

# Kinetics Theory: Haber-Bosch and Steam Reforming

Edward Beck, Yasmi Chibber, Adam Morad, Khushi Shah,  
Owen Sotak



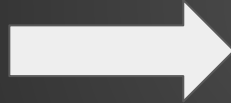
A. JAMES CLARK  
SCHOOL OF ENGINEERING

# Why is Kinetics Important?

Kinetics is the study of the rates and processes of chemical reactions

Chemical engineers view kinetics from the lens of:

- Temperature
- Pressure
- Composition
- Flow rates
- Reynolds number

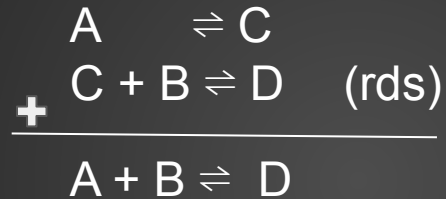


Optimize:

- Efficiency of reactors
- Concentration of desired product
- Profit from chemical reactions

# Core Kinetics Concepts

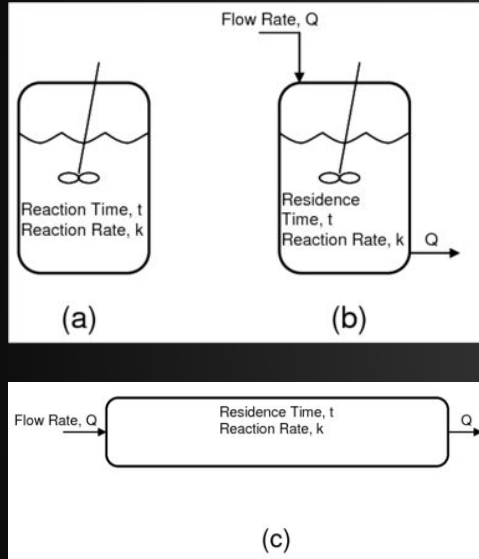
The study of kinetics fundamentally relies on the reaction mechanism and its elementary steps



Following the Power Law:  $r = kC_B C_C$

- Power Law can often *oversimplify* the kinetics due to it ignoring the reversibility of a reaction, as well as potential unidentified intermediates/elementary steps

# Reactor Types and Design Equations



| Reactor Type                                    | Mole Balance<br>Accum = In - Out<br>+ Gen                       | Algebraic<br>Form             | Integral Form                       | Reaction Type | Example Uses                                 |
|---|---|-------------------------------|-------------------------------------|---------------|--|
| Batch Reactor                                   | $\frac{dC_j}{dt} = 0 - 0 + r_j$<br>$C_A \frac{dX_A}{dt} = -r_A$ | -                             | $t = C_{A0} \int_0^{X_A} -r_A dX_A$ | Homogeneous   | Bioreactors,<br>polymerization               |
| Continuous<br>Stirred-Tank<br>Reactor<br>(CSTR) | $0 = F_{j0} - F_j + Vr_j$                                       | $V = F_{A0} \frac{X_A}{-r_A}$ | -                                   | Homogeneous   | Petrochemicals<br>, gas-phase<br>reactions   |
| Plug Flow<br>Reactor (PFR)                      | $\frac{dF_j}{dV} = r_j$<br>$F_{A0} \frac{dX_A}{dV} = -r_A$      | -                             | $V = F_{A0} \int_0^{X_A} -r_A dX_A$ | Heterogeneous | Steam<br>reforming,<br>ammonia<br>synthesis] |

# Steam Reforming (History)

The Billingham site produced syngas from coke gasification (40% efficiency, high energy loss).

1936

Introduced Raschig ring catalysts (better gas flow) and ZnO desulfurization.

1960-1980s

ICI developed SRATIO modeling to optimize steam-to-carbon (S:C) ratios and prevent carbon formation

2000s-Present

Before 1928

ICI built the first large methane reformer, used early nickel catalysts, but faced sulfur poisoning issues.

1950s

Focused on scaling up reformers to increase hydrogen production, efficiency, and durability through naphtha reforming and modular designs.

1980-2000s

Concentrating Ni on the outer layer improved reaction rates while reducing metal waste.

# Process

- Fuel
  - Mainly methane (natural gas); can also use ethanol, propane, or naphtha.
- Oxidant
  - Steam ( $H_2O$ ) reacts with methane to produce hydrogen and carbon monoxide.
- Catalyst & Reactor
  - Nickel (Ni) on alumina ( $Al_2O_3$ ) catalyst is packed into a fixed-bed reactor.

