

Sustainable Energy Transformation Technologies, SH2706

Lecture No 2

Title:

Biological and Chemical Energy

Henryk Anglart

Nuclear Engineering Division

Department of Physics, School of Engineering Sciences

KTH

Autumn 2022

Outline

- Energy in matter
- Biological energy
- Chemical energy

Energy in Matter

- There are many places in matter where energy can be stored in various forms
- **Internal energy** is located in various bindings present in matter, such as:
 - neutron and proton binding in nucleus (nuclear energy)
 - electron binding in atom
 - atom bindings in molecules
 - binding between molecules
- Additional internal energy, called thermal energy, is stored in motions of particles (atoms/molecules)
- Rest mass energies of constituent particles are also included into internal energy

Thermal Energy

- Thermal energy (\mathcal{U}) represents one of the components of internal energy (E_i), and refers to the energy contained in relative motion of particles in a macroscopic system
- It shouldn't be confused with heat (Q), which is thermal energy in transition from one system to another
- Temperature (T) is a relative measure of the amount of thermal energy of a system, but the relationship between them is very complex and will be discussed in lectures devoted to thermodynamics

Energy Stored in Molecules

- Binding atoms in molecules is another place where internal energy can be stored
- For example, dissociation of water requires energy:



- The first step requires 493 kJ/mol and the second 424 kJ/mol
- This energy can be retrieved when we “burn” hydrogen (reversed process used in fuel cells – to be discussed)

Biological Energy

- Living organisms require energy
- Plants use photosynthesis to convert solar energy into chemical energy, used to support live processes and grow
- A human needs 1700 kcal/d to support essential life activities
- Humans with active life style need 3000-3500 kcal/d

Photosynthesis

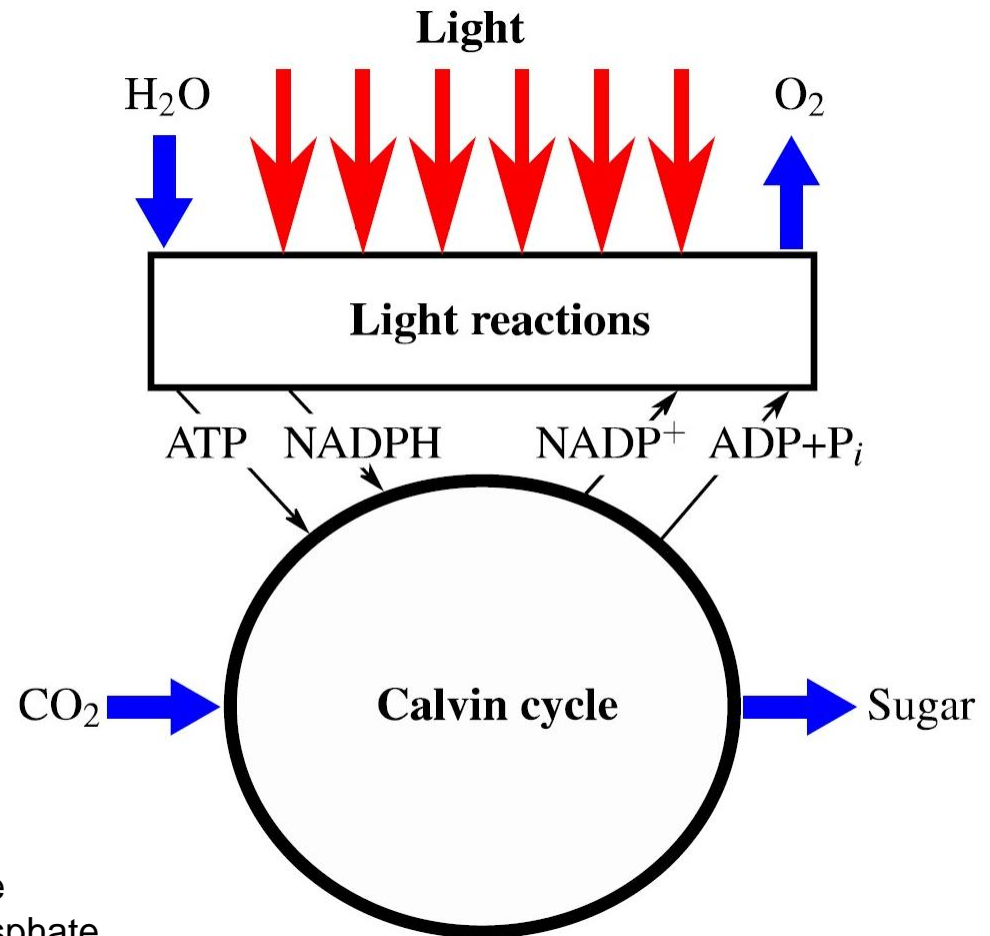
Photosynthesis type C-3 binding CO₂ in Calvin's cycle

