Autothermal Reforming of Methane for Hydrogen Production

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Background:

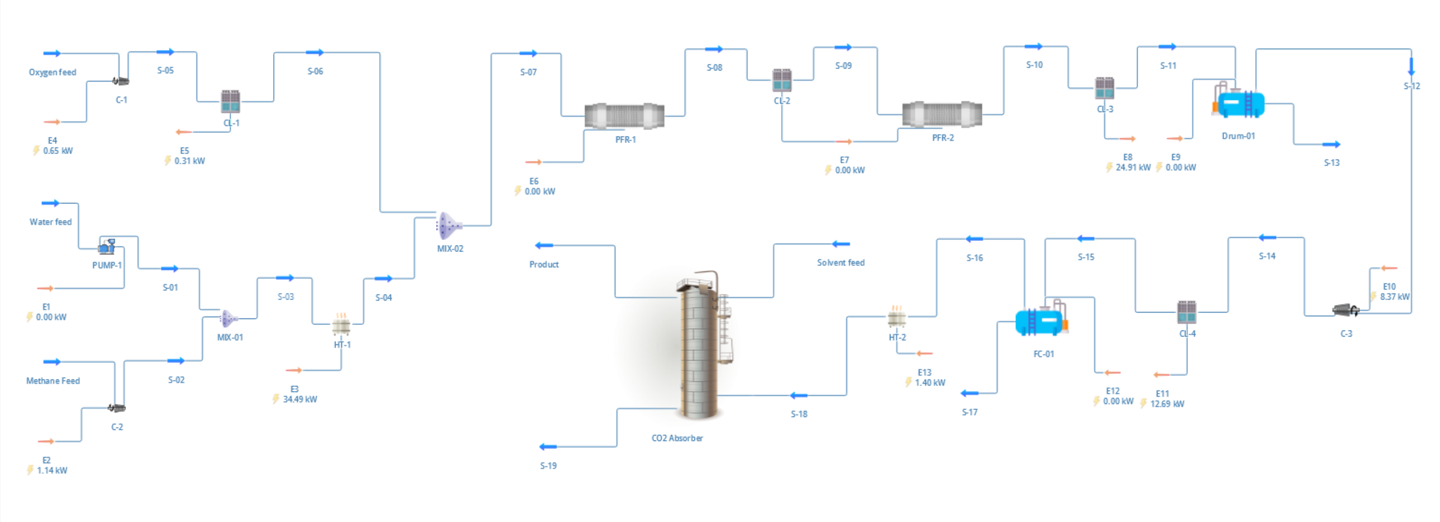
Beside conventional steam methane reforming, autothermal reforming (ATR) is an advanced hydrogen-production process that combines steam reforming and the partial oxidation of methane to generate syngas (a mixture of H_2 and CO). Unlike traditional steam reforming, which is strongly endothermic and requires a large external heat supply, ATR balances the endothermic reforming reaction with the exothermic heat from oxidation. This makes the overall process thermoneutral or slightly exothermic. As a result, ATR units are generally more compact, simpler in design, and more energy-efficient compared to conventional steam reformers and standalone partial-oxidation systems.

Description

This flowsheet converts methane into hydrogen using an autothermal reforming (ATR) approach, where methane reacts with oxygen and steam to produce a hydrogen-rich gas. In the simulation, 1 kmol/hr of methane (16.04 kg/hr), 2 kmol/hr of water (36.03 kg/hr), and 0.55 kmol/hr of oxygen (17.60 kg/hr) are mixed, compressed to 3 bar, and heated before entering PFR-1, the main reformer whose reaction kinetics follow the model reported by Luneau et al. Inside this reactor, partial oxidation and steam reforming occur simultaneously, producing syngas that exits at around 360 °C and 3 bar with a hydrogen mole fraction of about 0.59. The gas then flows to PFR-2, which serves as a mild water-gas-shift section to slightly increase the hydrogen content. Afterward, the stream is cooled and flashed at 50 °C and 3 bar to remove condensed water, then compressed to 15 bar to meet the absorber inlet requirements. Final purification occurs in the CO_2 absorption column, where the syngas contacts a circulating n-decane solvent (3601 kg/hr at 15.2 bar and 40 °C) that selectively absorbs CO_2, and the overhead product leaves the column with a hydrogen mole fraction of 0.98, corresponding to 98% purity hydrogen.

