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978-1-107-00286-9 - Analytic Combustion: With Thermodynamics, Chemical Kinetics, and Mass Transfer
Anil W. Date
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# 1 Introduction

## 1.1 Importance of Thermodynamics

Ever since humans learned to harness power from sources other than what their own muscles could provide, several important changes have occurred in the way in which societies are able to conduct civilized life. Modern agriculture and urban life are almost totally dependent on people's ability to control natural forces that are far greater than their muscles could exert. We can almost say that one of the main propellants of modern society is the increased availability of nonmuscle energy.

Pumping water to irrigate land and supply water to towns and cities; excavation of ores, oil, and coal, and their transport and processing; and transport of grains, foods, and building materials as well as passengers on land, water, and in the air are tasks that are exclusively amenable to nonmuscular energy. In fact, the extent of goods and services available to a society (measured in gross domestic product, GDP) are almost directly related to the per capita energy consumption. This is shown in Figure 1.1 for the years 1997 [36] and 2004 [120]. The figure also shows that over these seven years, the GDP of all countries increased, but the developed countries achieved reduced per capita energy consumption through technological improvements, compared with the developing countries.[1]

At the dawn of civilization (about the sixth millennium BCE), heavy tasks were performed by gangs of slaves and animals. Huge structures, such as the pyramids (about 2650 BCE), and in the reletively more recente times, Taj Mahal, (about 1650) were constructed in this manner. The power of the wind and the flowing water were probably harnessed only by about the sixth century CE through sails and windmills. Early windmills were used mainly for grinding grains and for sawing wood. No fuel was burned in use of these energy resources.

The most significant development in the use of nonmuscle energy came around 1712, when Newcomen in England developed the steam engine (see Figure 1.2), in which the piston and cylinder assembly performed the task of extracting power

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[1] Although the per capita energy consumption of India and China is low (owing to their large populations), the total energy consumption is about 45 percent of that of the United States, which is the largest consumer of absolute as well as per capita energy. In this sense, India, with about 16 percent of the world's population, consumes only 3 percent of the world's energy, whereas the United States, with 4.6 percent of the population, consumes almost 23 percent of the world's energy.

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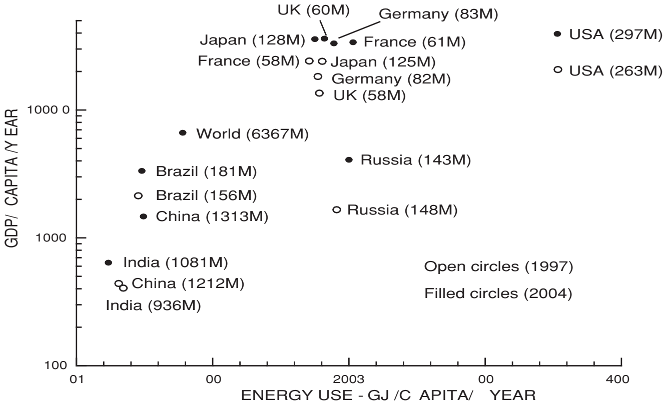

Figure 1.1. Dependence of GDP on per capita energy consumption. Figures in parentheses indicate population. GDP at constant 1987 dollars (1997 data) and 2004 dollars (2004 data).

and rejection of heat through condensation, and the boiler provided the pressurized steam. The energy required for generating steam was provided by burning coal (or any other fuel). The pressurized steam pushed the engine cylinder upward to execute the power stroke. The residual steam in the cylinder was then condensed by means of a water spray, thus enabling the return stroke. This engine developed approximately 15 HP.[2] The engine was used to drain water from mines by means of a reciprocating pump. The steam engine was a great advance because it brought a source of power of unprecedented magnitude dependent neither on muscle power nor on the vagaries of weather and geography.

Because of the simultaneous rise of modern science, improvements in energy conversion devices such as the Newcomen engine were brought about. Thus, in 1769, James Watt invented the idea of a separate condenser, increasing at least two- to threefold the availability of power from the same cylinder and piston assembly for the same amount of fuel consumption. Provision of a separate condenser always kept the engine cylinder hot, whereas in the Newcomen engine, the cylinder became cold after every charge of the cold water spray. The number of reciprocations (or the speed) of the engine could also now be increased.

