3A5 - Thermodynamics & Power Generation

Crib - 2025.

Q1)

(a) $dg = v\,dp - s\,dT$

$$\Rightarrow \left(\frac{\partial g}{\partial p}\right)_T = v \; ; \quad \left(\frac{\partial g}{\partial T}\right)_p = -\cancel{s} = -s$$

$$\left(\frac{\partial^2 g}{\partial T \partial p}\right) = \left(\frac{\partial v}{\partial T}\right)_p \; ; \quad \frac{\partial^2 g}{\partial p \partial T} = -\left(\frac{\partial s}{\partial p}\right)_T$$

These must be equal

$$\Rightarrow \boxed{\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T}$$

$$df = -p\,dv - s\,dT$$

$$\Rightarrow \left(\frac{\partial f}{\partial v}\right)_T = -p \; ; \quad \left(\frac{\partial f}{\partial T}\right)_v = -s$$

$$\frac{\partial^2 f}{\partial T \partial v} = -\left(\frac{\partial p}{\partial T}\right)_v \; ; \quad \frac{\partial^2 f}{\partial v \partial T} = -\left(\frac{\partial s}{\partial v}\right)_T$$

These two must be equal

$$\Rightarrow \boxed{\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v}$$

as required.

(b) $$P_r = \frac{\beta T_r}{(\alpha V_r - 1)} - \frac{\alpha}{V_r^2}$$ ②

(i) At critical point, there is no phase change if the substance is cooled isobarically or compressed isothermally.

This implies $\left(\frac{\partial p}{\partial v}\right)_T = 0$ & $\left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0$

Since the critical point is the point of inflection.

$$\left(\frac{\partial P_r}{\partial V_r}\right)_{T_r} = -\frac{\alpha \beta T_r}{(\alpha V_r - 1)^2} + \frac{2\alpha}{V_r^3}$$

& $$\left(\frac{\partial^2 P_r}{\partial V_r^2}\right)_{T_r} = \frac{2\alpha^2 \beta T_r}{(\alpha V_r - 1)^3} - \frac{6\alpha}{V_r^4}$$

@ Critical point $P_r = V_r = T_r = 1$

& the above two derivatives are zero

$\Rightarrow$ $\frac{\beta}{2} = (\alpha - 1)^2$ & $\frac{2\alpha\beta}{(\alpha-1)^3} = 6$

$\Rightarrow \beta = \frac{3(\alpha-1)^3}{\alpha}$

$$\frac{3}{2}\frac{(\alpha-1)^3}{\alpha} = (\alpha-1)^2$$

$\Rightarrow \boxed{\alpha = 3}$ using this gives $\beta = 8$.

Thus @ Critical point $\boxed{\alpha = 3 \ \& \ \beta = 8}$

(ii) $dh = vdp + Tds$ (from data book)

$$\left(\frac{\partial h}{\partial T}\right)_p = c_p = T\left(\frac{\partial s}{\partial T}\right)_p$$

for $c_p = f(T)$ only $\left(\frac{\partial c_p}{\partial p}\right)_T = 0$.

$$\left(\frac{\partial c_p}{\partial p}\right)_T = T\,\frac{\partial^2 s}{\partial p\,\partial T} = T\,\frac{\partial}{\partial T}\left(\frac{\partial s}{\partial p}\right)_T$$

Using the Maxwell relation in (a)

$$T\,\frac{\partial}{\partial T}\left(\frac{\partial s}{\partial p}\right)_T = T\,\frac{\partial}{\partial T}\left(\frac{\partial v}{\partial T}\right)_p$$

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{V_c}{T_c}\left(\frac{\partial V_r}{\partial T_r}\right)_{p_r} = \frac{V_c}{T_c}\,\frac{1}{\left(\partial T_r/\partial V_r\right)_{p_r}}$$

Rewriting the state equation as

$$\frac{(\alpha V_r - 1)\,p_r}{\beta} + \frac{\alpha}{\beta}\,\frac{(\alpha V_r - 1)}{V_r^2} = T_r$$

$$\Rightarrow \left(\frac{\partial T_r}{\partial V_r}\right)_{p_r} = \frac{\alpha p_r}{\beta} + \frac{\alpha}{\beta}\left(\frac{2}{V_r^3} - \frac{\alpha}{V_r^2}\right) \equiv F$$

$\therefore \left(\frac{\partial v}{\partial T}\right)_p = \frac{V_c}{T_c}\,\frac{1}{F}$ but F is not a function of T or T_r

Thus $\frac{\partial}{\partial T}\left(\frac{\partial v}{\partial T}\right)_p = 0$

$$\Rightarrow \left(\frac{\partial c_p}{\partial p}\right)_T = 0 \Rightarrow \boxed{c_p = f(T) \text{ only.}}$$

