Three – Stage Hydrogen Compression System. Simulating Study with Comsol Multiphysics

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Abstract: In the current paper, a mathematic and simulation study on a three-stage metal hydride hydrogen compressor is presented. Multistage metal hydride hydrogen compressor (MHHC) uses a combination of different materials as metal hydrides to increase the final compression ratio, while maximizing the absorption of both the supply pressures of each stage. We can predict the performance of such MHHC by solving simultaneously the differential equations of energy, mass and momentum conservation. This work is done by using Comsol Multiphysics (version 4.2) software . The materials used in the current study are $LaNi_5$, $MmNi_{4.6}Al_{0.4}$ and $Ti_{0.99}Zr_{0.01}V_{0.43}Fe_{0.99}Cr_{0.05}Mn_{1.5}$. For supply conditions 20^0C and 5 bar a compression ratio of 26:1 is achieved.

Keywords: Metal Hydride, Hydrogen Compression, Coupled Heat and Mass Transfer.

1. Introduction

Over the years, the investigation of new alternative fuels and energy technologies became important [1]. Hydrogen is the most promising energy carrier for the future. It is high energy effective and low polluting fuel [2]. Metal hydrides have long been studied as excellent mediums for hydrogen storage, due to their unique storage capability of storing hydrogen within their atomic structure, at room temperature [3].

Hydrogen compression is one of the most promising methods of storing hydrogen inside a metal hydride tank. The compression is based on the reversible hydrogen absorption/desorption ability of the metal hydrides [4]. When analyzing the use of metal hydrides for hydrogen thermal compression it is important to study the coupling of the four basic stages of a compression complete cycle; the first step is the absorption of hydrogen along with cooling of the metal hydride, followed by the sensible heating of the material. The third step is the desorption procedure of hydrogen along with heating and finally the material is cooling in order to reach the initial conditions [5].

The operation of a hydride compressor depends on heat and mass transfer inside the reaction bed during the absorption and the desorption process. Though, it is very essential the knowledge of the transfer characteristics. Some parameters which play a major role in hydrogen compression procedure are: Heat source and sink temperatures, operating pressures, cycle time and thermal parameters of the bed [6].

Over the past decade a great number of scientists have make efforts in the subject of MHHC and some great results were found [7-14]. In the present paper, a simulation study of a three stage MHHC is made. Once the combination of alloys for multistage MHHC is chosen it is necessary to study the coupled heat and mass transfer characteristics. This is performed by using COMSOL Multiphysics

multimedia package for finite method solution of differential equations. The alloys used in the current study are $LaNi_5$ at the first stage of the compression, $MmNi_{4.6}Al_{0.4}$ at the second stage and at the final stage of compression used $Ti_{0.99}Zr_{0.01}V_{0.43}Fe_{0.99}Cr_{0.05}Mn_{1.5}$

2. Numerical model

The geometry of the three-stage hydrogen compressor is shown in figure 1. In order to simplify the problem, the developed mathematical model is based on the following assumptions:

Temperature and pressure are uniform inside the reactors.

Thermal conductivity and specific heat of the hydride are assumed to be constant.

The medium is in local thermal equilibrium which implies that there is no heat transfer between solid and gas phases.

Radiative heat transfer and viscous dissipation are negligible.

Physical properties of the hydride bed are independent of temperature and hydrogen pressure.

Hydrogen treats as an ideal gas from a thermodynamic point of view.

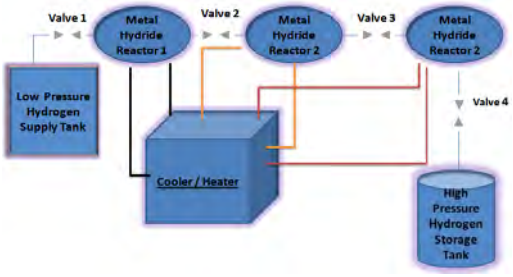

Figure 1. A simplified scheme of a three – stage metal hydride hydrogen compression system

2.1 Energy equation

Assuming thermal equilibrium between the hydride powder and hydrogen gas, a single energy equation is solved instead of separate equations for both solid and gas phases:

$$(\rho \cdot Cp)_e \cdot \frac{\partial T}{\partial t} + (\rho_g \cdot Cp_g) \cdot \bar{v}_g \cdot \nabla T = \nabla \cdot (k_e \cdot \nabla T) + m \cdot (\Delta H - T \cdot (Cp_g - Cp_s)) \quad \textbf{(1)}$$

The effective heat capacity is given by:

$$(\rho \cdot Cp)_e = (\varepsilon \cdot \rho_g \cdot Cp_g) + ((1-\varepsilon) \cdot \rho_s \cdot Cp_s) \quad \textbf{(2)}$$

for absorption and

$$(\rho \cdot C_p)_e = \rho_g \cdot Cp_g + \rho_s \cdot Cp_s \quad \textbf{(3)}$$

for desorption.