Stage 1: light reactions to capture the photon energy and make ATP¹ and NADPH² molecules

Stage 2: light-independent reactions using ATP and NADPH molecules to capture and reduce CO₂

This type of photosynthesis is called **oxygenic photosynthesis**.

- 1) energy carrier – **A**denosine **T**ri**P**hosphate
- 2) **N**icotinamide **A**denine **D**inucleotide **P**hosphate



Photosynthesis

- Oxygenic photosynthesis involves a complicated set of biochemical reactions with the following net conversion:



- The reaction indicates that, under action of $8n$ photons, n -water and carbon dioxide molecules produce a molecule of sugar and n molecules of oxygen
- On the other hand, **anoxygenic** photosynthesis uses electron donors other than water (occurs in purple bacteria and green sulphur bacteria in aquatic habitats)

Photosynthesis Efficiency

- The efficiency of photosynthesis for most plants is a fraction of 1%
- Only 40% of the energy in sunlight lies in the photosynthetically active frequency range
- The energy that is stored in structural material within the plant is substantially less than 1% of the incident sunlight, and typically around 0.25%.

Food Production - Example

- Estimate the efficiency of growing maize (corn), knowing that it is produced with harvest yield of 10 t/ha-y, it has energy density of 15 MJ/kg, and the average insolation is 200 W/m².
- Solution: We find the energy capture rate as 10000 kg/ha-y * 15 MJ/kg = 150 GJ/ha-y. The insolation gives 100x100 m²/ha * 200 J/s-m² * 365*24*3600 s/y = 63072 GJ/ha-y. Thus the efficiency is 150/63072*100% = 0.2378%

Bioenergy

- We discuss various forms of bioenergy:
 - biomass
 - biogas
 - biofuels
 - ethanol
 - biodisel

Biomass

- Biomass is any type of organic material derived from living or recently living organisms
- Biomass represents about 8% of global energy use
- It can be:
 - digested by bacteria to produce biogas (e.g. methane)
 - upgraded by thermal, chemical, biochemical, etc. processes (e.g. Fischer-Tropsch synthesis to convert biological syngas into liquid hydrocarbons)

Biomass - Example

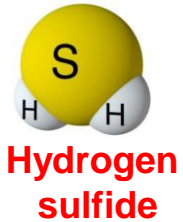
- Estimate the land needed to supply sustainably 40 EJ/y, by direct burning of biomass consisting of crops and trees that accumulated energy through photosynthesis at a rate of around 5 t/ha-y, with typical energy density of 12 MJ/kg.
- Solution: the energy supply rate is $5000 \text{ kg/ha-y} \times 12 \text{ MJ/kg} = 60 \text{ GJ/ha-y}$. Thus the total area needed is $40 \times 10^{18} \text{ J/y} / 60 \times 10^9 \text{ J/ha-y} = 6.7 \times 10^8 \text{ ha}$, which corresponds to about 14% of all forested land area on Earth.

