

2010 PART IIA 3A5
THERMODYNAMICS AND POWER GENERATION
PROFESSOR J B YOUNG

ENGINEERING TRIPOS PART IIA 2010

MODULE 3A5 – THERMODYNAMICS AND POWER GENERATION

SOLUTIONS TO TRIPOS QUESTIONS

J.B. YOUNG & C.A. HALL

1. (a) The exergy equation for the heater is,

$$\dot{m}(e_2 - e_1) = \int_1^2 \left(1 - \frac{T_0}{T}\right) d\dot{Q} - T_0 \dot{S}_{irrev} \quad (1) \quad (2) \quad (3)$$

Term (1) is the increase in the exergy flowrate of the gas. This represents the increase in the 'power potential' of the gas with respect to the dead state temperature T_0 .

Term (2) is the rate of exergy supply to the heater. It is positive because $d\dot{Q} > 0$.

Term (3) is the lost power due to irreversibilities occurring within the heater. $\dot{S}_{irrev} \geq 0$.

(b) From the definition of e ,

[15 %]

$$\dot{m}(e_2 - e_1) = \dot{m}[(h_2 - T_0 s_2) - (h_1 - T_0 s_1)] = \dot{m}[(h_2 - h_1) - T_0(s_2 - s_1)]$$

From the SFEE and $Tds = dh - vdp$,

$$d\dot{Q} = \dot{m} dh = \dot{m}(Tds + vdp)$$

Hence, for any gas,

$$\int_1^2 \left(1 - \frac{T_0}{T}\right) d\dot{Q} = \dot{m} \int_1^2 \left[dh - \frac{T_0}{T}(Tds + vdp) \right] = \dot{m}[(h_2 - h_1) - T_0(s_2 - s_1)] - \dot{m} \int_1^2 \frac{T_0}{T} v dp$$

Substituting in the exergy equation gives,

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

(c) The maximum power available from a steady-flow device connected between the outlet state 2 and the inlet state 1 is given by availability theory as,

[25 %]

$$\begin{aligned} [\dot{W}_X]_{\max} &= \dot{m}(e_2 - e_1) = \dot{m}(h_2 - h_1) - \dot{m}T_0(s_2 - s_1) \\ &= \dot{m}c_p(T_2 - T_1) - \dot{m}c_p T_0 \ln\left(\frac{T_2}{T_1}\right) + \dot{m}RT_0 \ln\left(\frac{p_2}{p_1}\right) \quad (\text{perfect gas}) \end{aligned}$$

For $R = 2.08$ kJ/kg K and $c_p = 5.19$ kJ/kg K,

$$\begin{aligned} [\dot{W}_X]_{\max} &= 10 \times 5.19 \times (1500 - 800) - 10 \times 5.19 \times 300 \times \ln\left(\frac{1500}{800}\right) + 10 \times 2.08 \times 300 \times \ln\left(\frac{4.5}{5.0}\right) \\ &= 36.33 \times 10^3 - 9.79 \times 10^3 - 0.66 \times 10^3 = 25.88 \times 10^3 \text{ kW} = 25.88 \text{ MW} \end{aligned}$$

[25 %]

The 'lost power' in the heater is,

$$\begin{aligned} T_0 \dot{S}_{irrev} &= -\dot{m} \int_1^2 \frac{T_0}{T} v dp = -\dot{m} RT_0 \int_1^2 \frac{dp}{p} = -\dot{m} RT_0 \ln\left(\frac{p_2}{p_1}\right) \\ &= -10 \times 2.08 \times 300 \times \ln\left(\frac{4.5}{5.0}\right) = 0.66 \times 10^3 \text{ kW} = 0.66 \text{ MW} \end{aligned}$$

Hence the exergy supply rate to the heater is,

$$\int_1^2 \left(1 - \frac{T_0}{T}\right) d\dot{Q} = \dot{m}(e_2 - e_1) + T_0 \dot{S}_{irrev} = 25.88 + 0.66 = 26.54 \text{ MW} \quad [10 \%]$$

(d) The characteristic equation of state of the new gas is,

$$g = c_p (T - T_0) - c_p T \ln\left(\frac{T}{T_0}\right) + RT \ln\left(\frac{p}{p_0}\right) + RTB(p - p_0)$$

