1 **(a)** **Define "Availability". How does "Exergy" differ from "Availability"?** [15%]

The availability change of a substance or a material stream, is defined as the maximum amount of work that could be extracted during the change. This is achieved by only exchanging heat with the environment at the temperature of the environment, and by using reversible processes. The absolute value of availability is meaningless without some reference state being imposed. Exergy is simply the availability, relative to the environment state, so that the change in exergy is equal to the change in availability. By including a reference state of the environment in the definition, absolute values of exergy can be stated, and these values represent the maximum amount of work a substance or stream could possibly do (i.e. Exergy = maximum work output when bringing substance into equilibrium with the environment).

(b) **(i)** **How much heat is absorbed by the power cycle per kmole of CO2 released?** [20%]

First need to calculate the composition of the stream leaving the combustion process, and the amount of air used.
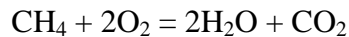
Carbon Balance:

$$n_{CO2} = n_{cH4,in} = 1 \ kmol \ s^{-1}$$

Hydrogen Balance:

$$4 = 2 * n_{H2o}$$

$$n_{H2o} = 2 \ kmol \ s^{-1}$$

$$CH_4 + 2O_2 = 2H_2O + CO_2$$

Stoichiometric combustion requires 2 kmols of Oxygen per kmol of methane, so the oxygen flow is $n_{O2,in} = 1.2 * 2 = 2.4 \ kmol \ s^{-1}$. This means the nitrogen flow is

$n_{N_2} = \frac{2.4}{0.21} * .79 \ kmol \ s^{-1} = 9.03 \ kmol \ s^{-1}$

Oxygen Balance: $n_{O2} = .2 * n_{O2,in} = .4 \ kmol \ s^{-1}$

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

$$Q = \overbrace{n_{co2}h_{CO2} + n_{N2}h_{N2} + n_{O2}h_{O2} + n_{H2O}h_{H2O}}^{Combustion \ exit \ at \ 250 \ C} - \overbrace{n_{CH4}h_{ch4} - n_{O2}h_{O2} - n_{N2} \ n_{N2}}^{inlet \ at \ 25 \ C}$$

$$Q = (1 * -384162 + 9.03 * 6597 + .4 * 6808 + 2 * -234083) - (1 * -74600 - 2.4 * 0 - 9.03 * 0)$$

$$Q = -715433.89 \ kJ \ s^{-1}$$

The negative sign implies this is a heat release (as expected). I.e. the heat release per kmole of CO_2 produced is
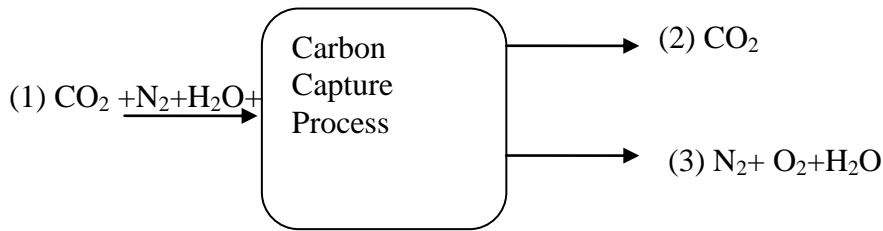
$$Q_1 = 715434 \ kJ \ kmol^{-1}$$

b) **(ii) How much work is generated per kmole of CO2 released?** [10%]

$$W_{total} = \eta_1 Q_1 + \eta_{Carnot}(1 - \eta_1)(Q_1)$$

$$W_{total} = Q_1(\eta_1 + (1 - \eta_1)(1 - T_e/T_1))$$

$$= Q_1(0.3 + 0.7(1 - 298/389)) = Q_1 0.464 = 331785 \ kJ \ kmol^{-1}$$

(c) **(i) If work, rather than heat were to be used to drive the capture plant, show that the minimum amount of work (W_{min}) per kmole of CO_2 needed to separate the flue gases, as shown in Fig.1, is about 8600 kJ $kmol^{-1}$?** **[15%]**

$(1)\ CO_2 + N_2 + H_2O + \longrightarrow$ Carbon Capture Process $\longrightarrow (2)\ CO_2$

