Hydrogen production via the Water-Gas Shift Reaction (WGSR)

Mr. Ivica MARJANOVIC
UPMC – Université Pierre et Marie Curie, Paris – CAPGEMINI, Paris

Background & Description:

This project investigates the simulation of hydrogen production through the Water-Gas Shift Reaction (WGSR), a crucial step in the broader Steam Methane Reforming (SMR) process, using process simulation tools. Hydrogen is a clean energy carrier with the potential to replace fossil fuels in transportation, power generation, and industrial processes. Due to its carbon-free combustion and high energy efficiency, hydrogen is increasingly recognized as a critical component of future sustainable energy systems.

The WGSR enhances hydrogen yield by converting residual carbon monoxide—produced during SMR—into carbon dioxide and additional hydrogen. This reaction not only improves process efficiency but also minimizes the emission of toxic CO gas.

The key chemical reaction involved is:

$$\mathbf{CO + H2O \rightarrow CO2 + H2}$$

This process consists of three main steps:

1. **High Temperature Shift (HTS):** Flue gases exiting the SMR unit, containing CO and unreacted steam, are passed into a high-temperature shift reactor operating between 500–700 K, where approximately 35% of the steam reacts, significantly increasing hydrogen production.
2. **Low Temperature Shift (LTS):** The gas stream is cooled to around 400 K and sent to a low-temperature shift reactor operating at 300–400 K. This stage enhances the hydrogen yield by an additional 2–3%, achieving near-complete CO conversion.
3. **Separation & Purification:** The outlet vapor is cooled and fed into a gas-liquid separator, condensing residual steam. The dry gas—rich in hydrogen—is further processed using Pressure Swing Adsorption (PSA) to isolate high-purity hydrogen.

The thermodynamic behavior of the system was modeled using suitable property methods, ensuring accurate representation of gas-phase equilibrium at various temperature regimes.

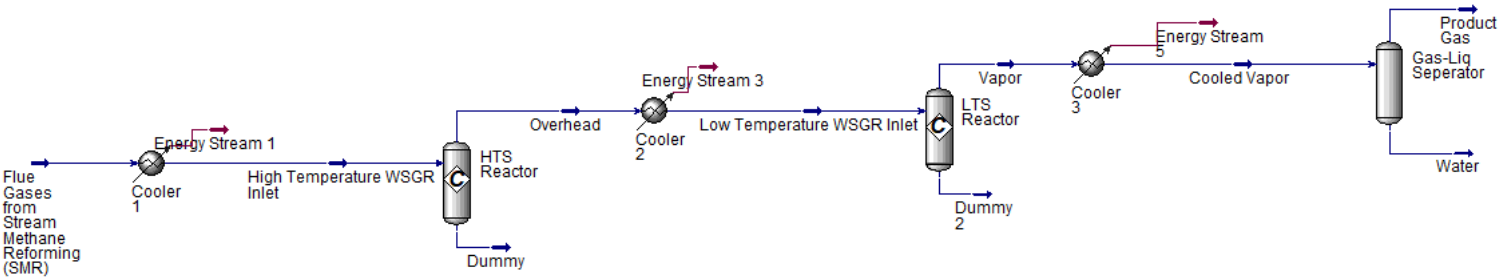
Simulations based on this model achieved a hydrogen molar yield of 0.4701 mol at the product stage, with complete conversion of carbon monoxide and minimal methane slip. These results confirm the efficacy of the WGSR in maximizing hydrogen output and minimizing emissions.

Although challenges such as reactor configuration and thermal integration were initially encountered, iterative optimization—especially around cooling stages and steam-to-carbon ratios—resulted in successful process convergence.

In parallel, the same WGSR process was simulated using Aspen HYSYS, with results comparable to those from open-source platforms like DWSIM. This reinforces the viability of both tools for simulating and optimizing hydrogen production workflows. In particular, DWSIM proves to be a cost-effective solution for chemical process modeling in resource-limited settings.

Thermodynamic package: A property method suited for gas-phase equilibrium (such as Peng-Robinson or SRK) was used for the WGSR system due to its capability to handle high-temperature, non-ideal gas behavior, and gas-phase reactions involving CO, CO_2, H_2, and steam.

Flowsheet



Results:

Master Property Tableau

Object	SMR	Dummy	Overhead	Dummy 2	Vapor	Water	Product Gas
T (K)	617.1	678.1	678.1	471.1	471.1	333.1	333.1
P (Pa)	4.053e5	4.053e5	4.053e5	4.053e5	4.053e5	4.053e5	4.053e5
Molar Flow (gmole/s)	4.709	0	4.709	0	4.709	0.5715	4.137
Molar Flow (CH4)	0.0161	-	0.0161	-	0.0161	0	0.0184
Molar Flow (O2)	0.0074	-	0.0074	-	0.0074	0	0.0085
Molar Flow (Nitrogen)	0.2835	-	0.2835	-	0.2835	0	0.3227
Molar Flow (H2O)	0.2423	-	0.1656	-	0.1656	0.9998	0.0504
Molar Flow (H2)	0.3183	-	0.3950	-	0.3950	0	0.4496
Molar Flow (CO)	0.0767	-	0	-	0	0	0
Molar Flow (CO2)	0.0556	-	0.1323	-	0.1323	0.0002	0.1506

Nb : Insignificant quantities (<0) of components in the product streams can be considered negligible, effectively approximating them to zero without impacting the overall process results or conclusions (see flowsheet).

References: Ibañez, J. F. C., Ergueta, P. L. A., Bilbao, M. B. G., & Cagigal, V. L. B. (2011). U.S. Patent No. 8,075,870. Washington, DC: U.S. Patent and Trademark Office