Introduction to Combustion

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Mechanical Engineering 483
***Alternative Energy
Engineering II***

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Reading

Tonight:

The online notes on combustion give the derivation of the equations that will be presented in lecture tonight.

Next two classes: Online notes on engineering economics give a summary of information on this topic. This is essentially a brief review of a typical course in engineering economics, such as the MSE 304 course at CSUN, which is required in many undergraduate engineering programs.

Homework

Second homework assignment due tonight.

Download problem set due next Monday, February 8.

Today's Class

- Review last class
- Modeling general fuels
- Air/fuel ratio and λ = relative ratio
- Products for complete combustion
- Exhaust species rates per unit heat input
- Combustion efficiency

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The simplified combustion analysis considered here is one of the main topics in the second thermodynamics course (ME 470). This presentation will provide the basic equations used to compute quantities such as air/fuel ratio, exhaust concentrations, pollutant species rates, and combustion efficiency. The lecture material will provide a summary of the equations used and the notes will show sample calculations. The final slide contains an example problem that will give you experience in doing the calculations.

There is a set of combustion notes on line that provides the derivation of the equations used here. These derivations use the basic principles of balanced chemical reactions from freshman chemistry and first-law energy balances from thermodynamics.

The concept of chemical energy is introduced here. In beginning thermodynamics courses the effect of combustion is modeled as a heat addition. In reality the heat addition comes from the conversion of chemical energy in the fuel into thermal energy.

The actual heat transfer from a furnace, gas turbine combustor or other practical combustion device is designed to be a small fraction of the chemical energy converted; it represents an energy loss. An ideal conversion from chemical energy to thermal energy would have no external heat loss.

Review Properties and First Law

- Real fluid properties and ideal gas law
- Heat and work definitions and signs
- Closed system first law: Q = ΔU + W = mΔu + ∫$_{path}$PdV
- Open system first law:

$$\frac{dE_{cv}}{dt} = \dot{Q} - \dot{W}_U + \sum_{inlets} \dot{m}_{inlet}\left(h_{inlet} + \frac{\vec{V}^2_{inlet}}{2} + gz_{inlet}\right)$$

$$- \sum_{outlets} \dot{m}_{outlet}\left(h_{outlet} + \frac{\vec{V}^2_{outlet}}{2} + gz_{outlet}\right)$$
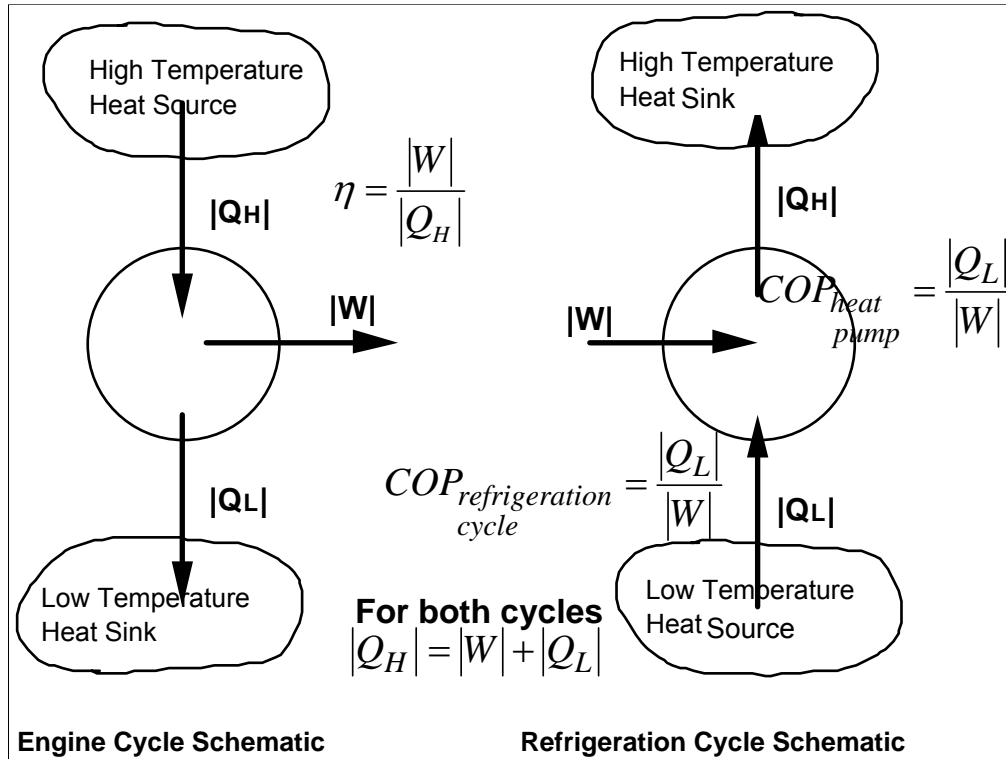
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Ideal gas: $PV = nR_uT$ where R_u, the universal gas constant, 8.31557 kJ/kgmol·K = R_u = 8.31557 kPa·m^3/kgmol·K = 10.7316 psia·ft^3/lbmol·R = 1.98588 Btu/lbmol·R. Engineering gas constant = R_u/M so PV = mRT.