Saving of fuel consumption brought the idea of *specific fuel consumption* (kg/s of fuel per kW of power, say, or kg/kJ) and *efficiency* (a dimensionless ratio of the rate of mechanical energy output to the rate of fuel energy input) of the energy conversion devices. This meant systematic measurement of the *energy value* (now called the *calorific value* or the *heat of combustion*) of the fuels (kJ/kg) and of the power developed. The horse power unit, for example, was invented by James Watt (1 HP $\equiv$ 0.746 kW).

Steam engines were used extensively in spinning and weaving machinery, in paper mills, and for pumping water from the mines. In 1807, Robert Fulton in the United States made a commercial steamboat that plied on the Hudson River and thus demonstrated the use of steam power for transport. Subsequently, steam was used for transport on land in the form of steam locomotives. This gave rise to a network of railways throughout the world.

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[2] For further details, see http://technology.niagarac.on.ca/people/mcsele/newcomen.htm.

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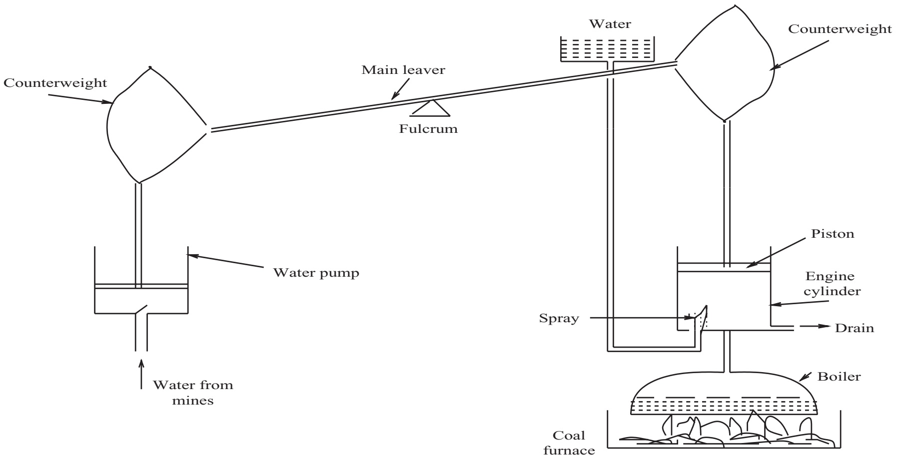

Figure 1.2. Schematic of Newcomen engine.

The steam engine, however, was an *external combustion* engine. By 1768, Street had proposed an *internal combustion* (IC) engine, in which vaporized turpentine was exploded in the presence of air.[3] Commercial use of the gas engine was delayed by almost a century. The gas ($H_2 + CO$) was derived from partial combustion of coal.

Then, in 1870, Otto invented the gasoline (or Petrol) engine. In both the gas and the gasoline engines, the fuel + air charge was ignited by either an electric spark or an external flame. Gasoline engines were soon followed by heavy-oil engines (invented by Diesel) in which the charge was ignited by a hot bulb or by contact, making use of the fact that air, when compressed to a high pressure (say, about fifteen times the atmospheric pressure), also increased its temperature. These developments occurred in Germany, France, and Britain.

The internal combustion engines were generally more compact and more efficient (Otto's engine had an efficiency of 15%) than the steam engines, and it appeared as though the steam engines would become obsolete. But, in 1884, Parsons[4] revived the use of steam by combining it with the principle of the windmill. Thus was born the idea of a *reaction steam turbine*. This machinery reduced the specific fuel consumption nearly by half and a large steam power plant became a reality. Such power plants find economic favor even today. The plant cycle is shown in Figure 1.3. The thermal efficiency of a plant is defined as

$$\eta_{th} = \frac{\text{net work (turbine} - \text{pump)}}{\text{heat input in the boiler}}. \tag{1.1}$$

Today's large power plants have efficiency as high as 40 percent. This means that a 500-MW plant will require 1250 MW of heat (or nearly 216 tons of coal per hour) and will release heat to the tune of 750 MW to the cooling water and, hence, to the environment. That is, allowing for a 7°C rise in cooling water temperature, nearly 25.6 tons of cooling water per second are required. The environmental consequences will be considered shortly.

