PART IIA 2007
3A5 Thermodynamics and power generation
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ENGINEERING TRIPOS PART IIA 2007

MODULE 3A5 – THERMODYNAMICS AND POWER GENERATION

SOLUTIONS TO TRIPOS QUESTIONS

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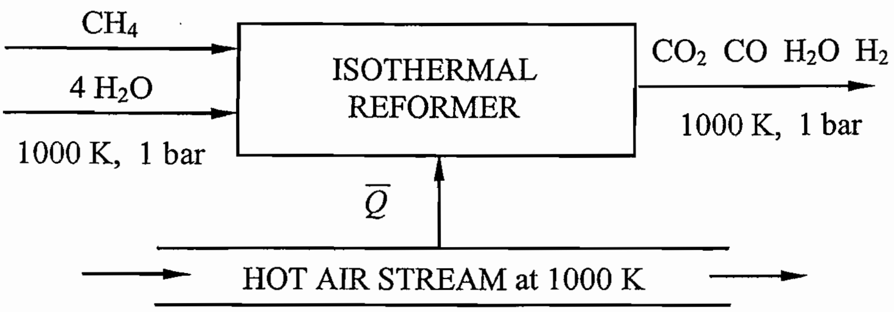
Q1



(a) The chemical reaction is :

$$CH_4 + 4\,H_2O \rightarrow a\,CO_2 + b\,CO + c\,H_2O + d\,H_2$$

Conservation of atomic C : $a + b = 1$ (i)

Conservation of atomic H : $2c + 2d = 12$ (ii)

Conservation of atomic O : $2a + b + c = 4$ (iii)

The equilibrium equation for the shift reaction (reaction 8 in the Data Book) is,

$$\left(\frac{p_{CO}}{p_0}\right)^{-1}\left(\frac{p_{H2O}}{p_0}\right)^{-1}\left(\frac{p_{CO2}}{p_0}\right)^{+1}\left(\frac{p_{H2}}{p_0}\right)^{+1} = K_{p8}(T)$$

where p_0 is standard pressure (1 bar). From the Data Book, $\ln(K_{p8}) = 0.366$, so $K_{p8} = 1.4419$. The partial pressures are,

$$p_{CO2} = \frac{a}{n}p, \quad p_{CO} = \frac{b}{n}p, \quad p_{H2O} = \frac{c}{n}p, \quad p_{H2} = \frac{d}{n}p,$$

where p is the actual mixture pressure (1 bar) and $n = a + b + c + d$. Hence,

$$\frac{ad}{bc} = K_{p8}(T) = 1.4419 \qquad \text{(iv)}$$

Assuming $a = 0.5063$ kmol as given in the question, eqs. (i) – (iii) give,

For CO : $b = 1 - a = 0.4937$ kmol

For H_2O : $c = 4 - b - 2a = 2.4937$ kmol

For H_2 : $d = 6 - c = 3.5063$ kmol

Substituting into the LHS of eq. (iv) gives,

$$\frac{ad}{bc} = \frac{0.5063\times3.5063}{0.4937\times2.4937} = 1.4419$$

which is in agreement with the RHS of eq. (4). [40 %]

(b) The SFEE applied to the reformer gives (per kmol CH_4 supplied),

$$\overline{Q} = (a\overline{h}_{CO2} + b\overline{h}_{CO} + c\overline{h}_{H2O} + d\overline{h}_{H2}) - (\overline{h}_{CH4} + 4\overline{h}_{H2O})$$

$$= 0.5063\overline{h}_{CO2} + 0.4937\overline{h}_{CO} - 1.5063\overline{h}_{H2O} + 3.5063\overline{h}_{H2} - \overline{h}_{CH4}$$

where all molar enthalpies are evaluated at 1000 K. By definition,

$$[\Delta\overline{H}^0_{1000}]_{ref} = \overline{h}_{CO} + 3\overline{h}_{H2} - \overline{h}_{CH4} - \overline{h}_{H2O}$$

$$[\Delta\overline{H}^0_{1000}]_{shift} = \overline{h}_{CO2} + \overline{h}_{H2} - \overline{h}_{CO} - \overline{h}_{H2O}$$

Hence,

$$[\Delta\overline{H}^0_{1000}]_{ref} + 0.5063[\Delta\overline{H}^0_{1000}]_{shift} =$$

$$0.5063\overline{h}_{CO2} + 0.4937\overline{h}_{CO} + 3.5063\overline{h}_{H2} - \overline{h}_{CH4} - 1.5063\overline{h}_{H2O} = \overline{Q}$$ [20 %]