Ideal gas relations apply at pressures that are low compares to the critical pressure and at temperatures that are high compared to the critical pressure. For real fluids we have to consider different phases, typically only liquid and gas, as well as mixtures of phases. Find properties from tables and compute mixed region properties from quality, x, the mass fraction of vapor in the liquid-vapor mixture.

Sign conventions: heat added to a system is positive; work done by a system is positive; heat rejected from a system is negative; work done on a system is negative.

Have different forms of the first law for closed (fixed mass) systems and open systems (sometimes called control volumes) that allow mass to enter and leave.

The diagram contains the following labels and equations:

Engine Cycle Schematic (left):
High Temperature Heat Source → $|Q_H|$ → circle → $|W|$ (work out), circle → $|Q_L|$ → Low Temperature Heat Sink

$$\eta = \frac{|W|}{|Q_H|}$$

Refrigeration Cycle Schematic (right):
High Temperature Heat Sink ← $|Q_H|$ ← circle ← $|W|$ (work in), Low Temperature Heat Source → $|Q_L|$ → circle

$$COP_{heat \atop pump} = \frac{|Q_L|}{|W|}$$

$$COP_{refrigeration \atop cycle} = \frac{|Q_L|}{|W|}$$

For both cycles
$$|Q_H| = |W| + |Q_L|$$

Engine Cycle Schematic   **Refrigeration Cycle Schematic**

Cycles are a fundamental concept in energy production and use.

In an engine cycle the device gets heat $|Q_H|$ from a high temperature source, performs a certain amount of work, $|W|$, then rejects heat $|Q_L|$ to a low temperature sink.

In a refrigeration cycle the device gets heat $|Q_L|$ from a low temperature source, has an input of a certain amount of work, $|W|$, then rejects heat $|Q_H|$ to a high temperature sink. In your home refrigerator the low temperature source is as the inside of the refrigerator. Work is done by an electric motor and the high temperature heat transfer is done by the coils in the back of the refrigerator.

Note that traditional cycle analysis does not use the usual sign conventions for heat and work; instead it uses quantities that are always positive. For both the engine and refrigeration cycles we can write $|Q_H| = |Q_L| + |W|$.

An engine cycle is rated by its efficiency, η, the ratio of work output to heat input. For a refrigeration cycle we would like to remove as much heat as possible from the low temperature source while doing the least amount of work. Thus the figure of merit for a refrigeration cycle, called the coefficient of performance, COP, is the ratio of the heat removed from the low temperature heat source to the work input.

The efficiency of an engine cycle is between zero and one. The COP for a refrigeration cycle may be greater than one.

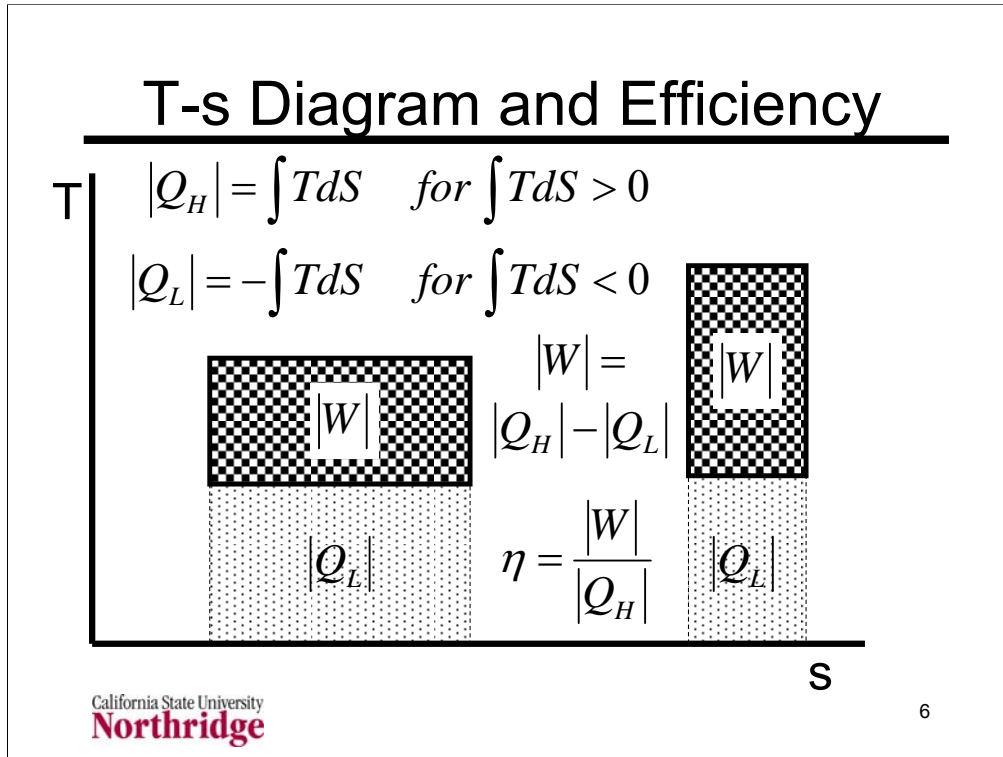The notation $|q_H|$ and $|q_L|$ are used for heat transfer per unit mass.