(iii) $du = Tds - Pdv$

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - p$$

from part (a) $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$

from the given state equation

$$p = \frac{p_c \beta T}{T_c(\alpha V_r - 1)} - \frac{\alpha p_c}{V_r^2}$$

$$\Rightarrow \left(\frac{\partial p}{\partial T}\right)_v = \frac{p_c}{T_c}\frac{\beta}{(\alpha V_r - 1)}$$

$$\Rightarrow \left(\frac{\partial u}{\partial v}\right)_T = \cancel{\frac{T p_c \beta}{T_c(\alpha V_r - 1)}} - \cancel{\frac{T p_c \beta}{T_c(\alpha V_r - 1)}} + \frac{\alpha p_c V_c^2}{V^2}$$

$$= \frac{\alpha p_c V_c^2}{V^2}$$

integrating from V_0 to V

$$\Rightarrow \boxed{\Delta u = \alpha p_c V_c^2 \left[\frac{1}{V_0} - \frac{1}{V}\right]}$$

Q2

(a) $C_4H_{10}O + a\left(O_2 + \frac{0.79}{0.21}N_2\right)$

$$\rightarrow 4CO_2 + 5H_2O + a\frac{0.79}{0.21}N_2$$

O atom balance gives $a = 6$.

So, the Stoichiometric reaction is

$$C_4H_{10}O + 6\left(O_2 + \frac{0.79}{0.21}N_2\right) \rightarrow 4CO_2 + 5H_2O + 6\frac{0.79}{0.21}N_2.$$

(b) Fuel: air = 1:2 molar ratio

$$C_4H_{10}O + 2\left(O_2 + \frac{0.79}{0.21}N_2\right)$$

$$\rightarrow b_1CO_2 + b_2CO + b_3H_2O + b_4H_2 + b_5N_2$$

$$\Rightarrow b = 2\frac{0.79}{0.21}\cancel{N_2} = 7.5238$$

C-atom : $b_1 + b_2 = 4 \Rightarrow b_2 = 4 - b_1$

H-atom: $2b_3 + 2b_4 = 10 \Rightarrow b_3 + b_4 = 5$

$b_4 = 5 - b_3$

O-atom: $2b_1 + b_2 + b_3 = 5$

$\Rightarrow b_1 + b_3 = 1 \Rightarrow b_3 = 1 - b_1$

$b_4 = 4 + b_1$

4 unknows & 3 relations, So we need 1 K_p relation.

Consider the water-gas shift reaction

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

Rxn 8.

@ $T = 1400K$

$\ln(K_p) = -0.767$

$$K_p = \frac{(p_{CO_2}/p_0)\,(p_{H_2}/p_0)}{(p_{CO}/p_0)\,(p_{H_2O}/p)} = \frac{b_1\, b_4}{b_2\, b_3}\,\frac{(p/p_0)^2}{(p/p_0)^2}$$

$$0.4644 = \frac{b_1\,(4+b_1)}{(4-b_1)\,(1-b_1)}$$

$$\Rightarrow 0.5356\, b_1 + 6.322 b_1 - 1.8576 = 0$$

$\Rightarrow \; b_1 = 0.2869$ Physically meaningful answer.

$b_2 = 3.7131$

$b_3 = 0.7131$

$b_4 = 4.2869$

$b_5 = 7.5238$

$\text{Sum} = \underline{\underline{16.5238}}$

mole fractions are

$X_{CO_2} = \frac{b_1}{\text{Sum}} = 0.0174$

$X_{CO} = 0.2247$

$X_{H_2O} = 0.0432$

$X_{H_2} = 0.2594$

$X_{N_2} = 0.4553$

$\underline{\underline{\Sigma = 1.000}}$

(C) No changes to X_i because of pressure change, since no pressure dependence appears in the K_p relation.

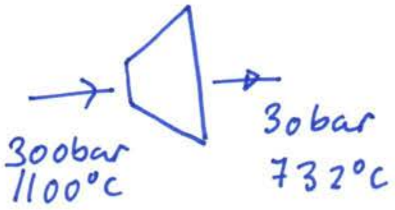
(d) H_2 Yield by shifting the water-gas shift reaction to the right by spraying water.

$CO + H_2O \rightleftharpoons CO_2 + H_2$ $\quad H_2O \uparrow \Rightarrow H_2 \uparrow$

by Le-chartelier principle.