Thermodynamic Package : Peng-Robinson 1978 (PR78)

The Flowsheet:



Results:

Master Property Table

Object	S-06	S-05	S-04	S-03	S-02	S-01	Oxygen feed	Water feed	Methane Feed	
Temperature	100	167.324	350	40.6678	133.085	25.0173	25	25	25	C
Pressure	3	3	3	3	3	3	1	1	1	bar
Mass Flow	17.5993	17.5993	52.073	52.073	16.0425	36.0306	17.5993	36.0306	16.0425	kg/h
Molar Flow	0.55	0.55	3	3	1	2	0.55	2	1	kmol/h
Molar Fraction (Mixture) / CH_4	0	0	0.333333	0.333333	1	0	0	0	1	
Molar Fraction (Mixture) / O_2	1	1	0	0	0	0	1	0	0	
Molar Fraction (Mixture) / CO_2	0	0	0	0	0	0	0	0	0	
Molar Fraction (Mixture) / CO	0	0	0	0	0	0	0	0	0	
Molar Fraction (Mixture) / H_2O	0	0	0.666667	0.666667	0	1	0	1	0	
Molar Fraction (Mixture) / H_2	0	0	0	0	0	0	0	0	0	
Molar Fraction (Mixture) / $C_{10}H_{22}$	0	0	0	0	0	0	0	0	0	

Object	S-15	S-14	S-13	S-12	S-11	S-10	S-09	S-08	S-07	
Temperature	-10	270.298	50	50	50	360.109	360	686.97	320.121	C
Pressure	15	15	3	3	3	3	3	3	3	bar
Mass Flow	54.4854	54.4854	15.1869	54.4854	69.6724	69.6724	69.6724	69.6724	69.6724	kg/h
Molar Flow	4.20758	4.20758	0.8426	4.20758	5.05019	5.05019	5.05019	5.05019	3.55	kmol/h
Molar Fraction (Mixture) / CH_4	8.56E-11	8.56E-11	4.57E-18	8.56E-11	7.13E-11	7.13E-11	7.13E-11	7.13E-11	0.28169	
Molar Fraction (Mixture) / O_2	0.0119273	0.01193	1.62E-07	0.011927	0.009937	0.00994	0.00994	0.009937	0.15493	
Molar Fraction (Mixture) / CO_2	0.237601	0.2376	0.00033	0.237601	0.198013	0.19801	0.19791	0.197914	0	
Molar Fraction (Mixture) / CO	7.17E-08	7.17E-08	6.43E-14	7.17E-08	5.98E-08	5.98E-08	9.87E-05	9.87E-05	0	
Molar Fraction (Mixture) / H_2O	0.0373852	0.03739	0.99967	0.037385	0.197939	0.19794	0.19804	0.198038	0.56338	
Molar Fraction (Mixture) / H_2	0.713087	0.71309	1.63E-06	0.713087	0.594111	0.59411	0.59401	0.594012	0	
Molar Fraction (Mixture) / $C_{10}H_{22}$	0	0	0	0	0	0	0	0	0	

Object	Solvent feed	S-19	S-18	S-17	S-16	Product	
Temperature	40	40.1734	30	-10	-10	39.2357	C
Pressure	3	15.2	15	15	15	15	bar
Mass Flow	3557.04	3601.29	51.6481	2.83733	51.6481	7.40032	kg/h
Molar Flow	25	26.3456	4.05062	0.156967	4.05062	2.70506	kmol/h
Molar Fraction (Mixture) / CH_4	0	6.16E-12	8.89E-11	4.29E-19	8.89E-11	7.31E-11	
Molar Fraction (Mixture) / O_2	0	0.0006	0.01239	1.75E-07	0.01239	0.0127	
Molar Fraction (Mixture) / CO_2	0	0.03725	0.24672	0.002336	0.246717	0.00669	
Molar Fraction (Mixture) / CO	0	2.50E-09	7.45E-08	2.58E-14	7.45E-08	8.72E-08	
Molar Fraction (Mixture) / H_2O	0	2.59E-05	0.00017	0.997663	0.000173	6.87E-06	
Molar Fraction (Mixture) / H_2	0	0.01324	0.74072	6.70E-07	0.74072	0.98019	
Molar Fraction (Mixture) / $C_{10}H_{22}$	1	0.94888	0	0	0	0.00041	

References:

I. Experiments and Modeling of Methane Autothermal Reforming over Structured Ni–Rh-Based Si–SiC Foam Catalysts — M. Luneau, E. Gianotti, N. Guilhaume, E. Landrivon, F. Meunier, C. Mirodatos, Y. Schuurman. *Industrial & Engineering Chemistry Research*, 2017.

II. NPTEL Course on Hydrogen Energy- Production, Storage, Transportation and Saftey by Prof. Pratibha Sharma, IIT Bombay.