$\longrightarrow (3)\ N_2 + O_2 + H_2O$

The minimum work needed is given by the availability change of the gases, i.e. in heat only rejected at the temperature of the environment, no irreversibililities. An availability balance for this kind of process gives

$$W_{min} + n_1\left(\underline{h}_1 - T_e\underline{s}_1\right) - n_2\left(\underline{h}_2 - T_e\underline{s}_2\right) - n_3\left(\underline{h}_3 - T_e\underline{s}_3\right) = 0$$

The separation process is isothermal, the gases are ideal, so there is no enthalpy change

$$W_{min} = T_e\left(n_1\underline{s}_1 - n_2\underline{s}_2 - n_3\underline{s}_3\right)$$

The molar entropy flow has two contributions, e.g.

$$n_1\underline{s}_1 = \sum_{species,k} n_{k,1}\left(\underline{s}_{pure,k} - Rln(y_{k,1})\right)$$

As the temperatures of the gases entering and leaving the control volume are the same, and no species react,

$$\sum_{species,k} n_{k,1}\left(\underline{s}_{pure,k}\right) = \sum_{species,k} n_{k,2}\left(\underline{s}_{pure,k}\right) + \sum_{species,k} n_{k,3}\left(\underline{s}_{pure,k}\right)$$

i.e. the pure contribution from the pure component part of the entropy cancels out. All the remains are the terms due to mixing.

$$\frac{W_{min}}{T_e} = \sum_{species,k} n_{k,1}\left(-Rln(y_{k,1})\right) - \sum_{species,k} n_{k,2}\left(-Rln(y_{k,2})\right) - \sum_{species,k} n_{k,3}\left(-Rln(y_{k,3})\right)$$

$$\frac{W_{min}}{RT_e} = \sum_{species,k} n_{k,1}\left(-ln(y_{k,1})\right) - \sum_{species,k} n_{k,2}\left(-ln(y_{k,2})\right) - \sum_{species,k} n_{k,3}\left(-ln(y_{k,3})\right)$$

Need to add up the molar flows * -ln(mol fraction) for each stream. Note that for the pure $CO2$ this would be zero.

	Stream 1			Stream 3		
	Molar flow (kmol/s)	Mole Fraction, y	-LN(mole fraction)*molar flow	Molar flow (kmol/s)	Mole Fraction, y	-LN(mole fraction)*molar flow
H2O	2	0.16	3.65	2	0.17	3.49
CO_2	1	0.08	2.52	0		
N_2	9.03	0.73	2.89	9.03	0.79	2.13
O_2	0.4	0.03	1.37	0.4	0.03	1.34
Total	12.43		10.43	11.43		6.96

Then

$$\frac{W_{min}}{RT_e} = 10.43 - 6.96 = 3.48$$

$$W_{min} = 3.48 * 8.318 * 298 = 8626 \; kJ \; kmol^{-1}$$

Notes on the answer: note that without rounding errors the answer is $8618 \; kJ \; kmol^{-1}$. It can also be shown that that the minimum possible separation work is

$$\frac{W_{sep}}{n_{CO_2}} = RT_e \left(ln\left(\frac{1}{1 - y_{CO2}}\right)\frac{(1 - y_{CO2})}{y_{CO2}} - ln(y_{CO_2}) \right)$$

c) (ii) **Show that, if the capture process is assumed to be reversible, the heat which must be diverted from the power cycle, Q_{cc}, is given by**

$$Q_{cc} = \frac{T_2 W_{min}}{T_e \left(1 - \dfrac{T_2}{T_1}\right)}$$

and calculate the loss in electrical work output caused by the addition of the carbon capture plant. [20%]

An availability balance over the proposed process gives,

$$n_1(h_1 - T_e s_1) - n_2(h_2 - T_e s_2) - n_3(h_3 - T_e s_3) + Q_{cc}\left(1 - \frac{T_e}{T_1}\right) - Q_{cc}\left(1 - \frac{T_e}{T_2}\right) = 0$$

(where it is noted that the heat rejected by the carbon capture process is the same as the heat it absorbs, since there is no change in enthalpy of the gas streams).