3(a)

i)



$\dot{W}_t = 360\,\text{MW}$

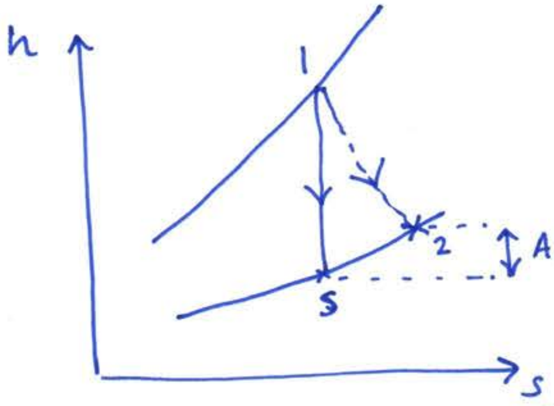
$\dot{m}(1839 - 1353) = 360 \times 10^3$

$\dot{m} = 740.74\ \text{kg/s}$ [2]

ii) $\text{Loss} = T_0 \Delta S_{irr} = (25+273) \times (-3.494 + 3.549) \times 740.74$

$= 12.1\ \text{MW}$ (or 16.4 kJ/kg) [2]

iii)



Exergetic loss $= T_0 \Delta S_{irr}$

Power loss due to irreversibility $\not\approx T_2 \Delta S_{irr}$

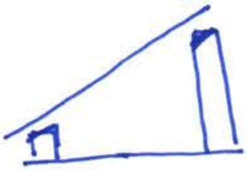
$T_2 \gg T_0$

if turbine were reversible additional power would be $\approx (732+273) \times (3.549 - 3.494)$

$= +55.3\ \text{MW}$ [2]

iv) $Q_{IN} = \dfrac{740.74}{104} = 7.12\ \text{m}^3/\text{s}$

$Q_{out} = \dfrac{740.74}{15.1} = 49\ \text{m}^3/\text{s}$

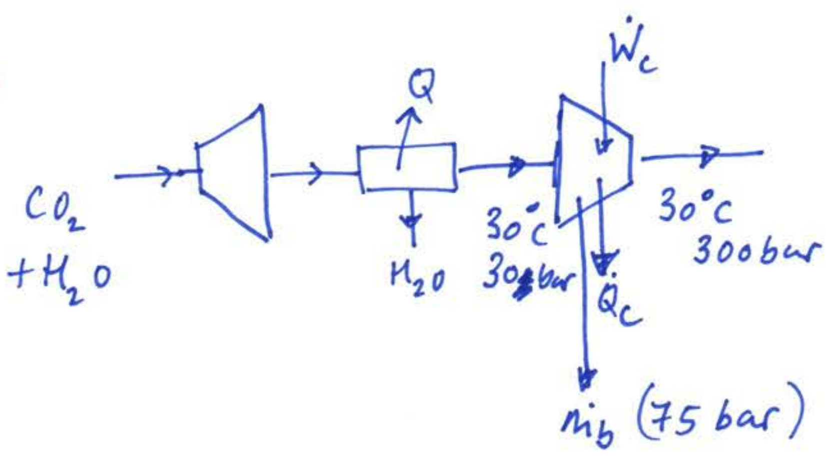


Blade height increases to accomodate larger volume flow

fluid densities much larger than for GT or ST → higher power density (small blade heights)

[2]

b)



i) Enthalpy drops because the fluid does not behave like an ideal gas → $h = f(p,T)$. The fluid is compressed from a gas to a super-critical state. Heat transfer outweighs shaft work input. [2]

ii) SFEE $$\dot m_b(290) + [\dot m_c - \dot m_b](250) - \dot m_c(480) = \dot W_c - \dot Q_c$$

$\dot m_c = 740.74 \times 0.97 = 718.5\ \text{kg/s}$

$\dot m_b = 26.6\ \text{kg/s}$

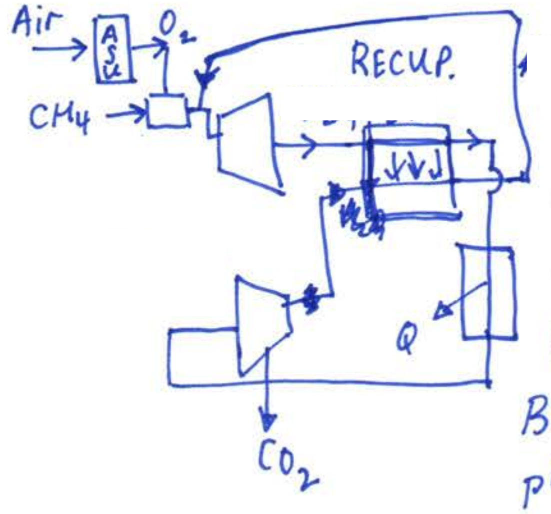
→ $-\dot Q_c = -164.2\,\text{MW} - 56\,\text{MW}$ $\quad \dot Q_c = \underline{220\,\text{MW}}$ (POSITIVE OUT) [2]

iii) if reversible $$\dot W_c = \dot m_b\left[290 - (303)(1.296) - 480 + (303)(2.039)\right] + (\dot m_c - \dot m_b)\left[250 - (303)(1.077) - 480 + (303)(2.039)\right]$$

$$(\dot W_c)_{REV} = \underline{43.5\,\text{MW}}$$

→ Work to overcome irrev = $\underline{12.5\,\text{MW}}$ [4]

c)



Produces high concentration CO_2 → easy to capture CO_2 compared with conventional power plant.

