Heat and Power Integration Opportunities in Methane Reforming based Hydrogen Production with PSA separation

Alberto Posada and Vasilios Manousiouthakis
Chemical Engineering Department, University of California, Los Angeles, CA 90095, USA
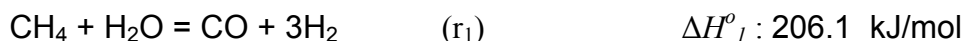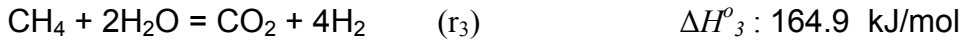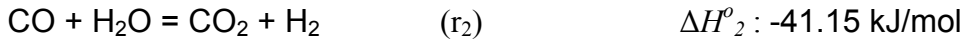
1. Introduction

Hydrogen is getting increasing attention by government and industry leaders, [1], as a very environmentally attractive and clean fuel because its oxidation leads only to water formation. There is abundance of hydrogen in nature, although it is only available for exploitation in a combined state, either in water, hydrocarbons, or coal [2]. Its recovery from these natural resources requires the addition of energy, [3]. The most common industrial process for production of hydrogen from methane is steam reforming, [2-4], which involves an overall endothermic reaction of methane and water to produce hydrogen, carbon dioxide and carbon monoxide in equilibrium with the reactants. Optimization of the use of energy in this process leads to reduction of the cost of production of hydrogen and therefore to a faster development of a hydrogen economy [1]. Tindall and King [5] have summarized important factors to keep in mind when designing steam reformers for hydrogen production that include recovering heat from the hot flue gas by preheating the reformer feed and the generation of steam by extracting heat from the reformer outlet process gas. Scholz [2] considers a process block diagram with a unit that he calls the steam/energy system where heat from the flue gas and from the reformed and converted product gas is used for generation of steam and heating of feed gas, water and combustion air. Shahani et al. [6] have suggested alternative design features that include: operating hydrogen plants as a source of steam (from waste heat recovery) apart from their primary purpose of producing hydrogen, on the basis that "up to a point, a steam reformer has the ability to produce steam more efficiently than a conventional boiler", and also generation of electricity for export from the steam produced. Rajesh et al. [7-8] have presented an integrated approach to obtain possible sets of steady-state operating conditions for improved performance of an existing plant, using an adaptation of a genetic algorithm that seeks simultaneous maximization of product hydrogen and export steam flow rates. Here we carry out heat and power integration studies for a conventional methane reforming based hydrogen production plant with the purpose of finding minimum hot/cold/electric utility cost.