$$n_1(h_1 - T_e s_1) - n_2(h_2 - T_e s_2) - n_3(h_3 - T_e s_3) + Q_{cc}\left(\frac{T_e}{T_2} - \frac{T_e}{T_1}\right) = 0$$

Comparing with the expression used to calculate the minimum work,

$$W_{min} + n_1(h_1 - T_e s_1) - n_2(h_2 - T_e s_2) - n_3(h_3 - T_e s_3) = 0$$

Gives

$$-W_{min} + Q_{cc}\left(\frac{T_e}{T_2} - \frac{T_e}{T_1}\right) = 0$$

Therefore

$$Q_{cc} = \frac{W_{min}}{\left(\dfrac{T_e}{T_2} - \dfrac{T_e}{T_1}\right)} \; or \; Q_{cc} = \frac{T_2 W_{min}}{T_e \left(1 - \dfrac{T_2}{T_1}\right)}$$

When the power station is fitted with the carbon capture plant, the total power output is given by

$$W_{total} = \eta_1 Q_1 + \eta_{Carnot}((1 - \eta_1)Q_1 - Q_{cc})$$

i.e. there is loss in power output of $\eta_{Carnot}(Q_{cc})$

$$Q_{cc} = \frac{358 * 8626}{298\left(1 - \frac{358}{389}\right)} = 130036$$

Then the work penalty is $\eta_{Carnot}(Q_{cc}) = \left(1 - \frac{298}{389}\right) * 130036 = 30419 \ kJ \ kmol^{-1}$

(iii) **If the heat rejected by the carbon capture plant could be recovered and used to generate work, what is the minimum energy penalty possible for the system shown? Comment on your answer in light of your answer to (c) (iii).** [20%]

If you could recover the energy rejected by the capture plant, the max work which could be generated from the recovered heat would be.

$$Q_{cc}\left(1 - \frac{T_e}{T_2}\right)$$

Therefore the energy penalty would be

$$Power \ loss = Q_{cc}\left(1 - \frac{T_e}{T}\right) - Q_{cc}\left(1 - \frac{T_e}{T_2}\right)$$

$$Power \ loss = Q_{cc}\left(\frac{T_e}{T_2} - \frac{T_e}{T}\right)$$

Which can be shown to be equal to Wmin – this is of course and obvious answer, since it represents the minimum amount of exergy loss in the process.

$$Power \ loss = Wmin$$

$$Power \ loss = Q_{cc}\left(\frac{T_e}{T_2} - \frac{T_e}{T}\right) = Wmin$$

The energy penalty from part (iii) was nearly 8% of the total (unabated power station output). The minimum power loss calculated from the above expression is much lower. However, recovering the heat from such a low temperature source is very difficult and would require very large heat exchangers, and thus probably not economic.

Examiner's comment:

Most candidates were able to do part (a) , which was very straight forward. The material and energy balances for part (b) were also generally well done. Part (c) proved to be very difficult for most the students. Most realised that minimum work was found by an availability balance, and noticed that the enthalpy change of the gases was zero. Very few were able to give a convincing proof of the expression for energy penalty (though the better students were able to complete this part).

2   (a)   (i)   When performing a lifecycle assessment (LCA), why are reference systems used?   [10%]

A reference system is used for comparison. Obtaining absolute values of the environmental burden can be difficult, whilst the change in environmental burden is more easily calculated, and in some cases more relevant. For example, for biofuels, the environmental impact should take into account the change in land use. In this case the reference system burden is that associated with the use of the land, if it wasn't used to grow the biofuel. Another use of reference system is to allow savings to be calculated, e.g. if a biofuel is used to displace petrol for transport, the LCA for the biofuel will take indicate a positive energy input and may not be particularly useful. If this is burden is compared with that which would have arisen if petrol was used, the difference allows meaningful comparisons to be made.