But air separation unit reduces plant efficiency (requires work)

Potential to have ~~ma~~ smaller plant size compared to conventional CCS.

[4]

4 a) 'Grey' H_2 → Steam methane reformation using natural gas

'Blue' H_2 → SMR + carbon capture

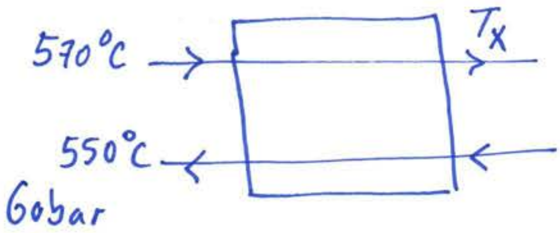
"Green" H_2 → Electrolysis with renewables

Using H_2 as replacement for CCGT → used for long term energy storage

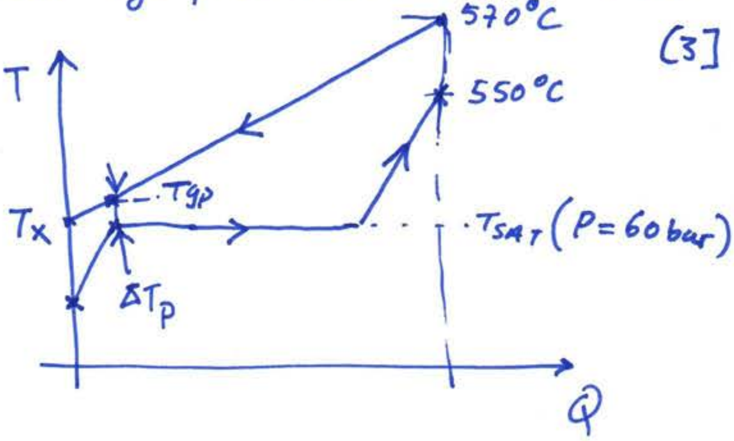
Need to consider both direct ~~impact~~ emissions and also 'round trip' emissions of production + distribution of fuel.

[3]

b)



i)



i) $T_{gp} = T_{SAT} + \Delta T_p = 275.58 + 15 = 290.58°C$ [2]

ii) $1.1\,(570 - 290.58) \times \dot{m}_g = \dot{m}_s\,(-1213.9 + 3541.3)$

[2]

$\rightarrow \dot{m}_s/\dot{m}_g = 0.1321$

iii)

$(-T_x + 290.58) \times 1.1 = \left(\frac{\dot{m}_s}{\dot{m}_g}\right) \times (1213.9 - 121.4)$

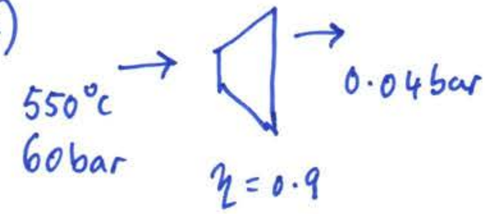
$\rightarrow \underline{T_x = 159.4°C}$

Need to ensure T_x above dew-point but scope to reduce T_x and increase heat transfer efficiency

$\eta_b = \frac{Q}{Q_{MAX}} = \frac{570 - 159.4}{570 - 28.96} = 75.9\%$

[3]

c)



from chart

$h_s = 2130$ kJ/kg

$\rightarrow \dfrac{h_2 - h_1}{h_s - h_1} = 0.9$

$h_2 = 0.9(2130 - 3550) + 3550$

$= 2272$ kJ/kg

$\dot{m}_s = 0.1321 \times 300 = 39.63$ kg/s

Power $= 39.63 \times [-2272 + 3550] = \underline{50.6 \text{ MW}}$

Max power $= \dot{m}(b_2 - b_1) = 39.63((h - T_0 s)_2 - (h - T_0 s)_1)$

$= 39.63\left[\left[3541.3 - (28.96 + 273)(7.0307)\right] - \left[121.4 - (28.96 + 273)(0.422)\right]\right] = \underline{56.4 \text{ MW}}$

losses mostly due to wetness + viscous dissipation in turbine

[8]

$\eta_{ov} = \eta_b \eta_2 + \eta_1(1 - \eta_b \eta_2)$

d) ~~i)~~ feed heating will reduce η_b

$\rightarrow \eta_{ov} \downarrow , T_x \uparrow$

[2]

~~[1]~~

~~ii) triple or dual steam levels will increase η_2~~

~~$\rightarrow \eta_{ov} \uparrow$~~

~~[1]~~