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[3] For the early history of gas engines, see http://www.eng.cam.ac.uk/DesignOffice/projects/cecil/engine.html and http://encyclopedia.jrank.org/GaG-GEO/GAS-ENGINE.html.

[4] For a brief history of steam turbines, see http://www.history.rochester.edu/steam/parsons/ and http://www.g.eng.cam.ac.uk/125/1875-1900/parsons.html.

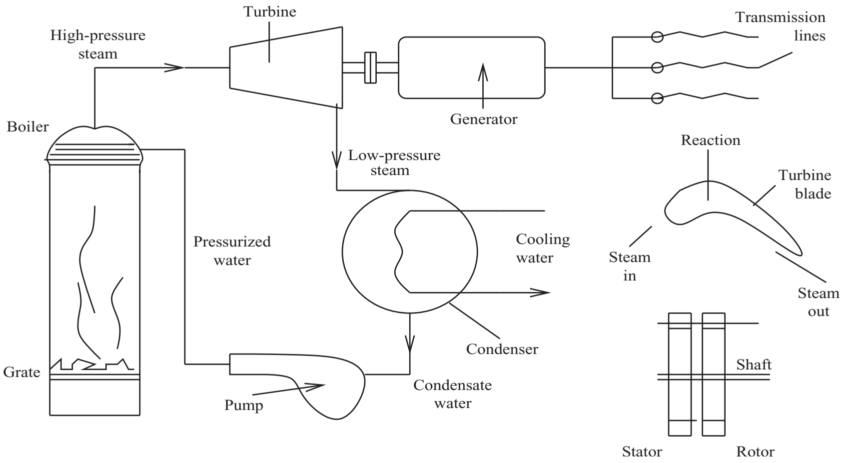

Figure 1.3. Schematic of a modern steam power plant cycle.

In 1910, the *gas turbine* (GT) became a reality. The GT was developed primarily for aircraft propulsion because it offered an alternative to the earlier IC engines in terms of a high power-to-weight ratio. Figure 1.4 shows a GT plant in which propulsive power output is effected either through a shaft coupling air-compressor and turbine, or directly through the propulsive force of a jet.

In many modern power stations, the gas and the steam turbine plants are coupled. This is possible because the exhaust from the gas turbine is typically available at 350 to 450°C. This temperature is in the range of temperatures of superheated steam employed in the steam power plant. As such, the main fuel is burned in the combustion chamber of a GT plant. The hot exhaust from the GT is used to produce steam (instead of burning fuel in a boiler), which is then expanded in a steam turbine. This combined plant typically records efficiencies on the order of 50 percent.

Fossil fuels, however, are not inexhaustible; thus the discovery of nuclear energy around 1915 was welcomed. The raw materials for nuclear energy are principally

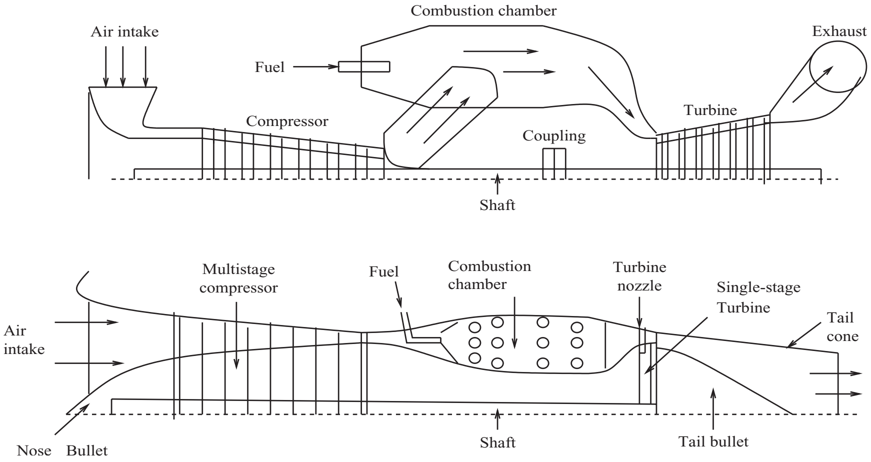

Figure 1.4. Gas turbine plant: (a) industrial GT engine (top figure); (b) GT jet engine (bottom figure).