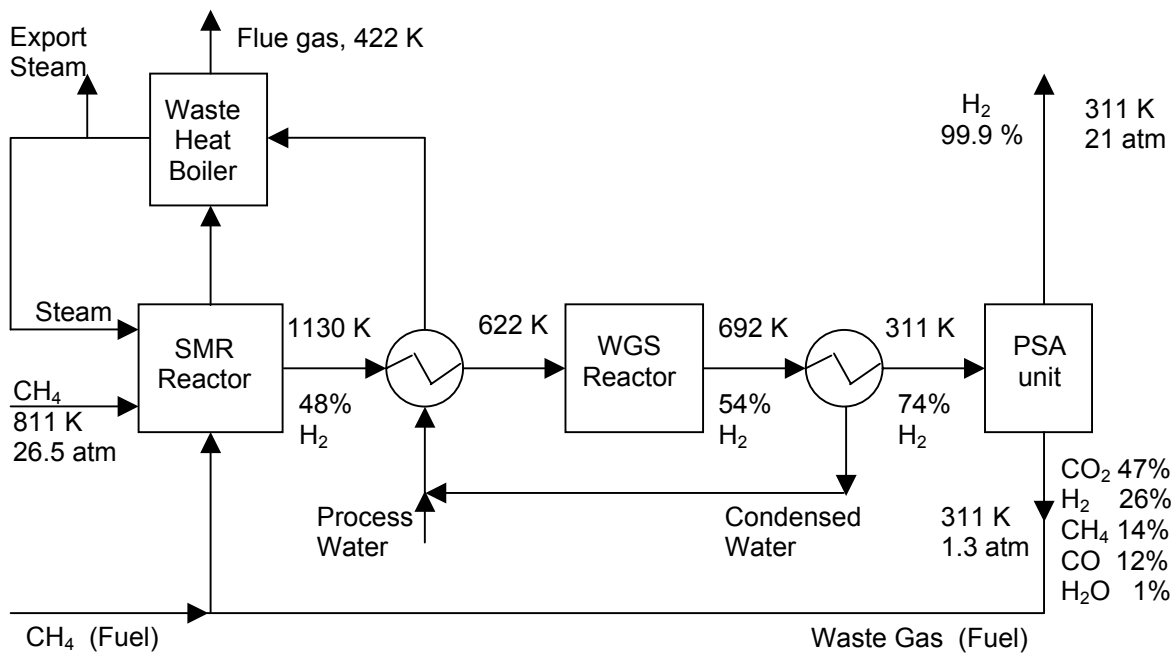## 2. Process description

A conventional methane reforming based hydrogen production plant can be represented with the block diagram in Fig. 1, [4, 8-10]. Hot methane and steam are fed to the steam methane reformer (SMR) where the reversible reactions (r_1), (r_2) and (r_3) are the main global reactions taking place:

$$CH_4 + H_2O = CO + 3H_2 \qquad (r_1) \qquad \Delta H^o_1 : 206.1 \ kJ/mol$$

$CO + H_2O = CO_2 + H_2$ (r_2) ΔH^o_2 : -41.15 kJ/mol

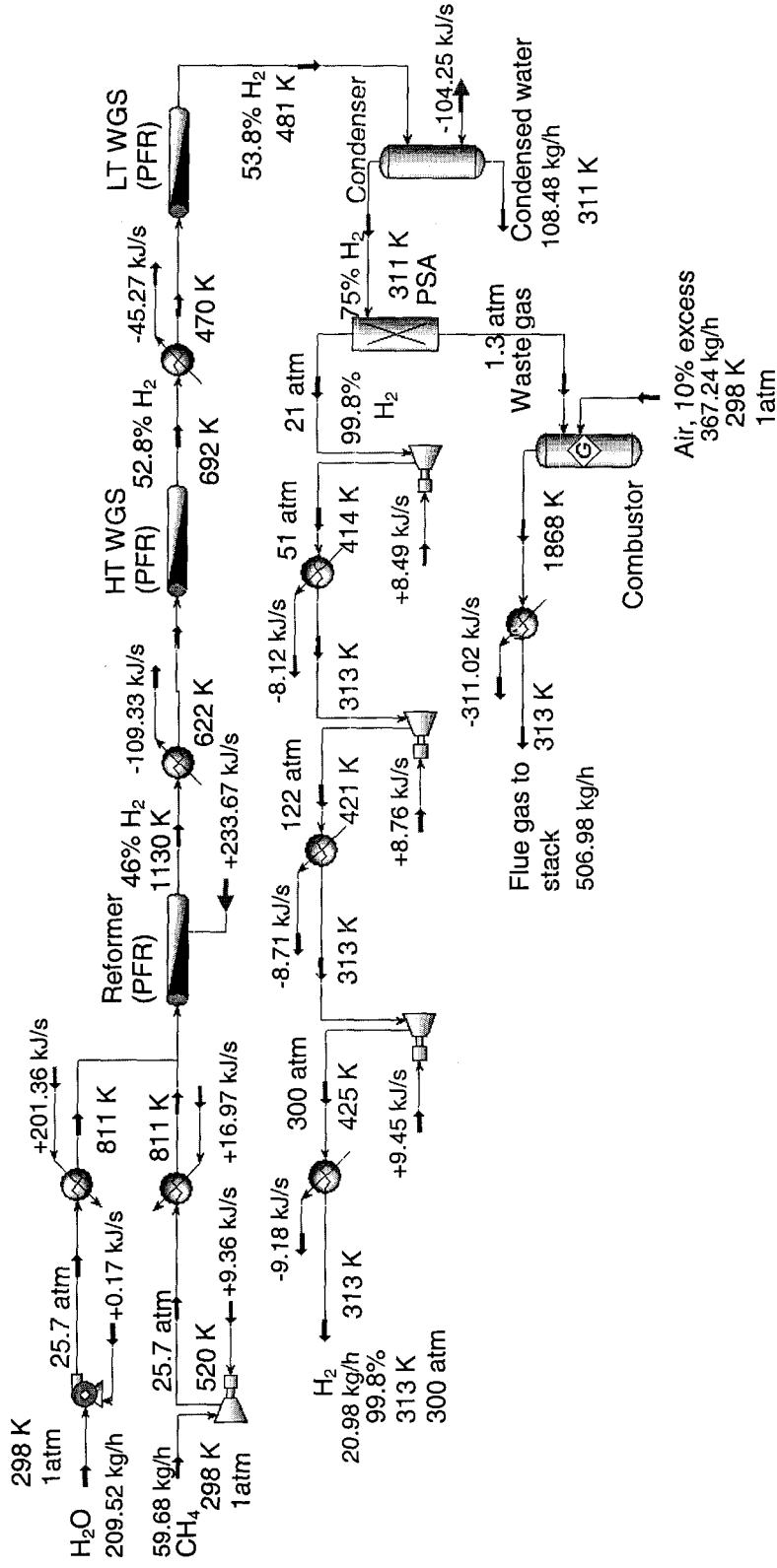$CH_4 + 2H_2O = CO_2 + 4H_2$ (r_3) ΔH^o_3 : 164.9 kJ/mol