The effective thermal conductivity is given by:

$$k_e = \varepsilon \cdot k_g + (1-\varepsilon) \cdot k_s \quad \textbf{(4)}$$

2.2 Mass balance for hydrogen

The mass balance equation for hydrogen gas inside the reactor is given by the equation of continuity:

$$\varepsilon \cdot \frac{\partial(\rho_g)}{\partial t} + div(\rho_g \cdot \vec{v}_g) = -m \quad \textbf{(5)}$$

From the assumption that hydrogen is treated as an ideal gas from a thermodynamic point of view, hydrogen density is considered from gases prefect law

$$\rho_g = \frac{P \cdot M_g}{R \cdot T} \quad \textbf{(6)}$$

2.3 Hydride mass balance

For the solid, a mass conservation equation is considered.

$$(1-\varepsilon)\cdot\frac{\partial \rho_s}{\partial t} = \mp m$$

(7)

Where (-) sign is used for absorption and (+) sign is used for the desorption process.

2.4 Momentum equation

Gases velocity can be expressed by Darcy's law. By neglecting the gravitational effect, the equation which gives the velocity of gas inside the tank is given by:

$$\vec{v}_g = -\frac{K}{\mu_g}\cdot grad(\vec{P}_g) \quad \textbf{(8)}$$

Where K is the permeability of the solid and μ_g is the dynamic viscosity of gas. The solid permeability is given by the Kozeny – Carman's equation

$$K = \frac{dp^2\cdot\varepsilon^3}{180\cdot(1-\varepsilon^2)} \quad \textbf{(9)}$$

From equations (6) and (8), the mass conservation equation of hydrogen becomes:

$$\frac{\varepsilon\cdot \mathrm{M}_g}{R\cdot T}\cdot\frac{\partial P_g}{\partial t} + \frac{\varepsilon\cdot M_g\cdot P_g}{R\cdot T}\cdot\frac{\partial}{\partial t}\cdot\frac{1}{T} - \frac{K}{v_g\cdot r}\cdot\frac{\partial}{\partial r}\cdot\frac{r\cdot\partial P_g}{\partial r} - \frac{K}{v_g}\cdot\frac{\partial^2 P_g}{\partial z^2} = -m$$

(10)

2.5 Kinetic expression

In the equations (1), (5), (7) and (10), the m term represents the amount of hydrogen that absorbed and desorbed inside the reactor.

For the absorption process:

$$m = C_a\cdot\exp[-\frac{E_a}{R_g\cdot T}]\cdot\ln[\frac{p_g}{P_{eq}}]\cdot(\rho_{ss}-\rho_s)$$

(11)

For the desorption process:

$$m = Cd\cdot\exp[-\frac{E_d}{R_g\cdot T}]\cdot(\frac{P_{eq}-p_g}{P_{eq}})\cdot(\rho_s-\rho_o)$$

(12)

C_a and C_d are pro-exponential constants for absorption and desorption respectively, E_a and E_d are the absorption/desorption activation energy, ρ_{ss} is the saturation density for hydride, and ρ_o is the initial metal hydride density.

2.6 Equilibrium Pressure

Initially, all three reactors are in equilibrium with the hydrogen gas. The hydride equilibrium pressure is estimated by using van't Hoff law:

$$\ln P_{eq} = \frac{\Delta \mathrm{H}}{R_g\cdot T} - \frac{\Delta S}{R_g} \quad \textbf{(13)}$$

2.7 Coupled mass and energy balance:

The temperature and the pressure of the hydrogen gas in the combined space immediately after the opening of the valve given by the following equations adopted by [12]:

$$T_{ind} = \frac{n_A\cdot Cg_A\cdot T_A + n_B\cdot Cg_B\cdot T_B}{n_{gi}\cdot Cg_i} \quad \textbf{(14)}$$

and

$$p_{ind} = \frac{n_{gi}\cdot R\cdot T}{V_A+V_B} \quad \textbf{(15)}$$

2.8 Boundary and Initial Conditions

At time t=0, all three reactors are in equilibrium with hydrogen gas. Initially the densities of the hydrides inside the reactors 1,2 and 3 are

$$\rho_{m,A} = \rho_{m,B} = \rho_{m,C} = \rho_{in}$$

The initial temperatures for all the reactors are:

$$T_A = T_B = T_C = T_0$$

The geometry and the boundaries of the reactors are show in Figure 3. In Figure 3a, there is a heat flux procedure between the external heat source (bath) and the chosen walls, which describes from the heat flux condition:

$$-\vec{n} \cdot k_e \cdot \nabla T = h \cdot (T - T_f)$$

where h is the heat flux coefficient.