Second Law

- There exists an extensive thermo-dynamic property called the entropy (with the symbol, S) defined as follows:
- dS = (dU + PdV)/T
- For any process in a system dS ≥ dQ/T, and, for an isolated system
- $\Delta S_{\text{isolated system}} \geq 0$
- **Impossible:** 100% efficient engine cycle and refrigeration cycle with |W| = 0

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The second law provides a qualitative statement about limitations on cycles and it provides a mathematical tool, the entropy, to compute the efficiency of ideal cycles. We can use this tool, with the inequality relation that dS ≥ dQ/T, to determine the ideal case as the case in which dS = dQ/T. This is known as the reversible cycle. The maximum efficiency occurs in a reversible cycle.

For reversible heat transfer, dQ = TS so that Q = ∫Tds. If we can plot a reversible process on a diagram that has entropy as the abscissa and temperature as the ordinate (T-s coordinates or a T-s diagram) then the heat transfer is the area under the plot for that process.

No actual cycle is truly reversible, but we can try to approach reversibility as closely as possible within the constraints of cost. At some point the extra cost of making a device that is more nearly reversible outweighs the cost of the energy saved.

T-s Diagram and Efficiency

T

$$\left|Q_H\right| = \int TdS \quad for \int TdS > 0$$

$$\left|Q_L\right| = -\int TdS \quad for \int TdS < 0$$

$$\left|W\right| = \left|Q_H\right| - \left|Q_L\right|$$

$$\left|W\right|$$

$$\left|Q_L\right|$$

$$\eta = \frac{\left|W\right|}{\left|Q_H\right|}$$

$$\left|Q_L\right|$$

S

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The temperature-entropy or T-s diagram is often used to plot cycles because it shows provides a visual way of comparing cycle efficiency, once you are familiar with the underlying relations.

Recall that for a reversible process Q = ∫TdS. When we draw an ideal (reversible) cycle on a T-s diagram we can apply this equation. When the integral is positive, we have a heat input giving $|Q_H|$. Then the integral is negative we have the heat rejected so that $|Q_L|$ = –∫TdS. An engine cycle always operates in a clockwise manner. Each cycle can be viewed as stating in the upper left corner, then proceeding to the upper right corner and so on until the cycle is complete.

The chart uses the Carnot cycle, shown as the dark checked rectangles, as an example. There are only two parts of the cycle in which there is a heat transfer. Along the top part of the cycle, where the temperature is constant at a value T_H the integral gives $|Q_H|$ = $T_H \Delta S$. The lower portion gives $|Q_L|$ = –$(T_H)(-\Delta S)$ = $T_L \Delta S$. The difference between $|Q_H|$ and $|Q_L|$ is the net cycle work, |W|.

The area corresponding to $|Q_H|$ is the sum of two different areas shown on the diagram: the dark checkered area for the original cycle and the lower area. The lower area corresponds to $|Q_L|$. The difference between the two, which is the area in the cycle, is the work. The ratio of the cycle area to the total area (cycle area plus area beneath the cycle) is the efficiency.

Which of the two cycles has a greater efficiency?

Cycle Analysis

- The following assumptions define idealized versions of practical cycles
  - There are no line losses; the outlet state (i.e. thermodynamic properties) from one device is the same as the inlet state to the next device.
  - work devices are reversible and adiabatic so they have constant entropy (isentropic).
  - Heat transfer devices have no pressure loss and are reversible so Q = ∫Tds
  - Outlet states from devices with two phases are saturated liquids or vapors.

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These assumptions give the highest efficiency for a given set of cycle conditions. In practice they are not met and the degree to which they are not met gives the difference between the actual or maximum cycle efficiency and the actual cycle efficiency.

These assumptions can also be applied to the analysis of a refrigeration cycle to compute the maximum coefficient of performance.

Last class period we looked at a variety of cycles:

The **Rankine cycle** and its variants are used to model the process in a steam-electric power plant. Higher temperatures and pressures in the steam generator provide higher efficiencies, but reheating has to be used to ensure that there is not an excessive amount of water in the final stages of the turbine. Feedwater heaters are used to increase efficiency.

The **Otto cycle** models the operation of gasoline engines. The simple analysis shows that the efficiency is related to the compression ratio, CR, which is the ratio of the maximum cylinder volume to the minimum cylinder volume. This equation, $\eta = 1 - 1 / (CR)^{k-1}$, overstates the efficiency, but does show a correct trend of efficiency with compression ratio.

The **Brayton cycle** models gas turbine engines. The simple analysis shows that the efficiency is related to the pressure ratio, PR, which is the ratio of the engine pressure in the combustor to the minimum engine pressure at the compressor inlet and turbine outlet This equation, $\eta = 1 - 1 / (PR)^{(k-1)/k}$, overstates the efficiency, but does show a correct trend of efficiency with pressure ratio.