(ii)   Briefly describe when the problem of allocation arises in LCA, and the method of allocation by substitution.   [20%]

When there are co-products produced by the system, it becomes necessary to apportion the total environmental burden between these co-products. Ideally, this should be based on physical relationships, but this is not usually possible. Simply proportioning by price or energy content is one way forward, but somewhat arbitrary. The preferred method of allocation is by substitution (which is formally equivalent to extending the system boundary to avoid allocation). Credits are assigned to each co-product, equal in value to the burden which would have arisen if these products had been produced elsewhere in the market place. I.e. by burden of a co-product is equal to that saved by preventing someone else from producing the same good. This is easy when the co-product is itself produced as a primary product elsewhere.

b)   A business proposes to reduce its environmental burden by using biodiesel (with a calorific value of 30 MJ kg^{-1}) to fire the existing boiler in its premises (which currently runs on natural gas). Taking a functional unit as 1 GJ of heat delivered to the premises (and using the data below) calculate

(i)   The overall saving in global warming potential (GWP).   [20%]

(ii)   The overall saving in fossil energy requirement   [10%]

(i)GWP calculation (for a functional unit of 1000 MJ of heat)

1000 MJ of heat requires $\frac{1000}{30} = 33.3$ kg of the biodiesel.

Direct production of GWP is $\frac{1000}{30} * 3 = $ <mark>+100</mark> kg CO_2equivalent

Now we consider credits for the co-products. The co-products can displace $30 * \frac{1000}{30} = 1000$ MJ of heat, which would otherwise have come from burning coal in the power-station. The coal combustion produces $\frac{}{4}$ kg of CO_2 per MJ of heat, so the saving the saving in CO2 is $\frac{1000}{4} = $ <mark>250 kg</mark> CO2equivalent.

For each kg of biodiesel produced the amount of CO2 release due to land use change is

$$6000 \frac{kgCO_2}{ha \times yr} \times \frac{0.8}{1000} \frac{ha \times yr}{kg fuel} = 6000 \times \frac{0.8}{1000} \frac{kgCO_2}{kg fuel}$$

However, only half of the biodiesel has come from a crop grown on virgin grass land, so the Co2 burdens is

$$6000 \times \frac{0.8}{1000} \times \frac{1000}{30} \times \frac{1}{2} = +80 \ kg \ CO2 equivalent$$

Comparing with the reference system of burning gas in the boiler. Producing 1000 MJ of heat would result in $0.06 * 1000 = 60$ kg of CO2 released.

Therefore the overall GWP is

Direct	100
Converting the land	80
Displacing coal	-250
Comparing with reference system burning natural gas	-60
TOTAL	-130 kg CO2 equivalent per 1000 MJ

The total saving is 130 kg CO2 per 1000 MJ per year, or 3.9 kg of CO2 per kg of biodiesel.

(ii)Fossil energy (for a functional unit of 1000 MJ of heat delivered)

1000 MJ of heat requires $\frac{1000}{30} = 33.3$ kg of the biodiesel. The direct energy input is $20 * \frac{1000}{30} = 667$ MJ of fossil energy.

For each kg of biodesieel produced the amount of energy you were previously using to to maintain the fallow land

$$6000 \frac{MJ}{ha \times yr} \times \frac{0.8}{1000} \frac{ha \times yr}{kg fuel} = 6000 \times \frac{0.8}{1000} \frac{MJ}{kg fuel}$$

However, only half of the biodiesel has come from a crop grown previously fallow land so the SAVING in energy is

$$6000 \times \frac{0.8}{1000} \times \frac{1000}{30} \times \frac{1}{2} = 80 \ MJ$$

Now we consider credits for the co-products. The co-products can displace $30 * \frac{1000}{30} = 1000$ MJ of heat, which would otherwise have come from burning coal in the power-station, giving a credit of 1000 MJ.

The reference system which burns gas, uses 1000 MJ. Therefore the overall LCA input of fossil energy is

$$667 - 80 - 1000 - 1000 = -1413 \text{ MJ}$$

Therefore the overall saving in fossil energy requirement is 1413 MJ per 1000 MJ per year, or 42 MJ per kg of biodiesel.

c) In light of your answers to (b) provide a critical assessment of the proposal and suggest whether or not the proposal should go ahead. You should also consider the wider issues that arise when using biofuels, and suggest how, if the aim was simply to reduce CO_2 emissions, the proposal could be modified. **[40%]**

Whilst the overall Lifecyle assessment looks favourable, giving both a saving in GWP and fossil energy, it is instructive to look at how those savings are made.