The boundaries between the metal hydride tank and the hydrogen flow canister are shown in Figure 3b. The boundary condition has set to continuity and described by the following condition:

$$-\vec{n} \cdot (k_{eq1} \cdot \nabla T_1 - k_{eq2} \cdot \nabla T_2) = 0$$

The boundary in which the low pressure supply tank is attached to the first reactor has set to convective flux and described with the condition:

$$-\vec{n} \cdot k_e \cdot \nabla T = 0$$

The boundaries for the coupled desorption – absorption processes are shown in Figure 3c and 3d. Figure 3c, shows the boundaries of the coupled reactors in which they related to each other. The condition in these boundaries has set as continuity. Figure 3d shows the boundaries of the tube which connects the two reactors. The boundary condition for this geometry set as thermal insulation for convection procedure and symmetry for pressure conditions and described by the following condition:

$$-n \cdot \vec{u} = 0, \vec{u} = -\frac{K}{n} \cdot \nabla P$$

3. Results

Figure 2 shows the geometry of the simulation metal hydride tanks. Every reactor has cylindrical shape with length at 0.45m and radius 0.0175m. The dimensions of the supply canister are length at 0.45m and radius 0.004m. The three stage hydrogen compression model consists of three reactor with different materials. The first reactor consists of $LaNi_5$, the second with $MmNi_{4.6}Al_{0.4}$ and the last reactor concludes $Ti_{0.99}Zr_{0.01}V_{0.43}Fe_{0.99}Cr_{0.05}Mn_{1.5}$. The basic thermodynamic properties of these materials are shown in Table 1

Properties	$LaNi_5$	$MmNi_{4.6}Al_{0.4}$	$Ti_{0.99}Zr_{0.01}V_{0.43}Fe_{0.99}Cr_{0.05}Mn_{1.5}$
Activation energy (J/mol)	32000	30000	31400
Enthalpy ΔH (J/mol)	28500	29000	20000
Entropy ΔS (J/molK)	103.2	107.2	97.0
Thermal Conductivity (W/Mk)	1.32	1.6	7.2

Table 1. Basic Thermal Properties of the Metal Hydride Materials.

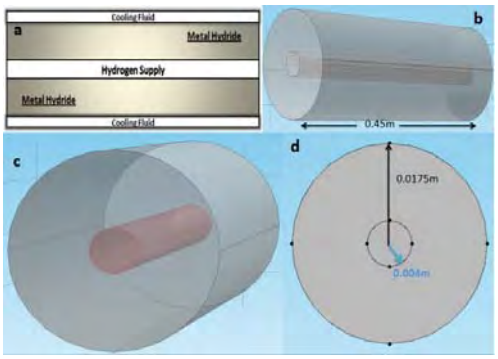

Figure 2. Figure 2a depict a two dimensional geometry of the reactor where the hydrogen supply canister and the cooling fluid flow are shown. 2b and 2c shows the 3D geometry of the reactors used in the model, with cylindrical shape. Figure 2d shows a vertical incision of the cylindrical reactor and the dimensions of the reactor.

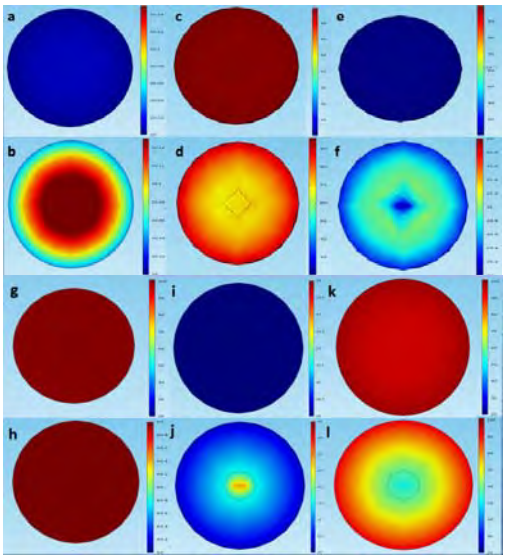

Figure 3. Simulating Results of the Temperature evolution in a three – stage MHHC