Introduction to Combustion

- Have several levels of analysis
  - Balanced chemical equation to determine species
    - Assume complete combustion
  - Energy balance to include chemical energies
  - Chemical equilibrium calculations
  - Chemical kinetics calculations
  - Computational fluid dynamics integrates flow, heat transfer, and chemical kinetics

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There is a range of analyses that can be done on combustion processes. At a basic level we know that chemical elements are conserved so we can write a simple chemical balance equation for the reaction of a fuel molecule with air. We can consider complex fuels by allowing non-integer amounts of atoms in our fuel "molecule". This allows us to represent the combustion of several fuels by a single chemical balance equation.

The assumption of complete combustion, where all the fuel carbon reacts to CO_2, all the fuel hydrogen reacts to H_2O, all the fuel sulfur reacts to SO_2, and all the fuel nitrogen reacts to N_2 is usually a reasonable one for well maintained lean combustion processes. It is a useful first approximation to the species balance and energy balance.

More extensive calculations can consider the thermochemical equilibrium. Computer codes are available to make these computations. These show that the combustion products at high temperatures have significant concentrations of other species such as CO and NO.

Chemical kinetics calculations use a set of ordinary differential equations to determine the rate of change of the species in an air-fuel mixture. Such calculations are limited to the simplest fuels.

Combustion processes usually occur in flow systems where there is a significant amount of turbulence. Sophisticated computer programs, known as computational fluid dynamics or CFD, can analyze such processes in principle, but a large amount of data are required.

Basic Fuel Analysis

- Apply to any fuel with any amount of the following elements: C, H, O, N, and S
- Covers most fossil fuels
  - Some natural gases have components such as helium and argon not covered
  - Ultimate analysis for liquid and solid fuels gives weight percent of each element, including mineral matter that forms "ash"
  - Gaseous fuels have molar analysis of each component in gas

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Fossil fuels, particularly coals, contain some amount of mineral matter that does not enter into the combustion process. The ultimate analysis of fuels, discussed on the next chart, gives the relative amounts, by mass, of carbon, hydrogen, oxygen, and mineral matter. The mineral matter does not provide any energy, but forms solids that either fall to the bottom of the combustion region (slag) or are emitted with the exhaust gas (fly ash).

The analysis of the combustion process deals with the conversion of the main fuel elements, C, H, O, N, and S into combustion products: CO_2, H_2O, SO_2, and N_2. The combustion products also contain excess O_2 and unreacted components of air such as N_2, Ar, and other trace species.

The goal of the analysis is to find the relative amounts of combustion products and determine combustion efficiencies.

Basic Fuel Analysis II

- General fuel formula: $C_xH_yS_zO_wN_v$

- Determine values of x, y, z, w, and v from ultimate analysis or analysis of gas mixtures

- Mineral matter included in ultimate analysis represented as %Ash or %MM

- For ultimate analysis x = wt%C/12.0107, y = wt%H/1.00794, z = wt%S/32.065, w = wt%O/16.0004, v = wt%N/14.0067

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When using data for an ultimate analysis we can arbitrarily set the mass equal to 100 kg or 100 lb_m depending on the units we are using. This arbitrary choice is called the basis of the calculation. We can use this arbitrary basis because we will state all results in terms of product species or energy release per unit mass of fuel. Hence arbitrary value of 100 (or any other value we choose) will cancel when we obtain per unit mass values.

Once we choose this basis we know that the mass of each element in the generic fuel formula is the weight percent from the ultimate analysis times 100 so simply the weight percent expressed as a number. For example a fuel with 85%wt carbon would have 85 kg of carbon in the assumed 100 kg of fuel. If we divide this 85 kg of carbon by the atomic mass of carbon (12.0107) we get the amount, x = 7.077, kilogram atoms of carbon atoms in one "mole" of our fuel formula. We can repeat this for each component in the ultimate analysis.

Note that the subscripts are usually not integers here. This is correct since we are representing a mixture, which has a non-integer composition, by a fuel formula that looks like a molecule. This is not really a molecule, but provides an approach to analyzing fuel mixtures that is exactly the same as our usual operations for balancing a chemical equation.

An example of converting a set of data on the ultimate analysis of a fuel to a fuel formula is shown on the following notes page.

Gas Mixture Analysis

Gas	Mole Fraction	Carbon	Hydrogen
CH_4	0.88	0.88	3.52
C_2H_6	0.07	0.14	0.42
C_3H_8	0.03	0.09	0.24
C_4H_{10}	0.02	0.08	0.2
Mixture	1	1.19	4.38

- Sum product of mole fraction times number of atoms in fuel (*e.g.*: $C_{1.19}H_{4.38}$)[11]

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Gas mixtures can also be analyzed by the general fuel formula, $C_xH_yS_zO_wN_v$ where the relative elemental amounts are computed as the mole fraction weighted sums of the elements in each species. In the example shown in the table above, the carbon content in the mixture is computed as follows:

1(.88) + 2(.07) + 3(.03) + 4(.02) = 1.19

and the hydrogen content is found as

4(.88) + 6(.07) + 8(.03) + 10(.02) = 4.38

An example of converting an ultimate analysis to a fuel formula is shown below:

Atom	Weight Percent	Atomic Weight	%wt / Atom Wt	Symbol
C	85.4	12.0107	7.110	x
H	14.4	1.00794	14.287	y
S	0.005	32.065	0.0002	z
O	0.19	15.9994	0.012	w
N	0.004	14.0067	0.0003	v
Ash	0.001	Not included in fuel "molecule" but part of fuel mass		

The resuting fuel formula is $C_{7.110}H_{14.287}S_{0.0002}O_{0.012}N_{0.0004}$. The minor components can be neglected in a simple analysis but the sulfur and nitrogen in the fuel play a role in pollutant emissions.

