

So to burn 1kmol of methane requires 2.2 mol of O₂ (10% excess). Giving a air flow into the process of $\frac{2.2}{.21} = 10.48$ kmol/s and $\frac{2.2}{.21} * .79 = 8.28$ kmol/s of N₂. For a basis of 1 kmol/s of CH₄ entering the boiler, the flows in are then

Inflows: $n_{ch4,in} = 1, n_{O2,in} = 2.2, n_{N2,in} = 8.28$

Outflows

Carbon balance: $n_{CO2} = 1$

Hydrogen balance: $n_{H2O} = 2$

Oxygen Balance: $n_{O2} = 0.2$

Now we can use the first law to work out how much heat is released

$$Q = \overbrace{n_{CO2}h_{CO2} + n_{N2}h_{N2} + n_{O2}h_{O2} + n_{H2O}h_{H2O}}^{\text{Combustion exit at 250 C}} - \overbrace{n_{CH4}h_{ch4} - n_{O2}h_{O2} - n_{N2}n_{N2}}^{\text{inlet at 25 C}}$$

$$Q = (1 * -384162 + 8.28 * 6597 + .2 * 6808 + 2 * -234083) - (1 * -74600 - 2.2 * 0 - 8.28 * 0)$$

$$Q = -721743.24 \text{ kJ s}^{-1}$$

Therefore to produce 1MJ of heat requires

$$\frac{1000}{721743.24} = 0.00139 \text{ kmol CH}_4, \text{ or } 0.00139 * 16 = 0.02224 \text{ kg.}$$

Each kmol of methane produces 1kmol of CO₂ (molecular mass 44), giving the GWP as

$$0.00139 * 44 + 0.1 * 0.02224 * 21 = 0.1079 \text{ kg CO}_2 \text{ equivalent.} \quad [20\%]$$

(b) Allocating the burden for the CHP by energy content, between the heat and the power produced is attractive only because of its simplicity. In practice it does not make much sense, since the waste heat from the power station has little thermodynamic or monetary value when rejected at the temperature of the environment. I.e. it cannot be used for anything. If the heat was rejected at a higher temperature it might make more sense, but even then would not reflect the actual usefulness of the heat. It is also difficult for us to assess the value of the heat, since there is a cost associated with taking it from the power station, i.e. the power station efficiency will fall. The best way to account for this over change in GWP consider the CHP and the office block as part of the same system. The overall change in GWP can then be calculated. This avoids allocation. Allocation by substitution is functionally equivalent to expanding the system boundary, and in this case would be equivalent to taking the heat from the power station, dropping the power station efficiency and setting burden for the heat to be that required for someone else on the grid to make up the difference in electrical power output owing to the drop in efficiency. These latter two methods are always preferred over

the allocating by energy content as it describes what actually happens. The actual changes can be modelled, based on how the plant will run. Some assumption about the homogeneity of the market would be required, which for the case of electricity is usually ok when you have grid connection.

[15%]

(c) CHP uses 0.22 MW initially with no heat integration, efficiency of 0.557, producing 0.12 MW electricity and 0.1 MW heat. If heat is taken the efficiency falls, and so the thermal input to the CHP must increase from Q_1 to Q_2 , where Q_1 and Q_2 are linked by.

$$Q_2 \left(1 - \frac{373}{673}\right) = Q_1 \left(1 - \frac{298}{673}\right)$$

$$Q_2 = \frac{5 Q_1}{4} = 0.275 \text{ MW}$$

Heat available to the office is $0.275 * \left(1 - \left(1 - \frac{373}{673}\right)\right) = 0.153 \text{ MW}$, however only 0.1MW can be used.

Now consider two cases

Case 1: CHP reject heat at 25 C and office uses gas

$$\text{GWP} = 0.22 * 0.07 + 0.1 * 0.1079 = 0.02619 \text{ kg CO}_2/\text{s}$$

Case 2: CHP reject at 100 C and office uses no gas

$$\text{GWP} = 0.275 * 0.07 = 0.01925 \text{ kg CO}_2/\text{s}$$

Therefore the saving is $0.02619 - 0.01925 = 0.00694 \text{ kg CO}_2/\text{s} = 0.00694 * 3600 * 24 * 365 = 218859.8 \text{ kg/year}$. I.e. 219 tonnes of CO_2 per year.

