of some fuels

	kcal/kg	MJ/kg
Firewood	2500-4500	10-19
charcoal	7500	31
Peat	3000-4500	13-19
Lignite	4000-6200	17-26
Bitominous coal	6800-9000	28-38
Coke	7000	29
Anthracite	8000-8500	33-36
Crude oil	10000	42
Combustible oil	9800	41
Kerosene (Aircraft	:)10400	44
Gasoline (automa	43	
Petrol (automative	44	
LPG (automative)	11000	46

	KCal/INITI°	IVIJ/KY
Natural Gas	8300	47
Methane	8570	50
Water Gas from coke	2700	
Water Gas from carburiz	zed 6000	
Blast Furnace Gas	1000	
Gas from oil(cracking)	11500-17	500
	Nm ³ a 0°0	С

kool/NIm3 N/ 1/kg

42 MJ correspond to:

Lift 1 ton of water up to 4300m Heat 1 ton of water of 10°C Evaporate 18 kg of water at p_{atm} Oxidizing 1 kg of oil Fission of 0.5 mg of uranium-235

The learning curve of fuel-to-power conversion technologies



The learning curve of fuel-to-power conversion technologies



 η_{II}

Thermodynamic efficiency of the best-available mature technology for primary energy conversion to work or electricity

The learning curve of fuel-to-power conversion technologies



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Review of basic concepts: Power-plant philosophy of best available flame-based fuel-to-power conversion technology



Overall thermodynamic efficiency

64%

$$\eta_{\rm II-overall} = \frac{\dot{W}_{\rm electric}}{\dot{E}x_{\rm fuel}} = \eta_{\rm II-combustion} \times \eta_{\rm II-thermal-cycle} \approx 64\%$$

Review of basic concepts: Power-plant philosophy of best available flame-based fuel-to-power conversion technology



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Review of basic concepts: Power-plant philosophy of best available flame-based fuel-to-power conversion technology



The role of Thermodynamics? The role of Nonequilibrium?

- History tell us about the future:
 - By the end of this century, power plants will be 85% efficient.
- Thermodynamics tells us:
 - By burning fossil fuels in flames, we cannot exceed 70%.
 - The bottleneck is in the irreversibility of flame combustion.
- History tells us we will overcome that! How?
 - We will gain a better control of fuel oxidation as it occurs or develop alternative oxidation paths that allow better control and less irreversibility,
 - We will gain better control of nonequilibrium states.
 - We will improve our nonequilibrium fluid dynamics, transport phenomena, chemical kinetics models of heterogeneous and multicomponent systems.

Review of basic concepts: one way to get around the inherent irreversibility of flames is by oxidating the fuel in fuel cells



Integrating SOFC in Thermal Cycles (without CO2 sequestration) may yield: Fuel-Cell Rankine Cycle, 72% Fuel-Cell Combined Brayton-Rankine Cycle, 75% Fuel-Cell Regenerative Brayton Cycle, 76%

Methods for the ALLOCATION

of energy consumption and CO₂ production in combined heat and power (CHP) production

and of heat and/or power production in hybrid multi-resource facilities

What fraction of the fuel consumed by a heat-and-power cogeneration facility should be allocated to the heat produced?

Why is it important?

The question is important in real estate, for buildings served by district heating systems where the heat is produced in CHP facilities.

Each country has its own specific certification process and criteria for evaluating the energy performance of residential buildings. In the United States, the Energy Performance Certificate (EPC)* or Home Energy Score* provides information about a building's energy efficiency and, therefore, it affects the building's commercial value. Among the parameters which determine the Home Energy Score is how much primary energy is consumed for heating.

*Similar indices adopted in various countries:
Italy: Attestato di Prestazione Energetica (APE)
France: Diagnostic de Performance Énergétique (DPE)
Germany: Verbrauchsausweis
United Kingdom: Energy Performance Certificate (EPC)
Australia: Nationwide House Energy Rating Scheme (NatHERS) or Building Sustainability Index (BASIX)
Canada: EnerGuide Rating System
Japan: Comprehensive Assessment System for Building Environmental Efficiency (CASBEE)
China: China Green Building Evaluation Standard (GBES)
India: Energy Conservation Building Code (ECBC) or Star Rating for Energy Efficiency of Buildings

Allocation problem in Heat&Power Cogeneration: α_W , α_Q , partial efficiencies, and PES



$$PES = \frac{W/\eta_{\rm W}^{\rm ref} + Q/{\rm COP}_{\rm Q}^{\rm ref} - F}{W/\eta_{\rm W}^{\rm ref} + Q/{\rm COP}_{\rm Q}^{\rm ref}}$$

Allocation problem in Heat&Power Cogeneration: α_W , α_Q , partial efficiencies, and PES



Allocation problem in CHP: Incremental Electricity-Centered Allocation



Allocation problem in CHP: Separate Production Reference Allocation



Allocation problem in CHP: Choice of reference values for η_W^{ref} and COP_Q^{ref}

SPR method:

Fixed values set by some local Authority



Exergy method:

Fixed values set by Thermodynamics

Effectively takes as references the REVERSIBLE heat engines!

