

## Executive Summary

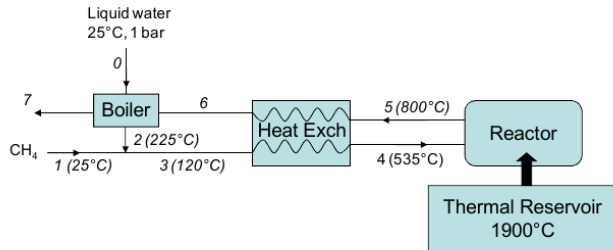


Figure 13.C-29: System for producing hydrogen

Figure 1: Hydrogen Reformer with heat recovery

The purpose of this assignment was to perform an analysis of a steady hydrogen producing system (see Figure 1) using the first and second laws of thermodynamics. The system takes equal molar flow rates of  $\text{CH}_4$  and  $\text{H}_2\text{O}$  and produces  $\text{H}_2$  and  $\text{CO}$  using a reactor, heat exchanger, and boiler. A thermal reservoir at  $1900^\circ\text{C}$  provides energy to the reactor to enable the chemical reaction. Table 1 summarizes all of the required values.

Table 1: Results

Temperature at state 6	$499.6^\circ\text{C}$
Temperature at state 7	$69.41^\circ\text{C}$
Second law efficiency of HX	72.98%
Thermal energy to reactor	84.99 MJ/kmol
Spec. exergy of $\text{H}_2$ at state 7	259.235 MJ/kmol
Overall second law efficiency	64.04%

All gases other than  $\text{H}_2\text{O}$  were assumed to be ideal gases. Negligible heat transfer occurred between the system and the environment, other than the heat transfer between the thermal reservoir and the reactor. Potential and kinetic energy of the flow through the pipes were also negligible, and there were no flow losses through the pipes. Additionally, it was assumed that the  $\text{CH}_4$  and  $\text{H}_2\text{O}$  were converted to  $\text{H}_2$  and  $\text{CO}$  with 100% efficiency, and that the flow rates were perfectly balanced so that no  $\text{CH}_4$  or  $\text{H}_2\text{O}$  exists in the exhaust.

Parts a and b of this assignment required the temperature at states 6 and 7 to be determined, respectively. The temperature at these locations was found by performing energy balances on both the heat exchanger and the boiler, using the first law of thermodynamics with simplifications as follows:

$$\sum_{i=1}^{\#inlets} n_i h_i = \sum_{i=1}^{\#outlets} n_i h_i \quad (1)$$

where  $n_i$  is the molar flow rate and  $h_i$  is the specific enthalpy of the reactant or product species, respectively. The

temperature at state 7 could be solved after the temperature at state 6 had been determined.

Part c required calculation of the second law efficiency of the heat exchanger. This calculation first required that the specific flow exergy at points 3, 4, 5, and 6 be calculated using the following simplified formula:

$$x_{if} = (h_i - h_0) - T_0(s_i - s_0) \quad (2)$$

in which  $x_{if}$  is the specific flow exergy at point  $i$  with respect to reference point 0,  $h_i$  and  $h_0$  are the specific enthalpies of the fluid at point  $i$  and reference point 0,  $T_0$  is the temperature at the reference point, and  $s_i$  and  $s_0$  are the specific entropies of the fluid at point  $i$  and reference point 0, respectively. The reference state was defined as the  $25^\circ\text{C}$  air outside of the system. The second law efficiency  $\eta_{2,HX}$  was then found using Equation 3.

$$\eta_{2,HX} = \frac{x_{4f} - x_{3f}}{x_{5f} - x_{6f}} \quad (3)$$

The thermal energy that had to be provided to the reactor from the thermal reservoir per mole of  $\text{H}_2$  was determined in Part D. This was done by performing an energy balance on the reactants and the products at states 4 and 5, respectively, which was simplified as follows:

$$Q_{\text{reservoir}} = n_{\text{H}_2} \left( \sum_{i=1}^{\#prod} n_i h_i - \sum_{i=1}^{\#react} n_i h_i \right) \quad (4)$$

where  $Q_{\text{reservoir}}$  is the heat energy added to the reactor from the hot reservoir per kmol of  $\text{H}_2$  produced ( $n_{\text{H}_2}$ ).

