STEAM ENGINES; THE RANKINE CYCLE

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problems 4.22 - 4.24.

A steam engine differs from the Otto and Diesel engines that we've looked at so far in that the working substance is not an ideal gas. A steam engine follows the Rankine cycle on a *PV* diagram, which looks like this:
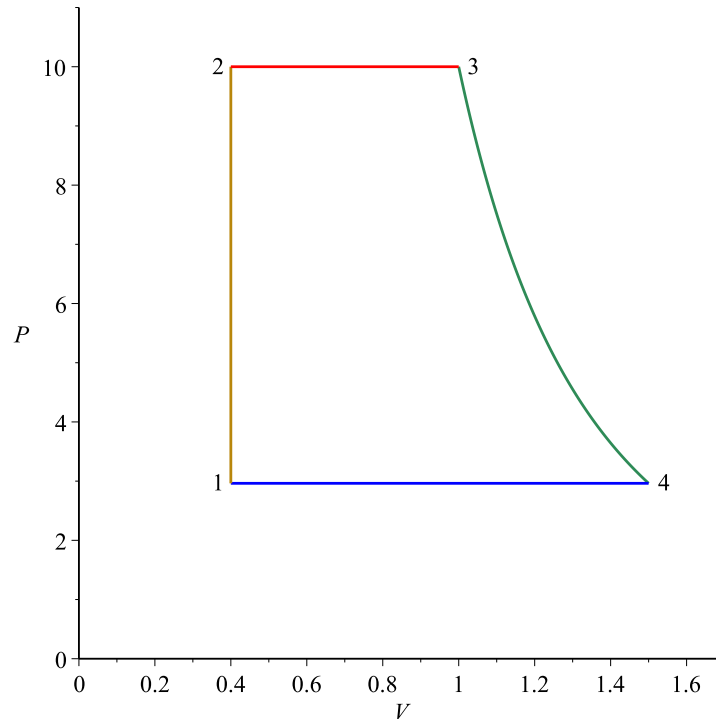
The working substance in a steam engine is, not surprisingly, steam, which is condensed to liquid water for part of the cycle. Starting at point 1, the water is in liquid form and is compressed at constant volume to a pressure P_2 at point 2. Liquid water doesn't change its volume much when compressed, so the constant volume is a good approximation.

Along edge 2 to 3, the water is boiled at constant pressure, producing steam which, by the time it reaches point 3, is superheated to a temperature much greater than its boiling point. This is the stage in which heat Q_h is

1

absorbed from the hot reservoir, which is typically produced by burning fuels such as coal or gas, or from nuclear power.

The edge 3 to 4 is the stage where the steam does work by turning a turbine (usually to produce electricity, although in the 19th century, steam engines were used in many other places, most nostalgically in steam trains). This stage is an adiabatic expansion to point 4.

Finally, the stage 4 to 1 condenses the steam back to liquid water at constant pressure, expelling waste heat Q_c.

The efficiency of the steam engine is defined in the usual way as

$$e = 1 - \frac{Q_c}{Q_h} \tag{1}$$

Although we have a nice, simple PV diagram for the Rankine cycle, we can't use it to calculate the efficiency directly, since we can't use any of the equations for an ideal gas. However, we can make a start by observing that the two edges along which heat is exchanged both occur at constant pressure, so the heats Q_c and Q_h are equal to the corresponding enthalpy changes along these edges:

$$e = 1 - \frac{H_4 - H_1}{H_3 - H_2} \tag{2}$$

The enthalpies can be read off from steam tables. Schroeder gives a couple of brief tables in his Tables 4.1 and 4.2; more complete tables can be found on the web. The two tables correspond to different parts of the diagram above. One table gives enthalpy and entropy values for saturated water and steam, which, for a given pressure, occurs at the boiling point of water (the boiling point decreases with decreasing pressure). Thus in this case, the temperature is determined by the pressure (or vice versa). This corresponds to points 1 and 4 since this is condensing phase, where the steam is being converted back into liquid water.

The other table gives values of entropy and enthalpy for superheated steam, which for a given pressure, is at a temperature above the boiling point. We can find the enthalpy for point 3 from here, given the pressure and temperature.

We can typically approximate the enthalpy at point 2 to be the same as that for point 1, so an approximate efficiency is

$$e \approx 1 - \frac{H_4 - H_1}{H_3 - H_1} \tag{3}$$

Example 1. We have a steam engine operating between temperatures of $20°$ C and $300°$ C with a maximum pressure of $P_3 = 10$ bars. To calculate the efficiency using the approximate formula, we need 3 enthalpies. H_1 can

be read off Schroeder's Table 4.1, since here we have water at $T = 20°$ C at its boiling point (implying a pressure of $P_1 = 0.023$ bar), so the enthalpy is

$$H_2 \approx H_1 = 84 \text{ kJ kg}^{-1} \tag{4}$$

Point 3 is in the superheated steam regime, so we can use Table 4.2 to find

$$H_3 = 3051 \text{ kJ kg}^{-1} \tag{5}$$

To get H_4, we use the fact that curve $3 \to 4$ is an adiabat, so the entropy of the steam is the same at points 3 and 4. From Table 4.2, we have

$$S_3 = 7.123 \text{ kJ K}^{-1}\text{kg}^{-1} \tag{6}$$

We need to find a mixture of water and steam at $20°$ C in Table 4.1 that has the same entropy. That is, the fraction x of water is given by

$$
\begin{align}
S_4 = S_3 &= xS_w + (1-x)S_s \tag{7} \\
7.123 &= 0.297x + 8.667(1-x) \tag{8} \\
x &= 0.184 \tag{9}
\end{align}
$$