From $dg = v dp - s dT$ we have,

$$s = -\left(\frac{\partial g}{\partial T}\right)_p = c_p \ln\left(\frac{T}{T_0}\right) - R \ln\left(\frac{p}{p_0}\right) - RB(p - p_0) \quad [10 \%]$$

From $g = h - Ts$ we have

$$h = c_p (T - T_0) \quad [10 \%]$$

Thus,

$$e = h - T_0 s = c_p (T - T_0) - c_p T_0 \ln\left(\frac{T}{T_0}\right) + RT_0 \ln\left(\frac{p}{p_0}\right) + RT_0 B(p - p_0)$$

Maximum power output from the GT cycle is,

$$\dot{m}(e_2 - e_1) = \dot{m} c_p (T_2 - T_1) - \dot{m} c_p T_0 \ln\left(\frac{T_2}{T_1}\right) + \dot{m} RT_0 \ln\left(\frac{p_2}{p_1}\right) + \dot{m} RT_0 B(p_2 - p_1)$$

This is exactly the same as for a perfect gas except for the final term :

$$\dot{m} RT_0 B(p_2 - p_1) = 10 \times 2.08 \times 300 \times (-0.1) \times (4.5 - 5.0) = 0.31 \times 10^3 \text{ kW} = 0.31 \text{ MW}$$

Hence, maximum power from the GT cycle is,

$$[\dot{W}_X]_{\max} = 25.88 + 0.31 = 26.19 \text{ MW} \quad [15 \%]$$

2. (a) A chemical reaction can be represented in the form $\sum \nu_i A_i = 0$, where ν_i is the stoichiometric coefficient of chemical species A_i . The condition for equilibrium is then,

$$\sum \nu_i \bar{\mu}_i(T, p_i) = 0$$

where $\bar{\mu}_i(T, p_i)$ is the chemical potential per mole of species A_i evaluated at temperature T and partial pressure p_i . For an ideal gas,

$$\bar{\mu}_i(T, p_i) = \bar{\mu}_i^0(T) + \bar{R}T \ln\left(\frac{p_i}{p_0}\right)$$

where $\bar{\mu}_i^0(T)$ is the chemical potential per mole at T and $p_0 = 1$ bar, and \bar{R} is the molar gas constant. Hence,

$$\sum \nu_i \bar{\mu}_i^0(T) = -\bar{R}T \sum \nu_i \ln\left(\frac{p_i}{p_0}\right) = -\bar{R}T \sum \ln\left(\frac{p_i}{p_0}\right)^{\nu_i} = -\bar{R}T \ln\left[\prod \left(\frac{p_i}{p_0}\right)^{\nu_i}\right]$$

By definition, $\Delta \bar{G}_T^0 = \sum \nu_i \bar{\mu}_i^0(T)$ and $K_p = \prod (p_i/p_0)^{\nu_i}$. Hence,

$$\Delta \bar{G}_T^0 = -\bar{R}T \ln(K_p) \quad [25 \%]$$

(b) For the reaction,



we have $\Delta \bar{H}_{298}^0 = -90.8$ MJ per kmol of CO, $\Delta \bar{G}_{298}^0 = -25.4$ MJ per kmol of CO.

Also, van't Hoff's equation is,

$$\frac{d}{dT}(\ln K_p) = \frac{\Delta \bar{H}_T^0}{\bar{R}T^2}$$

Integrating from 25 °C to 200 °C with $\Delta \bar{H}_T^0$ assumed to be constant gives,

$$\ln(K_p) - \ln(K_{p0}) = \frac{\Delta \bar{H}_T^0}{\bar{R}} \left(\frac{1}{T_0} - \frac{1}{T} \right)$$

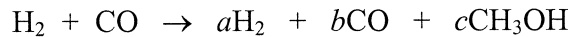
where $K_p = K_{p0}$ at $T = T_0 = 298.15$ K. From the result of part (a),

$$\ln(K_{p0}) = \frac{-\Delta \bar{G}_{298}^0}{\bar{R}T_0} = \frac{25.4 \times 10^3}{8.3143 \times 298.15} = 10.246$$

Thus, at 200 °C = 473.15 K,

$$\ln(K_p) = 10.246 - \frac{90.8 \times 10^3}{8.3143} \left(\frac{1}{298.15} - \frac{1}{473.15} \right) = -3.302 \rightarrow K_p = 0.03682 \quad [25 \%]$$

