Problem 4-13

Analyze the basic economics and show an I/O diagram for producing hydrogen from water, coal and natural gas. What production mode should be utilized to obtain production rates of 3×10^7 and 1×10^8 kg/yr?

Cost data:	Electricity:	\$ 0.05/kWh (Cost & Eval. Worksheet)
	H_2:	\$ 0.67/kg (Kirk-Othmer)
	O_2:	\$ 0.04/kg (Kirk-Othmer)
	Bituminous Coal:	\$ 0.0568/kg (eia.gov, 2018)
	Anthracite Coal:	\$ 0.1079/kg (eia.gov, 2018)
	Generic Coal:	\$ 0.055/kg (Cost & Eval. worksheet)
	Steam:	\$ 0.008/kg (Cost & Eval. Worksheet)
	Natural gas:	\$ 1.161/kg (Henry Hub Spot, 15 February 2018)
	Natural Gas:	\$ 1.289/kg (Cost & Eval. Worksheet)

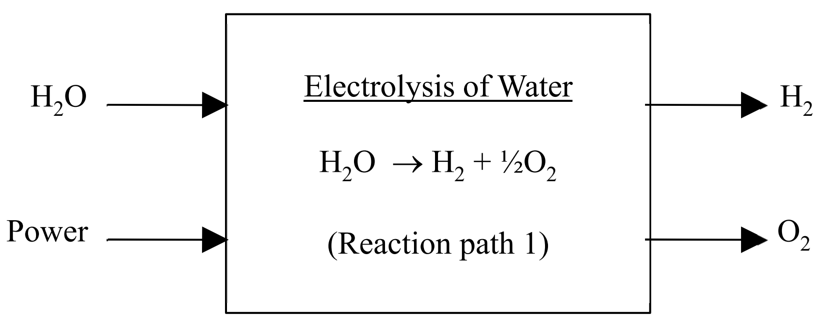
Solution:

Production Mode:

Cadets are often tempted to try to choose one of the four reaction pathways discussed below as the "production mode." In the present context, the authors' intent is quite specific, and "production mode," discussed on page 132 of the textbook, refers to batch versus continuous processing. The rule of thumb given in the book is that the production mode should be batch is the production rate is less than 5×10^5 kg/yr. Based on this rule of thumb, the production mode should be continuous at both 1×10^8 kg/yr and 3×10^7 kg/yr, since these rates are more than the cutoff for batch.

Production of Hydrogen from Water - Electrolysis:

The I/O diagram for the electrolysis of water is shown below:



Electrolysis is a *power-intensive* process, so the power is included in the I/O diagram. In order to account for the cost of electric power in the process, a factor is needed to convert from kg of hydrogen to kilowatt-hours of power. The key to calculating the power requirement is to realize that electrons are forced to move in a redox reaction by the application of external voltage and current (where power = voltage × current). It is also important to recognize that 2 moles of electrons move in the electrolysis circuit for every 1 mole of H_2 formed. The number of electrons is deduced from the change in oxidation numbers in the chemical reaction. The chemical reaction can be re-written with electrons included as:

$$H_2O + 2\ e^- \rightarrow H_2 + \tfrac{1}{2} O_2 + 2\ e^-$$

Electrolysis voltage is typically in the range of 1.85-2.05 volts [1]. Using the relationship that power equals voltage times current allows calculation of kW·hr per kg of H_2:

$$1.95\,\text{V} \cdot \frac{1\text{ amp}}{1\,\text{C/s}} \cdot \frac{96{,}485\text{ C}}{1\text{ mol e}^-} \cdot \frac{2\text{ mol e}^-}{1\text{ mol H}_2} \cdot \frac{1\,\text{W}}{1\text{ amp}\cdot\text{V}} \cdot \frac{1\,\text{kW}}{1000\,\text{W}} \cdot \frac{1\text{ h}}{3600\,\text{s}} \cdot \frac{1\text{ mol H}_2}{2.02\,\text{g}} \cdot \frac{1000\,\text{g}}{1\,\text{kg}} = \frac{51.75\text{ kW}\cdot\text{h}}{1\text{ kg H}_2}$$

At 1.1V, this is about ~29.3 kWh/kg H_2

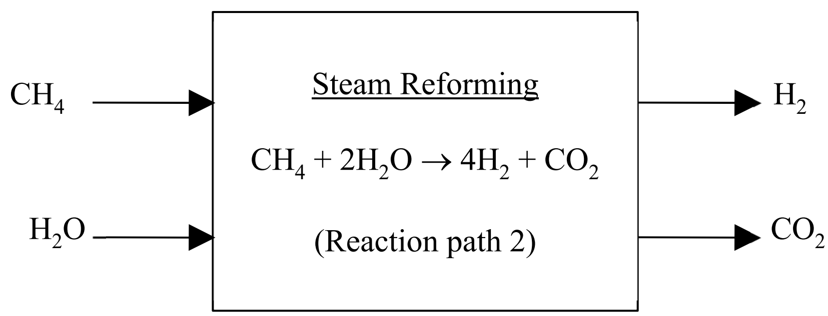
Electrolysis efficiencies are typically about 67% [2], so the actual conversion factor is:

$$\frac{51.75\text{ kWh/kg}\,H_2}{0.67} = 77.24\ \text{kWh/kg}\,H_2$$

With the addition of this conversion factor, the solution closely follows Example 4-2 in the book, and is shown below in the excel screen shots below, where we have assumed a basis of 1 kg of H_2. The analysis is shaded in gray and is labeled "reaction path 1." The price of hydrogen from this process is in excellent agreement with the range of \$2.70-\$3.00/kg H_2, reported by the National Renewable Energy Laboratory [3]. Additional economic data for hydrogen in Reference 5 give a value of ~\$1.00/kg H_2.

Production of Hydrogen from Natural Gas - Steam Reforming:

The I/O diagram for the steam reforming process is shown below, along with the balanced chemical reaction, where methane is chosen to represent natural gas.

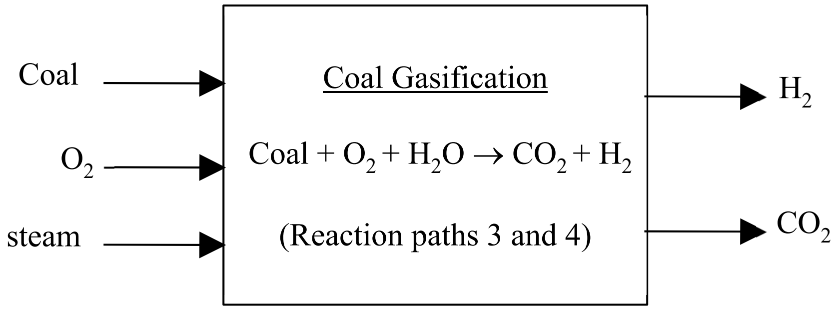


Since carbon monoxide (CO) has no commercial value, we have ignored it in the I/O analysis. This means that we are essentially ignoring the water-gas shift reaction in this analysis.

The economic analysis follows in the excel screen shots, where we have assumed a basis of 1 kg of H_2. The analysis is labeled "reaction path 2."

Production of Hydrogen from Coal - Coal Gasification:

The I/O diagram for the coal gasification process is shown below.



Coal is a diverse material, and the specific type of coal influences the I/O analysis. There are four general classes of coal, including anthracite, bituminous, sub-bituminous, and lignite [4]. The class of coal affects the process technology, since different coals vary considerably in terms of bulk physical properties and elemental composition. In this solution, we consider the reactions of anthracite and bituminous as separate reaction paths. In the analysis, we use separate molecular weights and balanced equations. The empirical formulas are found in Reference 4. Bituminous coal has empirical formula $C_{137}H_{97}O_9$ and FW = 1807.269 g/mol. Anthracite has empirical formula $C_{240}H_{90}O_4$ and FW = 3037.347 g/mol. Balanced reactions are as follows:

Bituminous: $4\ C_{137}H_{97}O_9 + 529\ O_2 + 2\ H_2O \rightarrow 548\ CO_2 + 196\ H_2$

Anthracite: $1\ C_{240}H_{90}O_4 + 237\ O_2 + 2\ H_2O \rightarrow 240\ CO_2 + 47\ H_2$

Water is included in the reactions even though the reactions can be balanced without it. This represents the water-gas shift reaction, which partly determines the amount of hydrogen formed.

The I/O analysis in excel for each of the four reactions is shown below:

Data Needed for Calculations:			Reaction Path (kg/kg H_2):			
Species	Power, kWh/kg	Price, $/kWh	1	2	3	4
e-	29.3	0.05	-29.30	----	----	----
Species	MW, kg/kgmol	Price, $/kg				
H_2	2.0	6.000	1.00	1.00	1.00	1.00
H_2O, liquid	18.0	0.000	-9.00	----	----	----
O_2	32.0	0.040	8.00	----	-43.18	-80.68
CH_4	16.0	1.295	----	-2.00	----	----
CO_2	44.0	0.000	----	5.50	61.51	112.34
H_2O, steam	18.0	0.008	----	-4.50	-0.09	-0.38
bituminous	1887	0.068	----	----	-19.26	----
anthracite	3037	0.118	----	----	----	-32.31
		product value	$6.32	$6.00	$6.00	$6.00
		reactant cost	-$1.47	-$2.63	-$3.03	-$7.04
		excess value	$4.86	$3.37	$2.97	-$1.04

Balanced Equations:

Reaction Path 1: Electrolysis

$H_2O + 2\ e^- \rightarrow H_2 + 1/2\ O_2 + 2\ e-$

Reaction Path 2: Steam reforming

$CH_4 + 2\ H_2O \rightarrow 4H_2 + CO_2$

Reaction Path 3: Bituminous coal gasification

4 C137H97O9 + 529 O2 + 2 H2O ---> 548 CO2 + 196 H2

Reaction Path 4: Anthricite coal gasification

1 C240H90O4 + 237 O2 + 2 H2O ---> 240 CO2 + 47 H2

Production mode: continuous or batch?