The specific exergy of the  $\text{H}_2$  exiting at state 7 is the flow exergy of  $\text{H}_2$  at that state. Since we are looking at a single species, the properties at state 7 are  $\text{H}_2$  specific and the dead state properties refer to the atmospheric species that contain hydrogen, which is only  $\text{H}_2\text{O}$ .

The second law efficiency for the system is the ratio of the exergy from the products over the exergy of the reactants and the heat supplied. Since the reactants and products heat and cool each other before entering the reactor, the exergy of the flows in and out of the reactor constitute the exergetic basis of the system as a whole. The equation used to determine second law efficiency for the system is therefore as follows:

$$\eta_{2,sys} = \frac{x_{\text{products}}}{x_{\text{reactants}} + x_{Q_{\text{reservoir}}}} \quad (5)$$

where  $\eta_{2,sys}$  is the second law efficiency of the system and  $x_{\text{products}}$  and  $x_{\text{reactants}}$  are the specific flow exergy of the products and reactants, respectively, found using Equation 2.  $x_{Q_{\text{reservoir}}}$  is the specific exergy supplied to the reactor, found by using:

$$x_{Q_{\text{reservoir}}} = Q_{\text{reservoir}} \left( 1 - \frac{T_0}{T_H} \right) \quad (6)$$

where  $T_H$  is the temperature of the thermal reservoir.

## EES program

### HW5

#### Equations

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\$UnitSystem SI Molar C Pa J Deg

System for steadily producing H<sub>2</sub> from CH<sub>4</sub> and H<sub>2</sub>O

GIVEN

Species

Reactants

$$me\$ = \text{'CH4'} \quad (7)$$

$$wa\$ = \text{'H2O'} \quad (8)$$

$$water\$ = \text{'Steam'} \quad (9)$$

Products

$$hy\$ = \text{'H2'} \quad (10)$$

$$cm\$ = \text{'CO'} \quad (11)$$

Mole Fractions

$$MW_m = MW(me\$) \quad (12)$$

Molecular weights

$$MW_w = MW(wa\$) \quad (13)$$

$$MW_h = MW(hy\$) \quad (14)$$

$$MW_c = MW(cm\$) \quad (15)$$

$$n_m = 1 \quad (16)$$

$$n_w = 1 \quad (17)$$

$$n_h = 3 \quad (18)$$

$$n_c = 1 \quad (19)$$

$$n_r = n_m + n_w \quad (20)$$

$$n_p = n_h + n_c \quad (21)$$

$$y_m = \frac{n_m}{n_r} \quad (22)$$

Mole fraction of Reactants

$$y_w = n_w/n_r \quad (23)$$

$$y_h = \frac{n_h}{n_p} \quad (24)$$

3 H<sub>2</sub> for 1 CO

$$y_c = n_c/n_p \quad (25)$$

$$MW_r = y_m \cdot MW_m + y_w \cdot MW_w \quad (26)$$

$$MW_p = y_c \cdot MW_c + y_h \cdot MW_h \quad (27)$$

$$mf_w = y_w \cdot MW_w/MW_r \quad (28)$$

Constant given values in process

$$T_{res} = 1900 \text{ [C]} \quad (29)$$

Temperature at hot thermal reservoir in C

$$P = 1 \cdot |1 \text{ 1}| \quad (30)$$

Pressure throughout entire process

## Partial Pressures

$$P_m = P \cdot y_m \quad (31)$$

$$P_w = P \cdot y_w \quad (32)$$

$$P_h = P \cdot y_h \quad (33)$$

$$P_c = P \cdot y_c \quad (34)$$

## State Points

$$T_{1..5} = 25, 225, 120, 535, 800 \quad (35)$$

## Temperature at first five state-points in C

$$T_0 = 25 \text{ [C]} \quad (36)$$

$$h_1 = h(\text{water}, T = T_1, P = P) \quad (37)$$

## Enthalpy at first states. By mole

$$h_2 = h(\text{water}, T = T_2, P = P) \quad (38)$$

$$h_3 = y_w \cdot h(\text{wa}, T = T_3) + y_m \cdot h(\text{me}, T = T_3) \quad (39)$$

$$h_4 = y_w \cdot h(\text{wa}, T = T_4) + y_m \cdot h(\text{me}, T = T_4) \quad (40)$$

$$h_5 = y_h \cdot h(\text{hy}, T = T_5) + y_c \cdot h(\text{cm}, T = T_5) \quad (41)$$

What about  $\dot{m}$ ??? Is it constant? Yes I think so.