(c) The actual reaction is,



$$\text{Conservation of atomic H} \quad 2a + 4c = 2 \quad (\text{i})$$

$$\text{Conservation of atomic C} \quad b + c = 1 \quad (\text{ii})$$

$$\text{Conservation of atomic O} \quad b + c = 1 \quad (\text{Redundant})$$

$$\text{Number of moles of products} \quad a + b + c = n \quad (\text{iii})$$

Partial pressures (p is the mixture pressure)

$$p_{\text{H}_2} = \frac{a}{n}p, \quad p_{\text{CO}} = \frac{b}{n}p, \quad p_{\text{CH}_3\text{OH}} = \frac{c}{n}p$$

The equilibrium constant is related to the partial pressures by,

$$K_p = \left(\frac{p_{\text{CH}_3\text{OH}}}{p_0} \right) \left(\frac{p_{\text{CO}}}{p_0} \right)^{-1} \left(\frac{p_{\text{H}_2}}{p_0} \right)^{-2} = \left(\frac{c}{n} \right) \left(\frac{n}{b} \right) \left(\frac{n}{a} \right)^2 \left(\frac{p_0}{p} \right)^2 = \frac{cn^2}{a^2b} \left(\frac{p_0}{p} \right)^2$$

From (i), (ii) and (iii),

$$c = \frac{1-a}{2}, \quad b = 1-c = \frac{1+a}{2}, \quad n = 1+a$$

Substituting into the equation for K_p gives,

$$K_p = \frac{(1-a)(1+a)^2}{a^2(1+a)} \left(\frac{p_0}{p} \right)^2 = \frac{(1-a^2)}{a^2} \left(\frac{p_0}{p} \right)^2$$

Thus,

$$a^2 \left[K_p + \left(\frac{p_0}{p} \right)^2 \right] = \left(\frac{p_0}{p} \right)^2$$

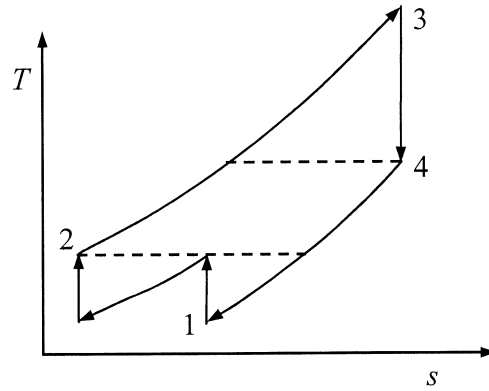
Setting $K_p = 0.03682$ and $(p_0/p) = 0.1$ gives,

$$a = 0.4622, \quad b = 0.7311, \quad c = 0.2689, \quad n = 1.4622$$

Mole fractions are : $X_{\text{H}_2} = 0.3161$, $X_{\text{CO}} = 0.5000$, $X_{\text{CH}_3\text{OH}} = 0.1839$

[50 %]

3. (a)2.



$$\frac{T_3}{T_4} = r_t$$

$$\frac{T_2}{T_1} = \sqrt{r_t}$$

[10 %]

Turbine work : $w_t = c_p(T_3 - T_4) \rightarrow \frac{w_t}{c_p T_1} = \left(\frac{T_3}{T_1} - \frac{T_4}{T_3} \frac{T_3}{T_1} \right) = \theta \left(1 - \frac{1}{r_t} \right)$

Compressor work : $w_c = 2c_p(T_2 - T_1) \rightarrow \frac{w_c}{c_p T_1} = 2 \left(\frac{T_2}{T_1} - 1 \right) = 2(\sqrt{r_t} - 1)$

Heat input : $q_{in} = c_p(T_3 - T_4) \rightarrow \frac{q_{in}}{c_p T_1} = \left(\frac{T_3}{T_1} - \frac{T_4}{T_3} \frac{T_3}{T_1} \right) = \theta \left(1 - \frac{1}{r_t} \right)$

Cycle efficiency : $\eta_c = \frac{w_t - w_c}{q_{in}} = \frac{\theta(1 - 1/r_t) - 2(\sqrt{r_t} - 1)}{\theta(1 - 1/r_t)}$

$$= 1 - \frac{2r_t(\sqrt{r_t} - 1)}{\theta(r_t - 1)} = 1 - \frac{2r_t}{\theta(\sqrt{r_t} + 1)}$$