Given:	m.t./yr	
3.00E+07 kg/yr	30,000	continuous
1.00E+08 kg/yr	100,000	continuous

Rule of thumb is that cutoff is 50 m.t. per year

Balanced Equations:

Reaction Path 1: Electrolysis

$H_2O + 2\,e^- \rightarrow H_2 + 1/2\,O_2 + 2\,e^-$

Reaction Path 2: Steam reforming

$CH_4 + 2\,H_2O \rightarrow 4H_2 + CO_2$

Reaction Path 3: Bituminous coal gasification

4 C137H97O9 + 529 O2 + 2 H2O ---> 548 CO2 + 196 H2

Reaction Path 4: Anthricite coal gasification

1 C240H90O4 + 237 O2 + 2 H2O ---> 240 CO2 + 47 H2

Production mode: continuous or batch?

Given:		m.t./yr	
3.00E+07	kg/yr	30,000	continuous
1.00E+08	kg/yr	100,000	continuous

Rule of thumb is that cutoff is 50 m.t. per year

Notes:

Basis for all calculations: 1 kg of H_2

Coal can be either bituminous, anthracite; lignite or subbituminous.

Cadets must provide empirical formula for coal used.

Reference for empirical formulas:

https://www.purdue.edu/discoverypark/energy/assets/pdfs/cctr/outreach/Basics8

-accessed Feb 7, 2022

Coal prices found at https://www.eia.gov/energyexplained/coal/prices-and-outlook.php

-accessed Feb 7, 2022

Natural gas price is available at https://www.eia.gov/naturalgas/weekly/

-accessed Feb 7, 2022

Steam price is 0.008$/kg from the "Cost and Evaluation Spreadsheet"

Water and carbon dioxide are assumed to have no value

The details of the stoichiometry calculations in the excel spreadsheet are shown below:

Calculation Details for Each Reaction Path:

1: Electrolysis	2: Steam Reforming	3: Bituminous gasification	4: Anthracite gasification
=-E8*C5			
=-(E8/C8)*(1/1)*C9			
=(E8/C8)*(0.5/1)*C10		=-(G8/C8)*(529/196)*C10	=-(H8/C8)*(237/47)*C10
	=-(F8/C8)*(1/4)*C11		
	=(F8/C8)*(1/1)*C12	=(G8/C8)*(548/196)*C12	=(H8/C8)*(240/47)*C12
	=-(F8/C8)*(2/4)*C13	=-(G8/C8)*(2/196)*C13	=-(H8/C8)*(2/47)*C13
		=-(G8/C8)*(4/196)*C14	
			=-(H8/C8)*(1/47)*C15
=E8*D8+E10*D10	=F8*D8+F12*D12	=G8*D8+G12*D12	=H8*D8+H12*D12
=E5*D5+E9*D9	=F11*D11+F13*D13	=G14*D14+G13*D13+G10*D10	=H15*D15+H13*D13+H10*D10
=E17+E18	=F17+F18	=G17+G18	=G19+G20

References:

1. E. Zoulias, E. Varkaraki, N. Lymberopoulos, C.N. Christodoulou, and G.N. Karagiorgis, "Review on Water Electrolysis," p. 1, accessed 12 February 2024. http://www.cres.gr/kape/publications/papers/dimosieyseis/ydrogen/A%20REVIEW%20ON%20WATER%20ELECTROLYSIS.pdf

2. B. Kroposki, J. Levene, K. Harrison, P.K. Sen, and F. Novachek, "Electrolysis: Information and Opportunities for Electric Power Utilities," p. 25, accessed 12 February 2024. https://www.nrel.gov/docs/fy06osti/40605.pdf

3. "Current (2009) State-of-the-Art Hydrogen Production Cost Estimate Using Water Hydrolysis," National Renewable Energy Laboratory, U.S. Department of Energy, p. 4, accessed 12 February 2024. https://www.hydrogen.energy.gov/pdfs/46676.pdf

4. Brian H. Bowen and Marty W. Irwin, "Coal Characteristics," The Energy Center at Discovery Park, Purdue University, p. 3, accessed 11 February 2024. https://www.purdue.edu/discoverypark/energy/assets/pdfs/cctr/outreach/Basics8-CoalCharacteristics-Oct08.pdf

5. "Hydrogen Fuel Cost vs Gasoline," http://heshydrogen.com/hydrogen-fuel-cost-vs-gasoline/, 2016, Hydrogen Energy Systems, LLC, accessed 11 February 2024.

6. M. Kaiho and O. Yamada, "Stoichiometric Approach to the Analysis of Coal Gasification Process," Chapter 16 in Stoichiometry and Materials Science - When Numbers Matter, Edited by Dr. A. Innocenti, INTECH, 2012, ISBN 978-953-51-0512-1, accessed 1 February 2024. https://cdn.intechopen.com/pdfs/35403/intech-stoichiometric_approach_to_the_analysis_of_coal_gasification_process.pdf