

Hydrogen and dry ice production through phase equilibrium separation and methane reforming[☆]

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Abstract

A clean hydrogen (99.9999%) and dry ice production process is proposed, which is based on phase equilibrium (PE) separation and methane reforming. Heat and power integration studies are carried out for the proposed process, by formulating and solving the minimum hot/cold/electric utility cost problem for the associated heat exchange network. The optimum operating cost of the proposed process is shown to be lower than the corresponding cost of the conventional PSA (pressure swing adsorption) based process, if the produced dry ice is sold for as low as 2 cents kg-dry-ice⁻¹ or if an equivalent CO₂ sequestration credit is conceded.

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1. Introduction

The highly efficient oxidation of hydrogen to water in fuel cells suggests it as an environmentally attractive transportation fuel, whose use could result in a positive health impact on city populations [1]. The most common industrial process for production of hydrogen from natural gas is steam reforming [2–4], which involves the endothermic transformation of methane and water to hydrogen, carbon dioxide and carbon monoxide. Following its formation, hydrogen must be separated from the other gases, to attain purity levels required for best performance and long operation of fuel cells [5]. This is especially the case for proton exchange membrane fuel cells (PEMFC), whose anode platinum catalyst has an extremely low carbon monoxide (CO) tolerance (only few ppm) [6]. Hydrogen concentration is increased prior to separation, through the use of water gas shift reactors where CO is partially consumed down to a low percentage as it reacts

with water to produce more H₂ and CO₂. Most of the remaining water is later separated by condensation. CO content can sometimes be reduced to few ppm either by using methanation [7] reactors, i.e. catalyzing the reaction of CO with H₂ to produce CH₄, or through CO preferential oxidation (PROX) [8] reactors, which require the addition of precisely measured amounts of air.

Conventional hydrogen production processes, however, [4,9–12] use pressure swing adsorption (PSA) technology for final hydrogen purification [13,14]. PSA achieves separation of CO, CO₂, CH₄ and H₂O from H₂, by adsorption of these components on a solid adsorbent at a relatively high pressure. The adsorbed species are then desorbed from the solid, by lowering the pressure and purging with high purity product hydrogen. The resulting PSA waste gas contains significant amounts of hydrogen and methane and is thus burned as a source of heat for the reformer. Continuous flow of hydrogen product is maintained by using multiple adsorption beds, whose adsorption/desorption cycles are properly synchronized.

In this work, a clean hydrogen (99.9999%) and dry ice production process is proposed, which is based on phase equilibrium (PE) separation and methane reforming. The pro-

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Nomenclature

c_{CUCj}	cost coefficient of cold utility with constant temperature number $j = 1, 2, 3$ ($\$ \text{kJ}^{-1}$)
c_{CUVj}	cost coefficient of cold utility with varying temperature number $j = 1, 2$ ($\$ \text{kg}^{-1}$)
c_{HU}	cost coefficient of hot utility ($\$ \text{kg}^{-1}$)
c_p	mass heat capacity ($\text{kJ kg}^{-1} \text{K}^{-1}$)
c_W	cost coefficient of electric utility ($\$ \text{kJ}^{-1}$)
C	dry ice selling price or CO_2 sequestration credit ($\$ \text{kg-dry-ice}^{-1}$)
$CUCj$	cold utility with constant temperature number $j = 1, 2, 3$
$CUVj$	cold utility with varying temperature number $j = 1, 2$
Den	denominator in reaction rate expressions
F	mass flow (kg s^{-1})
HE	heat exchanger subnetwork
HEP	heat engine and pump subnetwork
HU	hot utility
ΔH	enthalpy change (kJ s^{-1})
ΔH_m°	standard (25°C , 1 atm) heat of reaction r_m , $m = 1, 2, 3$ (kJ mol^{-1})
k_k	adsorption constant of species $k = \text{CH}_4, \text{H}_2\text{O}, \text{H}_2, \text{CO}$. Units are specified in Table A.1
k_m	rate coefficient of reaction r_m , $m = 1, 2, 3$. Units are specified in Table A.1
K_m	equilibrium constant of reaction r_m , $m = 1, 2, 3$. Units are specified in Table A.2
MUC	minimum utility cost
P_k	partial pressure of species $k = \text{CH}_4, \text{H}_2\text{O}, \text{H}_2, \text{CO}_2, \text{CO}$ (bar)
PE	phase equilibrium, PE based process
PSA	pressure swing adsorption, PSA based process
Q	heat flow (negative for cooling) (kJ s^{-1})
ΔS	entropy change ($\text{kJ K}^{-1} \text{s}^{-1}$)
r_m	reaction $m = 1, 2, 3$
r_{r_m}	rate of reaction r_m , $m = 1, 2, 3$ ($\text{kmol kg}_{\text{cat}}^{-1} \text{h}^{-1}$)
SMR	steam methane reformer
T	temperature (K)
T_i^H	high temperature of interval i in the hot temperature scale (K)
T_{i+1}^H	low temperature of interval i in the hot temperature scale (K)
ΔT_{min}	minimum approach temperature (K)
W	electricity (negative if produced) or work (negative if work is done by the fluid) (kJ s^{-1})
W_s	work provided to the HEP subnetwork (negative if work is produced) (kJ s^{-1})

Greek letters

α_i	variable indicative of presence of hot utility in interval i
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γ_{ji}	variable indicative of presence of cold utility with varying temperature number j in interval i , $j = 1, 2$
δ_i	available heat at interval i (kJ s^{-1})
δ_{CUCj}	heat transferred to cold utility $CUCj$ (kJ s^{-1})
η_i	fraction of cold composite stream from interval i used in the HE subnetwork
θ_i	fraction of hot composite stream from interval i used in the HE subnetwork
λ_{ji}	variable indicative of presence of cold utility with constant temperature number j in interval i , $j = 1, 2, 3$

Subscripts

C	cold composite stream
cat	catalyst
$CUCj$	cold utility with constant temperature number $j = 1, 2, 3$
$CUVj$	cold utility with varying temperature number $j = 1, 2$
H	hot composite stream
HU	hot utility
i	interval i for optimization problem
in	inlet temperature
j	utility number for optimization problem
n	number of intervals for optimization problem
out	outlet temperature
W	electric utility

Superscripts

C	cold temperature scale
$CUCj$	cold utility with constant temperature number $j = 1, 2, 3$
$CUVj$	cold utility with varying temperature number $j = 1, 2$
H	hot temperature scale
HU	hot utility

posed flow diagram avoids the following limitations of the PSA based process: (1) close to 12% [12] of the hydrogen produced in the reformer and the water gas shift reactors ends up in the PSA waste gas. (2) A considerable percentage of the methane fed into the reformer is not converted to hydrogen resulting in increased flows through all reaction and separation units; such percentage depends on the reformer operating conditions and it is around 20% [12] for pressure of 25.7 atm, outlet temperature of 1130 K and steam/ CH_4 molar ratio of 3.12 in the feed. (3) The unsteady operation of the adsorption (PSA) beds necessitates the use of precise and complex control systems to ensure continuous flow of clean hydrogen. In addition, heat and power integration studies of the proposed PE based process are carried out, with the purpose

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