[20%]

(d i) Now fuel input remains fixed at 2.2MW, the power station will reject heat and lose efficiency. The loss in electrical power will have to be made up by grid electricity.

Now consider two cases

Case 1: CHP reject heat at 25 C and produces 0.123 MW electricity and office uses gas

$$\text{Electricity} = 0.22 \left(1 - \frac{298}{673}\right)$$

$$\text{GWP} = 0.22 * 0.07 + 0.1 * 0.1079 = 0.02619 \text{ kg CO}_2/\text{s}$$

Case 2: CHP reject at 100 C and office uses no gas, grid supplies some electricity

$$\text{Electricity} = 0.22 \left(1 - \frac{373}{673}\right) = 0.098 \text{ MW}$$

So need an extra $0.123 - 0.098 = 0.025$ MW made up from the grid

$$\text{GWP} = 0.22 * 0.07 + 0.025 * \frac{0.53}{3.6} = 0.0191 \text{ kg CO}_2/\text{s}$$

Therefore the saving is $0.02619 - 0.0191 = 0.00709$ kg CO₂/s = $0.00709 * 3600 * 24 * 365 = 223590.24$ kg/year . I.e. 223 tonnes of CO₂ per year. [15%]

dii) The CHP runs at full power and produces electricity, the gas boiler is turned off. The heat pump uses grid electricity as it cannot tell the difference. Therefore can consider just the change in switching from the gas boiler

$$\text{Gas boiler: GWP} = 0.1 * 0.1079 \text{ kg CO}_2/\text{s} \frac{0.1}{3} * \frac{0.53}{3.6}$$

Heat pump: COP of 3 implies that we require .0333 MW of electricity. So $\text{GWP} = \frac{0.1}{3} * \frac{0.53}{3.6} = 0.00491$ kg CO₂

Therefore the saving is $0.1 * 0.1079 - 0.00491 = 0.00588$ kg CO₂/s or $0.00588 * 3600 * 24 * 365 = 185432$ kg CO₂ per year , i.e. 185 tonnes. [10%]

(e) Based on the figures, it looks like the heat pump wins in terms of overall saving. However, heat pumps are unlikely to always reach the projected COP, and are actually worse in winter when they have to pump heat across larger temperature difference. Given the nonlinearity of the COP with respect to temperature care must be taken with averages, in fact, to do the calculation correctly the heat and electricity requirements must be calculated on a moment by moment basis, then added up over the whole year. The CHP calculations can also suffer from this problem, in particular if the heat requirement is not steady. The GWP of grid electricity varies throughout the year, depending on the current grid mix. In winter when there is high demand, the GWP may be higher than that estimated using an average value. If more heat is required in winter, then using the average grid mix throughout the year in the above calculations will underestimate the GWP of the heat pump, and underestimate the cost of reducing the efficiency of the CHP by taking heat from it. Thus, there is an argument for using the current “average” grid mix in the calculations. An alternative view is to attempt to consider where each joule of electricity has come from, using a marginal analysis, i.e. when the heat pump is turn on (or extra grid electricity is needed) which power station must be turned on or throttle up to meet the extra demand. This is a complex analysis and varies throughout the year as the gas and coal prices vary.

2 (a)

First law

$$0 = \sum_{in} H_i - \sum_{out} H_j + \dot{Q} + \dot{W}$$

Here the summation represents the sum of total enthalpy flow over all input streams, i, and output streams, j.

Second law

$$0 = \sum_{in} S_i - \sum_{out} S_j + \frac{\dot{Q}}{T} + \dot{S}_{gen}$$

Combining

$$0 = \sum_{in} (H_i - T_e S_i) - \sum_{out} (H_j - T_e S_j) + \dot{Q} \left(1 - \frac{T_e}{T}\right) - T_e \dot{S}_{gen} + \dot{W}$$

$$0 = \sum_{in} (B_i) - \sum_{out} (B_j) + \dot{Q} \left(1 - \frac{T_e}{T}\right) - T_e \dot{S}_{gen} + \dot{W}$$

$$\sum_{out} (B_j) - \sum_{in} (B_i) = \Delta B = \dot{Q} \left(1 - \frac{T_e}{T}\right) - T_e \dot{S}_{gen} + \dot{W}$$

[10%]

(b) (i) Starting from

$$\sum_{out} (B_j) - \sum_{in} (B_i) = \Delta B = \dot{Q} \left(1 - \frac{T_e}{T}\right) - T_e \dot{S}_{gen} + \dot{W}$$

