Chapter 3

Fossil Fuels and Thermal Engines

3.1 Fossil Fuel Resources

There are three major types of fossil fuels:

- Those derived from naturally occurring petroleum forms, which include liquid oil, tar sands, and oil shales – by refining them, one obtains gasoline, diesel fuel, and aviation fuel (kerosene). Petroleum. Here, we will use the term crude oil for all the mined forms, and a general term of oil-products for all of the refined forms.

- Natural gas, which is essentially methane CH\textsubscript{4} with small admixtures of other gasses.

- Coal – all its types.

A unit measure used for oil and its liquid derivatives is a barrel (37.5 US gallons, or 119.24 liters). Because oil is now the “king” of fossil fuels, it has become a custom to express the amount of the other two fuels in units called Barrel of Oil Equivalent BOE. A BOE of coal is the amount of coal that releases, when burned, the same amount of energy as burning a barrel of oil (6.1 GJ)– it’s 200 kg, or 0.2 tonne of coal. For natural gas at normal pressure, one BOE is 5,800 cubic feet, or 164.23 cubic meters (the US Geological Service uses 6,000 cubic feet, or 170 cubic meters).
Comprehensive data concerning the resources and the consumption of fossil fuels can be found in several different Web documents – we recommend the Fossil Fuels site, a section of a larger Web document maintained by the Our World in Data, a project produced by the Oxford Martin Programme on Global Development at the University of Oxford, U.K., and is made available in its entirety as a public good.

**Resources:**
The global resources of recoverable oil (including liquid oil, tar sands, and shale oil) are estimated to be as high as about 1,700 billion barrels. The three countries possessing the largest oil deposits are Venezuela, Saudi Arabia, and Canada (with 300, 266.6, and 172.2 billion barrels, respectively). The US resources are estimated to be about 55 billion barrels.

The estimated global resources of natural gas are 187 trillion cubic meters, equivalent to 1,139 billion BOE.

The estimated coal resources, including all forms, from the high-quality (anthracite) to the lowest-quality lignite (also known as “brown coal”) are 1.1 trillion tonnes, or 5,500 billion BOE.

**Consumption:**
The data concerning various aspects of fossil fuels are often given in different units (which may be a nightmare for the reader, and even for an author of a text like this one). It’s easier to find annual production than annual consumption data – not a big problem, because most of the oil mined is promptly refined and consumed, so that one can safely assume that the production and consumption data are equal. But to make things worse, the production data in the Internet source quoted above are given in TWh, while we would prefer BOE data. Fortunately, on the Web, using Google or another search engine, one can find right away programs converting one kind of units to another kind. So, one such program informs us that:

\[ 1\text{TWh} = 588,235\text{BOE} \]

Fine! So, let’s begin with oil. In the Fossil Fuels site we read from a chart that in 2016 the annual production of crude was 51,000 TWh – and by
multiplying this number by the above conversion factor, we obtain almost exactly 30 billion barrels. Now, we take the global resources, 1,700 barrels – and we get that if oil is mined from now on at the same level as in 2016, the resources will be all gone about 57 years from now.

For the author of this text, who was born the at the same year as the WW II ended, for obvious reasons it’s not a threatening perspective – but if you, Dear Reader, are an undergraduate student, it may be a piece of bad news!

Let’s then look at natural gas. Again, the storage of natural gas is difficult (it may be stored in in a liquefied form, which is the called LNG, but it’s being done mostly for transporting the gas, not for storing it for a long period (a much better method of long-time storage is to keep the gas underground!). So, here we can again assume that the annual consumption and the annual production are equal. In the Fossil Fuels site we find that the annual production is 37,366 TWH, which converts to 21.98 billion BOE. By dividing the known reserves, 1,139 billion BOE, by the latter number, we obtain a period of about 51.8 years. Again, not very good news!

The last one on our list is coal. Since there is a serious danger that all oil and gas resources will be gone before the end of this century, perhaps coal is the “last resource” for future generations? Well, there are no reasons for too much optimism. In 2016, the production of all coal types was about 42,500 TWh, equivalent of 25.0 billion of BOE. Considering that the global resources are 5,500 billion BOE, we get 220 years. Do we? Not really! Because when all oil and natural gas resources are exhausted, coal must substitute for the two other missing fuels! It must be used in much higher annual rate, if we still want to generate as much power from fossil fuels as we did when oil and gas were still available!

Making estimates of how long the coal resources will last if coal indeed will be used to “fill the gap” left by exhausted oil and gas deposits is difficult – let’s not try to do that here, but let’s rather check what professionals claim. The problem is discussed, for instance, in this Web document. From the graph presented in this site, one can see that the authors of the document don’t even expect the coal resources to last beyond the end of this century!

There is always some room for optimism, because new deposits of fossil fuels are still being discovered. For instance, the recoverable oil reserves in the United States in 2005 were estimated as 29.9 billion barrels, and ten
years later, in 2015, as 50 billion barrels. Such a big change was due to two factors: new oil fields in North Dakota, and the invention of a new “fracking” technology that allows to pump more oil from deposits that were considered fully emptied. Similarly, the estimates of natural gas resources, which were 1200 trillion cubic feet in 2002, increased to over 2,400 trillion cubic feet in 2013. Again, it was due to discovering new gas fields and to developing new technologies of horizontal drilling and fracking.

On the other hand, people who are even strong enthusiasts of using fossil fuels should keep in mind that there are not mined with the sole purpose of burning them in power plants, smelters, heating furnaces, or gasoline, diesel, and jet engines. Oil and natural gas (and coal, to a lesser degree) are the basic raw material for many branches of chemical industry, making products of crucial importance for our lives: plastics, fertilizes, drugs, and dozens of others. If we keep burning fossil fuels as long as they are available, our lives may become miserable... And another important reason to start showing restraint in burning fossil fuels is that we are adding more and more CO$_2$ to the atmosphere. The concentration of CO$_2$ in the atmosphere is rapidly growing.

![Scripps Institution of Oceanography NOAA Earth System Research Laboratory](image)

Figure 3.1: Atmospheric CO$_2$ concentration at Mauna Loa Observatory.

The CO$_2$ concentration in atmospheric air is monitored at many observation posts around the globe – the best known of which is the one located at Hawai‘i, at the Mauna Loa volcano at the altitude of 4169 meters above the
sea level. Hawaii archipelago is located in the middle of the Pacific Ocean, far away from any big industrial center that might be able to create a local increase above the average concentration. On the graph in Fig. 3.1, one can see a steep curve with characteristic saw-teeth-like oscillations. This is the so-called *Keeiling Curve*, in which the saw-teeth-like features represent the *seasonal variations* of the carbon dioxide concentration. Why does it change with seasons? The answer is simple: in May, the concentration starts decreasing, which reflects the fact that the vegetation, grasses and trees, start growing new leaves, and they are rapidly absorbing CO$_2$ from the air. The process lasts for several months, producing a “dip” on the curve, until the leaves fall and start rotting – now, in turn, releasing CO$_2$ into the air.

Well, one may have some doubts concerning such an explanation. The spring starts in May, yes, but only at the northern hemisphere – and at the southern, it starts in 6 months later in the same calendar year, in November. So, the southern hemisphere vegetation should give rise to a similar “dip” phase-shifted by 6 month relative to that caused by the northern-hemisphere vegetation. Hence, the two effects should cancel each other!