Biogas

- Biogas is obtained by thermal gasification, e.g. by heating biomass in presence of oxygen, air, and/or water vapour
- This leads to breakdown of the molecular structure of the biological material into methane, CO_2 , CO , H_2
- Biological syngas is obtained by incomplete combustion
- Pyrolysis is heating in the absence of oxygen or air: releases gas containing H_2 , light hydrocarbons (methane, ethane), and liquid hydrocarbons

Biogas

- Raw biogas contains about 60% of methane, 39% of CO_2 and traces of H_2S : inadequate to use in engines
- H_2S is corrosive and would destroy the engine
- Methane in biogas can be concentrated via biogas upgrader to the same standards as fossil natural gas
 - is called then biomethane
- If concentrated and compressed, it can be used in vehicle transportation (Sweden, Switzerland, Germany)
- The air pollution produced by biogas is similar to that of natural gas
- Can be explosive when mixed with air with ratio 1:8-20



Ethanol

- Ethanol ($\text{C}_2\text{H}_5\text{OH}$) can be obtained from simple sugars through fermentation (biological transformation of sugars to alcohols, acids, or gases)
- For glucose we have: $\text{C}_6\text{H}_{12}\text{O}_6 \rightarrow 2\text{C}_2\text{H}_5\text{OH} + 2\text{CO}_2$
- The energy density of ethanol is approximately twice that of simple sugars due to the release of CO_2
 - pure ethanol has mass density 0.789 kg/l and energy density 23.4 MJ/l
- Main producers:
 - USA, maize-based, 54×10^9 l/y
 - Brazil, sugarcane-based, 24×10^9 l/y

Both maize and sugarcane can be used as food, so there are efforts to use cellulose instead

Ethanol - NEB

- Important metric for biofuels is NEB – **Net Energy Balance** \equiv (total energy out)/(total energy in)
- For example, sugarcane can be produced with rate at 180 GJ/ha-y
- This production requires substantial energy inputs:
 - fertilizers, planting, harvesting, transport, distribution, etc
- For Brazilian sugarcane plant, NEB \approx 8
- For US maize plant, NEB \approx 1.2-1.6 (difficult to process starches – cannot be directly fermented)
- For cellulosic ethanol NEB is still unclear

Biodiesel

- Biodiesel is a liquid fuel produced from vegetable oil and animal fat using purely chemical processes
- Since biodiesel can be produced from a wide range of different feedstocks, various mixtures of molecules exist in different batches
- Typical specific energy of biodiesel fuel is 37 MJ/kg
 - about 10% lower than for standard diesel fuel

Chemical Energy

- The enthalpy of a chemical reaction (called also heat of reaction ΔI_r) is defined to be the amount of energy that is absorbed ($\Delta I_r > 0$) or released ($\Delta I_r < 0$) as heat during reaction **Endothermic reaction** **Exothermic reaction**
- For example, consider the reaction:
Calcium carbonate (limestone) $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ (calcination)
Calcium oxide
- From thermodynamic tables we find that $\Delta I_r = +178.3$ kJ/mol
- In practical applications, chemists do not tabulate ΔI_r for all possible reactions
- Instead, so-called enthalpy of formation (ΔI^f) is tabulated for various compounds and **Hess's law** is used

Hess's Law

- **Hess's law** states that the reaction enthalpy for any reaction is equal to the sum of the enthalpies of formation of the products minus sum of the enthalpies of formation of the reactants:

$$\Delta I_r = \sum_{\text{products}} \Delta I^f - \sum_{\text{reactants}} \Delta I^f$$

Hess's Law Example

- Calculate the reaction enthalpy for calcination knowing that enthalpies of formation are as follows

Compound	Enthalpy of formation, kJ/mol
CaCO ₃	-1207
CaO	-635
CO ₂	-394

Solution: using Hess's law we have $\Delta I_r = \Delta I^f(\text{CO}_2) + \Delta I^f(\text{CaO}) - \Delta I^f(\text{CaCO}_3)$
 $= -635 + (-394) - (-1207) = +178 \text{ kJ/mol}$. \square

- Since $\Delta I_r > 0$, heat must be supplied to make the reaction go

HHV and LHV

- **Higher Heating Value (HHV)** of a fuel is defined as the negative of the reaction enthalpy (conducted at 25°C and 1 atm), when H₂O product is in the liquid form (condensed)
- **Lower Heating Value (LHV)** of a fuel is defined as the negative of the reaction enthalpy (conducted at 25°C and 1 atm), when H₂O product is in the gas form (not condensed water vapour)
- HHV is a few percent higher than LHV. For natural gas, the difference can be about 10% of HHV