Combustion Air

- Complete combustion converts C to CO_2, H to H_2O, S to SO_2 and N to N_2
  - Stoichiometric O_2 is minimum to give this
- Stoichiometric O_2 for $C_xH_yS_zO_wN_v$ is A = x + y/4 + z – w/2 moles O_2
- Usually have extra O_2 so total is λA
  - λ is ratio of actual O_2 to stoichiometric O_2
- Also have other dry air components: N_2, Ar, and CO_2 plus H_2O from humidity

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Composition of Dry Air (Molar mass = 28.966) from http://ic.ucsc.edu/~wxcheng/envs23/lecture5/air_compo.htm (accessed February 5, 2007)

Gas	Mole %	Mass %	Moles/mole O_2
Oxygen	20.947	23.20	1
Nitrogen	78.084	75.47	3.7277
Carbon Dioxide	0.036	0.046	0.0017
Hydrogen	0.00005	~ 0	0.000002
Argon	0.934	1.28	0.0446
Neon	0.0018	0.0012	0.0001
Helium	0.0005	0.00007	0.000024
Krypton	0.0001	0.0003	0.0000025
Xenon	9×10^{-6}	0.00004	4×10^{-7}

There 3.774 moles of other species per mole of O_2 in dry air. In the simplest combustion analyses these additional moles are assumed to be all nitrogen that is an inert. Other analyses will include argon, and sometimes CO_2, as a separate species. When N_2 is the only other air species in the analysis it can be assigned a fictitious molar mass of 28.163 (compared to the correct value of 28.0134) to have the correct mass of all other species in air. This is called "atmospheric" nitrogen.

The mass of air per mole of O_2 = 28.966 /0.20947 = 138.28

Air/Fuel Ratio for $C_xH_yS_zO_wN_v$

- Given λ and data to find x, y, z, w, and v
- First compute A = x + y/4 + z – w/2 = moles O_2/mole fuel
- $m_{fuel} = M_{fuel}$ / (1 – %Mineral in fuel)
  - M_{fuel} = 12.0107x + 1.00794y + 32.065z + 15.9994w + 14.0067v
  - $m_{fuel} = M_{fuel}$ = 100 for %Mineral = 0
- m_{air} =138.28λA
- Air/fuel ratio = m_{air}/m_{fuel}

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Air fuel ratio is commonly expressed on a mass basis. (For most liquid hydrocarbon fuels the stoichiometric air/fuel ratio is about 14.7.) Note that approach used to compute x, y, z, w, and v for an ultimate analysis essentially assumes that the chemical formula is based on 100 mass units. If there is no mineral matter (ash) in the fuel, his is equivalent to assuming a molar mass of 100, so it is not necessary to compute M_{fuel} in this case. If the ultimate analysis contains a value for %Ash and you use 100 mass units to convert the ultimate analysis to a fuel formula, then the fuel mass m_{fuel} = 100. Regardless of the number of mass units you chose to use in the ultimate analysis you can always compute $m_{fyel} = M_{fuel}$/(1 - %Ash).

Note the subtle difference between complete combustion and stoichiometric combustion. Complete combustion is when all the fuel C forms CO_2, all the fuel H forms H_2O, all the fuel S forms SO_2 and all the fuel N forms N_2. This cannot possibly occur unless the oxygen is equal to or greater than stoichiometric.

Although we can define a stoichiometric oxygen supply and have actual combustion with just this amount of oxygen, the stoichiometric oxygen supply does not guarantee complete combustion. Usually excess air is added. This excess air is usually expressed as a ratio to the stoichiometric oxygen requirement, λ. (For combustion with air the stoichiometric air requirement is called the theoretical air and λ, expressed as a percentage, is called the percent theoretical air.)

Complete Combustion Products

- $C_xH_yS_zO_wN_v + \lambda A(O_2 + 3.77\ N_2) \rightarrow xCO_2 + (y/2)H_2O + zSO_2 + (\lambda - 1)AO_2 + 3.77\lambda A + v/2)N_2$

- Measurements on wet/day basis done with/without product water

- Relate λ and product O_2

$$\frac{\%O_2|_{dry}}{100} = \frac{(\lambda - 1)A}{x + 4.77\lambda A - A + z + \dfrac{v}{2}}$$

$$\lambda = \frac{A + \dfrac{\%O_2|_{dry}}{100}\left[x - A + z + \dfrac{v}{2}\right]}{A\left(1 - 4.77\dfrac{\%O_2|_{dry}}{100}\right)}$$

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The balanced chemical equation shown above uses the simple approach where all other constituents of air are assumed to be N_2. Recall that when we do this, we have to use a fictitious molar mass of 28.163 for molecular nitrogen (N_2).