Yes, it would be so, but the thing is that most landmass, and most vegetation on Earth is on the northern hemisphere. Especially, the boreal forests of northern Russia (the “taiga”) and of northern Canada are much stronger CO$_2$ absorbers/emitters than anything that can be found in the southern hemisphere. For instance, the famous enormous rainforest in the basin of Amazon River is all *evergreen*, so that it does not contribute to the seasonal variation of CO$_2$. Therefore, the southern hemisphere vegetation plays only a minor role in the process.

However, if there were only seasonal variations, the Keeling Curve, when averaged, should be flat – but in fact, it’s rapidly growing. When the Author of this text for the first time learned about the CO$_2$ concentration in the atmosphere, it was 0.03% = 300 ppm, and now, 60 years later, it has already exceeded 400 ppm.

**So what?** – some people angrily ask. Where is the problem? Here we have come to one of the major controversies of our times. There is no doubt that the increasing concentration of CO$_2$ is *anthropogenic*, i.e., caused by the activity of us, humans. And in the scientific community, the majority of its members agree that the increasing concentration of CO$_2$ is responsible for global warming. In 2015, a United Nations Framework Convention on Climate Change was held in Paris. There was a consensus among the 195 participating nations (summarized in the document worked out by the
conference, the so-called Paris Agreement) that keeping the CO₂ emission at the current (or higher) rate will lead in the near future to a global temperature increase of 2°C over the pre-industrial level, i.e., the average global temperature at 1880. The participants declared to voluntarily mitigate the emission of CO₂ by their countries. It is not known exactly by how much the emission should be cut down to meet the goal – there is no well-established theory of how the CO₂ concentration in the atmosphere is correlated with the global temperature. The data on which the Paris Agreement recommendations has been based are published in a 2013 Intergovernmental Panel on Climate Change. The Paris Agreement recommendations are often termed the carbon budget. In short, it says that if we want to achieve a 50% probability of limiting warming to 2°C, we have to leave the majority (up to 80 percent) of our fossil fuels in the ground (for more details, see the Unburnable Carbon Section in the Fossil Fuels Web page. OK, if 80% of fossil fuels should stay in the ground – then, if they are mined at the current rate, they will “run out” much faster than we predicted above – or, the pace of mining them from the underground must be drastically reduced.

On the other hand, there are many groups of people (including some scientists) who argue that man-made global warming is a “hoax”. They use different arguments, or no arguments – there make no sense to quote them here, because this would be off-topic. The main point in this Section is: “How long will the fuel resources last?” – so the answer to this question depends not on who is right (those who believe in man-made global warming, or global warming skeptics?), but which one of those two groups will win the dispute. And the skeptics have many supporters – beginning from very-high placed politicians, to big business leaders whose profits are correlated with the rate of fuel extraction, and – last but not least – to people who live from mining fuels, i.e., simple coal miners or operators of gas or oil wells. The combined influence of such people on public opinion may be quite strong, and may decide, for instance, on who wins the elections.

So, it’s not possible to predict which group will take over. If the global warming skeptics, then mining of fossil fuels may last longer. Recently, the Trump Administration declared it would withdraw the United States from the Paris Agreement (it cannot happen immediately – the earliest possible effective withdrawal date by the United States cannot be before November 4, 2020, four years after the Agreement came into effect in the United States). It’s always possible that other countries may do the same. Regretfully, the only thing that one can do now is “to wait and see”.
3.2 How much energy there is in fossil fuels? How much CO$_2$ they produce?

A very important characteristic of each fossil fuel type is the *heat of combustion* – in other words, the amount of thermal energy released in the process of burning a mass unit of a given fuel. It is listed in the table below. In addition, we also give the data for several other substances which are not mined, but are widely used as fuels. The names of fossil fuels or fuels derived from them are shown in bold face, and of other fuels – in regular face.

The heat of combustion is given in the units of MJ/kg, and also of British Thermal Units per pound (BTU/lb). The latter is not a SI unit, but it is still very popular in the US.

Table 3.1. Heat of combustion of fuels

<table>
<thead>
<tr>
<th>Fuel</th>
<th>MJ/kg</th>
<th>BTU/lb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>141.80</td>
<td>61,000</td>
</tr>
<tr>
<td><strong>Methane (Nat. gas)</strong></td>
<td>55.50</td>
<td>23,900</td>
</tr>
<tr>
<td>Propane</td>
<td>50.35</td>
<td>21,700</td>
</tr>
<tr>
<td>Butane</td>
<td>49.50</td>
<td>20,900</td>
</tr>
<tr>
<td>Gasoline</td>
<td>47.30</td>
<td>20,400</td>
</tr>
<tr>
<td>Kerosene</td>
<td>46.20</td>
<td>19,860</td>
</tr>
<tr>
<td><strong>Diesel</strong></td>
<td>44.80</td>
<td>19,300</td>
</tr>
<tr>
<td>Ethanol</td>
<td>29.67</td>
<td>12,750</td>
</tr>
<tr>
<td>Methanol</td>
<td>22.65</td>
<td>9,740</td>
</tr>
<tr>
<td><strong>Coal (Anthracite)</strong></td>
<td>27.00</td>
<td>11,600</td>
</tr>
<tr>
<td>Coal (Lignite)</td>
<td>15.00</td>
<td>6,500</td>
</tr>
<tr>
<td>Wood</td>
<td>15.00</td>
<td>6,500</td>
</tr>
<tr>
<td><strong>Peat (dry)</strong></td>
<td>15.00</td>
<td>6,500</td>
</tr>
<tr>
<td><strong>Peat (dump)</strong></td>
<td>6.00</td>
<td>2,500</td>
</tr>
</tbody>
</table>

Hydrogen H$_2$ does not occur naturally. Large amounts of hydrogen are used in fertilizer industry for making ammonia NH$_3$. In the US, 95% of hydrogen used for this purpose is produced by a process called *natural gas reforming*. Hydrogen may be used as fuel in electric cars using *fuel cells* for converting it to electricity. They are real *zero-emission* cars (their exhaust is pure water vapor only), so they are ideal for California. However, because of their high price and a small number of refueling stations, they are not yet very popular:
until mid-2018, only slightly over 3,000 of them has been sold, mostly in big CA cities. And it has to be kept in mind that the cars are zero-emission ones, yes, but CO\textsubscript{2} is released to atmosphere when the fuel for them is produced by the natural gas reforming technology.

Propane (C\textsubscript{3}H\textsubscript{8}) and Butane (C\textsubscript{4}H\textsubscript{10}) are gases normally dissolved in crude oil, and released during the rectification process; they are transported and sold in a liquefied form, in pressurized tanks. They are used, e.g., as a popular fuel in gas grills.

Peat is a fossil fuel, yes, but a very “young” one. It formed at the end of the last Ice Age – not tens of millions years ago, like coal. There are few peat-fired power plants in the world, so, essentially, peat is a fossil fuel of only marginal importance.

3.2.1 How much CO\textsubscript{2} is released by burning various fuels

In the Table 3.1. we find how much thermal energy is released by burning a unit weight of various fuels – but an important question also is how much CO\textsubscript{2} is released in such processes. In fact, it’s easy to find out. The only skill one really needs for doing this is to know how to write the chemical equation of the combustion reaction\textsuperscript{1}.