HHV and LHV - Example

- Calculate the HHV and LHV for combustion of methane (CH_4)

Solution: HHV can be found from reaction $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$, where the enthalpies of formation for CH_4 , CO_2 and $\text{H}_2\text{O}(\text{l})$ are -74.8 kJ/mol, -393.5 kJ/mol and -285.8 kJ/mol, respectively. From Hess's law we get $\Delta I_r = 2\Delta I^f(\text{H}_2\text{O}(\text{l})) + \Delta I^f(\text{CO}_2) - \Delta I^f(\text{CH}_4) = 2(-285.8) + (-393.5) - (-74.8) = -890.3$ kJ/mol. Thus HHV ≈ 890 kJ/mol. LHV is found in a similar way, but the enthalpy of formation of water vapour (-241.8 kJ/mol) is taken instead of water liquid. Thus $\Delta I_r = 2\Delta I^f(\text{H}_2\text{O}(\text{g})) + \Delta I^f(\text{CO}_2) - \Delta I^f(\text{CH}_4) = 2(-241.8) + (-393.5) - (-74.8) = -802.3$ kJ/mol. The difference between the HHV and LHV is equal to latent heat of condensation of two moles of water at 25°C, which is exactly 88 kJ/mol. We note that the difference between the LHV and HHV is 10%. \square

Fossil Fuels - Coal

- In 2016⁸ global energy supply was ~~18.7~~^{14.3} Gtoe, of which:
 - Oil (31.9%)
 - coal (27.1%)
 - natural gas (22.1%)
- Coal still provides 38.4% of electricity
- Proven reserves of coal are about 890 billion tonnes, enough for ~~100~~¹³² years with current consumption
- Specific energy varies from ~10 MJ/kg (lignite) to ~35 MJ/kg (anthracite)

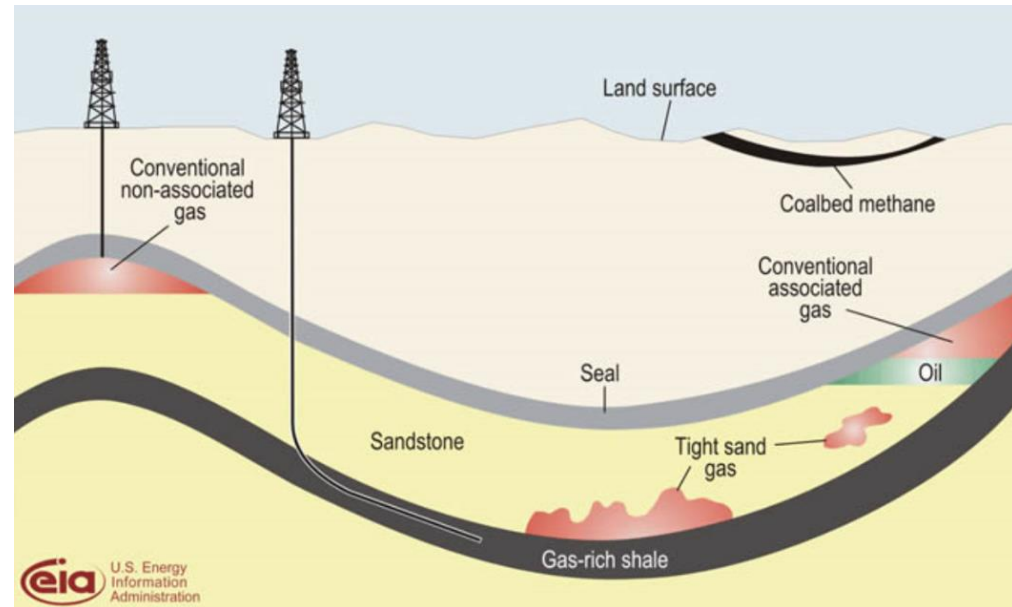
Petroleum

- The dominant role of oil results from its attractive features (high specific energy 42-44 MJ/kg, easy transport and storage)
- Crude oil contains a wide range of different hydrocarbons
- Crude oil is used to produce naphtha, gasoline, kerosene and heavier fuel oils (house heating, etc)
- To separate, distillation is used in refineries