Question 1: Find at state point 6 between HX and boiler

$$Q_{HX} = \frac{(h_4 - h_3)}{MW_r} \quad (42)$$

Heat rate of HX. Cold side. Use h not C because h is useful for reaction

$$Q_{HX} = \frac{h_5 - h_6}{MW_p} \quad (43)$$

Heat rate of HX. Hot side.

$$Ta = \frac{T_5 + T_6}{2} \quad (44)$$

$$cp_h = c_p(hy\$, T = Ta) \quad (45)$$

$$cp_c = c_p(cm\$, T = Ta) \quad (46)$$

$$cp_p = \frac{y_c \cdot cp_c + y_h \cdot cp_h}{MW_p} \quad (47)$$

$$Q_{HX} = cp_p \cdot (T_5 - T_6) \quad (48)$$

Get temperature with species enthalpy

$$cp_{h2} = c_p(hy\$, T = T_6) \quad (49)$$

$$cp_{c2} = c_p(cm\$, T = T_6) \quad (50)$$

$$cp_{p2} = (y_c \cdot cp_{c2} + y_h \cdot cp_{h2}) \quad (51)$$

Need the boiler balance for Question 1

in -out

$$n_w \cdot h_1 + n_h \cdot h(hy\$, T = T_6) + n_c \cdot h(cm\$, T = T_6) = n_w \cdot h_2 + n_h \cdot h(hy\$, T = T_7) + n_c \cdot h(cm\$, T = T_7) \quad (52)$$

$$h_7 = y_h \cdot h(hy\$, T = T_7) + y_c \cdot h(cm\$, T = T_7) \quad (53)$$

$$h_{h,out} = h(hy\$, T = T_7) \quad (54)$$

For question 5, exit enthalpy of hydrogen

Question 3: 2nd Law efficiency of HX.

Need the exergy at state pts 3, 4, 5, 6.

$$s_3 = y_w \cdot s(wa\$, T = T_3, P = P) + y_m \cdot s(me\$, T = T_3, P = P) \quad (55)$$

$$s_4 = y_w \cdot s(wa\$, T = T_4, P = P) + y_m \cdot s(me\$, T = T_4, P = P) \quad (56)$$

$$s_5 = y_h \cdot s(hy\$, T = T_5, P = P) + y_c \cdot s(cm\$, T = T_5, P = P) \quad (57)$$

$$s_6 = y_h \cdot s(hy\$, T = T_6, P = P) + y_c \cdot s(cm\$, T = T_6, P = P) \quad (58)$$

$$s_{h,out} = s(hy\$, T = T_7, P = P) \quad (59)$$

For question 5. exit entropy of hydrogen.

$$s_7 = s_{h,out} + y_c \cdot s(cm\$, T = T_7, P = P) \quad (60)$$

And the Dead State

$$y_o = 0.2032 \quad (61)$$

$$y_n = 0.78 \quad (62)$$

$$y_{wv} = 0.0165 \quad (63)$$

$$y_{co2} = 0.00035 \quad (64)$$

$$h_0 = y_o \cdot h('O2', T = T_0) + y_n \cdot h('N2', T = T_0) + y_{wv} \cdot h('H2O', T = T_0) + y_{co2} \cdot h('CO2', T = T_0) \quad (65)$$

$$h_{0,wa} = h(wa\$, T = T_0) \quad (66)$$

$$s_0 = y_o \cdot s('O2', T = T_0, P = P) + y_n \cdot s('N2', T = T_0, P = P) + y_{wv} \cdot s('H2O', T = T_0, P = P) + y_{co2} \cdot s('CO2', T = T_0, P = P) \quad (67)$$

$$s_{0,wa} = s(wa\$, T = T_0, P = P) \quad (68)$$

$$T_{0k} = \text{ConvertTemp}(C, K, T_0) \quad (69)$$

No Q across boundary in HX. These are the specific flow exergies for the states. All mass basis.

$$\psi_{f,3} = \frac{((h_3 - h_0) - T_{0k} \cdot (s_3 - s_0))}{MW_r} \quad (70)$$

$$\psi_{f,4} = \frac{((h_4 - h_0) - T_{0k} \cdot (s_4 - s_0))}{MW_r} \quad (71)$$

$$\psi_{f,5} = \frac{((h_5 - h_0) - T_{0k} \cdot (s_5 - s_0))}{MW_p} \quad (72)$$

$$\psi_{f,6} = \frac{((h_6 - h_0) - T_{0k} \cdot (s_6 - s_0))}{MW_p} \quad (73)$$

The second law efficiency is just the flow exergy of the cold side over the hot side (hot side supplies energy (exergy), cold side uses exergy).