How to write the equation of a combustion reaction?

Step One: The left side. On the left side of the equation, you put the chemical formula of a single molecule of the “fuel”. For instance: hydrogen occurs in diatomic molecules H\textsubscript{2}. Coal, with a not-so-bad approximation, can be though of as pure carbon, C. Natural gas is essentially methane, CH\textsubscript{4}. Gasoline is a mixture of a large number of different hydrocarbons, but a “good average” for it may be octane C\textsubscript{8}H\textsubscript{18}. For methanol and ethanol the respective formulas are CH\textsubscript{4}O and C\textsubscript{2}H\textsubscript{5}O. By the way, there are different methods of writing the chemical formulas, some people prefer writing them in a way that is similar to the actual arrangements of atoms in the molecule.

\textsuperscript{1}From his past experience in teaching the Energy Alternatives course at OSU, the Author knows that not all students taking this course have taken a basic chemistry course, either during their high school education, or at OSU. The term chemical reaction equation may sound scary to them – which is a wrong reaction(!), such equations are pretty simple indeed, and we here explain step-by-step how to write them.
Then, methanol is written as \( \text{CH}_3\text{OH} \), and ethanol as \( \text{CH}_3\text{CH}_2\text{OH} \). But in combustion reaction equations it does not matter which method you prefer: only the total number of atoms of each constituent element must be right. In an ethanol molecule, there are 2 atoms of carbon, 6 atoms of hydrogen, and one atom of oxygen. Note that those numbers are correct, no matter whether you use the \( \text{C}_2\text{H}_6\text{O} \), or the \( \text{CH}_3\text{CH}_2\text{OH} \) formula.

The other component necessary for combustion is oxygen, usually taken from the air. Oxygen, like hydrogen, also occurs in diatomic molecules \( \text{O}_2 \).

So, we can now start writing the left side of the combustion equation. Let’s take, for example, ethanol. So, we write down the formulas for ethanol and oxygen:

\[
\text{C}_2\text{H}_6\text{O} + x\text{O}_2 \rightarrow
\]

We don’t know yet how many oxygen molecules will be needed, so that we put \( x \).

**Step Two:** The right side. It’s even easier, because in the reactions of combustion of all fuels listed in Table 3.1, the only products of combustion may be carbon dioxide \( \text{CO}_2 \) and water \( \text{H}_2\text{O} \). We don’t know yet how many molecules of each of the two are created, so we put, as in “ordinary” equations, the symbols normally used for “unknown”, \( x \) and \( y \):

\[
\text{C}_2\text{H}_6\text{O} + x\text{O}_2 \rightarrow y\text{CO}_2 + z\text{H}_2\text{O}
\]

**Step Three:** Determining \( y \) and \( z \). It’s really easy. On the right side, we have a total of 2 carbon atom, so that two molecules of \( \text{CO}_2 \) can be created – and a total of 6 hydrogen atoms, so that three \( \text{H}_2\text{O} \) molecules can be created. Therefore:

\[
\text{C}_2\text{H}_6\text{O} + x\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}
\]

**Step Four:** Determining \( x \). We now count the total number of O atoms on the right side: in two \( \text{CO}_2 \) molecules there are four of them, and in three \( \text{H}_2\text{O} \) molecules there are three of them – seven altogether. And on the left side, one O atom already is in the \( \text{C}_2\text{H}_6\text{O} \) molecule. To get a total of seven on the left side, we need extra six, so that \( x \) must be 3. So, now we can write the final equation:

\[
\text{C}_2\text{H}_6\text{O} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}
\]
In a similar fashion, we can write the equation of combustion for methanol:

\[
\text{CH}_4\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}
\]

Here the situation is a bit more tricky, because, as you see, on the right side we have four oxygen atoms, and on the left side one is already in the methanol molecule, so we need three extra atoms of oxygen. Some people like to take it this way: *three atoms of oxygen are in one-and-one-half oxygen molecule.* Other people don’t like to use “half-molecules”, so they write instead:

\[
2\text{CH}_4\text{O} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 4\text{H}_2\text{O}
\]

Both ways are correct, and which one you want to use depends only on your personal preferences.

For coal, approximated as carbon, the equation is very simple:

\[
\text{C} + \text{O}_2 \rightarrow \text{CO}_2
\]

For gasoline, the equation is:

\[
\text{C}_8\text{H}_{18} + 12\frac{1}{2}\text{O}_2 \rightarrow 8\text{CO}_2 + 9\text{H}_2\text{O}
\]

which, if one doesn’t like “half-molecules”, can also be written as:

\[
2\text{C}_8\text{H}_{18} + 25\text{O}_2 \rightarrow 16\text{CO}_2 + 18\text{H}_2\text{O}
\]

**How to calculate how much CO**\text{2}**is created in a combustion reaction?** To do this, one has to first recall what the atomic mass \(m_a\) is: it’s the mass of an atom of a chemical element expressed in atomic mass units. For the hydrogen atom, \(m_a = 1\). A carbon atom is 12 times more massive than a hydrogen atom, so that for C \(m_a = 12\), and for an oxygen atom, O, \(m_a = 16\). For simple combustion reactions we consider in this Section, it’s all we need.

The *molecular mass* \(M\) of a molecule is the sum of the atomic masses of all the constituent elements. For instance, for \(\text{CO}_2\), \(M = 12 + 2 \times 16 = 44\). For \(\text{H}_2\text{O}\), one gets \(M = 2 \times 1 + 16 = 18\). For \(\text{O}_2\), \(M = 2 \times 16 = 32\). And for ethanol \(\text{C}_2\text{H}_6\text{O}\), \(M = 2 \times 12 + 6 \times 1 + 16 = 46\).

In a chemical reaction equation, the sum of all atomic masses on the left side must be equal to the sum on the right side. It’s yet another method of
checking whether the equation is correct. So, let’s look at the combustion equation of ethanol we have derived a moment ago:

$$C_2H_6O + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

For the left side, we get: $\sum M_{\text{left}} = 46 + 3 \times 32 = 142$. And for the right side, we get: $\sum M_{\text{right}} = 2 \times 44 + 3 \times 18 = 142$. So that, $\sum M_{\text{left}} = \sum M_{\text{right}}$, as expected, showing one more time that our combustion equation is correct.

Now, the calculation of the CO$_2$ mass becomes very simple. Let’s write the molecular masses instead of the chemical formulas:

$$\begin{align*}
46_{\text{fuel}} + 96_{\text{oxygen}} &= 88_{\text{CO}_2} + 54_{\text{H}_2\text{O}} \\
\text{(3.1)}
\end{align*}$$

Now, one can clearly see: the “input” is 46 mass units of ethanol, and the “output” is 88 mass units of CO$_2$. This gives us the proportion of the output CO$_2$ mass to the input ethanol mass units (we are not interested in the input oxygen and the output water). There must be the same proportion of masses, if we use kilograms, not atomic mass units. Denote the mass of CO$_2$ produced by the combustion of 1 kg of ethanol as $X$. We can write:

$$\frac{\text{CO}_2 \text{ mass (atomic units)}}{\text{Ethanol mass (atomic units)}} = \frac{88}{46} = \frac{X \text{ kg}}{1 \text{ kg}} \quad (3.2)$$

By solving this proportion, we get:

$$X = (1 \text{ kg}) \times \frac{88}{46} = 1.913 \text{ kg} \quad (3.3)$$

Ethanol is sometimes used as a fuel – e.g., in tourist stoves – but it’s definitely not a fuel used by electric power generating plants. Let’s then make similar calculations for two fuels that are used by such plants: coal and natural gas.