(c) The SFSE applied to the reformer gives (per kmol CH_4 supplied),

$$\Delta\overline{S}_{irrev} + \frac{\overline{Q}}{T} = a\overline{s}_{CO2} + b\overline{s}_{CO} + c\overline{s}_{H2O} + d\overline{s}_{H2} - \overline{s}_{CH4} - 4\overline{s}_{H2O}$$

where all molar entropies are evaluated at 1000 K and 1 bar (as instructed in the question). Proceeding as for (b) but replacing *h* with *s* gives,

$$\Delta\overline{S}_{irrev} = [\Delta\overline{S}^0_{1000}]_{ref} + 0.5063[\Delta\overline{S}^0_{1000}]_{shift} - \frac{\overline{Q}}{T}$$ [20 %]

(d) Evaluating $\overline{Q}$ and $\Delta\overline{S}_{irrev}$ gives,

$$\overline{Q} = 225.70 + 0.5063\times(-34.74) = 208.11 \text{ MJ/kmol } CH_4$$

$$\Delta\overline{S}_{irrev} = 0.2529 + 0.5063\times(-0.0317) - \frac{208.11}{1000} = 0.02874 \text{ MJ/(kmol } CH_4\text{) K}$$

If the environment is at $T_0 = 298.15$ K, then the lost work due to irreversible entropy creation in the reformer is $T_0\Delta\overline{S}_{irrev}$. Hence the maximum rational efficiency of a power plant supplied by methane at 25 °C and 1 bar is,

$$[\eta_{rational}]_{max} = 1 - \frac{T_0\,\Delta\overline{S}_{irrev}}{[-\Delta G^0_{298}]} = 1 - \frac{298.15\times0.02874}{800.70} = 0.9893 \equiv 98.93\ \%$$ [20 %]

This shows that the steam reforming of methane is a highly efficient conversion process.

Q2 (a) (i) From the definition $f = u - Ts$, we have $df = du - Tds - sdT$. Combining this with the Gibbs equation $Tds = du + pdv$ gives,

$$df = -pdv - sdT$$

Hence :

$$s = -\left(\frac{\partial f}{\partial T}\right)_v$$ [10 %]

(ii) From the given characteristic equation of state,

$$f = f_0(T) - RT\left[\ln(v) - \frac{B(T)}{v}\right]$$

we obtain,

$$s = -\left(\frac{\partial f}{\partial T}\right)_v = -\frac{df_0}{dT} + R\left[\ln(v) - \frac{B}{v}\right] - \frac{RT}{v}\frac{dB}{dT}$$

Hence,

$$u = f + Ts = f_0 - RT\left[\ln(v) - \frac{B}{v}\right] - T\frac{df_0}{dT} + RT\left[\ln(v) - \frac{B}{v}\right] - \frac{RT^2}{v}\frac{dB}{dT}$$

$$= f_0 - T\frac{df_0}{dT} - \frac{RT^2}{v}\frac{dB}{dT}$$ [25 %]

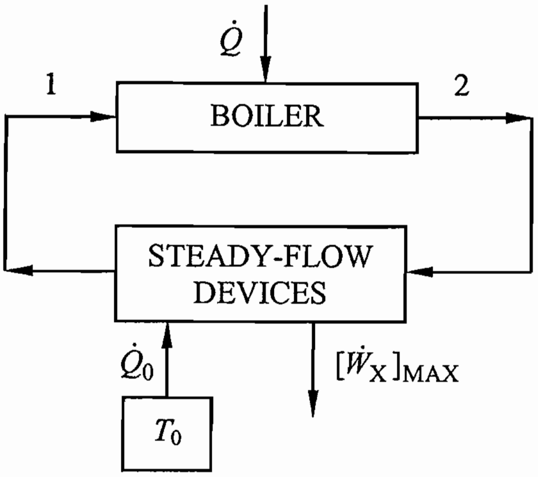
By definition,

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v = -T\frac{d^2 f_0}{dT^2} - \frac{R}{v}\frac{d}{dT}\left[T^2\frac{dB}{dT}\right]$$

Hence, the condition to be fulfilled in order that c_v is not a function of v is,

$$\frac{d}{dT}\left[T^2\frac{dB}{dT}\right] = 0$$ [15 %]

(b)