No work

$$\sum_{out} (B_j) - \sum_{in} (B_i) = \Delta B = \dot{Q} \left(1 - \frac{T_e}{T_{react}}\right) - T_e \dot{S}_{gen}$$

$$\sum_{out} H_j - \sum_{in} H_i = \Delta H = \dot{Q}$$

$$\Delta B = \Delta H \left(1 - \frac{T_e}{T_{react}}\right) - T_e \dot{S}_{gen}$$

$$\Delta H - T_e \Delta S = \Delta H \left(1 - \frac{T_e}{T_{react}}\right) - T_e \dot{S}_{gen}$$

$$-\Delta S = \Delta H \left(-\frac{1}{T_{react}} \right) - \dot{S}_{gen}$$

$$T_{react} = \left(\frac{\Delta H}{\Delta S} \right) + T_{react} \dot{S}_{gen}$$

$$\dot{S}_{gen} \geq 0$$

Hence

$$T_{react} \geq \left(\frac{\Delta H}{\Delta S} \right)$$

(note that some students might notice that this is equivalent to $\Delta G \leq 0$)

For this process,

$$\Delta H = 146616 + 0.5 * 160032 - (-26083) = 252715 \text{ kJ/kmol H}_2$$

$$\Delta S = 218 + 0.5 * 301 - (311) = 57.5 \text{ kJ/kmol H}_2/\text{K}$$

$$T_{react} > 252715/57.5 = 4395 \text{ K, hence feasible.}$$

[20%]

(ii) In the reactor, the exergy balance is

$$\sum_{out} (B_j) - \sum_{in} (B_i) = \Delta B = \dot{Q} \left(1 - \frac{T_e}{T_{react}} \right) + T_e \dot{S}_{gen}$$

$$\Delta H - T_e \Delta S = \Delta H \left(1 - \frac{T_e}{T_{react}} \right) + T_e \dot{S}_{gen}$$

$$252715 - 298 * 57.5 = 252715 * \left(1 - \frac{298}{4500} \right) - Loss$$

$$Loss = 235979.65 - 235580 = 400 \frac{\text{kJ}}{\text{kmol}}$$

The loss owing to finite temperature difference heat transfer is given by the difference in exergy between the heat added and that absorbed by the reactor

$$\Delta H \left(1 - \frac{T_e}{T_{col}} \right) - \Delta H \left(1 - \frac{T_e}{T_{react}} \right) = \Delta H \left(\frac{T_e}{T_{react}} - \frac{T_e}{T_{col}} \right)$$

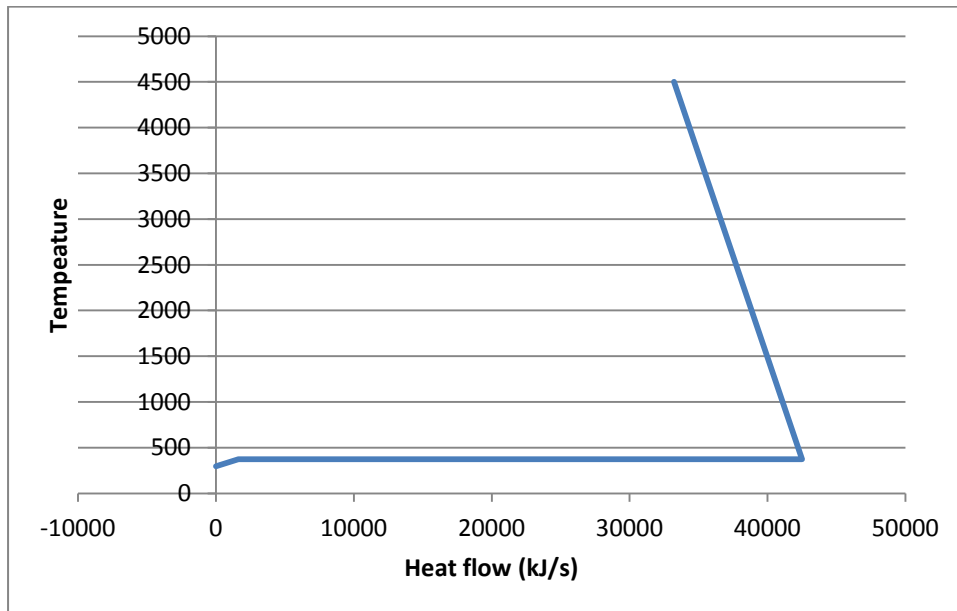
$$\Delta H \left(\frac{T_e}{T_{react}} - \frac{T_e}{T_{col}} \right) = 252715 \left(\frac{298}{4500} - \frac{298}{5000} \right) = 1673 \text{ kJ/kmol}$$