Let’s take anthracite, the highest-quality mined coal (over 95% of pure carbon), and ignore the 5% that may not be carbon. The equation of combustion is then pretty simple:

$$C + O_2 \rightarrow CO_2$$

The fuel input is 12 atomic mass units, the CO$_2$ output is 44 atomic mass units. Hence, the combustion of 1 kg of anthracite produces:

$$X = (1 \text{ kg}) \times \frac{44}{12} = 3.67 \text{ kg of CO}_2 \quad (3.4)$$
Natural gas, as mentioned, is almost pure methane CH$_4$. The equation of combustion is then:

$$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$$

The molecular mass of methane is 18 atomic mass units, so the mass $X$ of CO$_2$ created in the reaction is:

$$X = (1 \text{ kg}) \times \frac{44}{18} = 2.44 \text{ kg of CO}_2$$  \hspace{1cm} \text{(3.5)}$$

It’s only 2/3 of the CO$_2$ released by burning the same mass of coal. But one often hears that natural gas is a “much greener” fuel than coal, so perhaps you have expected a more significant difference?

But the difference is significant! The thing is that we should not look at the the amount of CO$_2$ released by burning a mass unit unit of a given fuel, but at the amount of CO$_2$ that needs to be released to the atmosphere for obtaining a unit measure – say, 1 GJ – of thermal energy by burning a given fuel. So, let’s see how such figures look like for coal and natural gas. Let’s take the data from Table 3.1 and from the calculations we have made, but for 1000 kg (a tonne) of fuel, not a single kilogram:

- The burning of 1000 kg of coal releases 27.0 GJ of heat, and 3670 kg of CO$_2$. Accordingly, for obtaining 1 GJ of heat from coal one has to “dump” $3670/27 = 136$ kg of CO$_2$ to the atmosphere.

- The burning of 1000 kg of natural gas releases 55 GJ of heat, and 2440 kg of CO$_2$. Therefore, for producing 1 GW of heat from natural gas one has to send $2440/55 = 44.4$ kg of CO$_2$ to the atmosphere.

As follows from the above, natural gas is “more than three times greener a fuel” than coal! In fact, in practice this ratio may be even higher, because of two reasons. First, we have made our calculations for anthracite, the highest quality coal. It’s the so-called smokeless coal$^2$. Only about 1% of all global coal resources are anthracite, the rest are lesser quality forms with lower heat of combustion than anthracite. A really “bad guy” is lignite, the

$^2$During the Civil War, the “blockade runners” – i.e., the Confederacy merchant ships trying to sneak through the blockade imposed by the Union – used anthracite as a fuel. Other types of coal were much cheaper, but they produced a lot of smoke, revealing the position of the “blockade runner” to the Union Navy ships enforcing the blockade.
so-called *brown coal*. With its heat of combustion as low as 15 MJ/kg, it may produce as much as 250 kg of CO\(_2\) for 1 GJ of heat, a score about five times worse than natural gas. Nonetheless, “brown coal” is willingly used by some European countries because huge rich deposits of this fuel are placed shallowly underground. Like the coal deposits in Montana – however, in Montana it’s a good quality coal, not the highly polluting lignite.

The other reason that the natural gas is much “greener” than coal is the difference in the efficiency of thermal engines using coal and those using natural gas as fuel. Coal is the standard fuel in power plants using steam turbines – currently, it’s the most popular type of thermal power plants. Here, coal is used to heat steam-generating boilers, from which steam is directed to turbines. The combined efficiency of such a system may be only somewhat higher than 30%. It means that the amount of CO\(_2\) created for producing 1 GW of electric energy may be as high as \((136 \text{ kg})/0.3 \sim 450 \text{ kg}\) of CO\(_2\). On the other hand, the efficiency of gas turbines, converting thermal energy from gas burning directly to mechanical energy, may be as high as 45% – and in some newest models of turbines, the record-high efficiency is 62%. Then, the production of 1 GJ of electric power releases only \((44.4 \text{ kg})/0.62 \sim 72 \text{ kg}\) of CO\(_2\). 72 kg as opposed to 450 kg, natural gas, if such gas turbines are widely used, may be 6.25 times “greener” than coal!

### 3.3 Heat Engines

Heat engines are devices that convert thermal energy to mechanical work. They are all around us. They may be quite annoying if you live in the center of a big city. There are many different types. Chronologically, the first types used in industry, used for pulling trains on railroads, and used for propelling commercial and navy vessels were piston steam engines. At the end of the 19\textsuperscript{th} century internal combustion engines were invented – gasoline and diesel engines – and they started gradually replacing steam engines. Some of the “steamers”, though, were die-hards: steam automobiles, the famous *Stanley Steamers*, were manufactured in the US until the mid-1920-s. Steam railway locomotives were still used in many countries even after the year 1950. And during the World War Two yhears, between 1941 and 1945, the American shipyards mass-manufactured, on an unprecedented scale, as many as 2710 cargo steamers, known as the *U.S. Liberty class* ships.
Steam turbines. However, the decline of the piston steam engines coincided with the emergence of a new steam engine type – namely, the *steam turbine*. They turned out to be particularly useful in devices where huge power was needed: for propelling the largest ships – and in power plants generating hundreds or thousands of megawatts of electric power. The first modern steam turbine was built in 1884 by Sir Charles Parsons (1854-1931). An generator connected to his turbine produced 7.5 kW of electric power. During his lifetime, the power of a single turbine units increased to 50 MW. Today, the two largest existing steam turbines are capable of generating 1,600 MW each.

In today’s global electric power generating system steam turbines are extremely important, indeed. Their main application is in conventional thermal power plants – those fueled by coal, natural gas, or oil. Also, all existing nuclear power plants utilize them: nuclear reactors are only generating heat, later used for making steam sent to turbines. And they are also vital component in some renewable energy systems – in solar power plants based on the technology of Concentrated Solar Power (CSP). Altogether, power plants using steam turbines generate more than 50% of electric power currently consumed worldwide.

Because of the leading role of turbines in power generation, we will not discuss the design or functioning of piston engines here, no matter what type they are - steam, petrol or diesel. For students who are strongly interested in such engines, we can recommend an instructive Web site in which 20 animated schemes of piston engines (plus one of a jet engine) are shown. It’s also recommended to pay special attention to the Newcomen Atmospheric engine in this Web page. You may also want to see this Web page. The Newcomen Engine, designed in 1712, was the very first thermal engine that found a wide application in mining industry (several hundred of them were built throughout the 18th Century. Their construction and the operation principle were very simple – not to say “primitive”. So why it’s worth paying attention to such an engine? Well, because of the simplicity of its operation, it’s pretty straightforward to calculate its thermal efficiency (pretty low!), and to discuss where most of the input thermal energy is wasted. It’s a good homework problem!