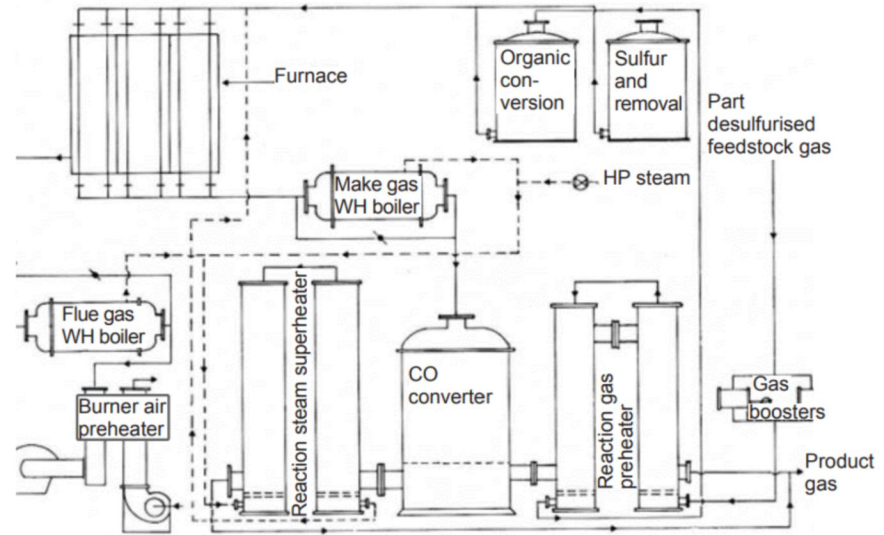


Fig. 3. The methane-steam plant flowsheet from Billingham 1936 (Reproduced with permission from (2))

# Process Conditions

## 1. Methane Pre-treatment

- a. Natural gas is desulfurized to remove sulfur compounds that poison catalysts.

## 2. Primary steam reforming rxn

- a.  $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ 
  - i. Very endothermic, High temperatures (700-1100 °C)
  - ii. Rate Limiting Step: activation of methane on Ni Catalyst surface

$$R_{smr} = 1.42 \times 10^3 \cdot \exp(-1.56 \times 10^5 / R_0 T) (P_{\text{CH}_4})^{1.29} (P_{\text{H}_2\text{O}})^{-0.53} \quad (\text{mol} / \text{m}^2 / \text{s})$$

## 3. Water - Gas Shift Reaction

- a.  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$
- b. Exothermic, low temperature favors  $\text{H}_2$  production -> Le Chatelier's principle

c.

$$r_{\text{CO}} = 2.96 \times 10^5 \exp\left(-\frac{47400}{RT}\right) \left(P_{\text{CO}} P_{\text{H}_2\text{O}} - \frac{P_{\text{CO}_2} P_{\text{H}_2}}{K_e}\right)$$

- d. Methanation (Reverse Reaction, Unwanted) ->  $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ 
  - i. At lower temp. -> competes with SMR

## 4. $\text{H}_2$ separation

- a.  $\text{CO}_2$  removed via absorption or membrane separation

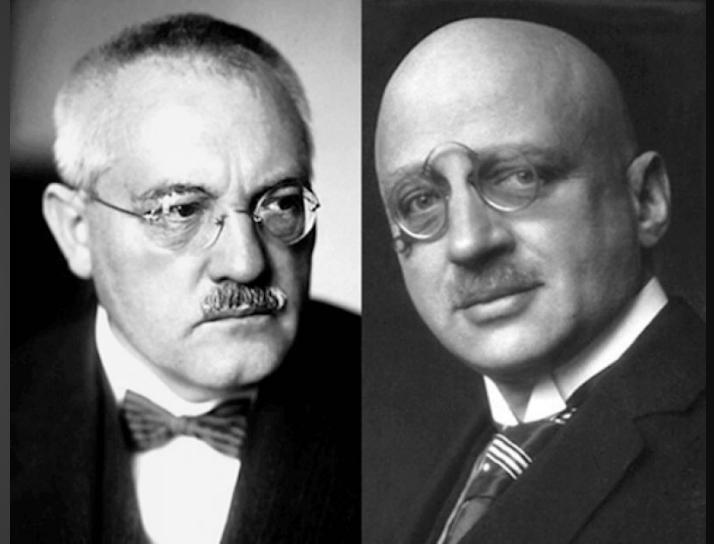
# Steam Reforming vs Other H<sub>2</sub> Production Methods