uranium ($U_{235}$) and thorium ($Th_{232}$). Easily extractable uranium[5] is available in few countries, such as the United States, Canada, Australia, South Africa, and Nigeria, whereas thorium is more widely available, but its extraction is much more difficult. Uranium is used in power plants that work on the principle of nuclear *fission*, in which heat generated (as a result of the fission reaction) is carried away by means of an inert gas ($CO_2$) or by light ($H_2O$) or heavy ($D_2O$) water. These carriers then pass on the heat to water in a steam generator, and the steam power plant cycle is executed. The next possibility is that of nuclear *fusion*, as opposed to fission. Here, the hydrogen atom is split, leading to a release of a large amount of energy. Because $H_2$ is plentiful (from water), there should be no shortage of raw material, in principle. However, it has not been conclusively demonstrated that the energy consumed in extracting hydrogen from water and preparing it for the fusion is less than that which can be released from its reaction with oxygen. The splitting reaction also requires very high temperatures (more than 100 million Kelvin) for sustenance [57]. Extensive use of nuclear energy is also beset with serious environmental concerns.

In view of the difficulties associated with the extensive use of nuclear energy through fission or fusion (there are also intermediate routes, such as the fast breeder reactors), there has emerged an opinion in favor of what are called *renewable* sources of energy, such as wind, solar thermal, solar–electric (or photovoltaic), and biomass. All these are manifestations of the principle source of energy, the sun. The availability of these sources, however, is uncertain (that is, they are seasonal and/or intermittent) and the energy is not highly concentrated in them as in fossil fuels. This means that the plants using these sources must be very large, incurring heavy initial (capital) costs, although the running costs may be low. Also, the energy conversion devices working on fossil fuels are not directly suitable for adaptations to these renewable sources. Modifications are needed in several aspects – for example, working fluids, engine cycles, and manufacturing techniques. Intelligent modifications can be devised only on the basis of the science of *thermodynamics*.

At this stage, therefore, we may define thermodynamics as *the science of energy and its conversion*. Many of the developments of the earlier devices were largely intuitive, lacking formalism. This, however, need not be the case anymore.

## 1.2 Laws of Thermodynamics

At the beginning of the nineteenth century, questions about specific fuel consumption were being thought of in terms of *work* (which the engineer wanted to get out of an engine or a plant) and *heat*, which, via the burning of a fuel, the engineer had to employ to produce work. What are the laws governing conversion of heat into work? Watt showed that by providing a separate condenser in the Newcomen engine, the specific fuel consumption could be reduced. Could the specific fuel consumption be reduced indefinitely – and if not, why not? In providing answers to such questions, the science of thermodynamics was born.

A practical answer to these questions was provided by Sadi Carnot in 1824. Through abstract reasoning, he perceived that the *temperature* provided the key. Difference in temperature was likened to two different levels of water, and the heat

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[5] Usable uranium from its raw ore is only 0.25% to 2% and therefore very expensive.

was likened to the flow of water resulting from the difference in levels. Just as the flow of water provided work in a water wheel, so did the heat engine provide work because of the flow of heat. This thought formed the basis of the second law of thermodynamics.

In one respect, Carnot was wrong, for whereas the same amount of water flows away from the water wheel, less heat is rejected by an engine or a power plant (see the estimates provided in the previous section) than supplied to it. Carnot can hardly be blamed for not noticing the essential difference between the water-substance and the heat, because in the engines of his day, the heat lost between supply and release amounted to less than 5 percent.

In 1850, Joule provided the answer to the lost heat – it had turned into work. The flow of heat thus could not be likened to the flow of water. Joule, of course, performed a reverse process, in which work was shown to have been completely converted to heat. This discovery formed the basis of the first law of thermodynamics. The explanation of the lost heat was thus only by inference that whereas work can be completely converted to heat, the reverse can also be exercised – but only at a premium.

The inference of the lost heat, though not completely clear at this stage, becomes clear when Carnot's and Joule's findings are combined – that is, when the first and second laws are combined. This recognition was made by Lord Thompson in Scotland and independently by Clausius in Germany. This forms a body of knowledge that is known today as *Classical*, *Macroscopic*, or *Equilibrium thermodynamics*. These terms essentially imply that one is dealing only with the bulk nature of matter as gas, liquid, or solid. Molecular and atomic structures are ignored.