Let’s go back to the steam turbine. Its spinning part, called *rotor*, is a sturdy shaft, on which a number of discs are mounted. Each discs has a number of
blades attached to its perimeter, as shown in the Fig. 3.2.

![Figure 3.2: The rotor of a steam turbine.](image)

Figure 3.2: The rotor of a steam turbine. Note that there are spaces between successive discs, into which *stators* (a.k.a. *diafragms*) are inserted when the rotor is mounted in its casing.

In between each pair of rotor discs, *stator discs*, or *diafragms* are inserted. Stator discs are similar to rotor discs, but they are fixed to the turbine casing and do not move during the turbine operation. Full discs, of course, couldn’t be inserted in between rotor discs – so, a “trick” is used, each disc consists of two “half-discs” inserted one from the right, the other from the left.

![Figure 3.3: A stator “half disc”.](image)

Figure 3.3: A stator “half disc”.

The role of the stators is explained pretty well by an animation in this *Technology Partnership* Web page. In the animated graph seen in the page.
right after it opens up, there is a picture of a steam turbine with two rotor disc, and one stator disc in between. The steam that leaves the nozzles, moving (if looked at from the top of the picture) “to the right”. It enters the spaces between the blades of the first rotor disc and passes some of its momentum to the blades. But in the process the steam is “redirected”: now, looking from the top of the picture, it moves “to the left”. But the next rotor disc again “expects” the incoming steam to move “to the right”. And this is why the stator disc is for: the steam enters the spaces between the blades moving “to the left”, but due to the curvature of the blades, it’s redirected and leaves the stator disc “moving to the right”.

Figure 3.4: A graph explaining the role of the stator blades in a steam turbine.

Another graph explaining the role of the stator blades is shown in the Fig. 3.4. The rotor blades are the blue ones, and the stator blades are red. The steam arrinet eving from the left is first “redirected” up by the red static blades – so that they can “push” the blue rotor blades “upwards”. But after exiting the rotor, the steam moves “downwards”. So, another passage between static blades redirects it “upwards” again – and so on.
In the Fig. 3.2 one can see that the turbine rotor has a sophisticated shape – at the far end (it’s where the steam enters) it has a small diameter, which gradually increases, and becomes much larger where the steam exits. Why is it so? The orange curve in Fig. 3.4, which shows how the pressure changes along the turbine shaft. Also, as the steam gradually passes its energy to the turbine rotor, its temperature drops. Decreasing pressure of a gas causes it to expand in volume; decreasing temperature has an opposite effect. But in a steam turbine the pressure drop has a far stronger effect than the temperature drop – therefore, the net effect is that the volume of the steam strongly increases in the course of its passage through the turbine – and therefore the last rotor disc is so much larger than the first one.

The turbine is only one part of a complete thermal power plant. A simplified scheme of a complete installation is shown in the Fig. 3.5. It must include, of course, a “steam source”. By tradition, it’s called boiler. In the old days, the boilers were huge water tanks mounted on the top of coal furnaces. Inside the tank, water was boiling – usually at pressure much higher than the atmospheric pressure. After “doing its work” in the engine, the exhaust steam was simply released into the air. When most water was used up, the tank had to be opened and refilled with fresh water. It was an inconvenient and time-consuming procedure. A significant improvement was the invention of a condenser. Now, the system became a “closed-loop” one: the exhaust steam was cooled down so it condensed back to liquid water, which was then re-injected by a special pump back into the boiler.

![Figure 3.5: A simplified scheme of a modern coal-fired thermal power plant.](image-url)
Next, the engineers realized that a big-volume boiler was not necessary. Once the water circulated, a tank could be replaced by a system of coiled tubes. It had an additional advantage that higher pressure could be used. So, water could be heated up to higher and higher temperatures — up to the so-called critical point, which for water occurs at 374°C (647 K), at pressure 218 times the atmospheric pressure. And it was good, considering that the efficiency of a turbine increases with the increasing steam temperature (it will be discussed in closer detail in the next Section).

Finally, the engineers realized that not only liquid water could be heated. *If increasing the steam temperature improves the efficiency, why don’t we heat up the steam even more? —* was their thinking. What was needed for that, was just adding more tubes to the “tank-less” boiler. And so the newest-generation boilers were born. They produce the so-called superheated steam, of temperature about 550°C (823 K).

Also, the furnaces underwent a gradual evolution: in the old days, the coal was shuffled manually into them by workers called *stokers* — you may see them, e.g., in this YouTube clip about the *Titanic* steam engines, starting at 1 minute 38 seconds (by the way, in the same YouTube one can hear that the steam pressure in the boilers supplying the *Titanic’s* giant piston-engines was 215 pounds per square inch (PSI), which is 14.6 atmospheres — and today the inlet steam pressure in state-of-the-art steam turbines may be more than 10 times higher).

Gradually, the stokers were replaced by conveyor belts. And in the most advanced installations, coal is first the coal is first pulverized into fine dust, and then injected into the furnace using a jet of compressed air.

The alternative of using coal is to fuel the boilers with oil and natural gas. Especially, the latter option is attractive, because — as was shown in the preceding section — natural gas produces at least 3 times less CO₂ than coal for the same amount of power generated. Another reason is the ease of fuel transportation, gas can be delivered to the plant by a pipeline. Therefore, more and more coal-fired power plants in the US are being converted to natural gas fuel.

**Gas turbines.** The conversion of a coal-fired power plant to a gas-fired one involves changing the coal-burning furnace to a system of gas burners. The other parts of the boiler may stay. However, in principle it’s possible to make a “deep conversion” in which the entire boiler and even the steam turbine is removed. The steam turbine may be replaced by a gas turbine that does not
need any boiler!

In a gas turbine, air and natural gas of ambient temperature are pumped into a combustion chamber, where they are ignited. Natural gas is essentially a pure methane \( \text{CH}_4 \), and air is a mixture of 21% of oxygen \( \text{O}_2 \), 78% of nitrogen \( \text{N}_2 \), and 1% of argon \( \text{Ar} \). Nitrogen and argon do not take part in the combustion reaction, and methane and oxygen change in the process to \( \text{CO}_2 \) and water vapor. Due to the high heat of combustion of natural gas, the temperature of the mixture of gases after the reaction is as high as 1600°C, and its pressure increases considerably. From the combustion chamber, it passes to the turbine, which has a very similar design to a steam turbine. The main difference is the temperature. In the latter, the inlet steam temperature is 550°C, or sometimes a bit higher – but it’s still a temperature tolerated by steel. In a gas turbine, the blades must tolerate a much higher temperature of inlet gases, so they have to be made of special alloys. But besides, the design and operation of both types of turbines are very similar.

As mentioned, the largest existing steam turbines can produce as much power as 1600 MW. Currently, single-unit gas turbines with record-high performance made by Siemens yield lees, nearly 600 MW – but as far as their efficiency is concerned, they outperform steam turbines. The latter, when running on extremely high-temperature steam, may reach up to 35% efficiency, while from a single-unit gas turbine one can get even 45%. And this is not the end, because gas turbines offer the possibility of working in combination with steam turbines, and then the efficiency of such a co-generation assembly may exceed 60%. How such a combination is set up, is explained in the Fig. 3.6.

