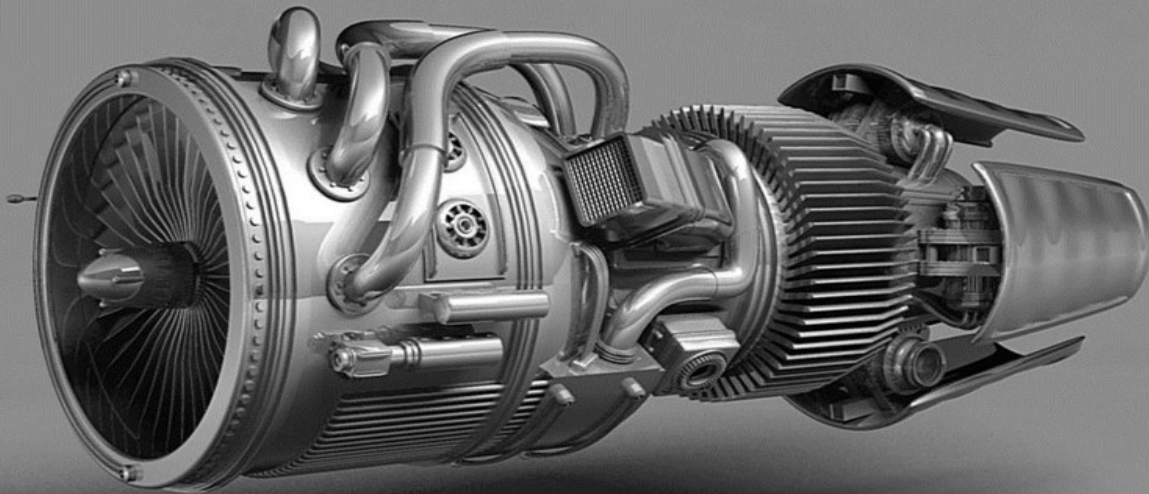


Thermodynamics



MSc – Thermal Power and Fluids Engineering
Dr Amir Keshmiri – The University of Manchester

TOPIC OF SPECIAL INTEREST*

Fuel Cells

Fuels like methane are commonly burned to provide thermal energy at high temperatures for use in heat engines. However, a comparison of the reversible works obtained in the last two examples reveals that the exergy of the reactants (818 MJ/kmol CH_4) decreases by 288 MJ/kmol as a result of the irreversible adiabatic combustion process alone. That is, the exergy of the hot combustion

*This section can be skipped without a loss in continuity.

gases at the end of the adiabatic combustion process is $818 - 288 = 530$ MJ/kmol CH_4 . In other words, the work potential of the hot combustion gases is about 65 percent of the work potential of the reactants. It seems that when methane is burned, 35 percent of the work potential is lost before we even start using the thermal energy (Fig. 15–34).

Thus, the second law of thermodynamics suggests that there should be a better way of converting the chemical energy to work. The better way is, of course, the less irreversible way, the best being the reversible case. In chemical reactions, the irreversibility is due to uncontrolled electron exchange between the reacting components. The electron exchange can be controlled by replacing the combustion chamber with electrolytic cells, like car batteries. (This is analogous to replacing unrestrained expansion of a gas in mechanical systems with restrained expansion.) In the electrolytic cells, the electrons are exchanged through conductor wires connected to a load, and the chemical energy is directly converted to electric energy. The energy conversion devices that work on this principle are called **fuel cells**. Fuel cells are not heat engines, and thus their efficiencies are not limited by the Carnot efficiency. They convert chemical energy to electric energy essentially in an isothermal manner.

A fuel cell functions like a battery, except that it produces its own electricity by combining a fuel with oxygen in a cell electrochemically without combustion, and discards the waste heat. A fuel cell consists of two electrodes separated by an electrolyte such as a solid oxide, phosphoric acid, or molten carbonate. The electric power generated by a single fuel cell is usually too small to be of any practical use. Therefore, fuel cells are usually stacked in practical applications. This modularity gives the fuel cells considerable flexibility in applications: The same design can be used to generate a small amount of power for a remote switching station or a large amount of power to supply electricity to an entire town. Therefore, fuel cells are termed the “microchip of the energy industry.”

The operation of a hydrogen–oxygen fuel cell is illustrated in Fig. 15–35. Hydrogen is ionized at the surface of the anode, and hydrogen ions flow through the electrolyte to the cathode. There is a potential difference between the anode and the cathode, and free electrons flow from the anode to the cathode through an external circuit (such as a motor or a generator). Hydrogen ions combine with oxygen and the free electrons at the surface of the cathode, forming water. Therefore, the fuel cell operates like an electrolysis system working in reverse. In steady operation, hydrogen and oxygen continuously enter the fuel cell as reactants, and water leaves as the product. Therefore, the exhaust of the fuel cell is drinkable-quality water.