Natural Gas

- Most natural gas resources contain methane
 - with smaller fractions of ethane, propane, butane
 - and traces of higher hydrocarbons, nitrogen, CO₂, water vapour, oxygen, hydrogen sulphide, and even helium



**Natural gas
used in
transportation**



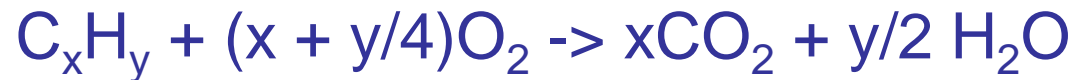
Combustion Reactions

- Combustion reactions are particularly important, since through them energy is retrieved from various chemical and biological fuels
- For example, the combustion reaction of methane is $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$ (*g*- gas, *l*- liquid)
- We can calculate the reaction enthalpy using Hess's law
- The negative of the reaction enthalpy, in which H_2O product is liquid, is defined as the **Higher Heating Value**

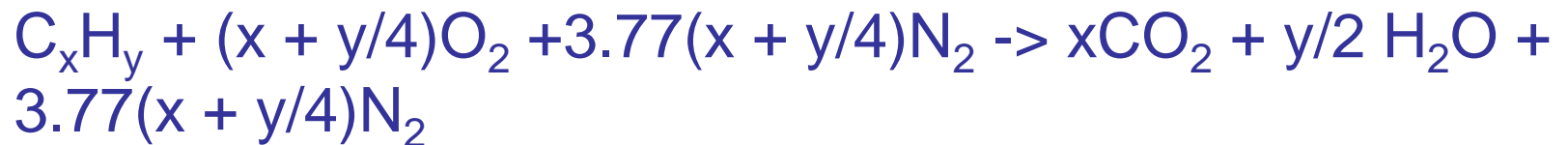


Combustion of Hydrocarbons

- Stoichiometric combustion of hydrocarbon in oxygen is as follows



- Practically all combustion uses air as oxygen source and the chemical formula becomes



- Here the nitrogen to oxygen volume ratio is 3.77
- Even though nitrogen doesn't participate in combustion, its inclusion shows the composition of the flue gas

Combustion of Gasoline

- We replace gasoline with iso-octane for simplicity
- The complete combustion of two moles of iso-octane with oxygen can be described as
$$2\text{C}_8\text{H}_{18} + 25\text{O}_2 \rightarrow 16\text{CO}_2 + 18 \text{H}_2\text{O}(l)$$
- Here we assume H_2O is liquid
- Using Hess's law we obtain the enthalpy of combustion for one mole:

$$\Delta I_c(\text{C}_8\text{H}_{18}) = 8\Delta I^f(\text{CO}_2(g)) + 9\Delta I^f(\text{H}_2\text{O}(l)) - \Delta I^f(\text{C}_8\text{H}_{18}). \quad (3.7)$$

Substituting the following enthalpies of formation: $\Delta I^f(\text{CO}_2(g)) = -394$ kJ/mol, $\Delta I^f(\text{H}_2\text{O}(l)) = -286$ kJ/mol and $\Delta I^f(\text{C}_8\text{H}_{18}) = -250$ kJ/mol, we obtain $\Delta I_c(\text{C}_8\text{H}_{18}) = -5.476$ MJ/mol. Since the molar mass of iso-octane is 114 g/mol, its specific energy density (positive by convention) is $E_c = 47.5$ MJ/kg.

CO₂ Emission from Gasoline Combustion

Question: what is the approximate CO₂ emission (in kg) resulting from combustion of 1 l (or 0.75 kg) of gasoline? (use iso-octane as a model)

Ans: (a) 0.6 kg
(b) 1.5 kg
(c) 2.3 kg

Combustion of Ethanol

- The complete combustion of ethanol with oxygen can be described as



- Here we assume H_2O is liquid. Using Hess's law we obtain the enthalpy of combustion for one mole:

$$\Delta I_c(\text{C}_2\text{H}_5\text{OH}) = 2\Delta I^f(\text{CO}_2(g)) + 3\Delta I^f(\text{H}_2\text{O}(l)) - \Delta I^f(\text{C}_2\text{H}_5\text{OH}). \quad (5.9)$$

Substituting the following enthalpies of formation: $\Delta I^f(\text{CO}_2(g)) = -394$ kJ/mol, $\Delta I^f(\text{H}_2\text{O}(l)) = -286$ kJ/mol and $\Delta I^f(\text{C}_2\text{H}_5\text{OH}) = -278$ kJ/mol, we obtain $\Delta I_c(\text{C}_2\text{H}_5\text{OH}) = -1.368$ MJ/mol. Since the molar mass of ethanol is 46 g/mol, its specific energy density (positive by convention) is $E_c = 29.7$ MJ/kg.