This equation can be checked to show that all chemical elements are conserved. This is simple to do for C, H, N, and S. To see that it is correct for O, we have to use the definition of A = x + y/4 + z – w/2. The elemental balance for oxygen can be done for O_2. We first note that both sides of the equation have λA moles of O_2 which cancel. We are then left with the following sum of O_2 for all species on the right side: x + y/4 + z – A = w/2, which is the amount of O_2 left on the right side of the equation after cancelling the λAO_2.

Many analytical instruments require water in the combustion products to be removed prior to analysis. Because of this, the exhaust measurements are commonly made on a dry basis. The equations on this slide show how the exhaust mole fraction can be used to determine λ.

The equation for the dry oxygen mole fraction can be seen to be the ratio of the moles of oxygen in the exhaust $(\lambda - 1)A$ divided by the total number of dry moles, D = x + z + $(\lambda - 1)$A + 3.77λA + v/2.

Note that the SO_2 dry mole fraction can be expressed by the following equation, analogous to the equation for the oxygen mole fraction: y_{SO2} = z/[x + z + $(\lambda - 1)$A + 3.77λA + v/2]

Regulatory Measurements

- Correct measured value, C_{meas}, to concentration, C_{std}, at standard exhaust O_2 concentration $[\%O_2]_{std}$ to prevent compliance by dilution

$$C_{std} = C_{meas} \frac{20.9 - [\%O_2]_{std}}{20.9 - [\%O_2]_{meas}}$$

- Typical values for $[\%O_2]_{std}$ are 0, 3 (for boilers) and 15 (diesel engines and gas turbines)

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When emission standards are stated on a concentration (or mass or mole fraction basis) they are often corrected to some standard oxygen concentration that is typical of the device in question. A zero oxygen concentration is used to determine the actual flow rate as shown in the following slides.

Boilers in a range of sizes typically operate at a small amount of excess oxygen that is characterized for regulatory purposes as the amount that produces an exhaust concentration of 3% O_2. Diesel engines are operated much leaner and gas turbines operate even leaner than diesel engines. The correction to 15% O_2 is generally used for gas turbines. It is sometimes used for diesel engines, but other levels are used here as well.

Emission Standards

- Emission standards, E, mass of pollutant per unit heat input

$$E_i = \rho_{i,d} F_d \frac{20.9}{20.9 - \%O_{2,d}}$$

- Calculation method uses F-Factor, F_d
  - F_d is exhaust volume flow / heat input
  - E is emissions in ng/J or lb/MMBtu
  - $\rho_{i,d}$ is dry mass partial density ng/m^3 or lb$_m$/ft^3
  - $\%O_{2,d}$ is dry mole percent O_2 in exhaust
- F_d = (8710, 9190) ft^3/MMBtu for (gas, oil)

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The volume measurements shown above are at standard conditions of 68°F = 20°C and atmospheric pressure.101.325 kPa = 14.696 psia. Such standard conditions are commonly abbreviated as scf for standard cubic feet or scm for standard cubic meters. To emphasize the use of dry measurements, the abbreviations dscf or dscm are sometimes used to denote dry standard cubic feet or dry standard cubic meters.

Some values of F_d from http://www.epa.gov/ttn/emc/promgate/m-19.pdf (accessed February 6, 2007) are shown below

Fuel	dscm/J	dscf/MMBtu
Anthracite Coal	2.71×10^{-7}	10,100
Bituminous Coal	2.63×10^{-7}	9,780
Lignite	2.65×10^{-7}	9,860
Oil	3 2.47×10^{-7}	9,190
Natural Gas	2.34×10^{-7}	8,710
Propane	2.34×10^{-7}	8,710
Butane	2.34×10^{-7}	8,710
Wood	2.48×10^{-7}	9,240
Wood Bark	2.58×10^{-7}	9,600

Emission Standards II

- Values for F_d for typical fuels found from EPA method 19 (reference below)
    - http://www.epa.gov/ttn/emc/promgate/m-19.pdf
- Can also be computed from ultimate analysis (%C, %H, etc.)

$$F_d = \frac{K\left(K_C\%C + K_H\%H + K_O\%O + K_S\%S + K_N\%N\right)}{Q_c}$$

- Q_c is higher heating value
- K values in notes page

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The constants in the equation for computing the factor, F_d, from the ultimate analysis are shown below. Two sets of values, one in SI units the other in engineering units, are given. Note that in the equation the values of the ultimate analysis are expressed as a percentage, not as a decimal. Thus a value for %C = 84% would be entered in the formula as 84 **not as .84**.

The units for the higher heating value (Q_c) are Btu/lb$_m$ or kJ/kg.

K = Conversion factor, 10^{-3} (kJ/J)/(%) [10^6 Btu/million Btu].

K_C = (9.57 scm/kg)/% [(1.53 scf/lb)/%].

K_H = (22.7 scm/kg)/% [(3.64 scf/lb)/%].

K_N = (0.86 scm/kg)/% [(0.14 scf/lb)/%].

K_O = (2.85 scm/kg)/% [(0.46 scf/lb)/%].

K_S = (3.54 scm/kg)/% [(0.57 scf/lb)/%].