Both are quite small, though finite temperature difference accounts for the majority of irreversibility. The temperature is high and the temperature difference is small, so exergy destruction is small. For the reactor, the reaction is running very close to equilibrium. [20%]

(c) (i) Note that the water boils, but the data provided gives us the DH per mol. Must break the water preheat into three temperature intervals.

| Interval | | Sum of heat capacity flows | | Heat flows | | | Cumulative heat flow |
|------------|----------|----------------------------|-------|------------|---------|--------|----------------------|
| Start temp | End temp | hot | cold | Qhot | Qcold | Total | |
| 4500 | 373.15 | 53.95 | 51.70 | 222644 | -213358 | 9285 | 9285 |
| 373.15 | 373.15 | | | 0 | -40879 | -40879 | -31594 |
| 373.15 | 298 | 53.95 | 75.5 | 4054 | -5674 | -1619 | -33213 |
| | | | | 226698 | -259911 | | |

The first interval can dump heat to the 373.-373 interval, but this interval cannot dump heat below. The largest deficit is 33213 KJ, which must come from the hot utility. With the heat from the utility, the cascade looks like,



The pinch is at 298 K. Note that a sketch of this would be sufficient for the next part.

[20%]

(ii) Exergy supply from the hot source is

$$\int_0^{33213} 1 - \frac{298}{5000} dQ = 31234$$

Exergy absorbed by the cold streams heating up =

$$\begin{aligned} \int_0^{1619} 1 - \frac{298}{T_w} dQ + \int_{1619}^{33213} 1 - \frac{298}{373.15} dQ &= 1619 - 21.55 \int_{298}^{373} -\frac{298}{T} dT + 6362 \\ &= 1619 - 21.55 * 298 * \ln\left(\frac{373.15}{298}\right) + 6362 = 6536 \end{aligned}$$

(note that for water heating up $dQ = 21.55 dT$, since some of the water can be preheated by the hot gasses)

Therefore the loss in exergy is $31234 - 6536 = 24698 \frac{\text{kJ}}{\text{kmol}} H_2$ [20%]

(d) It is possible to split water into hydrogen and oxygen using work at a must lower temperature, e.g. using a electrochemical process. One feature of the proposed process is that the reactor does not reject heat. If some heat were added and then rejected at a lower temperature, then the criteria derived previously is not valid. Adding extra heat and rejecting it at lower temperature is equivalent to producing work, thus allowing the water splitting to proceed at a lower temperature. Many such processes have been proposed, including the sulphur iodine cycle which takes heat at ~ 1000 C. For example you could generate electricity, then use an electrolyser to split the water at room temperature. [10%]

3. Write brief notes on the following. It may be helpful to illustrate your answers with appropriate sketches.

(a) *The arguments for and against exploiting solar power in the UK, given that at present, it is possible for home owner to place solar panels on their roof and obtain a “feed-in” tariff for any electricity they generate.* [20%]

The feed in-tariff pays homeowners for every kWh they produce, and thus a strong incentive to install solar panels. This tariff reduces the economic pay-back time down to around ~10 years. In terms of energy payback, solar panels in the UK are marginal. The latitude of the UK means that the solar resource available isn't very large. Compared to the energy input required to make the panels, the energy generated over the expected lifetime is not hugely greater. One thing that the UK does have in its favour is the fact that electricity can be fed back into the grid, this reduces the balance of systems required to support a solar installation. From an energy balance point of view, a very larger proportion of the embodied energy in an off grid installation is associated with batteries etc... The Grid in the UK means that the intermittency of the solar power isn't a problem, especially a solar is never going to provide a large proportion of grid electricity (unlike wind). Thus there is an economic incentive, but the environmental benefit, whilst positive, is marginal and funds might be better spent on alternative improvements.

