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:	\$ 4.67/kg (Google – average market price of hydrogen)
	O_2:	\$ 0.04/kg (Kirk-Othmer)
	CO:	\$ 0.20/kg (Google – average market price of carbon monoxide)
	Bituminous:	\$ 0.108/kg (eia.gov, 8 February 2025)
	Anthracite:	\$ 0.171/kg (eia.gov, 8 February 2025)
	Generic Coal:	\$ 0.055/kg (Cost & Eval. worksheet)
	Steam:	\$ 0.008/kg (Cost & Eval. Worksheet)
	Natural gas:	\$ 1.344/kg (Henry Hub Spot, 3 February 2025)
	Natural Gas:	\$ 1.289/kg (Cost & Eval. Worksheet)

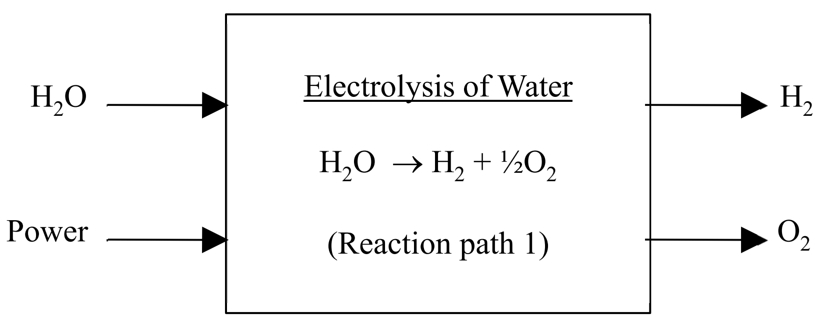
Solution:

<u>Production Mode:</u>

Cadets are often tempted to try to choose one of the four reaction pathways as the "production mode." Important Note: 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.

<u>Production of Hydrogen from Water - Electrolysis:</u>

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]. However, in general chemistry, the valtage in the table of half reactions in the RDC is 1.2291 V, so we will use that value.

Using the relationship that power equals voltage times current allows calculation of kW·hr per kg of H_2:

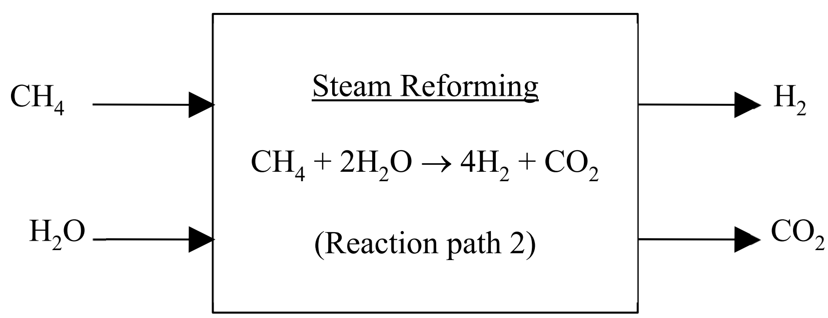
$$1.2291\,\text{V}\cdot\frac{1\text{ amp}}{1\,\text{C/s}}\cdot\frac{96{,}485\text{ C}}{1\text{ mol e}^-}\cdot\frac{2\text{ mol e}^-}{1\text{ mol H}_2}\cdot\frac{1\,\text{W}}{1\text{ amp}\cdot\text{V}}\cdot\frac{1\,\text{kW}}{1000\,\text{W}}\cdot\frac{1\text{ h}}{3600\,\text{s}}\cdot\frac{1\text{ mol H}_2}{2.02\,\text{g}}\cdot\frac{1000\,\text{g}}{1\,\text{kg}}=\frac{32.7\text{ kW}\cdot\text{h}}{1\text{ kg H}_2}$$

At 1.95V, this is about ~51.9 kWh/kg H_2, but 32.7 is the value in the spreadsheet.

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 somewhat lower value of ~\$1.00/kg H_2, but this price is somewhat dated

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.