Burning the gas in the boiler results in a 60 kg of CO_2 released, which is less than the CO_2 released just to produce the bio-fuel. In fact, the only reason a CO_2 saving exists is because the co-products have such a high calorific value, and the energy they produce is used to displace a fuel with a very high CO_2 footprint (i.e. Coal). It would actually be more sensible to burn the bio-diesel in the power station, since for every MJ of heat provided by the biodiesel this would save 0.25 kg of CO_2, compared with 0.06 if it was used in the boiler. This would increase the CO_2 saving by 1000*(.19) = 190 kg of CO_2 saving, compared to that calculated above.

It is therefore clear, that when the system as whole is considered, burning the biodiesel in the factory is a very poor idea. The fuel should instead be used to displace the highest CO_2 foot print fuel, i.e. the coal. However, burning the biodiesel in the PowerStation is still not optimal, since there are significant inputs required to produce the biodiesel. Biomass can be co-fired directly without this processing. Approximately half of the input of energy for the biodiesel is related to processing the fuel (the other half is related to the agriculture). Thus, the greatest fossil fuel saving, and lowest GWP when the biomass crop is simply combusted in the power-station.

It is worth noting that there might be some argument for using the biodiesel as a transport fuel, since you cannot use processes biomass as transport fuel, but using it for heating does not make sense.

In terms of the wider issues, the amount of land needed to grow the crop is an issue. Whilst on a small scale, it probably isn't a worry, if a large proportion of the UK's energy came from biomass, there would simply not be enough land. The use of agricultural land to produce fuel also poses a moral dilemma, since this land could have been used to grow food. Given that there are people in the world without enough to eat, using food for fuel is questionable. Biofuels have already had some affect on food prices. An alternative, but equally undesirable outcome is to bring virgin land into production. Already, large areas of tropical rainforest in South East Asia have been converted to agricultural land, and apart from the large CO_2 burden associated with land use change, this also threatens bio-diversity. If you are going to grow a biofuel crop, then the land use must be minimised by maximising yields of crops. First generation biofuels have a very poor yield as only part of the crop is used, and benefits are only possible when the co-products are fully utilised. Second generation fuels may use more of the crop. However, this still will not produce the benefits of simply burning the biomass in a power station to displace coal.

Examiner's comment:

Most candidates were able to give a reasonable explanation to part (a) of the question about reference systems and allocation methods. One or two students totally missed the point, giving totally spurious explanations. The calculation in part (b) where students were required to use allocation by substitution separated the stronger students, with a few students able to do everything correctly (most were able to make some attempt). One or two candidates did not seem to understand the difference between embodied energy and calorific value. The proposal in the question was not very sensible, using a high value liquid biofuel to displace relatively clean gas, yet when asked to comment on whether the proposal should go ahead very few pointed this out. Many of the students correctly spotted that most of the energy benefit came from the co-products, and that more environmental benefit could be gained by burning everything in the power station. Students correctly identified land use and competition for food as important issues. In hindsight, the wording of the question could have been ambiguous with the phrase "biodiesel from rapeseed (with a calorific value of 30 MJ/kg)" perhaps a little misleading (i.e. the calorific value was that of biodiesel). However, this did not appear to have caused any problems with students correctly taking the calorific value of the biodiesel as 30 MJ/kg.

3.   (a)   Describe the   principles which govern the operation of solar photovoltaic panel, and with reference to a suitable equivalent circuit explain the function of a Maximum Power Point Tracker.   **[25%]**