Figure 3.6: 1 – electric generators, 2 – steam turbine, 3 – condensor, 4 – pump, 5 – steam generator, 6 – gas turbine
The idea is simple: the exhaust gases from a gas turbine are still pretty
hot (450 - 650°C, which is an ideal steam temperature for a modern steam
turbine. Therefore, the exhaust gases are used for generating steam – much
like in a boiler in a conventional power plant using steam turbines only. In
practice, the power ratio of the two turbines making a “tandem” is close to
2:1. For instance, a typical combination is a 400 MW set consisting of a
270 MW primary gas turbine and a 130 MW secondary steam turbine. On
April 28, 2016, a plant in Bouchain, France, was certified by Guinness
World Records as the world’s most efficient combined cycle power plant at
62.22%. However, General Electric is expecting to break the 65% level soon.
Note that 65% means generating twice as much electricity from the same
amount of gas fuel than a plant using steam turbines only would do. As
you see, heat (or, rather thermal energy) from steam can be transformed to
mechanical energy. And there is a range of other heat engine types that can
be employed to perform many useful tasks (e.g., power your car).

3.4 The Efficiency of Thermal Engines

3.4.1 The First Law of Thermodynamics.

As we have seen, heat (or, rather thermal energy) from fuels can be trans-
formed to mechanical energy. And there is a range of thermal engine types
that can be “employed” to perform many useful tasks (e.g., power your car).

It is essentially what The First Law of Thermodynamics states. It’s the
good guy, everybody is happy with it. But it’s not the only law that governs
the transformation of heat to work. The other one is the Second Law of
Thermodynamics, and this is the bad guy.

This Section is mainly about the Second Law and its consequences – but
before we start talking about it, we should briefly recapitulate what the First
Law says in a more exact manner. We need some definitions:

- **A system:** A system: a single body, or more bodies that are in contact
  with one another.

- **Internal Energy:** There is a physical quantity called the internal
  thermal energy of a system or “internal energy” in short. Convention-
  ally, it is denoted as $U$. 

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• Energy may be added to the system, thus increasing its $U$. (we call such a process “heating”) – either through a contact with another system, or by performing work on the system (for instance: if the system is a portion of gas, one way of performing work on it is compressing it).

• Energy may be taken away from a system, thus lowering its $U$ (we call such a process “cooling”) – either through a contact with another system, or by causing the system to perform work (for instance: if the system were a gas, it would perform work by expanding). However, the process of taking energy away can not continue forever, when all energy is taken away, the system reaches the absolute zero point, at which its temperature is zero Kelvins (0 K).

Now, we can write the First Law in mathematical terms: essentially, it’s the Energy Conservation Law, but expressed in a way specifically applying to thermal phenomena:

$$\Delta U = \Delta Q + \Delta W$$ (3.6)

where:

$\Delta U$: The total change in the system internal energy.

$\Delta Q$: The change of $U$ due to transfer of heat (heat flowing in or out from another system, in contact with the system considered).

$\Delta W$: The change of $U$ due to mechanical work done on the system, or the work delivered by the system (then, negative).

**Important:** A common misconception is to confuse heat with the internal energy. Internal energy is the amount of energy contained by the system. Heat is the energy that flows in or out from/to a warmer/cooler body which is in contact with the system.

### 3.4.2 Entropy.

The First Law was an easy part. But in order to explain what the Second Law talks about, we have to introduce the notion of Entropy.

Entropy is widely regarded as one of the most difficult concepts in university physics curriculum. It’s a parameter that characterizes the state of a
thermal system. Other state parameters are the internal energy $U$, volume $V$, the amount of substance (usually expressed as the number of moles $N$ – a mole consists of $6.022 \times 10^{23}$ molecules$^3$ of a given substance). Furthermore, the temperature $T$, and the pressure $p$. They are all “intuitively clear”, right?

In contrast, entropy, conventionally denoted as $S$, is an abstract function. It’s mathematically defined, and the definition is not very complicated. Namely, if a portion of heat $\Delta Q$ is transferred in or out of a body of temperature $T$ (either an individual body, or a body being a part of a larger system, otherwise isolated) the change $\Delta S$ in the body’s/system’s entropy is:

$$\Delta S = \frac{\Delta Q}{T} \quad (3.7)$$

So, by adding heat one can increase the entropy of a system, and by removing heat e.g., through contact with a cooler body one can lower the systems entropy.

**An Example.** Perhaps a good thing to do now would be to discuss a simple example. OK, consider a 1 kg sample of ordinary water, $\text{H}_2\text{O}$. At very low temperature it’s a solid piece of ice. If we start adding heat to it by small portions $\Delta Q$, each time its entropy will grow by $\Delta S = \Delta Q / T$, according to the Equation 3.7. But when we add heat, we also add energy, right? So, after each step, the temperature will also grow a bit.

![Figure 3.7: Change of entropy of a sample of water, when heat is gradually added by small portions.](image)

---

$^3$Why such an “exotic” number? Well, once it has been decided that a mole of hydrogen, the simplest of all elements, would be the number of hydrogen atoms in a mass unit, a gram (g). And there are $6.022 \times 10^{23}$ atoms in a gram of hydrogen – it’s called the Avogadro Number. Then it has been decided that a mole of any other pure substance is the Avogadro Number of molecules of this substance.
As the process continues, the temperature will gradually increase, as illustrated in the Fig. 3.7 – until it reaches the ice melting point \( T_f = 273 \) K. In order to melt a mass unit of ice, one has to add an amount of heat called the heat of fusion, equal 334 kJ/kg. Now, the temperature stops growing, until the small portions \( \Delta Q \) add up to 334 kJ. But the entropy keeps growing during the process, as shown by the vertical part of the curve in the Fig. 3.7. During the entire melting process, it increases by 334kJ/273K = 1.22 kJ/K.

After all ice changes to water, the temperature starts increasing again, until it reaches the boiling temperature \( T_b = 373 \) K. Again, the temperature stops growing, because in order to change one kg of liquid water to water vapor, the energy of 2256 kJ is needed. So, again the temperature stops growing, until all small portions \( \Delta Q \) add up to this value – but the entropy in the course of this process increases by 2256kJ/373K = 6.05 kJ/K, creating another “vertical jump” on the curve. After that, the temperature of water, now in gas (vapor) form, will start increasing.

The purpose of the above example is to show that entropy can be calculated. In the Web one can find tables and online calculators.

**Another example** The process of water heating described above is reversible. If we started to take away small portions of heat, we would return to the original state along the same curve. There are, however, processes that cannot be reversed – called irreversible. Consider the following example: there are two 1 kg blocks of aluminum, placed into a container that is totally impermeable to heat – no heat can flow in or flow out. The blocks initially do not touch one another. The temperature of one of them (Block 1) is \( T_1 \), and of the other (Block 2) is \( T_2 \), with \( T_1 > T_2 \).

The relation between the amount of heat \( \Delta Q \) that flows in or out of aluminum, and the change \( \Delta T \) of its temperature is caused by the process is:

\[
\Delta Q = C_{Al} \Delta T \quad \text{or} \quad \Delta T = \frac{\Delta Q}{C_{Al}} \quad (3.8)
\]

where \( C_{Al} \) is a “material constant” called heat capacity. For Aluminum, its value is 900 J/kg·K.