| Method                       | Process   | Efficiency (%) | CO <sub>2</sub> Emissions            | Scale           |
|------------------------------|---|----------------|--------------------------------------|-----------------|
| <b>Steam Reforming (SMR)</b> | $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}$ | 65–75%         | High (unless carbon capture is used) | Large-scale     |
| <b>Electrolysis</b>          | $\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}_2$              | 60–80%         | Zero (if renewable energy is used)   | Small to medium |
| <b>Ammonia Cracking</b>      | $\text{NH}_3 \rightarrow \text{H}_2 + \text{N}_2$                     | 60–70%         | Low                                  | Medium          |
| <b>Biological Hydrogen</b>   | Microbial fermentation  | 10–30%         | Low                                  | Small-scale     |



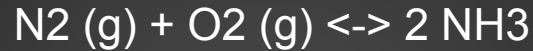
# Haber-Bosch Process (History)

- Revolutionized the agricultural industry in 1913
- Haber dealt with  $\text{NH}_3$  production and Bosch dealt with scaling production
- More than 159 million tons of ammonia are produced yearly
- Population growth to current level would not be possible without this



# Haber-Bosch Process (Math)

Overall reaction:



Langmuir adsorption model:

$$K_A = \theta_A^m / P_A (1 - \theta_{\text{total}})^m$$

$\theta_A$  : fraction of catalyst sites occupied by species A

$P_A$  : partial pressure of A

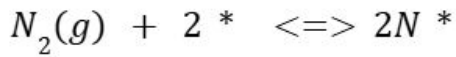
$m$  : exponent and stoich coefficient

$1 - \theta_{\text{total}}$  : fraction of free sites on the catalyst

$K_A$  : adsorption equilibrium constant, depends on temperature and catalyst properties

# Haber-Bosch Process (Math)

How to determine m:



$$\Theta_{total} + \Theta_{empty} = 1$$

$$K_A = \Theta_A^m / P_A (\Theta_{empty})^m$$

$$K_N = \Theta_N^2 / P_N (\Theta_{empty})^2$$

$$K_H = \Theta_H^2 / P_H (\Theta_{empty})^2$$

$$\Theta_N = K_N^{1/2} P_N^{1/2} \Theta_{empty}$$

$$\Theta_H = K_H^{1/2} P_H^{1/2} \Theta_{empty}$$



$$\Theta_{NH_3} = K_{NH_3} P_{NH_3} \Theta_{empty}$$

$$\Theta_{total} = \Theta_N + \Theta_H^3 + \Theta_{NH_3}$$

$$1 = \Theta_{empty} + \Theta_N + \Theta_H^3 + \Theta_{NH_3} = \Theta_{empty} + K_N^{1/2} P_N^{1/2} \Theta_{empty} + K_H^{3/2} P_H^{3/2} \Theta_{empty}^3 + K_{NH_3} P_{NH_3} \Theta_{empty}$$

$$\Theta_{empty} (1 + K_N^{1/2} P_N^{1/2} + K_H^{3/2} P_H^{3/2} + K_{NH_3} P_{NH_3}) = 1$$

$$\Theta_{empty} = 1 / (1 + K_N^{1/2} P_N^{1/2} + K_H^{3/2} P_H^{3/2} + K_{NH_3} P_{NH_3})$$

$$1 - \Theta_{total} = 1 / (1 + K_N^{1/2} P_N^{1/2} + K_H^{3/2} P_H^{3/2} + K_{NH_3} P_{NH_3})$$

# Haber-Bosch Process (Math)

How to find rate of reaction:

$$r = k \theta_N \theta_H^3 \theta_{NH_3}$$

$$r = k^* K_N^{1/2} P_N^{1/2} (1 - \theta_{total})^* K_H^{3/2} P_H^{3/2} (1 - \theta_{total})^3 K_{NH_3}^{1/2} P_N^{1/2} (1 - \theta_{total})$$

$$r = k^* K_N^{1/2} P_N^{1/2} K_H^{3/2} P_H^{3/2} K_{NH_3}^{1/2} P_N^{1/2} K_{NH_3} P_{NH_3} (1 - \theta_{total})^5$$

Competitive adsorption:

Let's say that the NH3 term is more present

We can simplify the  $(1 - \theta_{total})$  term:

$$\text{Let } K_N P_N, K_H P_H \ll K_{NH_3} P_{NH_3}$$

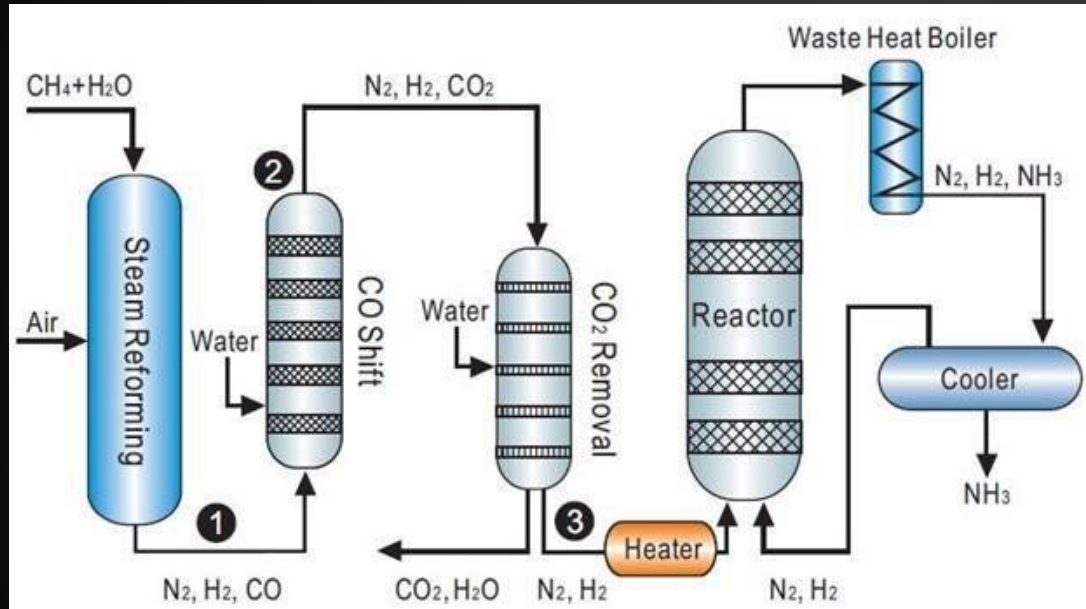
$$(1 - \theta_{total}) = 1/(1 + K_{NH_3} P_{NH_3}) \text{ therefore } \theta_{empty} = 1/(1 + K_{NH_3} P_{NH_3})$$

$$r = k^* K_N^{1/2} P_N^{1/2} K_H^{3/2} P_H^{3/2} K_{NH_3}^{1/2} P_N^{1/2} K_{NH_3} P_{NH_3} (1/(1 + K_{NH_3} P_{NH_3}))^5$$

# Haber-Bosch Process (Math)

$$r = k^* K_N^{1/2} P_N^{1/2} K_H^{3/2} P_H^{3/2} K_{NH_3}^{1/2} P_N^{1/2} K_{NH_3} P_{NH_3} (1/(1 + K_{NH_3} P_{NH_3}))^5$$

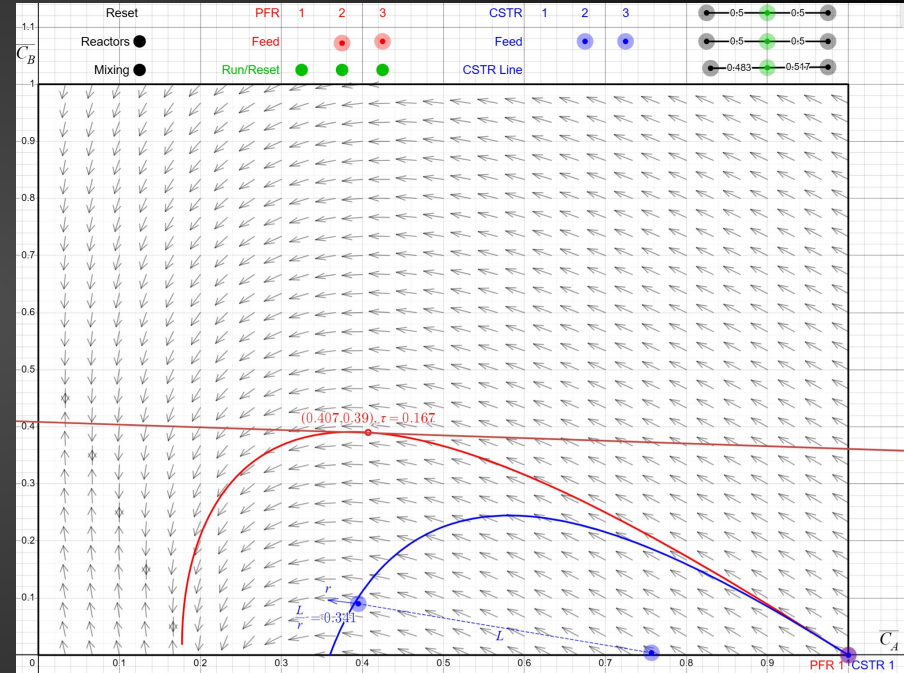
# Haber-Bosch Process (flowsheet)