The kinetics of these reactions on a $Ni/MgAl_2O_4$ catalyst have been studied by Xu and Froment [11]. The overall reactor operation requires that heat be provided to the reformer, and this is done through combustion of methane (fuel) and PSA waste gas. Hydrogen is produced together with all the other species and its conversion is further increased in the water gas shift (WGS) reactor(s) where only the exothermic reaction (r_2) is catalyzed at temperatures lower than that of the reformer. Keiski et al. [12] studied the kinetics for the high temperature water gas shift reaction on a Fe_3O_4-Cr_2O_3 catalyst for temperatures around 600 K and Rase [13] proposed a kinetic model for the low temperature water gas shift reaction on a copper-zinc oxide catalyst for temperatures below 560 K. Most of the water is separated by condensation as the gas stream is cooled down to almost ambient temperatures before entering the pressure swing adsorption (PSA) unit where hydrogen can be purified to 99.999+% [14-15]. Species other than hydrogen are selectively adsorbed on a solid adsorbent (e.g. activated carbon, 5A zeolite, [15]) at a relatively high pressure by contacting the gas with the solid in a packed column in order to produce a hydrogen enriched gas stream. The adsorbed species are then desorbed from the solid by lowering the pressure and purging with high purity product hydrogen, and the PSA waste gas is in this way generated. Continuous flow of product is maintained by using multiple, properly synchronized adsorption beds. Combustion of the PSA waste gas and methane (fuel) is used to provide heat for the reformer, and also for the preheating of feeds and the generation of export steam, as an effort to recover the waste heat from the still-hot gases leaving the reformer, [2, 5-6].

Fig 1. Conventional process for methane reforming based hydrogen production.