The value for C_d on the previous chart is stated as ng/m^3 or lb$_m$/ft^3. Typically the emission measurements are mole fractions such as y_i for species i. To convert this to the partial mass density ρ_i use the following calculation: $\rho_{d,I}$ = $y_{d,i}M_iP/R_uT = y_{d,i}P/R_iT$ where P is the standard pressure of 101.325 kPa = 14.696 psia, R_u is the universal gas constant = 8.31447 kPa·m3/kgmol·K = 10.7316 psia·ft3/lbmol·R, T = standard temperature = 288.15 K = 518.67 R, M_i is the molar mass of species i, and R_i is the engineering gas constant = R_u/M_i. (The standard temperature used here is 15°C = 59°F; other standard temperatures can be used; a standard pressure of 14.3 psia is sometimes used.)

Calculation Summary

- Need $\rho_{i,d}$, F_d and %$O_{2,d}$ to compute E_i

$$E_i = \rho_{i,d} F_d \frac{20.9}{20.9 - \%O_{2,d}}$$

- Measured dry mole fractions of O_2 and species i, $y_{i,d}$, ($y_i = 10^{-6} ppm_i$)
  - $\rho_{i,d} = y_{i,d} M_i P_{std}/RT_{std}$
- F_d computed from ultimate analysis or default values are used
- If %O_2 not measured

$$\frac{\%O_2|_{dry}}{100} = \frac{(\lambda - 1)A}{x + 4.77\lambda A - A + z + \frac{v}{2}}$$

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This slide recapitulates the equations provided on previous slides to outline the steps in calculating the pollutant emissions rate in mass per unit heat input, E. The three parts to the formula from slide 16 are found by various ways as outlined here.

The partial mass density of the pollutant species is found from the ideal gas law as discussed on the previous notes page. Note that pollutant concentrations are often given in parts per million (ppm) which is a mole fraction multiplied by 10^6.

The F_d factor can be taken from the default values on the notes page for slide 16 or can be computed from an ultimate analysis using the formula on slide 17 with the associated K values on the notes page for that slide.

The exhaust oxygen concentration is typically measured. If measurements are not available or you are making a design calculation, the dry exhaust concentration of oxygen can be found from the formula on slide 14 which is copied here. The items in that formula are the ultimate analysis calculation results x, y, z, w, v found from the formulas on slide 10. The stoichiometric oxygen moles per fuel mole, A = x + y/4 + z – w/2, is found on slide 13. The relative air/fuel ratio, λ, is assumed to be known if the exhaust oxygen is not measured.

Example Calculation

- The exhaust from a combined cycle power plant has exhaust concentrations (dry) of 2.8% O_2 and 9 ppm NOx. What is the NOx rate in lb_m/MMBtu.
  - $\rho_{i,d} = y_{i,d}M_iP_{std}/R_uT_{std}$ $y_i = 10^{-6}ppm_i$
- F_d = 8710 ft³/MMBtu for gas

$$E_i = \rho_{i,d}F_d\frac{20.9}{20.9-\%O_{2,d}} = \frac{0.011\,lb\,NOx}{MMBtu}$$

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See calculation
details in notes page   19

We compute the partial density from the mole fraction (after multiplying the ppm by 10^{-6} to get $y_{i,d}$.)

$$\rho_{i,d} = \frac{y_{i,d}M_iP_{std}}{R_uT_{std}} = \frac{\dfrac{9x10^{-6}\,lbmol\,NOx}{lbmol}\dfrac{46.0065\,lb\,NOx}{lbmol\,NOx}(14.696\,psia)}{\dfrac{10.7316\,psia\cdot ft^3}{lbmol\cdot R}(518.67\,R)} = \frac{1.0832x10^{-6}\,lb\,NOx}{ft^3}$$

Note the convention that the molar mass used for NOx is that of nitrogen dioxide (NO_2).

Note also that the volume used here is the hypothetical volume of the dry exhaust at standard conditions. The units for cubic feet at standard conditions are often specified as SCF. The abbreviation DSCF for (dry standard cubic feet) is also used to emphasize that the measurements are made for the dry exhaust.

Once we find the partial density we use the standard value that F_d= 8710 ft³/MMBtu (sometimes written as 8710 DSCF/MMBTU as noted above) for natural gas to get the emission rate per unit heat input.

$$E_i = \rho_{i,d}F_d\frac{20.9}{20.9-\%O_{2,d}} = \frac{1.0832x10^{-6}\,lb\,NOx}{ft^3}\frac{8710\,ft^3}{MMBtu}\frac{20.9}{20.9-2.8} = \frac{0.011\,lb\,NOx}{MMBtu}$$