[20 %]

Specific work : $\frac{w}{c_p T_1} = \frac{w_t - w_c}{c_p T_1} = \theta \left(1 - \frac{1}{r_t} \right) - 2(\sqrt{r_t} - 1)$

[5 %]

(b) For $\eta_c > \eta_{joule}$ we require,

$$1 - \frac{2r_t}{\theta(\sqrt{r_t} + 1)} > 1 - \frac{1}{r_t} \rightarrow 2r_t^2 - \theta\sqrt{r_t} - \theta < 0$$

We try $r_p = 26.4 \rightarrow r_t = r_p^{(\gamma-1)/\gamma} = 26.4^{0.4/1.4} = 2.548$

For $\theta = 5$ and $r_t = 2.548$: $2r_t^2 - \theta\sqrt{r_t} - \theta = 0.002 \cong 0$

Hence $\eta_c > \eta_{joule}$ for $r_p < 26.4$

[20 %]

(c) The heat exchanged in the recuperator is given by,

$$q_{ex} = c_p(T_4 - T_2) \quad \rightarrow \quad \frac{q_{ex}}{c_p T_1} = \left(\frac{T_4}{T_3} \frac{T_3}{T_1} - \frac{T_2}{T_1} \right) = \left(\frac{\theta}{r_t} - \sqrt{r_t} \right)$$

For zero heat exchange,

$$r_t^{3/2} = \theta = 5 \quad \rightarrow \quad r_t = 2.924 \quad \rightarrow \quad r_p = r_t^{\gamma/(\gamma-1)} = 42.75 \quad [10 \%]$$

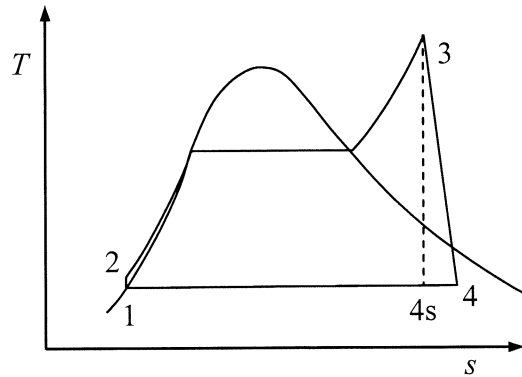
In order to match the efficiency of the Joule cycle some recuperation is required to make up for the efficiency penalty of intercooling. (Intercooling of an ideal cycle increases specific work output but decreases efficiency. Recuperation increases efficiency.) The heat transferred q_{ex} increases as the pressure ratio is reduced and hence the pressure ratio where there is no recuperation ($r_p = 42.75$) is significantly greater than that where the cycle efficiencies match ($r_p = 26.4$). [15 %]

(d) (i) With a non-isentropic turbine $w/(c_p T_1)$ will decrease, $q_{ex}/(c_p T_1)$ will increase (higher T_4), and η_c will decrease.

(ii) With a recuperator effectiveness of less than unity $w/(c_p T_1)$ will stay the same, $q_{ex}/(c_p T_1)$ will decrease and η_c will decrease.

(iii) With recuperator pressure losses $w/(c_p T_1)$ will reduce (lower pressure ratio across the turbine), $q_{ex}/(c_p T_1)$ will increase (higher T_4), and η_c will decrease. [20 %]

4.



(a) Neglecting the feed pump work, the cycle efficiency is,

$$\eta_c = \frac{h_3 - h_4}{h_3 - h_1}$$

Hence : $h_4 = h_3 - \eta_c(h_3 - h_1) = 3450.4 - 0.39 \times (3450.4 - 121.4) = 2152.1 \text{ kJ/kg}$

Actual dryness fraction : $x_4 = \frac{h_4 - h_1}{h_{fg}} = \frac{2152.1 - 121.4}{2553.7 - 121.4} = 0.835$ [15 %]

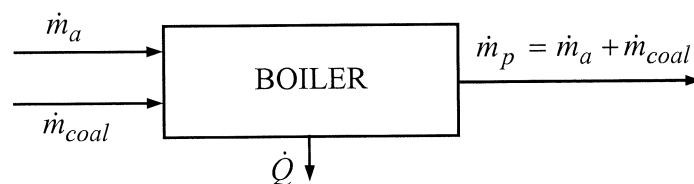
For an isentropic turbine expansion,

$$x_{4s} = \frac{s_3 - s_1}{s_{fg}} = \frac{6.523 - 0.422}{8.473 - 0.422} = 0.758$$