LT WGS
(PFR)

53.8% H_2
481 K

Condenser

−104.25 kJ/s

Condensed water
108.48 kg/h
311 K

75% H_2 311 K   PSA

21 atm

−45.27 kJ/s

470 K

HT WGS
(PFR)   52.8% H_2

692 K

99.8%
H_2

51 atm   414 K

+8.49 kJ/s

1.3 atm
Waste gas

Air, 10% excess
367.24 kg/h
298 K
1 atm

Combustor

1868 K

−8.12 kJ/s   313 K

−109.33 kJ/s

622 K

+233.67 kJ/s

1130 K

Reformer   46% H_2
(PFR)

122 atm   421 K

+8.76 kJ/s

−8.71 kJ/s   313 K

−311.02 kJ/s

313 K

Flue gas to
stack
506.98 kg/h

G

+201.36 kJ/s

811 K

+0.17 kJ/s

25.7 atm

811 K

25.7 atm

520 K

+9.36 kJ/s   +16.97 kJ/s

298 K
1 atm

H₂O
209.52 kg/h
298 K
1 atm

59.68 kg/h
CH_4

300 atm   425 K

+9.45 kJ/s

−9.18 kJ/s   313 K

H_2
20.98 kg/h
99.8%
313 K
300 atm

Fig 2. Process flow diagram of HYSYS simulation for conventional methane steam reforming based hydrogen production. Magnitudes of energy flows are shown as positive (+) for heating or work done on the fluid and as negative (−) for cooling.

3. Process simulation

The process has been simulated using AspenTech's process engineering software HYSYS® version 3.1 [16]. The process flow diagram of the simulation done in HYSYS is presented in Fig. 2. The process feed consists of liquid water and methane gas at ambient temperature. Reactions (r_1), (r_2) and (r_3) take place in the reformer, simulated as a plug flow reactor (PFR) with the kinetic models propose by Xu and Froment [11] producing a gas with 46% (molar) H_2. Heat, in the amount of 233.67 kJ/s, is provided to the reformer. A high temperature water gas shift reactor (HT WGS) is used to raise the concentration of hydrogen to 52.8%, and a low temperature water gas shift reactor (LT WGS) provides an additional 1% increase in hydrogen content. Only the exothermic reaction (r_2) takes place in these last two reactors, which are simulated as adiabatic PFRs using the kinetic models proposed by Keiski et al. [12] and Rase [13], respectively.

Hydrogen purification starts with the condensation and flash separation of liquid water by cooling down the gases, and is finalized in the PSA unit with adsorption of grand majority of the remaining contaminant gases, resulting in the production of 20.98 kg/h of a gas stream with 99.8% H_2 at 21 atm. The hydrogen produced from the PSA unit is compressed in three stages up to 300 atm, which is within typical storage pressure for hydrogen powered vehicles and related hydrogen fueling stations.

4. Optimization problem

The approach proposed by Holiastos and Manouisouthakis [17] for the calculation of the minimum hot/cold/electric utility cost for heat exchange networks is here applied to the conventional methane reforming based hydrogen production process. The problem statement is, [17]: given a set of process streams with specified flow rates, inlet temperatures, and fixed outlet target temperatures; hot and cold utility streams with known temperatures and unit costs; and electrical (work) utility with known unit cost; identify, among all possible heat exchange/pump/engine networks, the minimum total (hot/cold/electric) utility cost necessary to accomplish the desired changes.

For the application at hand the set of process streams is defined by the material streams in the process flow diagram of Fig. 2. The specifications of the hot, cold and electric utilities considered available are defined in Table 1. Hot and cold utilities not allowed to be used for work. The objective function is the sum of the costs of hot, cold and electric utilities.

Table 1
Utilities specification

Utility[a]	T_{in} (K)	T_{out} (K)	$c_{p\text{-}avg}$[b] (kJ/kg-K)	Cost ($/kg)	Cost ($/kJ)
HU: CH$_4$ combustion gas	T_{in}^{HU} = 2168	T_{out}^{HU} = 313	c_{pHU} = 1.44	c_{HU} = 1.724 x 10^{-2}	6.45 x 10^{-6}
CU: cooling water	T_{in}^{CU} = 298	T_{out}^{CU} = 308	c_{pCU} = 4.31	c_{CU} = 8 x 10^{-5}	1.85 x 10^{-6}
W: Electricity	---	---	---	---	c_W = 1.25 x 10^{-5}

a: HU: hot utility, CU: cold utility, W: electric utility or work.
**b**: Average mass heat capacity.