- As can be seen ethanol has lower energy density than iso-octane (and gasoline)

CO₂ Emission from Ethanol Combustion

Question: what is the approximate CO₂ emission (in kg) resulting from combustion of 1 l (or 0.789 kg) of ethanol?

Ans: (a) 0.4 kg
(b) 1.5 kg
(c) 2.1 kg

Combustion of Coal

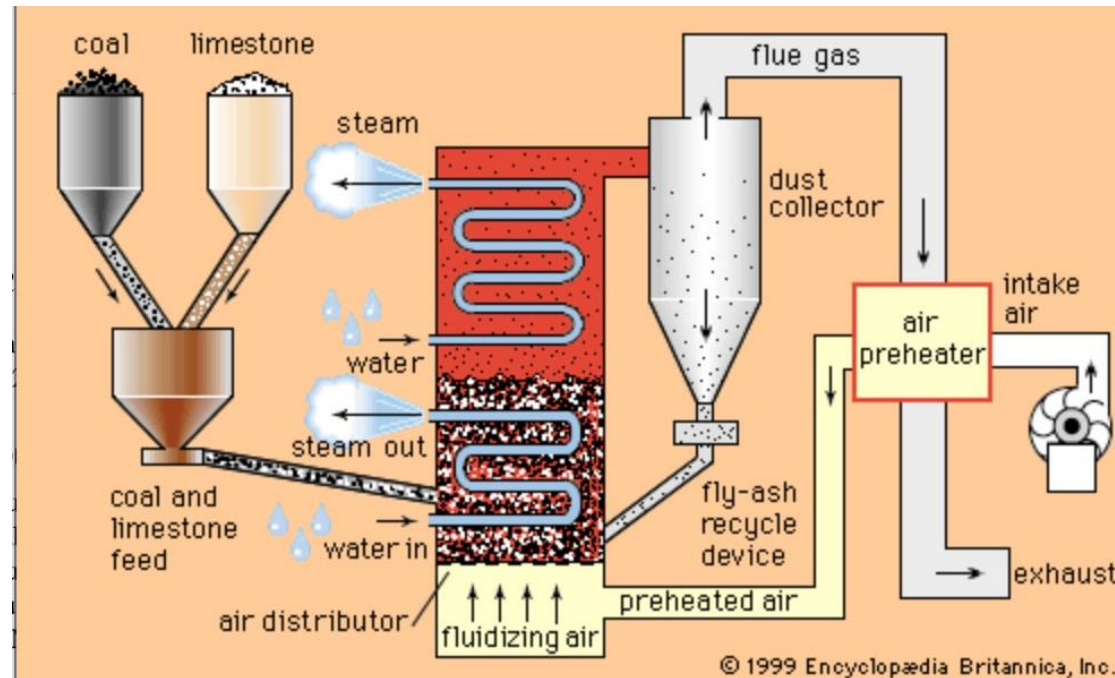
- Chemical reaction describing coal combustion can be simplified as:
 - $2\text{C-H} + 3/2\text{O}_2 \rightarrow \text{H}_2\text{O} + 2\text{CO}$
(for incomplete combustion)
 - $2\text{C-H} + 5/2\text{O}_2 \rightarrow \text{H}_2\text{O} + 2\text{CO}_2$ (for complete combustion)
- Here C-H is a simplified formula for coal
- The real coal combustion reaction includes carbon, sulphur, hydrogen, oxygen, nitrogen and moisture