The fuel cell was invented by William Groves in 1839, but it did not receive serious attention until the 1960s, when fuel cells were used to produce electricity and water for the Gemini and Apollo spacecraft. Today they are used for the same purpose in the space shuttle missions. Despite the irreversible effects such as internal resistance to electron flow, fuel cells have a great potential for much higher conversion efficiencies. At present, fuel cells are available commercially, but they are competitive only in some niche markets because of their high cost. Fuel cells produce high-quality electric power efficiently and quietly while generating low emissions using a variety of fuels such as hydrogen, natural gas, propane, and biogas. Recently many fuel cells have been installed to generate electricity. For example, a remote police station in Central Park in New York

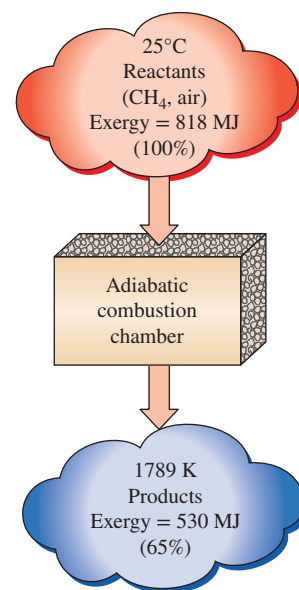


FIGURE 15–34

The availability of methane decreases by 35 percent as a result of the irreversible combustion process.

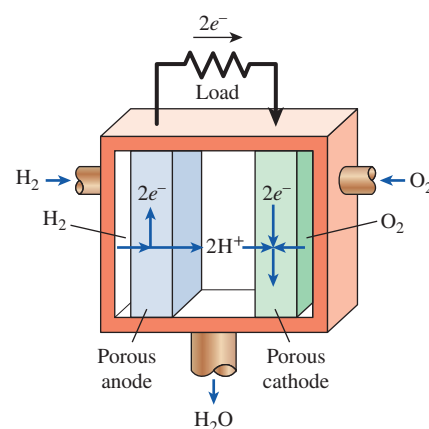


FIGURE 15–35

The operation of a hydrogen–oxygen fuel cell.

City is powered by a 200-kW phosphoric acid fuel cell that has an efficiency of 40 percent with negligible emissions (it emits 1 ppm NO_x and 5 ppm CO).

Hybrid power systems (HPS) that combine high-temperature fuel cells and gas turbines have the potential for very high efficiency in converting natural gas (or even coal) to electricity. Also, some car manufacturers are planning to introduce cars powered by fuel-cell engines, thus nearly doubling the efficiency from about 30 percent for the gasoline engines to up to 60 percent for fuel cells. Intense research and development programs by major car manufacturers are underway to make fuel-cell cars economical and commercially available in the near future.

SUMMARY

Any material that can be burned to release energy is called a *fuel*, and a chemical reaction during which a fuel is oxidized and a large quantity of energy is released is called *combustion*. The oxidizer most often used in combustion processes is air. The dry air can be approximated as 21 percent oxygen and 79 percent nitrogen by mole numbers. Therefore,

$$1 \text{ kmol O}_2 + 3.76 \text{ kmol N}_2 = 4.76 \text{ kmol air}$$

During a combustion process, the components that exist before the reaction are called *reactants* and the components that exist after the reaction are called *products*. Chemical equations are balanced on the basis of the *conservation of mass principle*, which states that the total mass of each element is conserved during a chemical reaction. The ratio of the mass of air to the mass of fuel during a combustion process is called the *air–fuel ratio* AF:

$$\text{AF} = \frac{m_{\text{air}}}{m_{\text{fuel}}}$$

where $m_{\text{air}} = (NM)_{\text{air}}$ and $m_{\text{fuel}} = \sum (N_i M_i)_{\text{fuel}}$.

A combustion process is *complete* if all the carbon in the fuel burns to CO₂, all the hydrogen burns to H₂O, and all the sulfur (if any) burns to SO₂. The minimum amount of air needed for the complete combustion of a fuel is called the *stoichiometric* or *theoretical air*. The theoretical air is also referred to as the chemically correct amount of air or 100 percent theoretical air. The ideal combustion process during which a fuel is burned completely with theoretical air is called the *stoichiometric* or *theoretical combustion* of that fuel. The air in excess of the stoichiometric amount is called the *excess air*. The amount of excess air is usually expressed in terms of the stoichiometric air as *percent excess air* or *percent theoretical air*.

During a chemical reaction, some chemical bonds are broken and others are formed. Therefore, a process that involves chemical reactions involves changes in chemical energies.

Because of the changed composition, it is necessary to have a *standard reference state* for all substances, which is chosen to be 25°C (77°F) and 1 atm.

The difference between the enthalpy of the products at a specified state and the enthalpy of the reactants at the same state for a complete reaction is called the enthalpy of reaction h_R . For combustion processes, the enthalpy of reaction is usually referred to as the enthalpy of combustion h_C , which represents the amount of heat released during a steady-flow combustion process when 1 kmol (or 1 kg) of fuel is burned completely at a specified temperature and pressure. The enthalpy of a substance at a specified state due to its chemical composition is called the *enthalpy of formation* \bar{h}_f . The enthalpy of formation of all stable elements is assigned a value of zero at the standard reference state of 25°C and 1 atm. The *heating value* of a fuel is defined as the amount of heat released when a fuel is burned completely in a steady-flow process and the products are returned to the state of the reactants. The heating value of a fuel is equal to the absolute value of the enthalpy of combustion of the fuel,

$$\text{Heating value} = |h_C| \quad (\text{kJ/kg fuel})$$

Taking heat transfer *to* the system and work done *by* the system to be positive quantities, the conservation of energy relation for chemically reacting steady-flow systems can be expressed per unit mole of fuel as

$$Q - W = \sum N_p (\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p - \sum N_r (\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r$$

where the superscript ° represents properties at the standard reference state of 25°C and 1 atm. For a closed system, it becomes

$$Q - W = \sum N_p (\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v})_p - \sum N_r (\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v})_r$$