5. Results and discussion

The optimization problem is solved using the linear programming software MINOS 5.5. [18]. The calculated minimum utility cost (MUC), expressed as per kg of hydrogen produced, is included in the bottom row of Table 2, where complete results are summarized. The values in the first column of Table 2 correspond to the conventional process without any integration analysis (no optimization). The second column corresponds to the results after heat (no power) integration of the process and the third column corresponds to the results after heat and power integration. The utility cost of the conventional process is 19 cents/kgH$_2$ and a 36% reduction is achieved after heat integration; a small utility profit can even be generated after heat and power integration due to electricity produced in excess of process needs.

Table 2
Heat and power integration results

Resource Use[a]	Conventional Process	Heat Integration	Heat and Power Integration
CH$_4$ (kg/kgH$_2$)	3.05	2.84	2.84
CO$_2$ (kg/kgH$_2$)	8.25	7.71	7.71
HU (kJ/gH$_2$)	10.7	0	0
CU (kJ/gH$_2$)	22.3	24.2	15.1
W (kJ/gH$_2$)	6.2	6.2	-3.0
MUC ($/kgH$_2$)	0.19	0.12	-0.01

a: CH$_4$: methane consumed as raw material and hot utility. CO$_2$: carbon dioxide generated from combustion of methane and PSA waste. HU: hot utility consumed. CU: cold utility consumed. W: electricity consumed (negative if produced). MUC: minimum utility cost.
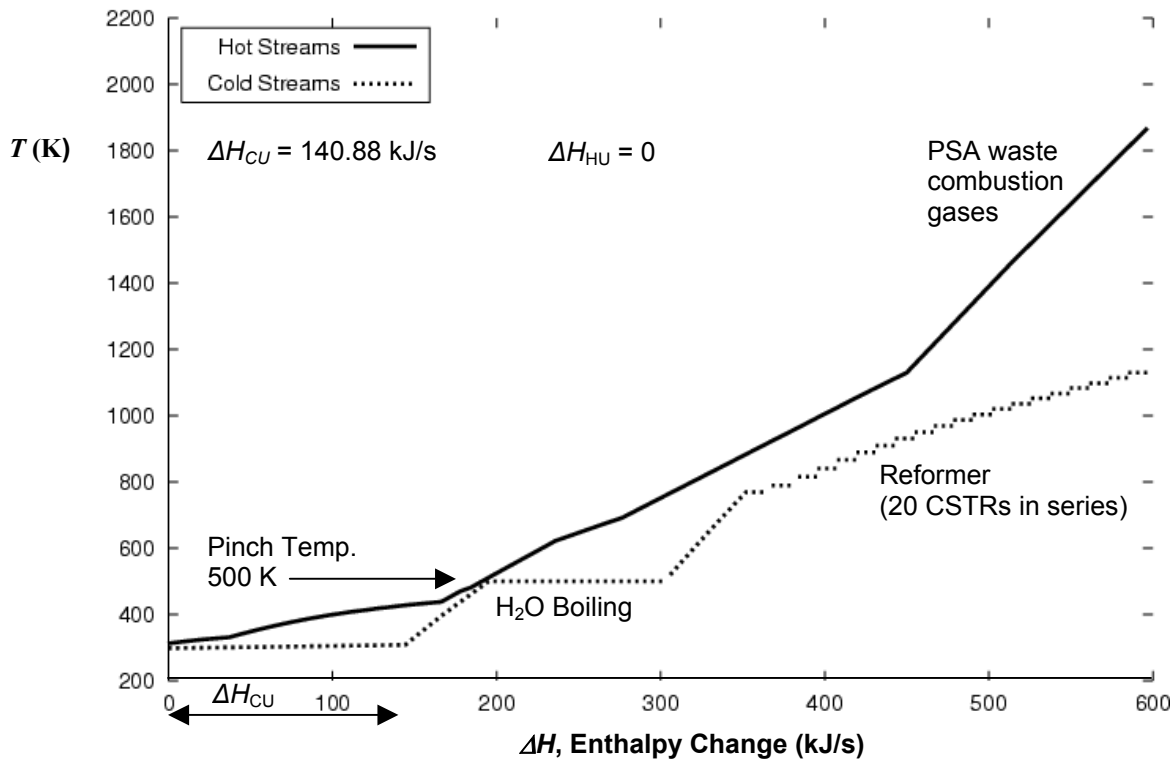
Fig 3. Enthalpy diagram of the optimal HE network of the methane reforming based hydrogen production process after heat integration. $\Delta T_{min} = 10$ K.