If we now bring the two blocks together to establish thermal contact between them, heat will start flowing from Block 1 into Block 2. The process will last until the temperature of both gets equal. Call this temperature \( T_{12} \). An obvious guess is that it is equal to the arithmetic average of \( T_1 \) and \( T_2 \),
i.e.,

\[ T_{12} = \frac{T_1 + T_2}{2} \]

To check whether it’s a right guess, let’s calculate the heat transferred out of Block 1 and heat transferred into Block2. The energy conservation law states that they must be equal! OK, let’s then see. First, we find the change of the temperature of Block 1. An algorithm for a temperature change \( \Delta T \) is always: the final temperature minus the initial one. So, we get:

\[ \Delta T_1 = T_{12} - T_1 = \frac{T_1 + T_2}{2} - T_1 = -\frac{T_1 - T_2}{2} \]

So that the heat transfer out of Block 1 is, according to the Eq. 3.8:

\[ \Delta Q_{\text{out of Block 1}} = -C_{\text{Al}} \frac{T_1 - T_2}{2} \]

In a similar fashion, we get:

\[ \Delta T_2 = T_{12} - T_2 = \frac{T_1 + T_2}{2} - T_2 = \frac{T_1 - T_2}{2} \]

and:

\[ \Delta Q_{\text{into Block 2}} = C_{\text{Al}} \frac{T_1 - T_2}{2} \]

So, everything is correct – the same amount flows out of Block 1 (therefore the minus sign) as it flows in Block 2.

However, let’s now see what happens with the entropy. Let’s focus on the very beginning of the process, when only a tiny amount of heat \( dQ \) managed to get out of Block 1, and into Block 2. So, the change of entropy of Block 1 is \( dS_1 = -dQ/T_1 \) (minus, because \( dQ \) flows out of Block 1), and of Block 2 is \( dS_2 = dQ/T_2 \). The total change of entropy of the system of two block is the sum of the two:

\[ dS_{\text{tot}} = dS_1 + dS_2 = -\frac{dQ}{T_1} + \frac{dQ}{T_2} = dQ \left[ -\frac{1}{T_1} + \frac{1}{T_2} \right] = dQ \left[ \frac{T_1 - T_2}{T_1 T_2} \right] \]

Note that the last right-hand expression in square brackets is a non-zero positive number. It means that the entropy of the two-block system increases in the course of the process. But not only during the initial short period –
the same math remains valid for any moment until the heat stops flowing. So, the conclusion is that this process of heat exchange between the blocks increases the entropy of the two-block system.

The exchange of heat between two bodies is always an irreversible process: the heat flows spontaneously from the warmer to the cooler body, but the opposite may never happen. There are many other types of irreversible thermodynamic processes, and all have one in common: if such processes occur in thermally isolated system (often called adiabatic by professionals), the entropy of the system always increases. Entropy may stay constant only if all processes in an adiabatic system are fully reversible. And the entropy in an adiabatic system can never ever decrease!

3.4.3 The Second Law of Thermodynamics

Why do we pay so much attention to entropy? Why is it so important? Well, it’s because the entropy is – let’s use such a metaphor – the “leading character” in the Second law of Thermodynamics.

One scientist once counted all non-identical formulations of the Second Law he was able to find – and his result was about one hundred. But non-identical does not mean that they are different: no, no, they are all equivalent! They all convey exactly the same information, only the differently (sometimes, very differently!) formulated. In some of them entropy is explicitly mentioned, and in some of them it is not. For instance, one of the Author’s favorite formulation of the Second Law is: It is not possible to build a Perpetual Motion Machine of the Second Kind.

In fact, what the second law states, is expressed in the last paragraph of the preceding Section. In a more compact form, one can say: In a closed thermodynamic (adiabatic) system, the entropy may either remain constant, or increase. Or, even in a compacted form:

In a closed thermodynamic (adiabatic) system, \( \frac{dS(t)}{dt} \geq 0 \)

If the time derivative of a function of time is zero, it means that the function does not change in time; and if the derivative is greater than zero, it means that its value is increasing in time.

Why does the Author so stubbornly stress each time that the Second Law applies only to thermally isolated, i.e., adiabatic systems? Because he knows from his long teaching practice that students often forget to add this
clause. The Author himself forgot about it at the thermodynamics exam at his senior year. Fortunately, other answers were correct, so the exam ended up with a B. Some instructors treat the omission of this clause as a cardinal error (not the Author, remembering his own fault – he believes that giving the student “another chance” is a better way of dealing with the problem).

In a system which is not thermally isolated, the entropy may decrease. Take a glass of water and on a cold winter day leave it outside. Water will freeze, its entropy will lower considerably. It’s all OK.

3.4.4 Sad Consequences of the Second Law

After the First Law has been discovered, some people started thinking: if heat is equivalent to mechanical work, we should be able to take a big reservoir of thermal energy – such as, e.g., an ocean – and extract work from it. There is so much thermal energy in any ocean that there should be enough mechanical work for everybody for thousands of years!

A machine that would extract thermal energy from oceans and convert it to usable work was given the name of Perpetual Motion Machine of the Second Kind (PMMoSK). The first kind was a machine that would produce work out of nothing.

Some inventors seriously believed that making such a machine would be possible. They spent much time working on projects and prototypes. The failure of all such efforts was certainly one of the factors that helped to discover the second law of thermodynamics.

Who has “derived” the Second Law? Not a human scientist. It was Mother Nature who decided that things should be that way. The role of human scientist was only that by analyzing a wide variety of facts they reached a firm conclusion that there is such a law of nature.\(^4\)

A simple explanation why it is not possible to build a PMMoSK is presented in the Fig. 3.8. Consider an isolated homogeneous system. An amount of work \(\Delta W\) can be added to it to increase its internal energy \(U\) – the result is the same as if one added an equivalent amount of heat \(\Delta Q\), so that the

\(^4\)In fact, other laws of physics were discovered in the same way. For instance, Newton did not “derive” his famous second law of dynamics, \(F = m \cdot a\). By analyzing observations, he concluded that there is such a law of nature. And many generations of physicist later strengthened his conclusion by performing zillions of tests. Something derived by scientists may only be a theorem, not a law.
Figure 3.8: Adding work to a homogeneous isolated system is possible – but extracting energy at the expense of its energy $U$ is not.

entropy of the system increases by $\Delta S = \Delta W/T$. The increase of entropy is permitted by the Second Law, so everything is OK with the process. But not with an opposite one! Extracting a portion of work $\Delta W$ from the system would be equivalent with taking a portion of entropy $\Delta S = \Delta W/T$ away from it – so, in consequence, to lowering the system entropy, which is strictly forbidden by the Second Law.

### 3.4.5 The Efficiency of an Ideal Thermal Engine

But there are devices converting heat to mechanical work! Yes, there are. There are ways of outsmarting the Second Law. But for a price!

Consider an isolated system (Fig. 3.9) containing a heated body. The only way of extracting work from a heated body of temperature $T_h$ is to build a more complicated system that would make it possible to keep the entropy at a constant level. The “trick” is as follow: the system should contain, in addition, a “heat engine” that draws a “portion” of heat $\Delta Q_h$ from the heated body, and converts some part of it – very important, some part of it only! – to mechanical work. And there must be a cold body or a “heat sink” of temperature $T_c$ necessarily lower than $T_h$ where the remaining heat can be absorbed (“dumped”).