(i) From availability theory,

$$[\dot{W}_X]_{MAX} = \dot{m}(b_2 - b_1) = \dot{m}[(h_2 - T_0 s_2) - (h_1 - T_0 s_1)] \qquad [15\ \%]$$

(ii) This equation can be expressed as,

$$[\dot{W}_X]_{max} = \dot{m}\int_1^2 dh - \dot{m}T_0 \int_1^2 ds$$

Introducing $Tds = dh - vdp$ gives,

$$[\dot{W}_X]_{max} = \dot{m}\int_1^2 \left(1 - \frac{T_0}{T}\right) dh + \dot{m}\int_1^2 \frac{T_0}{T} v\,dp$$

From the SFEE (neglecting changes in KE and PE) $d\dot{Q} = \dot{m}\,dh$. Hence,

$$[\dot{W}_X]_{max} = \int_1^2 \left(1 - \frac{T_0}{T}\right) d\dot{Q} - \left(-\dot{m}\int_1^2 \frac{T_0}{T} v\,dp\right) \qquad [25\ \%]$$

$$\int_1^2 \left(1 - \frac{T_0}{T}\right) d\dot{Q} = \dot{E}_Q$$

This is the exergy supply rate to the boiler (*i.e.*, the power potential of the heat transferred to the steam).

$$-\dot{m}\int_1^2 \frac{T_0}{T} v\,dp = T_0\,\Delta\dot{S}_{irrev}$$

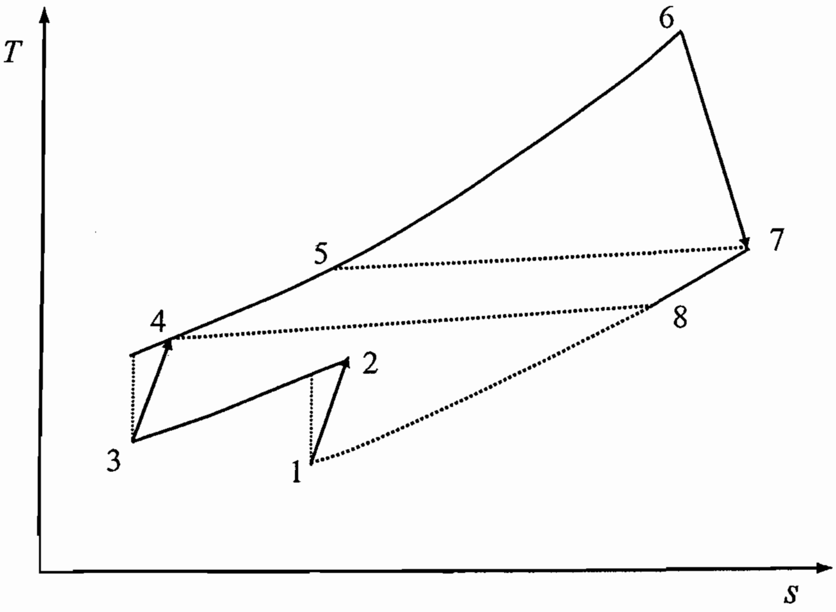
This is the lost power due to entropy creation in the boiler (due to the frictional pressure drop). [10 %]

Q3 (a) (i) Adding an intercooler increases the specific work output (because the compressor work input is decreased while the turbine work remains constant). In general, the overall efficiency is reduced. (Actually, depending on the polytropic efficiencies of the compressors, it may be possible to realise a small increase in overall efficiency for very low LP compressor pressure ratios.)

(ii) Adding a recuperator increases the overall efficiency because the fuel requirement is reduced while the specific work output is unchanged. (Actually, the specific work is very slightly reduced because less fuel is required so the mass flowrate through the turbine is reduced.)

(iii) Adding an intercooler and a recuperator gives the best of both worlds as the overall efficiency and the specific work output are increased. [25 %]

(b)



(i) For the LP compressor, $p_1 = 1$ bar, $T_1 = 298.15$ K, $p_2 = 3$ bar. Hence,

$$T_2 = T_1\left(\frac{p_2}{p_1}\right)^{(\gamma_a-1)/(\eta_p\gamma_a)} = 298.15\times\left(\frac{3.0}{1.0}\right)^{0.4/(0.9\times1.4)} = 422.57 \text{ K}$$

For the HP compressor, $p_3 = 3$ bar, $T_3 = 313.15$ K, $p_4 = 9$ bar. Hence,

$$T_4 = T_3\left(\frac{p_4}{p_3}\right)^{(\gamma_a-1)/(\eta_p\gamma_a)} = 313.15\times\left(\frac{9.0}{3.0}\right)^{0.4/(0.9\times1.4)} = 443.83 \text{ K}$$