The enthalpy diagram of the optimal HE (Heat Exchanger) network of the process after heat integration is presented in Fig. 3. The solid line corresponds to the hot composite curve and the dashed line represents the cold composite curve. The minimum approach temperature considered here is $\Delta T_{min} = 10$ K, being the smallest temperature difference that two streams leaving or entering a heat exchanger can have. It is attained at the pinch temperature of 500 K. The use of cold utility is 140.88 kJ/s; and hot utility is not required if heat integration is accomplished, which means that there is no need to burn additional methane to generate heat for the reformer as it is usually done in the conventional process. This brings not only a 36% reduction in utility cost but also a 6.5% reduction in carbon dioxide emission.

The optimal HEP (Heat Engine and Pump) subnetwork, obtained after heat and power integration, produces a net work of 53.72 kJ/s. If it is assumed that 100% of this work is converted into electricity, the amount of electricity generated is in excess of the process needs (36.24 kJ/s), and if this excess is sold, a small utility profit of 1 cent/kgH$_2$ is generated after covering the cost of the cold utility. Hot utility is again not needed after heat and power integration, suggesting that the production of a large quantity of export steam (10-12 ton of

steam/ton H_2, [19]) from conventional hydrogen plants, could be seen as the result of unnecessary combustion of additional methane (fuel).

6. Conclusions

Heat and power integration studies have been carried out for a conventional methane reforming based hydrogen production plant with capacity of 20.98 kgH$_2$/h. Heat and power integration results in utility profit due to electricity production in excess of process needs. Heat integration alone results in a 36% reduction in utility cost. Operation at the minimum hot/cold or hot/cold/electric utility cost doesn't require hot utility (methane (fuel)), with a consequent reduction of carbon dioxide emissions of 6.5%.

Notation:

c_{CU} : Cost coefficient of cold utility, $/kg
c_{HU} : Cost coefficient of hot utility, $/kg
c_p : Mass heat capacity, kJ/kg-K
c_W : Cost coefficient of electric utility, $/kJ
CU : Cold utility
HE: Heat Exchanger
HEP: Heat Engine and Pump
HU: Hot utility
HT WGS: High Temperature Water Gas Shift reactor
LT WGS: Low Temperature Water Gas Shift reactor
MUC: Minimum Utility Cost
PSA: Pressure Swing Adsorption
SMR: Steam Methane Reformer
r_j : Reaction j = 1, 2, 3.
T : Temperature, K
W: Electricity (negative if produced) or Work (negative if work is done by the fluid)
WGS: Water Gas Shift reactor(s)

Greek letters:

ΔT_{min} : Minimum approach temperature, K
ΔH^o_j : Heat of reaction (r_j), j = 1, 2, 3; kJ/mol
ΔH : Enthalpy change, kJ/s

Subscripts and superscripts:

CU : Cold utility
HU : Hot utility
in : inlet temperature
out : outlet temperature
W : Electric utility

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