The entropy taken from the heated body is:

$$\Delta S_h = \frac{\Delta Q_h}{T_h} \tag{3.9}$$

The engine is using some part of $\Delta Q_h$ to do work $\Delta W$, so that the remaining
Figure 3.9: An isolated system containing hot body, an ideal thermal engine, and a cold body, used for deriving the equation for the maximum possible thermal engine efficiency.

The amount of heat “to be dumped” to the cold body is:

\[ \Delta Q_c = \Delta Q_h - \Delta W \]

So the entropy \( \Delta S_c \) passed to the cold body is:

\[ \Delta S_c = \frac{\Delta Q_c}{T_c} = \frac{\Delta Q_h - \Delta W}{T_c} \quad (3.10) \]

The total entropy cannot decrease, so it must be:

\[ \Delta S_c = \Delta S_h \]

By substituting for \( \Delta S_c \) and \( \Delta S_h \) the results from the Eqs. 3.9 and 3.10, we get:

\[ \frac{\Delta Q_h}{T_h} = \frac{\Delta Q_h - \Delta W}{T_c} \quad (3.11) \]
By performing simple algebraic operations, one can convert the above to:

\[
\frac{\Delta W}{\Delta Q_h} = 1 - \frac{T_c}{T_h}
\]  

(3.12)

Note that the left side of the above equation is the ratio of the mechanical energy delivered by the heat engine to the thermal energy taken from the hot body – in other words, it is the **efficiency of converting the input heat to the output mechanical energy**. We can write then:

\[
\epsilon_{\text{conv}} = 1 - \frac{T_c}{T_h}
\]

(3.13)

Or, we often prefer to express the efficiency in percents, then this equation takes the form:

\[
\epsilon_{\text{conv}}[\%] = \left(1 - \frac{T_c}{T_h}\right) \times 100\%
\]

(3.14)

This result is known as the Carnot Law\(^5\), in honor of Nicolas Lonard Sadi Carnot (1796-1832), a French engineer whose works published in 1824 contributed greatly to discovering the Second Law of Thermodynamics and to understand the role of entropy in thermal phenomena.

What has been said by now, may raise one question: is it possible to build an engine? Is it possible to build an engine consistent with all the assumptions used in the considerations above? It’s a good question! But, fortunately, the answer is yes. A “prototypical” engine of such kind, known as the Carnot Engine, uses a gas as the “working fluid”. Later, many other types of Carnot Engines were conceived, not necessarily using a gas working fluid.

“Sadi” was perhaps a good middle name for the discoverer of this “law”, because, regretfully, it brings us a sad message... Namely, no heat engine can attain a higher efficiency of converting thermal energy to work than that permitted by the **Carnot Law**. The consequence are not so pleasant... Let’s consider a modern power plant, which uses steam turbines. The highest temperature of steam from “state of the arts” flame-heated boilers is \(t \approx 650^\circ\text{C}\), which translates to \(650 + 273 = 923\text{ K}\). And an often used “heat sink” is river, lake or sea water, usually of temperature \(\sim 20^\circ\text{C} = 293\text{ K}\). We get:

\[
\epsilon = 1 - \frac{293\text{K}}{923\text{K}} = 0.683
\]

\(^5\)As noted before, from an orthodox viewpoint it should not be called a *law*, but rather a *theorem*. But it is difficult to overcome a tradition. The Author will not try, and therefore the formulation **Carnot Law** will be used further on.
It means that only about then 68% of the thermal energy “invested” is converted to work, and about 32% “goes down the drain”, i.e., is dumped in the heat sink. Not a brilliant performance, you may think, but one can survive with such an efficiency...

3.4.6 Even sadder news...

But there are more bad news for you: namely, the “Carnot efficiency” is correct only in highly idealized situations. One can build engines which would obey the Carnot Law, yes look at the following Web sites: e.g., a NASA Web site, the renowned “Hyperphysics” site, or this site in Electropaedia (I like the British “Electropaedia”, one can find good “non-nonsense” articles over there).

However, such laboratory-built engines have to work extremely slowly in order to deliver output work consistent with the Carnot Law. “Extremely slowly” means that they, yes, deliver work – but not power. And power is what we really need! We need engines that produce maximum power from a given amount of thermal energy! To make the long story short: one can make power-maximizing heat engines, there is even a special theory of such engines in thermodynamics, they are called “endoreversible heat engines”. The thing is that their operation involves processes which the science of thermodynamics recognizes as irreversible and their nasty effect is that they produce an additional portion of entropy. This extra entropy also has to be removed from the engine, so that even more heat has to be “dumped” into the heat sink. The result is that even less heat can be converted to output work. In short, the efficiency of a power-maximizing heat engine is given by the Chambadal-Novikov formula:

$$\epsilon_{C-N} = 1 - \sqrt{\frac{T_c}{T_h}}$$  \hspace{1cm} (3.15)

Novikov and Chambadal are the two gentlemen who in 1957 independently did pioneering theoretical studies on power-maximizing engines. The theory is quite complicated, it will not make sense to discuss its details over here if you are interested, you may find more in the following Web sources: Endoreversible thermodynamics, or in this article – as well as in references listed in these two sources. The bad news is that, as noted, the above theory is “pretty complicated” but the good news is that the final theoretical formula is pretty similat to the
Carnot Equation note that there is only an extra square root symbol! So, it’s not the original Carnot’s equation, but the Chambdal-Novikov formula we should use for estimating the efficiency of practical heat engines. In the example we have considered above, we should use:

\[ \epsilon_{C-N} = 1 - \sqrt{\frac{293K}{923K}} = 0.437 \]  

(3.16)

It means that not 35% energy released from burning fuel, but as much as 54% of this energy “goes down the drain”!

Table 3.2. Comparison of the real efficiency of thermal plants with calculations using the Carnot and the Chambdal-Novikov formulae (the symbol \( \nu \) means the same as \( \epsilon \) in the text).

<table>
<thead>
<tr>
<th>Power Plant</th>
<th>( T_c ) (°C)</th>
<th>( T_h ) (°C)</th>
<th>( \eta ) (Carnot)</th>
<th>( \eta ) (Endoreversible)</th>
<th>( \eta ) (Observed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>West Thurrock (UK) coal-fired plant</td>
<td>25</td>
<td>565</td>
<td>0.64</td>
<td>0.40</td>
<td>0.36</td>
</tr>
<tr>
<td>CANDU (Canada) nuclear power plant</td>
<td>25</td>
<td>300</td>
<td>0.48</td>
<td>0.28</td>
<td>0.30</td>
</tr>
<tr>
<td>Larderello (Italy) geothermal power plant</td>
<td>80</td>
<td>250</td>
<td>0.33</td>
<td>0.178</td>
<td>0.16</td>
</tr>
</tbody>
</table>

As follows from the data in the table (from the Wikipedia site linked above), the Chambadal-Novikow formula yields results that are pretty close to the real thermal efficiencies attained in real power plants. But the 44% efficiency appears to be even too high for most existing thermal power plants, due to extra losses of heat in not-too-well engineered installations the real efficiency in such plants is seldom higher than 30%. 70% of thermal energy released goes down the drain!

70% of thermal energy released by burning fossil fuels is lost!

(not engineers should be blamed, but Mother Nature and her 2nd Law – but we can stop this wastage by using energy from other sources!)