Confirmed correct! Moran p393

$$\eta_{2,HX} = \frac{\psi_{f,4} - \psi_{f,3}}{(\psi_{f,5} - \psi_{f,6})} \quad (74)$$

Cold over hot.

Question 4: Amount of thermal energy from 1900 C reservoir per mole H<sub>2</sub> kJ/kmol H<sub>2</sub>

$$h_h = h(hy\$, T = T_5) \quad (75)$$

Specific enthalpy of each species on either side of the reactor

$$h_c = h(cm\$, T = T_5) \quad (76)$$

$$h_w = h(wa\$, T = T_4) \quad (77)$$

$$h_m = h(me\$, T = T_4) \quad (78)$$

$$q_{net} = (n_h \cdot h_h) + (n_c \cdot h_c) - ((n_w \cdot h_w) + (n_m \cdot h_m)) \quad (79)$$

First law balance of the reactor

$$Q_{reservoir} = q_{net}/n_h \quad (80)$$

Divide by the number of mols of H<sub>2</sub>

Question 5: Specific exergy of H<sub>2</sub> at 7 in kJ/kmol

$$\psi_{H7} = (h_{h,out} - h_{0,wa} - T_{0k} \cdot (s_{h,out} - s_{0,wa})) \cdot \left| 0.001 \frac{\text{kJ}}{\text{J}} \right| \quad (81)$$

Question 6: 2nd law efficiency of process

$$\psi_{Qcv} = Q_{reservoir} \cdot \left( 1 - \frac{T_{0k}}{\text{ConvertTemp}(C, K, T_{res})} \right) \cdot y_h \quad (82)$$

Now Qcv is on a per product rather than per H2 basis

Get properties at dead state

$$S_{R,0} = n_m \cdot s(me\$, T = T_0, P = P) + n_w \cdot s(wa\$, T = T_0, P = P) \quad (83)$$

$$S_{P,0} = n_h \cdot s(hy\$, T = T_0, P = P) + n_c \cdot s(cm\$, T = T_0, P = P) \quad (84)$$

$$H_{R,0} = n_m \cdot h(me\$, T = T_0) + n_w \cdot h(wa\$, T = T_0) \quad (85)$$

$$H_{P,0} = n_h \cdot h(hy\$, T = T_0) + n_c \cdot h(cm\$, T = T_0) \quad (86)$$

Get properties at reaction inlet and outlet temp

$$S_R = n_m \cdot s(me\$, T = T_4, P = P) + n_w \cdot s(wa\$, T = T_4, P = P) \quad (87)$$

$$S_P = n_h \cdot s(hy\$, T = T_5, P = P) + n_c \cdot s(cm\$, T = T_5, P = P) \quad (88)$$

$$H_R = n_m \cdot h(me\$, T = T_4) + n_w \cdot h(wa\$, T = T_4) \quad (89)$$

$$H_P = n_h \cdot h(hy\$, T = T_5) + n_c \cdot h(cm\$, T = T_5) \quad (90)$$

$$\psi_R = H_R - H_{R,0} - T_{0k} \cdot (S_R - S_{R,0}) \quad (91)$$

$$\psi_P = H_P - H_{P,0} - T_{0k} \cdot (S_P - S_{P,0}) \quad (92)$$

$$\eta_{2,sys} = \frac{\psi_P}{\psi_{Qcv} + \psi_R} \quad (93)$$

## Solution

### Variables in Main program

$cm\$ = 'CO'$	$cp_c = 32596 \text{ [J/kmol-K]}$
$cp_{c2} = 31674 \text{ [J/kmol-K]}$	$cp_h = 30064 \text{ [J/kmol-K]}$
$cp_{h2} = 29614 \text{ [J/kmol-K]}$	$cp_p = 3605 \text{ [J/kg-K]}$
$cp_{p2} = 30129 \text{ [J/kmol-K]}$	$\eta_{2,HX} = 0.7298 \text{ [-]}$
$\eta_{2,sys} = 0.6407 \text{ [-]}$	$hy\$ = 'H2'$
$h_0 = -4.128 \times 10^6 \text{ [J/kmol]}$	$h_{0,wa} = -2.418 \times 10^8 \text{ [J/kmol]}$