(b) *The mechanisms by which photosynthetic plants are able to exploit solar power and the limits this places on the efficiency of biomass as a renewable resource.* [40%]

Plants have evolved the ability to split water using light. The reaction takes place in the thylakoid membranes, and is somewhat analogous the way in a solar photovoltaic panel works, in that light is used to drive a charge separation. In green plants, light interacts with photosystem 2 and causes water to split into $2H^+$ and O_2 gas (i.e. oxygenic photosynthesis). The H^+ is inside the thylakoid lumen and increases the $[H^+]$ inside. The electron released from this reaction is give high energy/potential (from the photons) and is then passed between various molecules in the membrane down a potential gradient (the electron transport chain) to photosystem 1, using this energy to pump additional H^+ inside the lumen. At photosystem one, the electron is reexcited with light energy and passed down a potential gradient to $NADP^+$ reductase, where the electron is used to make NADPH by combining $NADP^+$ with H^+ (outside the lumen). NADPH is used elsewhere in the cell as a reducing agent. ATP is produced by letting the H^+ ions, which are in excess inside the lumen, bleed down a potential gradient via ATP synthase. The energy generated from this ion pump is used to convert ADP to ATP, an energy store used in the cell.

CO_2 is not fixed as the primary product of the light reactions. Instead, the ATP and NADPH are used in the calvin cycle to fix the CO_2 . These so called “dark” reactions take place independently of the light reaction. This cycle produces triose-phosphate, this is later converted into sugars and other cellular components. A key enzyme in this cycle is Rubisco.

This process is limited in the following ways

- Only photons of a high enough energy are able to excite electrons and cause light reactions. This means that only ~5% of solar radiation is photosynthetically active (400-700 nm).
- It takes ~12 (as a minimum) photosynthetically active photons to fix one carbon dioxide. This places an upper limit on photosynthetic efficiency of ~12%.

- Plants respire.
- Oxygen inhibits photosynthesis at low CO₂ concentrations by binding to Rubisco and causing photo-respiration.
- The calvin cycle is temperature dependant, hence temperature often limits plant growth, not light availability.
- High temperatures mean the plants loose too much water, so often close their stomato (pores used to gather CO₂) when it is hot. Hence they do not photosynthesis (note some plants can store CO₂, via carbon concentrating mechanisms for later use).
- Plants are greedy and often absorb more light than they can possibly use. This leads to photosynthetic efficiency decreasing with light level.

(c) *The key features of solar collectors used in solar thermal power system compared to those for domestic heating systems.*

The aim of domestic solar heating system is to produce hot water a < 100 C. A solar collector often has a maximum temperature which occurs when heat losses match the heat gain. Typically a solar collector consists of a “black” highly absorbing material, beneath a layer of glass or plastic which is transparent to visible light (and most of the solar spectrum), but absorbs infra-red (i.e. the radiation emitted by the hot collecting surface). In more advanced systems, the gap may even be under vacuum. For such a panel the rate of heat absorption is given by

$$P = I\tau_g\alpha_{absorber} - (C_1\delta T + C_2\delta T^2)$$

Where I is the insolation (W/m²) which is limited to ~1kW for a surface perpendicular to the sun. τ_g is the transmissivity of the glass cover to solar spectrum radiation, $\alpha_{absorber}$ is the absorbance of receiver to solar spectrum radiation. Heat losses and emission for the panel are difficult to model, hence this is often characterised using a polynomial fit in terms of the temperature difference from the surroundings. For a given solar collector the max temperature difference is given by P=0, and is clearly strongly dependant on I. Thus systems which only receive an isolation I are limited in the maximum temperature they can produce.

Solar thermal power stations require heat at as high a temperature as possible in order to give reasonable efficiencies. The energy usually being used to generated steam and then fed to steam turbine cycle. Thus top temperature limits efficiency. The limit on the temperature is removed by increasing the solar flux to the collector by concentrating the radiation. This is done using mirrors. Parabolic trough collectors put the absorber at the focuss of a parabolic trough. This has the added advantage that the trough can be moved throughout the day to maximise heat collection. A parabolic dish can move in two axis so can keep perpendicular to the sun throughout the day. However, it is difficult with a dish to integrate the steam cycle with the small collector as the focus (sterling engines have been proposed instead). In the most extreme case, solar towers consist of mirrors on the ground focussing sunlight onto a central collector; these can reach temperatures in excess of 1000 C. On characteristic of concentrating system is that only the direct component of the sunlight can be concentrated, thus they do not work well on cloudy days.