- 1) Steam Reforming Process
- 2) Water-Gas Shift Reaction using PFR or PBR
- 3) CO<sub>2</sub> and H<sub>2</sub>O Removal using PSA
- 4) N<sub>2</sub> and H<sub>2</sub> pass by another PBR
- 5) NH<sub>3</sub> exits system and N<sub>2</sub> and H<sub>2</sub> are recycled

# Kinetics Simulation in Desmos

- X and Y axis indicate the concentration of the different components normalized over the concentration of the feed.
- Gray arrows indicate the rate vector, which is modified by the rate law and the stoichiometry of the reactions.
- The red and blue lines indicate PFRs and CSTRs respectively.



# How to use the Desmos Simulation

$$r_1(x, y) = k_1 e^{-\frac{E_1}{R_c T}} \frac{K_{P1} P_P (K_{H1} P_H)^2}{(1 + K_{P1} P_P + K_{H1} P_H + K_{K1} P_K + K_{A1} P_A)^3}$$

$$r_2(x, y) = k_2 e^{-\frac{E_2}{R_c T}} \frac{K_{P2} P_P K_{H2} P_H}{(1 + K_{P2} P_P + K_{H2} P_H + K_{K2} P_K + K_{A2} P_A)^2}$$

Stoichiometry

$$r_A(C_A, C_B) = -r_1(C_A, C_B)$$

$$r_B(C_A, C_B) = r_1(C_A, C_B) - r_2(C_A, C_B)$$

Rate vector slope

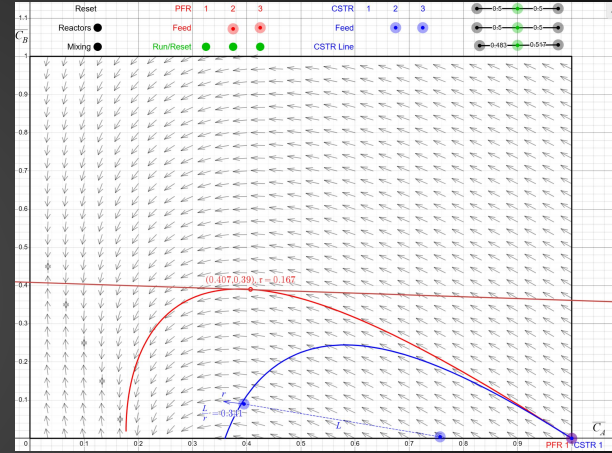
$$R(C_A, C_B) = \frac{r_B(C_A, C_B)}{r_A(C_A, C_B)}$$

- Modify the rate laws and stoichiometry to change the rate field.
- Place PFR and CSTR onto a proper concentration for feed and click run.
- Using the inverse lever arm rule and the lines in the top right, a mixture of the two reactors outputs can be found.



# Optimizing in Desmos Simulation

- Using an objective function it is possible to find an optimized point in the PFR and CSTR Curves in order to maximize or minimize certain parameters.