A solar cell consist of p-n junction in a semi conducting material. Where the n and p materials meet, the holes and free electrons in the semi-conductor cancel out, creating a region depleted of charge, and setting up a potential gradient across the junction. When exoposed to light, photons with an energy E=hv greater than the band gap of the material, can cause the electrons in the bonds to be promoted to the conduction band, creating a mobile "hole" and free electron. If this process happens in the region depleted of charge, the holes will flow down the potential gradient and the electrons up it, effectively acting as a current pump. Thus a solar cell is effectively a diode, which is exposed to light. The equivalent circuit for the solar cell is
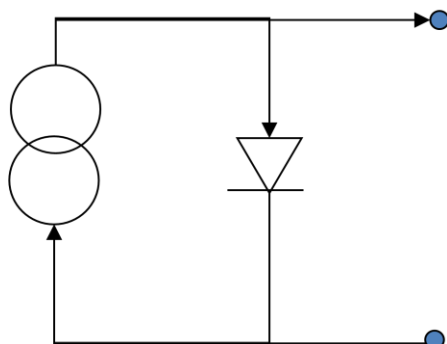
Which has the following characteristics
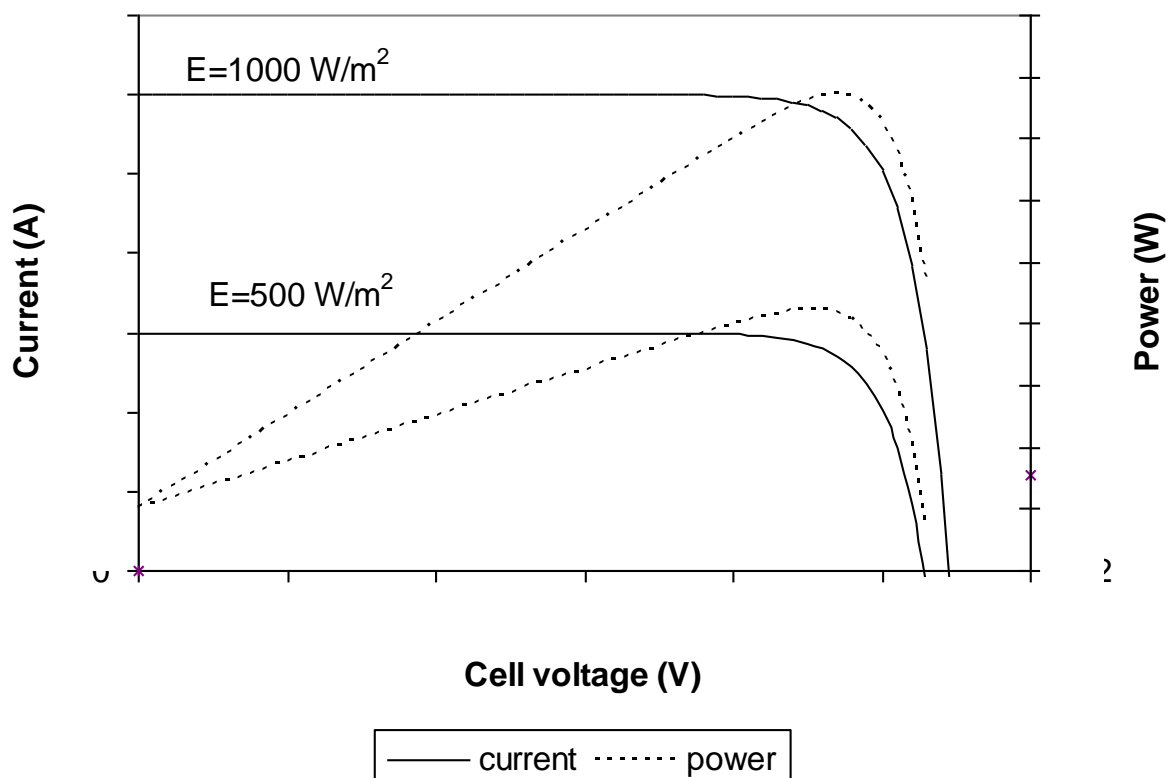
The voltage seen by the cell depends on the load attached. As the load voltage increases the power drawn goes up, however some current is diverted via the diode. When the voltage reaches a certain threshold, the current through the diode dominates, and the current through the load falls, reducing the amount of power which can be drawn. There is a very sharp drop off in power, after the maximum. A maximum power point tracker is a device which sits between the load and the cell, and keeps the cell voltage at its optimum to ensure maximum power is generated.