For the turbine, $p_6 = 9$ bar, $T_6 = 1575$ K, $p_7 = 1$ bar. Hence,

$$T_7 = T_6\left(\frac{p_7}{p_6}\right)^{\eta_p(\gamma_p-1)/\gamma_p} = 1575\times\left(\frac{1.0}{9.0}\right)^{0.9\times0.35/1.35} = 943.24 \text{ K}$$

For the recuperator, $\dot{m}_p c_{pp} > \dot{m}_a c_{pa}$. Hence the effectiveness is defined by,

$$\varepsilon = \frac{(T_5 - T_4)}{(T_7 - T_4)}$$

Thus the air temperature at combustor inlet is,

$$T_5 = T_4 + \varepsilon(T_7 - T_4) = 443.83 + 0.75\times(943.24 - 443.83) = 818.39 \text{ K} \qquad [25\ \%]$$

(ii) SFEE for the combustion chamber is,

$$(\dot{m}_a + \dot{m}_f)h_p(T_6) = \dot{m}_a h_a(T_5) + \dot{m}_f h_f(T_0)$$

Defining the air-fuel ratio $A = \dot{m}_a/\dot{m}_f$ and rearranging,

$$(A+1)[h_{p6} - h_{p0}] - A[h_{a5} - h_{a0}] = Ah_{a0} + h_{f0} - (A+1)h_{p0} = -\Delta H_{298}^0$$

Hence,

$$A = \frac{-\Delta H_{298}^0 - c_{pp}(T_6 - T_0)}{c_{pp}(T_6 - T_0) - c_{pa}(T_5 - T_0)}$$

$$= \frac{50\times10^3 - 1.100\times(1575-298.15)}{1.100\times(1575-298.15) - 1.005\times(818.39 - 298.15)} = 55.116 \qquad [25\ \%]$$

(iii) Per kg of air entering the LP compressor :

LP compressor work $= c_{pa}(T_2 - T_1) = 1.005\times(422.57 - 298.15) = 125.04$ kJ/kg

HP compressor work $= c_{pa}(T_4 - T_3) = 1.005\times(443.83 - 313.15) = 131.33$ kJ/kg

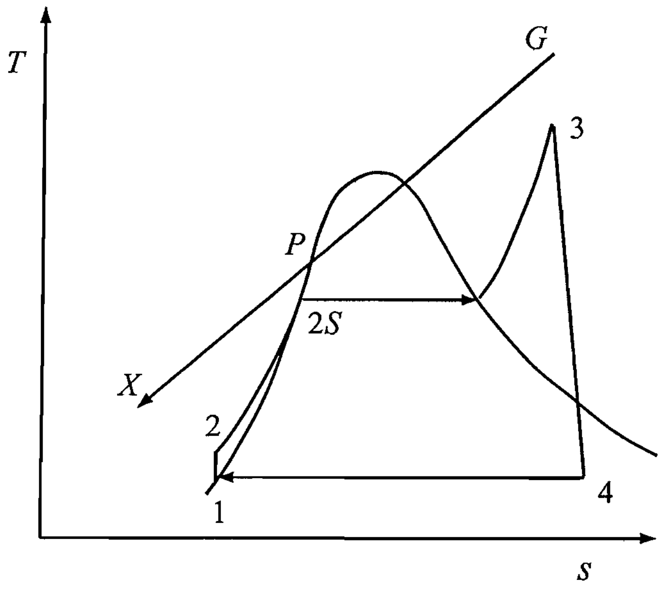
Turbine work $= \dfrac{(A+1)}{A}c_{pp}(T_6 - T_7) = \dfrac{56.116}{55.116}\times1.100\times(1575.0 - 943.24) = 707.55$ kJ/kg

Net work output $= 707.55 - 125.04 - 131.33 = 451.18$ kJ/kg air entering.