Hence : $h_{4s} = h_1 + x_{4s}h_{fg} = 121.4 + 0.758 \times (2553.7 - 121.4) = 1965.1 \text{ kJ/kg}$

Turbine isentropic efficiency : $\frac{h_3 - h_4}{h_3 - h_{4s}} = \frac{3450.4 - 2152.1}{3450.4 - 1965.1} = 0.874$ [15 %]

(b) Rate of heat input to cycle = $\dot{Q} = \frac{600}{0.39} = 1538.5 \text{ MW}$



SFEE for the boiler,

$$(\dot{m}_a + \dot{m}_{coal})h_p(T_p) - \dot{m}_a h_a(T_0) - \dot{m}_{coal} h_{coal}(T_0) = -\dot{Q}$$

From the definition of ΔH_{298}^0 (where the products are at temperature T_0),

$$(\dot{m}_a + \dot{m}_{coal})h_p(T_0) - \dot{m}_a h_a(T_0) - \dot{m}_{coal} h_{coal}(T_0) = \dot{m}_{coal} \Delta H_{298}^0$$

Subtracting the equations,

$$(\dot{m}_a + \dot{m}_{coal})[h_p(T_p) - h_p(T_0)] = -\dot{Q} - \dot{m}_{coal} \Delta H_{298}^0$$

Now $\dot{m}_a = 20\dot{m}_{coal}$ and c_p for the products is 1.10 kJ/kg K. Hence,

$$\dot{m}_{coal} [21c_p (T_p - T_0) + \Delta H_{298}^0] = -\dot{Q}$$

Thus,

$$\dot{m}_{coal} = \frac{-1538.5 \times 10^3}{21 \times 1.10 \times (140 - 25) - 24.0 \times 10^3} = 72.08 \text{ kg/s} \quad [25 \ %]$$

$$\text{Overall efficiency} = \frac{\dot{W}_{net}}{\dot{m}_{coal} [-\Delta H_{298}^0]} = \frac{1538.5 \times 0.39}{72.08 \times 24.0} = 0.347 \quad [5 \ %]$$

$$\text{Mass of carbon captured annually} = 0.5 \times 72.08 \times 0.8 \times 3600 \times 24 \times 365 = 9.092 \times 10^8 \text{ kg}$$

$$\text{Mass of CO}_2 \text{ captured annually} = 9.092 \times 10^8 \times \frac{44}{12} \times 10^{-3} \times 10^{-6} = 3.33 \text{ Mtonnes} \quad [10 \ %]$$

(c) Adding a direct contact feedheater causes an increase in the mean temperature of heat addition to the cycle which results in an increase in cycle efficiency. A higher cycle efficiency implies a higher overall efficiency and hence a smaller coal supply rate for the same power output. Adding a stage of steam reheat would also improve the cycle efficiency because this also increases the mean temperature of heat addition. [15 %]

(d) The main challenges for large-scale CO₂ capture and storage are: (i) Extracting the CO₂ from the boiler exhaust gases (requires a costly amine scrubbing plant, which will reduce overall efficiency), (ii) Pumping the CO₂ at high pressure to the storage location (again requires energy and plant) and (iii) Locating a suitable storage location (such as a subsurface porous rock formation) and ensuring it will safely hold all the CO₂ for hundreds of years. [15 %]

ENGINEERING TRIPOS PART IIA 2010
MODULE 3A5 – THERMODYNAMICS AND POWER GENERATION

ANSWERS

1. (c) 25.88 MW, 26.54 MW
(d) $s = c_p \ln\left(\frac{T}{T_0}\right) - R \ln\left(\frac{p}{p_0}\right) - RB(p - p_0)$, $h = c_p(T - T_0)$, 26.19 MW
2. (b) (ii) $X_{\text{H}_2} = 0.316$, $X_{\text{CO}} = 0.500$, $X_{\text{CH}_3\text{OH}} = 0.184$
3. (c) 42.75
4. (a) 0.835, 0.874
(b) 72.1 kg/s 0.347, 3.33MtCO₂

J.B. Young & C.A. Hall