(b) Write brief notes to explain following points to an engineering colleague who is not versed in IC engine technology. You may wish to illustrate your arguments with suitable diagrams where appropriate

> **(i)   Why the crank angle over which combustion takes place is roughly independent of engine speed in a spark ignition engine.   [10%]**

The combustion occurs at a turbulent flame front and the burn rate depends on the area of the flame front (locally burning at the laminar rate). The kinetic energy of the gas in the entering the engine is initially stored in the swirling motion, but rapidly breaks up into turbulence before the ignition. As the engine speed increases, the kinetic energy in the swirling gases increases, increasing the amount of turbulent mixing. Thus, higher speed engines have fater burning rate, due to having more rapid turbulent mixing. In fact, the rate of flame wrinkling is roughly proportional to engine speed, so burn rate is proportional to engine speed.

> **(ii)   Why a throttle is needed to vary the load of a spark ignition engine.   [15%]**

In a gasoline engine, there is a premixed air/fuel mixture. Spark ignition engines must operate with a nearly stoichiometric air to fuel ratio. Failure to do so will result in poor combustion characteristics (e.g. the fuel won't ignite). Away from stiochometry the flame kernels near the spark will extinguish rather than grow. Thus, when operating at part load, the amount of fuel injected into the engine is restricted, and the air flow to the cylinders must be throttled to ensure the correct air to fuel ratio. In addition, the three way catalyst on the exhaust only works when the combustion is very close to stoichiometric. This throttling reduces the efficiency considerably.

> **(i)   Why the compression ratio of a spark ignition engine is limited.   [15%]**

In addition, the compression ratio of spark ignition engines is restricted by the fact that the fuel may "explode" before the flame front has had chance to reach the unburned fuel, leading to knocking. When the cylinder begins to compress the air/fuel mixture, a chain of events begins which will eventually lead to the fuel spontaneously igniting after an induction time (which is controlled by the chemistry). Ideally, all of the fuel will burn in a more controlled manner as the flame front moves from the spark through the cylinder. If the cylinder is too large, some regions of the mixture have time to spontaneously ignite, before the flame can reach them. Thus, the compression ratio of an engine is limited, and a spark ignition engine can only be made bigger by scaling up the number of cylinders, rather than using larger cylinders. Cylinders are typically as large as possible, whilst still preventing knocking, whilst having the lowest surface are to volume ratio to minimise heat losses (heat transfer scales with surface area, whilst work output scales with cylinder volume).

(ii)   With reference to your answers to (ii) and (iii), the factors which affect the relative efficiency of diesel vs spark ignition engines.   [15%]

In contrast to a spark ignition engine, in a diesel engine, there is no need to throttle the air flow, since the combustion process does not rely on flame front moving throughout the cylinder. Instead, combustion takes place in a jet of fuel droplets which are sprayed into the engine. The combustion is spontaneous and limited by the rate of fuel evaporation. The requirement that the air to fuel ratio be close to stiochiometric is removed. This requires fuels with different ignition characteristics to gasoline engines. Removing the throttle means that a diesel engine can operate at a higher efficiency at part load compared to the same size gasoline engine. Since, pre-ignition and knocking are no longer an issue, diesel engines can be made much larger and have a higher compression ratio. This increases the cycle efficiency, and means that very cylinders are possible, where the surface area to volume ratio in the cylinder is very low.
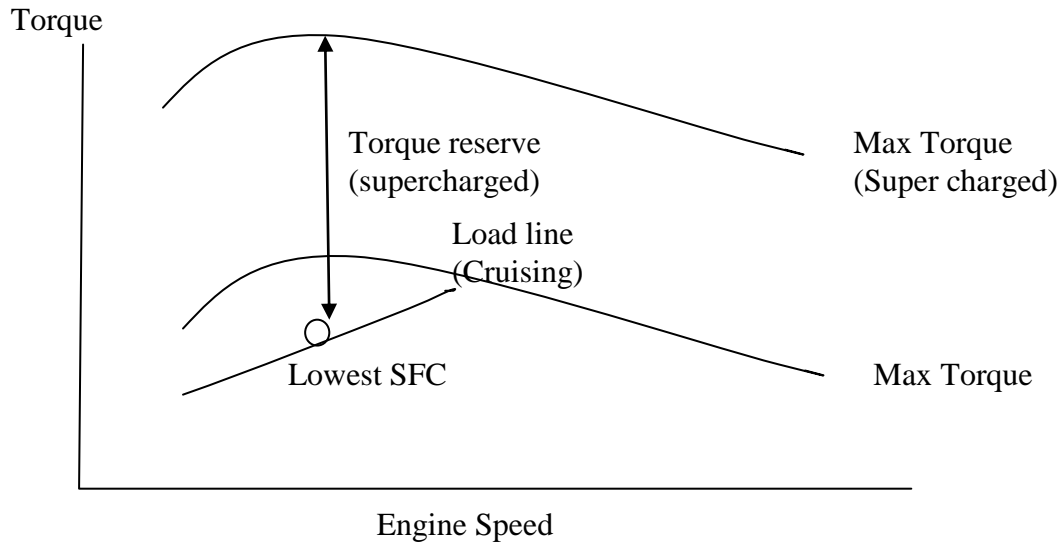
(i)   How turbo-charging an internal combustion engine can improve the specific fuel consumption, but may introduce other problems.   [20%]