Overall efficiency of plant :

$$\eta_{overall} = \frac{A w_{net}}{[-\Delta H_{298}^0]} = \frac{55.116\times451.18}{50\times10^3} = 0.497 \qquad [25\ \%]$$

Q4



Dead State

$T_0 = 298.15\text{ K}$

$p_0 = 1\text{ bar}$

(a) $T_G = 650 + 273.15 = 923.15$ K. Hence, steady-flow exergy of gas at state (G) is,

$$\dot{E}_G = \dot{m}_g e_G = \dot{m}_g[(h_G - h_0) - T_0(s_G - s_0)] = \dot{m}_g c_{pg}\left[(T_G - T_0) - T_0 \ln\left(\frac{T_G}{T_0}\right)\right]$$

$$= 150\times1.25\times\left[(923.15 - 298.15) - 298.15\times\ln\left(\frac{923.15}{298.15}\right)\right] = 54006\text{ kW}$$ [15 %]

(b) Applying the SFEE to the HRSG from gas inlet to pinch point,

$$\dot{m}_g(h_G - h_P) = \dot{m}_g c_{pg}(T_G - T_P) = \dot{m}_s(h_3 - h_{2S})$$

$T_P = 295.01 + 273.15 + 15 = 583.16$ K. Hence,

$$\dot{m}_s = \frac{\dot{m}_g c_{pg}(T_G - T_P)}{(h_3 - h_{2S})} = \frac{150\times1.25\times(923.15 - 583.16)}{(3399.5 - 1317.2)} = 30.614\text{ kg/s}$$ [10 %]

(c) (i) Power input to feed pump,

$$\dot{W} = \dot{m}_s(h_2 - h_1) = 30.614\times(181.9 - 173.8) = 248\text{ kW}$$ [5 %]

(ii) Applying the SFEE to the HRSG from gas inlet to gas outlet,

$$\dot{m}_g(h_G - h_X) = \dot{m}_g c_{pg}(T_G - T_X) = \dot{m}_s(h_3 - h_2)$$

Hence, the gas exit temperature is,

$$T_X = T_G - \frac{\dot{m}_s(h_3 - h_2)}{\dot{m}_g c_{pg}} = 923.15 - \frac{30.614\times(3399.5 - 181.9)}{150\times1.25} = 397.79\text{ K}$$

Thus, the steady-flow exergy of the gas at state (X) is,

$$\dot{E}_X = \dot{m}_g e_X = \dot{m}_g [(h_X - h_0) - T_0 (s_X - s_0)]$$

$$= \dot{m}_g c_{pg} \left[(T_X - T_0) - T_0 \ln\left(\frac{T_X}{T_0}\right) \right]$$

$$= 150 \times 1.25 \times \left[(397.79 - 298.15) - 298.15 \times \ln\left(\frac{397.79}{298.15}\right) \right] = 2564 \text{ kW} \qquad [20\,\%]$$

(iii) The 'lost power' in the HRSG is given by,

$$\dot{W}_L = T_0 [\dot{m}_s (s_3 - s_2) - \dot{m}_g (s_G - s_X)]$$

$$= T_0 \left[\dot{m}_s (s_3 - s_2) - \dot{m}_g c_{pg} \ln\left(\frac{T_G}{T_X}\right) \right]$$

$$= 298.15 \times \left[30.614 \times (6.727 - 0.592) - 150 \times 1.25 \times \ln\left(\frac{923.15}{397.79}\right) \right] = 8934 \text{ kW} \qquad [15\,\%]$$

(iv) For the adiabatic steam turbine,

$$\dot{W} = \dot{m}_s (h_3 - h_4) = 30.614 \times (3399.5 - 2215.8) = 36238 \text{ kW}$$

$$\dot{W}_L = \dot{m}_s T_0 (s_4 - s_3) = 30.614 \times 298.15 \times (7.082 - 6.727) = 3240 \text{kW} \qquad [10\,\%]$$

(v) Heat transferred from steam in condenser,

$$\dot{Q} = \dot{m}_s (h_4 - h_1) = 30.614 \times (2215.8 - 173.8) = 62514 \text{ kW}$$

$T_{cond} = 41.51 + 273.15 = 314.66$ K. Hence, exergy of heat transferred is,

$$\dot{E}_Q = \dot{Q}\left(1 - \frac{T_0}{T_{cond}}\right) = 62514 \times \left(1 - \frac{298.15}{314.66}\right) = 3280 \text{ kW} \qquad [15\,\%]$$

(d) Net Power output (steam turbine – feed pump) = 36238 – 248 = 35990 kW

Total lost power (steam turbine + HRSG) = 3240 + 8934 = 12174 kW

Total exergy out (gas exhaust + condenser heat) = 2564 + 3280 = 5844 kW

Sum total = 54008 kW

This agrees with the exergy supplied (54006 kW) to 4 significant figures. [10 %]