Figure 3 shows the temperature evolution of the three – stage MHHC. During the absorption process of the first reactor, due to the exothermal nature of the reaction, the temperature inside the reactor increases with time until the reaction end, and then the temperatures decrease to the equilibrium temperature which is equal to the external heat source temperature. The hydiding reaction inside the first reactor seems to fully end after 3000s, and a sensible heating of the reactor occurs, in order the dehydriding process to take place. During the initial stages of absorption and desorption a sudden increase and decrease of temperature inside the reactor is observed respectively. 3a and b shows the temperature of the first reactor at the hydriding process at the end of the reaction (a) and at the first 400s (b). Figure 3c and d shows the temperature evolution at the dehydriding process of the first reactor for the first coupled reaction. 3c shows the temperature at the end of the reaction and 3d at the beginning of the reaction after the sensible heating process. Figure 3e and f shows the temperature for the desorption of the second reactor for the coupling process. 3e shows the temperature at the end of the reaction while 3f at the first 20s of the reaction. Figure 3g and h show the dehydriding process of the second reactor for the second coupling process. 3g shows the temperature at the end of the process, while 3h at the beginning. 3i shows the temperature at the end of the absorption process of the third reactor and 3j at the beginning. Finally, 3k shows the temperature at the end of the desorption of the third reactor and 3l at the beginning.

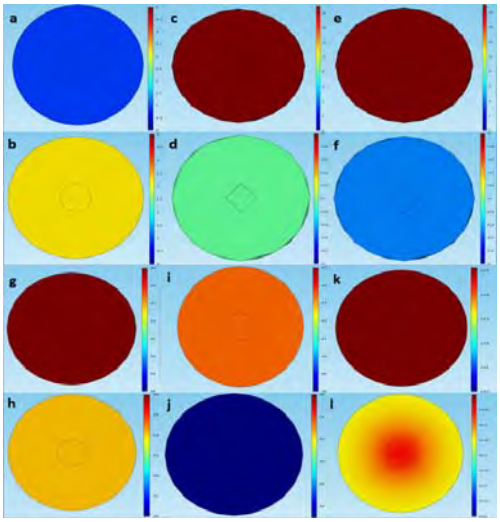

Figure 4. Simulating Results of the Pressure Evolution in a three – stage MHHC

Figure 4 shows the pressure evolution inside the metal hydride tanks. Initially, supply pressure from the low pressure supply tank is at 5bar, and attached to the first reactor. The reactor has an external heat source temperature at 20^0C and when the valve opens, the exothermic reaction begins and the first reactor starts to absorb the supplied hydrogen. As far

as the hydriding process continues there is a gradually reduction of the pressure inside the first reactor because an amount of hydrogen is stored inside the hydride structure voids. As a consequence, at the end of the absorption process the pressure is at 0.92bar. As mentioned before, before the desorption of the first reactor, a sensible heating process occurs to help the dehydriding process to take place. 4a and b shows the pressure of the first reactor at the hydriding process at the end of the reaction (a) and at the first 400s (b). Figure 4c and d shows the pressure evolution at the dehydriding process of the first reactor for the first coupled reaction. 4c shows the pressure at the end of the reaction and 4d at the the first 50s of the reaction after the sensible heating process. Figure 4e and f shows the temperature for the desorption of the second reactor for the coupling process. 4e shows the temperature at the end of the reaction while 4f at the first 50s of the reaction. Figure 4g and h show the dehydriding process of the second reactor for the second coupling process. 4g shows the pressure at the end of the process, while 4h at the first 350s. 4i shows the pressure at the end of the absorption process of the third reactor and 4j at the first 350s. Finally, 4k shows the temperature at the end of the desorption of the third reactor and 4l at the beginning.

4. Conclusions

A simplified lumped model of a three – stage metal hydride hydrogen compression system developed and presented in this work. The first part of this work focused on using a simple but reliable mathematical model which describes the hydrogen compression system. This model based on the solution simultaneously of the energy, mass and momentum differential equations with the proper initial values and boundary conditions. The second part of the work mainly based on construction of a 3D model of a three stage metal hydride hydrogen compressions system and the extraction of some interesting conclusions from this model. The above work done by using COMSOL multiphysics software.

5. References

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6. Nomenclature

Cp: Specific Heat (J/kgK)
u : Gas Velocity (m/s)
Ea: Absorption Activation Energy (J/mol)
Ed: Desorption Activation Energy (J/mol)
K: Permeability (m^2)
P: Pressure (bar)
T: Temperature (K)
t: Time(s)
R: Gas Global Constant, (8.314 J/molK)
d_p: Particle Size (m)

Greek Symbols
ΔH: Reaction Enthalpy (J/mol)
ε: Porosity
ΔS: Reaction entropy (J/molK)
λ: Thermal Conductivity(W/mK)
μ_g: Dynamic Viscosity (kg/ms)
ρ: Density(kg/m^3)

Subscripts
eq: Equilibrium
g: Gas
m: Metal
o: Initial
s: Solid – Hydride
ss: Saturation