Simplified Analyses

- Simple analysis to find mass of sulfur, SO_2, carbon, or CO_2 per unit fuel mass or heat input

$$\frac{m_S}{m_{fuel}} = \frac{wt\% S}{100} \qquad \frac{m_{SO_2}}{m_{fuel}} = \frac{wt\% S}{100} \frac{M_{SO_2}}{M_S} = 1.9979 \frac{wt\% S}{100}$$

$$\frac{m_C}{m_{fuel}} = \frac{wt\% C}{100} \qquad \frac{m_{CO_2}}{m_{fuel}} = \frac{wt\% C}{100} \frac{M_{CO_2}}{M_C} = 3.6642 \frac{wt\% C}{100}$$

$$\frac{m_C}{Q_{fuel}} = \frac{1}{Q_c} \frac{m_C}{m_{fuel}} \quad \frac{m_{CO_2}}{Q_{fuel}} = \frac{m_{CO_2}}{m_{fuel}} \quad \frac{m_S}{Q_{fuel}} = \frac{1}{Q_c} \frac{m_S}{m_{fuel}} \quad \frac{m_{SO_2}}{Q_{fuel}} = \frac{m_{SO_2}}{m_{fuel}}$$

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Simplified calculations of the mass of pollutant species can be made for SO_2 and CO_2 by assuming that all the sulfur in the fuel reacts to SO_2 and that all the carbon in the fuel reacts to CO_2. These are reasonable assumptions, with only a small (~1%) error.

The weight percent of sulfur or carbon (divided by 100 to give a weight fraction) gives the proportion of these elements in the fuel. Multiplying the fraction of sulfur in the fuel by the ratio of the molar mass of SO_2 to the molar mass of sulfur (64.0638 / 32.065) gives the result shown above. For practical purposes this molar mass ratio can be set to 2.

In a similar fashion, multiplying the fraction of carbon in the fuel by the ratio of the molar mass of CO_2 to the molar mass of carbon (44.0095 / 12.0107) gives the result shown above for the mass of CO_2 pre unit mass of fuel.

If the equations for the mass of carbon, sulfur, CO_2 or SO_2, per unit mass of fuel, are divided by the heat of combustion of the fuel, the result is the mass of carbon, sulfur, CO_2 or SO_2, per unit heat input from the fuel. Combining the equations on the chart gives the following results.

$$\frac{m_{CO_2}}{Q_{fuel}} = \frac{3.6642}{Q_c} \frac{wt\% C}{100} \qquad \frac{m_{SO_2}}{Q_{fuel}} = \frac{1.9979}{Q_c} \frac{wt\% S}{100}$$

Natural gas, with a higher value of Q_c and a lower value of wt% C compared to coal has lower emissions of CO_2 per unit heat input.

Combustion Efficiency

- How much heat of the amount possible in the fuel is actually used?

$$\eta_{comb} = \frac{|q|}{|q|_{max}} = 1 - \frac{\left[1+\frac{Air}{Fuel}\right]}{Q_c}\int_{T_{in}}^{T_{out}} c_{p_{Air}} dT' - \frac{xf\Delta h_{CO}}{M_{fuel}Q_c}$$

- Air/fuel is the air to fuel (mass) ratio
- $C_{p,air}$ = 0.24 Btu/lb$_m$·R = 1.005 kJ/kg·K
- f = molar exhaust ratio CO/(CO + CO$_2$)
- x = carbon atoms in fuel formula, C$_x$H$_y$…
- Q$_c$ = heat of combustion (Btu/lb$_m$ or kJ/kg)
- Δh_{CO} 282,990 kJ/kgmol = 121,665 Btu/lbmol

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The combustion efficiency analysis, whose results are shown here, is based on the assumption that the heat capacity of the fuel plus air is the same as the heat capacity of the exhaust, both of which are taken to be the heat capacity of air. This is not such a bad assumption since the fuel/air mixture is about 94% air and the main component of exhaust gases is nitrogen.

The Δh_{CO} term is the enthalpy difference that could have been obtained by burning one mole of CO in the exhaust to CO$_2$. It's value is 282,990 kJ/kgmol = 121,665 Btu/lbmol.

Either higher or lower heating values can be used for Q$_c$ and the combustion efficiency should be stated as a percent of the HHV or LHV as appropriate. Usually the lower heating value is used since the product water is in the vapor phase.

The heat capacity values for air shown in the slide are room temperature values. The assumption of a constant heat capacity is consistent with the assumption that the heat capacity of air applies to both the reactants and products. However, if there is a large temperature difference between the inlet and exit temperatures, a set of air tables can be used to find the integrated heat capacity.

In-Class Exercise

- Biomass fuel w HHV = 19,136 kJ/kg, and an ultimate analysis: wt%C = 48.55%, wt%H = 5.33%, wt%O = 45.30%, wt%S = 0.01%, wt%, N = 0.81% burned in air with λ = 1.4; T_{in} 25°C, T_{out} = 330°C; dry combustion gases have 12 ppm NOx and a $CO/(CO + CO_2)$ ratio of 1%.
  - Find: air/fuel ratio, product distribution, g NOx/MJ, and combustion efficiency

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All calculations request here are similar to those given in example calculations in the notes pages here. The usual order for the required calculations is shown below:

1. Find the fuel formula, $C_xH_yO_wS_zN_v$ from the example in the notes.

2. Follow example for calculating the air/fuel ratio.

3. Follow example for determining the $\%O_2$ calculation and the F factor, F_d for the given elemental composition.

4. Use the combustion efficiency formula that includes the effect of outlet temperatures that are higher than the inlet temperature and the effect of exhaust CO on combustion efficiency.