In addition, the main concerns are associated with the *before* and *after* of a process undergone by an identified bulk substance. The process may be heating, cooling, expansion, compression, phase-change, or a chemical reaction. The identified substance in thermodynamics is called the *System*. The terms "before" and "after" of a process are identified with the change in the state of the system.

The state of a system in thermodynamics is represented in terms of properties of the system. The basic properties are pressure, temperature, volume, and composition. The system is also characterized by several other properties, such as energy, entropy, availability, and enthalpy, which are derived from the basic properties. The formal definition of thermodynamics can thus be given as:

> *Thermodynamics is the science of relationships among heat, work, and the properties of the system.*

Because thermodynamics is concerned with the change in the states of a system, the in-between events are left out. Thus, in a chemical reaction, for example, the initial reactants and the final products represent the change in the state of the material substance (in this case, a mixture of several components or chemical species). In practical equipment, however, the product state is dependent on the rate of change. Thermodynamics does not deal with the rate of a process. The sciences that describe the rate of a process are largely empirical. Heat Transfer, Mass Transfer, Fluid Mechanics, and Chemical Kinetics are such empirical sciences that become necessary to design practical equipment. In fact, these rates can be explained by taking a microscopic view of matter, in which interactions between molecules and atoms are

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Table 1.1. *Primary energy consumption (including electricity) in Million Tons of Oil Equivalent (MTOE), 2001*

| Country | Oil | Nat. Gas | Coal | Nuclear | Hydro | Total |
|---|---|---|---|---|---|---|
| USA | 896 | 578 | 546 | 183 | 48 | 2251 |
| Japan | 248 | 71 | 103 | 73 | 20 | 515 |
| France | 96 | 38 | 12 | 96 | 18 | 258 |
| Germany | 132 | 75 | 85 | 39 | 6 | 336 |
| UK | 77 | 87 | 40 | 20 | 2 | 226 |
| China | 232 | 25 | 519 | 4 | 54 | 834 |
| India | 97 | 25 | 173 | 4 | 16 | 314 |
| World | 3517 | 2220 | 2243 | 601 | 585 | 9156 |

studied. Then, these interactions are essentially statistical, and the ideas developed in kinetic theory and quantum theory must be invoked. This body of knowledge is called *Statistical Thermodynamics*. The laws of Classical thermodynamics deal only with bulk matter.

## 1.3 Importance of Combustion

Throughout the world, since the early 1970s, much concern has been expressed about the impending *energy crisis*. By this term, it is meant that the fuels used to generate most of the energy used by humans are running out. Simultaneously, there has also been another concern – namely, the *environmental crisis*. Geographically, economically, and politically speaking, both these crises have global as well as local dimensions [91].

Table 1.1 provides estimates of primary energy use in different countries. Primary energy signifies coal, oil, natural gas, hydropower, and nuclear sources, and electricity is taken as secondary energy (converted to Tons of Oil Equivalent [TOE] based on 38% oil-to-electricity conversion) [107]. These estimates include all sectors of the economy, such as domestic, industrial, agriculture, transport, and infrastructure/construction sectors. The table shows that in 2001, for the world as a whole, 38.4 percent of the energy came from oil, about 24 percent each from natural gas and coal, about 6.6 percent from nuclear energy, and 6.4 percent from hydropower sources. For individual countries, however, there is considerable variation. For example, in France, nearly 37 percent of energy comes from nuclear power, whereas for most other countries nuclear energy provides less than 10 percent, and in India and China, less than 2 percent. In fact, India and China, with limited nuclear, hydro, and natural gas energy, rely almost exclusively on oil and coal.

These estimates preclude biomass and other non-conventional or renewable energy sources, largely because their use is extremely small in most countries. However, in countries such as India and China, for example, biomass contributes additional 16 percent to 20 percent to energy consumption. Finally, although the share of India and China in total world consumption was 3.4 percent and 9.1 percent, respectively, in 2001, it is estimated that by 2030, this share will rise to 8 percent and 16 percent, respectively.