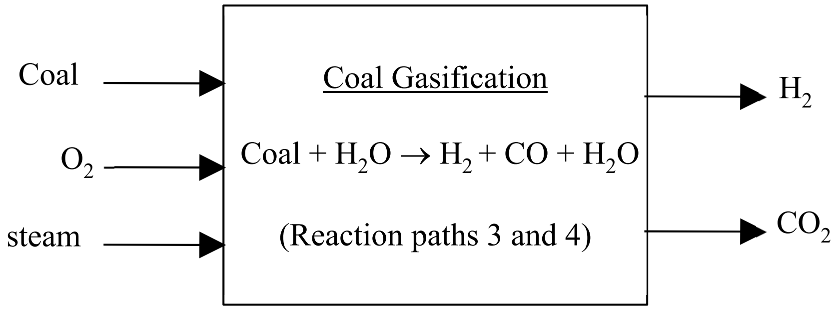


Since carbon monoxide (CO) has no commercial value, we have ignored it in the I/O analysis. This means that we are essentially ignoring the water-gas shift reaction in this analysis.

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:

$$C_{137}H_{97}O_9 \ + \ 209.7\ H_2O \ \rightarrow \ 137\ CO \ + \ 176.5\ H_2 \ + \ 81.7\ H_2O$$

Anthracite:

$$C_{240}H_{90}O_4 \ + \ 337.4\ O_2 \ \rightarrow \ 240\ CO \ + \ 281\ H_2 \ + \ 101.4\ H_2O$$

Water is included in the reactions at a ratio of 2 kg per kg of coal to ensure efficient gasification and maximize hydrogen production.[7] This means that water is produced as a product. This product water is not included in the economics.

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-	32.7	0.05	32.70	----	----	----
Species	MW, kg/kgmol	Price, $/kg				
H_2	2.0	4.670	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	----	----	----
CH_4	16.0	1.384	----	2.00	----	----
CO_2	44.0	0.000	----	5.50	----	----
CO	28.0	0.200	----	----	10.87	11.96
H_2O, steam	18.0	0.008	----	4.50	10.69	10.81
bituminous	1887	0.108	----	----	5.35	----
anthracite	3037	0.171	----	----	----	5.40
		product value	$4.99	$4.67	$6.84	$7.06
		reactant cost	$1.64	$2.80	$0.66	$1.01
		excess value	$3.36	$1.87	$6.18	$6.05

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-CoalCharacteristics-Oct08.pdf
-accessed Feb 8, 2025
Coal prices found at https://www.eia.gov/energyexplained/coal/prices-and-outlook.php
-accessed Feb 8, 2025
Natural gas price is available at https://www.eia.gov/naturalgas/weekly/
-accessed Feb 8, 2025
Steam price is 0.008$/kg from the "Cost and Evaluation Spreadsheet"
Water and carbon dioxide are assumed to have no value
Power of 32.7 kWh/kg assumes a minimum electrolysis voltage of 1.23V given in class.
Coal gasification produces CO and H2 in an incomplete combustion. (Lesson 13 Slide 25.)
About 1.5 to 2.0 kg of steam are used per kg of coal; 2kg/kg is assumed here.

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			
	=(F8/C8)*(1/4)*C11		
	=(F8/C8)*(1/4)*C12		
		=(G8/C8)*(137/176.5)*C13	=(H8/C8)*(240/281)*C13
	=(F8/C8)*(2/4)*C14	=(G8/C8)*(209.7/176.5)*C14	=(H8/C8)*(337.4/281)*C14
		=(G8/C8)*(1/176.5)*C15	
			=(H8/C8)*(1/281)*C16
=E8*D8+E10*D10	=F8*D8+F12*D12	=G8*D8+G13*D13	=H8*D8+H13*D13
=E5*D5+E9*D9	=F11*D11+F14*D14	=G15*D15+G14*D14	=H16*D16+H14*D14
=E18-E19	=F18-F19	=G18-G19	=H18-H19

References:

1. E. Zoulias, E. Varkaraki, N. Lymberopoulos, C.N. Christodoulou, and G.N. Karagiorgis, “Review on Water Electrolysis,” p. 1, accessed 8 February 2025. 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 8 February 2025. 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 8 February 2025. 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 8 February 2025. 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 2025.

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 8 February 2025. https://cdn.intechopen.com/pdfs/35403/intech-stoichiometric_approach_to_the_analysis_of_coal_gasification_process.pdf.

7. Google search - how much steam is used in coal gasification reaction?, accessed 13 February 2025.