Also from Table 4.1, we can now find the enthalpy of this mixture

$$
\begin{align}
H_4 &= xH_w + (1-x)H_s \tag{10} \\
&= 0.184 \times 84 + 0.816 \times 2538 \tag{11} \\
&= 2086 \text{ kJ kg}^{-1} \tag{12}
\end{align}
$$

The efficiency is therefore

$$e = 1 - \frac{2086 - 84}{3051 - 84} = 0.325 \tag{13}$$

Example 2. How good is the approximation $H_1 \approx H_2$ we used above? We can get an estimate as follows. Enthalpy is defined as

$$H = U + PV \tag{14}$$

so an infinitesimal change in enthalpy is

$$dH = dU + PdV + VdP \tag{15}$$

The change in energy is given by the thermodynamic identity (for constant particle number) as

$$dU = TdS - PdV \tag{16}$$

so

$$dH = TdS + VdP \qquad (17)$$

Along edge $1 \rightarrow 2$, the volume is (approximately; water does compress a little when the pressure is increased) constant, but what about the entropy change? If we assume that this compression is approximately adiabatic (I'm not 100% sure we can do this, but it seems like we're merely increasing the pressure and keeping the temperature and volume constant, so there doesn't appear to be much heat flow involved here), then the entropy is also roughly constant, so

$$dH \approx VdP \qquad (18)$$

The values given in Schroeder's tables are all for 1 kg of water, which occupies $V = 10^{-3}$ m^3 so for the numerical example given in Schroeder's book, where the pressure increases from 0.023 bar to 300 bars, the enthalpy change from 1 to 2 is

$$\Delta H_{1 \rightarrow 2} \approx 300 \times 10^5 \times 10^{-3} = 3 \times 10^4 \text{ J kg}^{-1} = 30 \text{ kJ kg}^{-1} \qquad (19)$$

Schroeder's example uses $P_1 = 0.023$ bar (giving $T_1 = 20°$ C), $P_2 = 300$ bars and $T_3 = 600°$ C. This changes the efficiency given by Schroeder to

$$e = 1 - \frac{1824 - 84}{3444 - 114} = 0.467 \qquad (20)$$

Which is slightly less than the value of 0.48 when we assume $H_1 = H_2$.

Example 3. We can see the effect of changing the key values in a steam engine by starting with the values given in the previous example. We'll use the approximation $H_2 \approx H_1$.

First, we reduce the maximum temperature to $500°$ C. This changes H_3 to (using Table 4.2):

$$H_3 = 3081 \text{ kJ kg}^{-1} \qquad (21)$$

To find H_4, we need to redo the interpolation from Example 1. The entropy at point 3 is

$$S_3 = 5.791 \text{ kJ K}^{-1}\text{kg}^{-1} \qquad (22)$$

We want a mixture of water (at a fraction x) and steam at 20°C that has the same entropy, so

$$\begin{align}
S_4 = S_3 &= xS_w + (1-x)S_s \tag{23}\\
5.791 &= 0.297x + 8.667(1-x) \tag{24}\\
x &= 0.344 \tag{25}
\end{align}$$

The resulting enthalpy is

$$\begin{align}
H_4 &= xH_w + (1-x)H_s \tag{26}\\
&= 0.344 \times 84 + 0.656 \times 2538 \tag{27}\\
&= 1694 \text{ kJ kg}^{-1} \tag{28}
\end{align}$$

with a modified efficiency of

$$e = 1 - \frac{1694 - 84}{3081 - 84} = 0.463 \tag{29}$$

Next, we reduce the maximum pressure to 100 bars (with the high temperature back to 600° C). Again, this affects H_3

$$H_3 = 3625 \text{ kJ kg}^{-1} \tag{30}$$

To find H_4, we need to redo the interpolation from Example 1. The entropy at point 3 is

$$S_3 = 6.903 \text{ kJ K}^{-1}\text{kg}^{-1} \tag{31}$$

We want a mixture of water (at a fraction x) and steam at 20°C that has the same entropy, so

$$\begin{align}
S_4 = S_3 &= xS_w + (1-x)S_s \tag{32}\\
6.903 &= 0.297x + 8.667(1-x) \tag{33}\\
x &= 0.211 \tag{34}
\end{align}$$

The resulting enthalpy is

$$\begin{align}
H_4 &= xH_w + (1-x)H_s \tag{35}\\
&= 0.211 \times 84 + 0.789 \times 2538 \tag{36}\\
&= 2020 \text{ kJ kg}^{-1} \tag{37}
\end{align}$$

with a modified efficiency of

$$e = 1 - \frac{2020 - 84}{3081 - 84} = 0.354 \tag{38}$$

Finally, with the original high temperature and pressure, we reduce the minimum temperature to 10° C. This gives

$$H_1 = 42 \text{ kJ kg}^{-1} \tag{39}$$

To find H_4, we need to redo the interpolation from Example 1. The entropy at point 3 is

$$S_3 = 6.233 \text{ kJ K}^{-1}\text{kg}^{-1} \tag{40}$$

We want a mixture of water (at a fraction x) and steam at 10°C that has the same entropy, so

$$
\begin{aligned}
S_4 = S_3 &= xS_w + (1-x)S_s & (41)\\
6.233 &= 0.151x + 8.901(1-x) & (42)\\
x &= 0.305 & (43)
\end{aligned}
$$

The resulting enthalpy is

$$
\begin{aligned}
H_4 &= xH_w + (1-x)H_s & (44)\\
&= 0.305 \times 42 + 0.695 \times 2520 & (45)\\
&= 1764 \text{ kJ kg}^{-1} & (46)
\end{aligned}
$$

The efficiency is

$$e = 1 - \frac{1764 - 42}{3444 - 42} = 0.494 \tag{47}$$

The first two changes produce an efficiency lower than the original of 0.48, but increasing the temperature range increases the efficiency slightly.

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