$h_c = -8.641 \times 10^7$ [J/kmol]	$h_h = 2.291 \times 10^7$ [J/kmol]
$h_{h,out} = 1.288 \times 10^6$ [J/kmol]	$h_m = -4.916 \times 10^7$ [J/kmol]
$H_P = -1.769 \times 10^7$ [J/kmol]	$H_{P,0} = -1.105 \times 10^8$ [J/kmol]
$H_R = -2.727 \times 10^8$ [J/kmol]	$H_{R,0} = -3.164 \times 10^8$ [J/kmol]
$h_w = -2.235 \times 10^8$ [J/kmol]	$me\$ = \text{'CH4'}$
$mf_w = 0.529$ [-]	$MW_c = 28.01$ [kg/kmol]
$MW_h = 2.016$ [kg/kmol]	$MW_m = 16.04$ [kg/kmol]
$MW_p = 8.515$ [kg/kmol]	$MW_r = 17.03$ [kg/kmol]
$MW_w = 18.02$ [kg/kmol]	$n_c = 1$ [-]
$n_h = 3$ [-]	$n_m = 1$ [-]
$n_p = 4$	$n_r = 2$
$n_w = 1$ [-]	$P = 100000$ [Pa]
$\psi_{H7} = 259235$ [kJ/kmol]	$\psi_P = 4.745 \times 10^7$ [J/kmol]
$\psi_{Qcv} = 5.500 \times 10^7$ [J/kmol]	$\psi_R = 1.907 \times 10^7$ [J/kmol]
$P_c = 25000$ [Pa]	$P_h = 75000$ [Pa]
$P_m = 50000$ [Pa]	$P_w = 50000$ [Pa]
$Q_{HX} = 1.083 \times 10^6$ [J/kg]	$q_{net} = 2.550 \times 10^8$ [J/kmol]
$Q_{reservoir} = 8.499 \times 10^7$ [J/kmol]	$s_0 = 194321$ [J/kmol-K]
$s_{0,wa} = 188818$ [J/kmol-K]	$s_{h,out} = 134699$ [J/kmol-K]
$S_P = 741903$ [J/kmol-K]	$S_{P,0} = 589667$ [J/kmol-K]
$S_R = 457932$ [J/kmol-K]	$S_{R,0} = 375178$ [J/kmol-K]
$Ta = 649.8$ [C]	$T_0 = 25$ [C]
$T_{0k} = 298.2$ [K]	$T_{res} = 1900$ [C]
$wa\$ = \text{'h2o'}$	$water\$ = \text{'Steam'}$
$y_c = 0.25$ [-]	$y_{co2} = 0.00035$ [-]
$y_h = 0.75$ [-]	$y_m = 0.5$ [-]
$y_n = 0.78$ [-]	$y_o = 0.2032$ [-]
$y_w = 0.5$ [-]	$y_{wv} = 0.0165$ [-]

**Key Variables**

$\eta_{2,HX} = 0.7298$ [-]	<i>Second law efficiency of HX</i>
$\psi_{H7} = 259235$ [kJ/kmol]	
$Q_{reservoir} = 8.499 \times 10^7$ [J/kmol]	
$\eta_{2,sys} = 0.6407$ [-]	

**Arrays Table: Main**

Row	$h_i$ [J/kmol]	$\psi_{f,i}$ [J/kg]	$s_i$ [J/kmol-K]	$T_i$ [C]
1	1.889E6 {1.889E6}			25 {25}
2	5.268E7 {5.268E7}			225 {225}
3	-1.548E8 {-1.548E8}	-8.903E6 {-8.903E6}	197548 {197548}	120 {120}
4	-1.363E8 {-1.363E8}	-8.370E6 {-8.370E6}	228966 {228966}	535 {535}
5	-4.422E6 {-4.422E6}	275129 {275129}	185476 {185476}	800 {800}
6	-1.364E7 {-1.364E7}	-455192 {-455192}	175404 {175404}	499.6 {499.6}
7	-2.634E7 {-2.634E7}		185121 {185121}	69.41 {69.41}