80  $.0562434 + .1624712y + .046068x + .005\tau = z$

81  $z = 0.19309$

0.193 ● .1935

# Haber-Bosch Batch Reactor Simulation in MATLAB

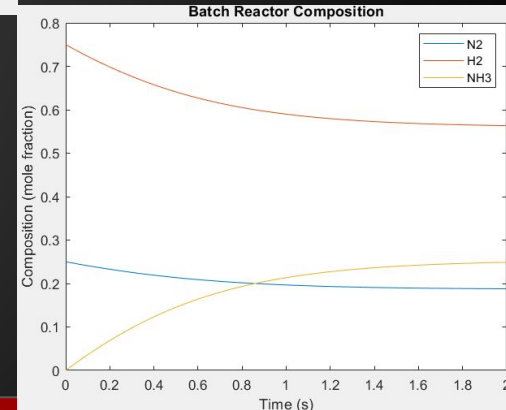
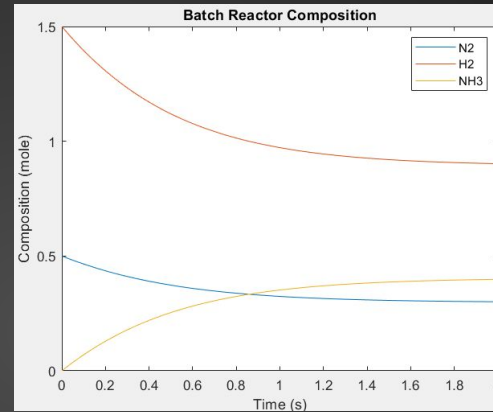
Define reaction rates in terms of both species, operating conditions, and the ODE to solve

```
% Reaction rate, in kmol N2/(m3xs), p in atm, T in K; from Eqn 27.8 of Seider
r = @(T, p) 1e4 * exp(-91000 / (R * T)) * p(N2)^0.5 * p(H2)^1.5 *
1.3e10 * exp(-140000 / (R * T)) * p(NH3);

% Reaction rate, in mol NH3/(m3xs), input p in bar, T in K.
r = @(T, p) r(T, p / 1.013) * 2 * 1000;

% Operating conditions: temperature, pressure, initial volume, catalyst loading
T = 600; % K
tf = 2; % Final time
P = 100; % bar
V = R * T / P / 1e5; % m^3/mole ... 1/density
ninit = [0.5 1.5 0]; % Initial moles of N2, H2, NH3
cat = sum(ninit) * V; % Catalyst volume in m^3

% ODE for batch reaction: dn/dt
dndt = @(t, n) cat * nu * r(T, n / sum(n) * P);
```



# References

**Desmos Graphing Calculator.** *Desmos*; Desmos Studio, Inc. Available at <https://www.desmos.com/calculator/qrjrbg3gqt> (accessed Feb 2025).

**Vallance, C.** *Kinetics at Surfaces*; University of Oxford. Available at <https://vallance.chem.ox.ac.uk/pdfs/KineticsAtSurfaces.pdf> (accessed Feb 2025).

**Genetic Literacy Project.** Fritz Haber and Carl Bosch: The Chemists Who Revolutionized Fertilizer Production, Changing Agriculture Forever. *Genetic Literacy Project*, Jan 29, 2021. Available at <https://geneticliteracyproject.org/2021/01/29/fritz-haber-and-carl-bosch-the-chemists-who-revolutionized-fertilizer-production-changing-agriculture-forever/> (accessed Feb 2025).

# References

**Hill, C. G., Jr.** *An Introduction to Chemical Engineering Kinetics & Reactor Design*; University of Ulm, 2021. Available at

<https://himatekkim.ulm.ac.id/id/wp-content/uploads/2021/06/Charles-G.-Hill-Jr-An-Introduction-To-Chemical-Engineering-Kinetics-Reactor-Design.pdf> (accessed Feb 2025).

**U.S. Department of Energy.** Hydrogen Fuel Basics. *Energy.gov*. Available at

<https://www.energy.gov/eere/fuelcells/hydrogen-fuel-basics> (accessed Feb 2025).

# References

**Starr, F.** *ICI Steam Reformer History*; Johnson Matthey, Available at

<https://fredstarr.com/wp-content/uploads/ICI-Steam-Reformer-History-Johnson-Matthey.pdf> (accessed Feb 2025).

**Liu, K.; Song, C.; Subramani, V.** Water Gas Shift Reaction—A Review. *Int. J. Hydrogen Energy* **2003**, 28 (10), 1103–1113. Available at

<https://www.sciencedirect.com/science/article/pii/S0378775303006141> (accessed Feb 2025).

**IOP Science.** Investigation of Hydrogen Production. *J. Phys.: Conf. Ser.* **2016**, 745 (3), 032147. Available at

# References

**IOP Science.** Investigation of Hydrogen Production. *J. Phys.: Conf. Ser.* **2016**, 745 (3), 032147. Available at

<https://iopscience.iop.org/article/10.1088/1742-6596/745/3/032147/pdf> (accessed Feb 2025).

**YouTube.** Fundamentals of Hydrogen Production. Available at

<https://www.youtube.com/watch?v=GEvORJhjjBE> (accessed Feb 2025).

**Wiley Analytical Science.** Advances in Chemical Kinetics for Industrial Applications. *Biotechnol. Bioeng.* **2021**, 118 (3), 1300–1315. Available at

<https://analyticalsciencejournals.onlinelibrary.wiley.com/doi/full/10.1002/bit.27230> (accessed Feb 2025).