Engines are typically sized to give a performance which allows rapid acceleration. This means that under normal "cruising" conditions the engine is only operating a part load, under conditions which are far from the most fuel efficient operating point. This gives the engine a "torque reserve" for rapid acceleration. A smaller engine, by contrast would not have such a torque reserve and would be unacceptable for the consumer, but would not need to operate at part load. This can be seen from the engine characteristics give below.
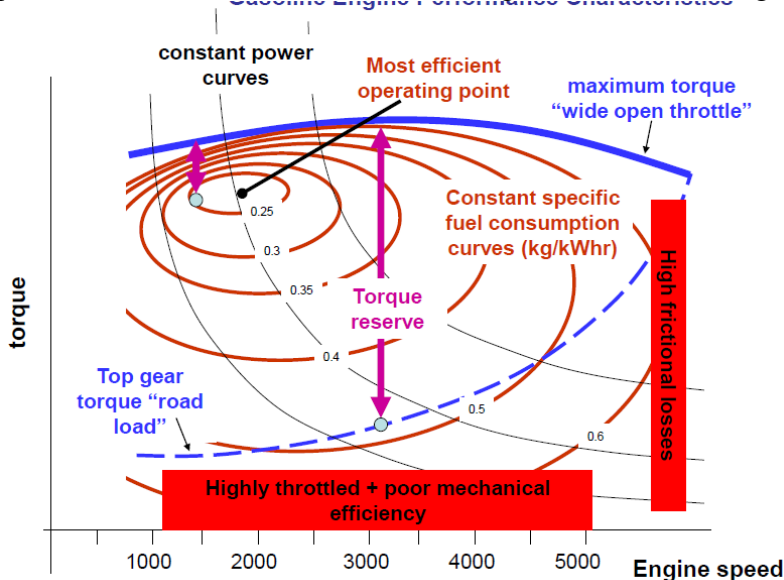
The power output of an engine is limited by the amount of air which can admitted to the cylinder (not the amount of fuel). Thus a smaller engine can be made more powerful by compressing air as it enters the engine (more moles of gas per unit volume at a higher pressure). This is achieved using a small compressor, on the air inlet (i.e. a turbo charger).

The effect of supercharging the engine is shown below.

Torque

Torque reserve
(supercharged)

Max Torque
(Super charged)

Load line
(Cruising)

Lowest SFC

Max Torque

Engine Speed

Thus, a small engine is ideally suited to most driving conditions, and when acceleration is needed, the supercharger changes the characteristics of the engine to those of a larger engine.

The disadvantages are:
- additional cost and complexity of the engine
- Applying this to petrol engines can be difficult as the amount of turbocharging is limited by knocking.
- The time delay needed to spin up the turbo can result in an unacceptable lag when accelerating. This can also lead to worse emissions as there may not be sufficient fuel air in the cylinder to combust the additional fuel during the transient.
- Sizing a turbocharger for all engine conditions is difficult. A small turbo will give a good boost a low rpm and low air flows, but will provide too much boost at high rpm. A large turbo has the opposite problem.

Examiner's comment:

Mostly well answered. One of two of the weaker candidates seemed to have little understanding of either topic addressed by the question. Most students were able to describe how a solar PV panel function. Most students had some understanding of how engines work, and the factors which determine engine design (e.g. knock and spark ignition vs. compression ignition).