 $\eta_{\rm w}^{\rm ref} \approx 1$

$$\operatorname{COP}_{Q}^{\operatorname{ref}} = 1 / \left(1 - \frac{T_{\operatorname{env}}}{T_{Q}} \right)$$

Allocation problem in CHP: "fair" reference values in a given local area

STALPR Method*: Self-Tuned-Average-Local-Productions-Reference

Adopt reference efficiencies



that are representative of the actual average efficiencies

 η_{W}^{loc} COP_Q^{loc}

of the energy production portfolio (typically the local area where the cogenerator itself is located) with which the resulting efficiencies of the cogenerator





* G.P. Beretta, P. Iora, and A.F. Ghoniem, Energy, Vol. 44, pp. 1107-1120 (2012)

Parameters of the local area						
η^{sep}_W			52 %			
COP _Q ^{sep}		-	90 %			
Parameter of the	ch	p pl	ant			
	(CC	BPST			
$\sigma_{chp} = \frac{W_{chp}}{Q_{chp}}$	1	.2	0.2			
$\eta_{chp} = \frac{W_{chp} + Q_{chp}}{P_{F,chp}}$	7	78% 85%				
Reference values for SPR						
$\eta_{\mathrm{W}}^{\mathrm{ref}}$			52 %			
COP _Q ^{ref}			90 %			



0/	IEC		Exergy		SPR	
70	η^{chp}_W	COP _Q ^{chp}	$\eta^{chp}_{\rm W}$	COP _Q ^{chp}	η^{chp}_W	COP _Q ^{chp}
CC	52	354	50	234	63.0	109
BPST	52	101	29	137	55.1	95.4





%	IEC		Exergy		SPR	
	η^{chp}_{W}	$\operatorname{COP}_Q^{\operatorname{chp}}$	η^{chp}_{W}	$\operatorname{COP}_Q^{\operatorname{chp}}$	η^{chp}_W	COP _Q ^{chp}
CC	52	354	50	234	63.0	109
BPST	52	101	29	137	55.1	95.4

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0/	IEC		Exergy		SPR	
% 0	η^{chp}_{W}	COP _Q ^{chp}	η^{chp}_{W}	$\operatorname{COP}_Q^{\operatorname{chp}}$	η^{chp}_W	COP _Q ^{chp}
CC	52	354	50	234	63.0	109
BPST	52	101	29	137	55.1	95.4





0/	IEC		Exergy		SPR	
[%] 0	η^{chp}_{W}	COP _Q ^{chp}	η^{chp}_{W}	COP _Q ^{chp}	η^{chp}_W	COP _Q ^{chp}
CC	52	354	50	234	65.4	101
BPST	52	101	29	137	55.1	95.4





0/	IEC		Exergy		SPR	
70	η^{chp}_{W}	$\operatorname{COP}_Q^{\operatorname{chp}}$	η^{chp}_{W}	COP _Q ^{chp}	η^{chp}_W	COP _Q ^{chp}
CC	52	354	50	234	65.4	101
BPST	52	101	29	137	54.5	95.7

0/	IEC		Exergy		STALPR	
70	η^{chp}_{W}	COP _Q ^{chp}	η^{chp}_{W}	$\operatorname{COP}_Q^{\operatorname{chp}}$	η^{chp}_W	COP _Q ^{chp}
CC	52	354	50	234	69.2	92.0
BPST	52	101	29	137	54.4	95.8

What fraction of the electrical energy produced in a hybrid solarfossil power plant should qualify as 'renewable electricity'?

Why is it important?

The question is important because several government programs (in the United States and in most other countries) provide economic incentives* for the production of electricity from solar, wind, and other renewable energy sources. In "hybrid facilities" where these renewable sources are combined/integrated with fossil fuels, the access to these incentives depends on how much of the produced electricity is recognized as renewable.

It is also relevant for multi-fuel power plants or hybrid CHP facilities.

*Examples: Investment tax credits Production tax credits Accelerated depreciation Cash grants Loan programs Grants and loan guarantees to agricultural producers and rural small businesses Renewable energy tax-credit bonds

Allocation problem in Hybrid Facilities: $\beta_{\rm F}$, $\beta_{\rm O}$, partial efficiencies, and PES

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Slide 10.39

Allocation problem in Hybrid Facilities: $\beta_{\rm F}$, $\beta_{\rm Q}$, partial efficiencies, and PES

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Slide 10.40

Allocation problem in Hybrid Facilities: Incremental Fossil-Centered Allocation

Allocation problem in Hybrid Facilities: Separate Production Reference Allocation

Allocation problem in Hybrid Facilities: Choice of reference values for η_F^{ref} and η_R^{ref}

Exergy method:

Effectively takes as references the REVERSIBLE heat engines!

$$\eta_{\rm F}^{\rm ref} \approx 1$$

$$\eta_{\rm R}^{\rm ref} \approx 0.93$$

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