Table 1.2. *Carbon emissions, 1996 (GDP in constant 1987 U.S. dollars)*

| Country | Total emissions Mt of C/yr | Emission per capita kg of C/capita/yr | Emission/GDP kg of C/GDP |
|---|---|---|---|
| USA | 1407 | 5270 | 0.26 |
| Russia | 496 | 3340 | 2.01 |
| Japan | 307 | 2460 | 0.1 |
| Germany | 228 | 2790 | 0.15 |
| France | 93 | 1600 | 0.09 |
| UK | 148 | 2530 | 0.19 |
| China | 871 | 730 | 1.62 |
| India | 248 | 270 | 0.65 |
| Brazil | 68 | 430 | 0.2 |
| Indonesia | 81 | 410 | 0.62 |
| World | 6250 | 1090 | NA |

Finally, it is important to recognize that with rising populations, world energy consumption is expected to rise by nearly 35 percent to 40 percent over the next thirty years. A large contribution to this increase is likely to come from the expanding economies of India and China.

Accompanying the current and expected increase in energy use is the concern for environment expressed in terms of two effects: (1) air–water–land pollution and (2) global warming. The first effect can be countered through local pollution abatement measures, but the second effect has global dimensions and is not easily tractable. Global warming (including unavoidable climate change) is caused by accumulation[6] of the so-called greenhouse gases (GHG$_s$), $CO_2$, $CH_4$, $N_2O$, and chlorinated fluorocarbons (CFCs) and aerosols in the atmosphere.[7] The GHGs, while allowing the solar radiation to warm the earth's surface, essentially trap the reflected outgoing solar radiation from the earth in the lower atmosphere (less than about 6 to 7 km above the earth), thus raising the earth's temperature still further. It is estimated that $CO_2$ concentrations have increased from about 280 ppm at the start of the industrial era to about 330 ppm today [36]. According to mathematical global warming models, this change implies an 0.5°C to 1.0°C rise in the earth's temperature. The actual measured temperature values from 1855 to 1999 have confirmed this temperature rise. Such model predictions have been used to assess the likely earth temperature up to the year 2100. The most optimistic scenarios predict further temperature rise of about 1.5°C, whereas the most pessimistic scenarios predict about 3.5°C to 5.0°C in temperature rise.

In climate-change literature, $CO_2$ is considered to be the major carrier of carbon into the atmosphere. The overall effect of GHGs is estimated in terms of carbon emissions. Table 1.2 provides estimates of emissions in different countries. The table shows that the United States and other industrialized countries have high per capita carbon emissions. France has relatively lower emissions, however, because of its heavy reliance on nuclear energy. Again, following expected high economic growth,

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[6] $CO_2$ emitted today has a residence time in the atmosphere of about a century.

[7] Burning 1 kg of coal releases 3.4 kg of $CO_2$. Thus, a 500-MW power plant will release $216 \times 3.4 \simeq 735$ tons of $CO_2$ per hour.

carbon emissions from India and China are expected to rise. Also, high values of emissions per GDP in Russia, China, India, and Indonesia suggest that fossil fuels are not burned efficiently in these countries. Again, carbon emissions from biomass burning are taken to be zero because growth of biomass by photosynthesis is a natural, solar-energy–driven $CO_2$ sink.

It is important to correlate $CO_2$ emissions in terms of intensity of energy use indicators. This has been done by Kaya [107]. The correlation reads

$$\mathrm{CO_2}\ \frac{\mathrm{kg}}{\mathrm{year}} = \mathrm{population} \times \frac{\mathrm{GDP}}{\mathrm{population}} \times \frac{\mathrm{energy}}{\mathrm{GDP}} \times \frac{\mathrm{CO_2}}{\mathrm{energy}} - \mathrm{sequestration}. \tag{1.2}$$

In this correlation, (GDP/population) represents the standard of living, (energy/GDP) represents energy intensity of the economy, ($CO_2$/energy) represents carbon intensity of the primary energy, and sequestration (when applied) represents the amount of $CO_2$ prevented from entering the atmosphere by capture and sequestration. This implies $CO_2$ capture at the site of its generation (say, a power plant) by a chemical process or, simply, by absorbing $CO_2$ in deep oil/gas reservoirs, oceans, or aquifers. Using information from Tables 1.1 and 1.2, it is possible to estimate the emission rate (see exercise). The correlation in Equation 1.2 suggests that to reduce carbon emissions, population, energy intensity, and standard of living may have to be reduced unless sequestration becomes economically attractive. Unfortunately, estimates at present predict an increase between 20 percent and 45 percent in the cost of net energy production if sequestration is applied.