**Flue gas from coal combustion
before desulfurization**

Fluidized Bed Combustion

- In Fluidized Bed Combustion (FBC) technology, strong jets of air are passing upward through coal
- Due to more efficient heat transfer, combustion occurs at lower temperature (800 – 900 C)
- This suppresses the formation of nitrogen oxides (NO_x)

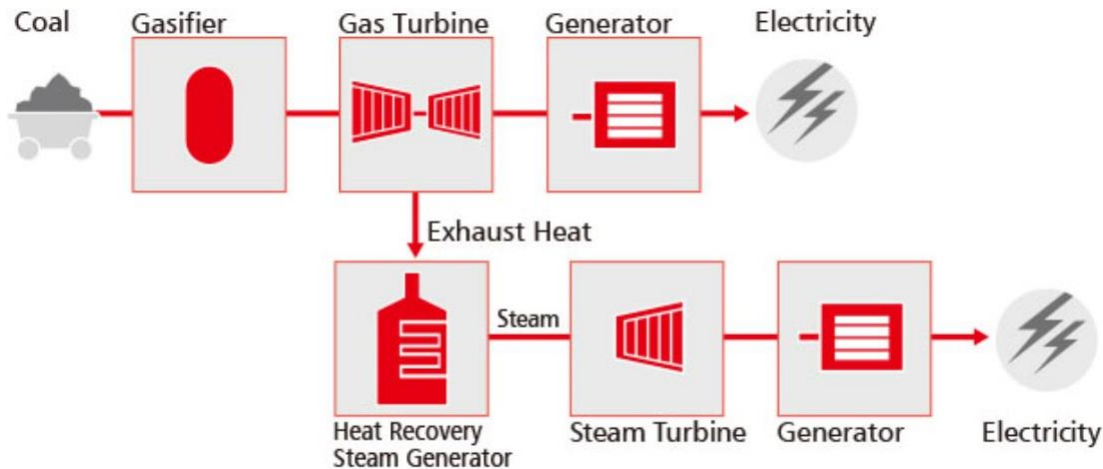


Integrated Gasification Combined Cycle

- In an Integrated Gasification Combined Cycle (IGCC) plant, a coal gasification system is integrated into a combined cycle plant
- Coal gasification starts with steam reforming:
$$\text{C} + \text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{CO} \text{ (endothermic reaction)}$$

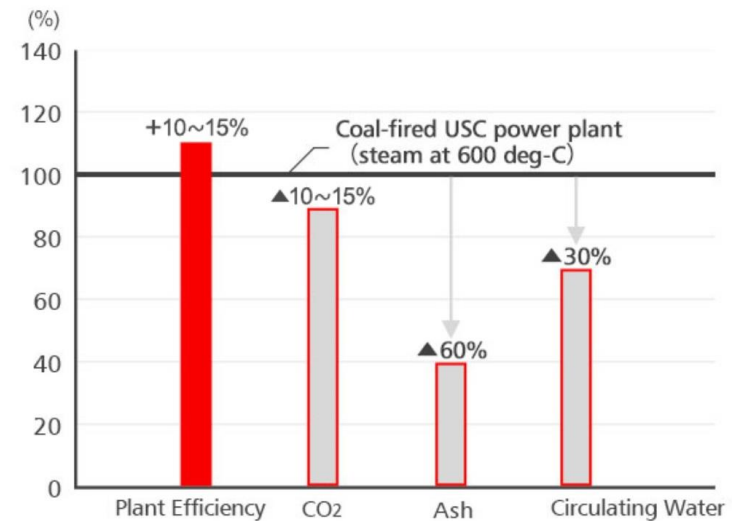
(coke + steam → hydrogen + carbon monoxide = water gas)
- The final resulting gas is a mixture of H_2 , CO and CO_2
- The process is expensive and complicated, but improves the cycle efficiency

IGCC



**Schematic diagram
of Integrated
Gasification
Combined Cycle
(IGCC) plant**

Benefits of IGCC



Summary

- Energy is stored in various bindings in matter (nucleons, electrons, atoms, molecules)
- Bioenergy results from transformation of the sunlight energy in photosynthesis into energy-containing organic matter
- Important metric for bioenergy is NEB (Net Energy Balance)
- Hess law is used to evaluate chemical energy
- Using bioenergy and chemical energy incurs emissions