Fossil fuels are finite. Therefore, it is of interest to estimate current reserves of the main primary energy sources. Table 1.3 shows proven estimates of primary energy reserves available in 2004 and the expected time of exhaustion if the resource was used at the current level of consumption.[8] The lifetime (or the time of exhaustion) of a reserve is estimated from

$$\mathrm{Lifetime\ (yrs)} = R^{-1}\left[\ln\left\{R \times \left(\frac{Q_T}{C_0}\right) + 1\right\}\right], \tag{1.3}$$

where $R$ is the percentage rate of growth of consumption per year, $Q_T$ is the total reserve (J, tons, $m^3$, barrels), and $C_0$ is the present rate of consumption per year (J, tons, $m^3$, barrels/yr).

At a time when the fossil fuels are running out, it is important that the maximum energy extractable from a fuel in a given device is indeed extracted. In other words, engineers seek to obtain nearly 100 percent combustion efficiency. In practical devices, however, it is not just sufficient to burn fuels with high efficiency but it is also necessary to ensure that the products of combustion have a particular temperature and chemical composition. Temperature control is necessary to achieve downstream process control, as in many metallurgical, chemical, and pharmaceutical

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[8] There is considerable difficulty in estimating energy reserves. *Proven reserves* implies economic viability of extraction and processing. This does not include known possibilities of availability of a resource. For example, it is known that uranium is available from the sea bed and deeper earth's crust, but its economic viability is not known.

Table 1.3. *World reserves of primary energy (2004).*

| Source | Estimated reserves | Time to exhaustion |
|---|---|---|
| Oil* | 1000–1227<br>billion barrels | 100<br>years |
| Natural gas | 120–180<br>trillion $m^3$ | 250<br>years |
| Coal | 1000–1100<br>billion tons | 250<br>years |
| Uranium | 1.3–11.0<br>million tons | 20–170<br>years |

* 1 barrel of oil = 136 kg of oil.

industries. Composition control is also necessary for meeting the strict environmental pollution norms. According to the U.S. 2000 National Ambient Air Quality Standards (NAAQS) [36], the permissible levels of pollutants are CO (9–35 ppm), $NO_2$ (0.053 ppm), $O_3$ (0.12 ppm), $SO_2$ (0.03–0.14 ppm), and particulate matter (PM) (50–150 $\mu g/m^3$). Excessive amounts of CO can have neurological effects, can cause visual acuity problems, headache, dizziness, or nausea, and can lead to acid rain afflicting flora and fauna. $NO_2$ and $SO_2$ can cause pulmonary congestion or nasal and eye irritation or coughs and can result in weathering and corrosion from the formation of nitric and sulfuric acids. Excessive PM can lead to asthma and throat and lung cancers, and can have other brain and neurological effects. PM can also cause visibility impairment owing to light scattering of small particles. Ozone ($O_3$) is a photo-oxidant, having a strong oxidizing capacity in the presence of sunlight. It can cause vegetation damage and can affect crop yields. All these pollutants are released from fossil fuel combustion and, therefore, their concentrations in products of combustion must be restricted.

Combustion is also important in fire prevention. Forest fires and fires in oil wells and mines are some examples. Such fires not only destroy valuable energy source, but also contribute to carbon emissions. Combustible material (wood, paints, other synthetic materials) used in buildings can catch fire from electric sparks or any other cause. Plastics and other organic materials are used extensively in modern society. Even clothing made from cotton or synthetic yarns can catch fire. Prevention and extinction of fires is an important task performed by engineers.[9]

## EXERCISES

**1.** Calculate the values of specific fuel consumption (kg/kJ ) and efficiency in each of the following:

   (a) A man working on a hand loom can produce 6.5 N-m of work per second for 8 hours in a day. His daily food intake is 1.5 kg (energy value of food = 3700 kcal/kg).

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[9] It is estimated that there are more than 220,000 forest fires per year in different parts of the world, destroying more than 6.5 million *hectares* of forest. In China, for example, anywhere between 20 and 100 million tons of coal are lost because of coal fires at the mines (Anupama Prakash, http://www.gi.alaska.edu/prakash/coalfires/introduction.html).