On efficiency of metal hydride extraction of hydrogen from a mixture with methane

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Abstract. Extraction of hydrogen from dilute mixtures with natural gas differs from traditional separation processes, since hydrogen is the minor component with low partial pressure. Metal hydrides absorb hydrogen selectively and can be used for purification. Exergy analysis shows that the metal hydride separation of binary mixture of a gas with hydrogen has a maximum at hydrogen content of 5-15%, and the main factors affecting efficiency are the need to spend heat to compensate the reaction enthalpy and pressure losses of methane during filtration through the metal hydride bed. We have experimentally demonstrated successful separation of the hydrogen (10%) – methane (90%) mixture at inlet pressure of 9.5 bar by the LaNi$_{4.8}$Mn$_{0.3}$Fe$_{0.1}$ intermetallic compound in one step with roundtrip (absorption/desorption) hydrogen recovery of 74% and absorption hydrogen recovery of 76%, which is close to the value of 77% calculated based on the thermodynamic analysis.

1. Introduction

Hydrogen-methane mixtures draw attention due to an idea of injection of hydrogen into natural gas network, thus lowering the need of huge investment in the development of hydrogen infrastructure. The power-to-gas process links the power grid with the gas grid by converting surplus power into a grid compatible gas via hydrogen production by water electrolysis and conversion to CH$_4$ via methanation [1]. Several technological and economic barriers exist, and currently operation of power-to-gas plants is not economically viable under current market conditions [2].

Extraction of hydrogen from dilute mixtures with natural gas differs from traditional separations [3], since hydrogen concentration is low. Production of pure hydrogen from a gas mixture containing 60–90 mol% H$_2$ by pressure swing adsorption (PSA) processes has become the state-of-the-art technology, but it is not generally attractive to recover hydrogen, when H$_2$ is a minor component [4].

For hydrogen separation several processes with enhanced sorption were proposed, which use a mixture of a conventional catalyst and a sorbent that is selective to one of the products of the reaction, including the use of metal hydrides [5].

Metal hydrides are known to selectively absorb hydrogen, and hydrogen separation is one of their applications [6]. Most of the investigations were performed on laboratory scale, and scale up studies are essential to take metal hydride applications into commercial market [7].

Our goal is to demonstrate hydrogen extraction from a dilute mixture with methane and to perform exergy analysis of the process in order to find main factors contributing to exergy losses and quantitatively compare them.
2. Experiment
Metal hydride purification technique is illustrated by a scheme in figure 1 (at the left). A feed (point 1), which is the initial mixture of methane and hydrogen, is supplied to a reactor inlet and filtrated through a metal hydride bed. If the partial pressure of hydrogen in the feed is higher than equilibrium pressure of hydrogen absorption, hydride formation starts inside the bed, methane and unreacted hydrogen leave outlet of the reactor (point 2), and absorption enthalpy is removed by cooling (point 4). Purified hydrogen (point 3) is obtained by reactor heating (point 5).

In experiments we use an experimental metal hydride reactor for hydrogen purification and storage RSP-8e [8]. A reaction chamber consists of coaxial steel tubes with outer diameters of 40 mm and 18 mm and length of 400 mm, a space between the tubes is filled with 1 kg of LaNi_{4.8}Mn_{0.3}Fe_{0.1} intermetallic alloy, and the inner tube is cooled or heated by a by silicon oil CAS: 63148-62-9 from a Julabo FP45-HE thermostat. Nominal hydrogen capacity of the reactor is 110 st.L. The reactor is installed in an experimental test bench, and the simplified scheme of experiments is presented in the right part of figure 1. Gas supply is provided from cylinders (hydrogen, hydrogen/methane mixture, nitrogen and helium for purge). Inlet and outlet gas flows are controlled and measured by Bronkhorst EL-FLOW Select mass flow meters/controllers (FR), outlet gas composition is measured by a AG-0012 thermal conductivity gas analyzer (GA), pressure inside the reactor and the gas supply line is measured by Aplisens pressure transmitters model PC28 (P_{in}, P_1 and P_2), temperatures were measured by thin film platinum sensors Heraeus M422, 1 kΩ (inside the metal hydride bed T1 – T3 and in gas space over the bed T4, coolant inflow T_{in} and outflow T_{out}). The test bench has connections to a vacuum system and an automatic control system using LabView software.

Figure 1. Scheme of the metal hydride separation of a binary mixture (left) and simplified scheme of experiments (right): FR – mass flow meters/controllers; GA - thermal conductivity gas analyser; P – pressure gauges; T – temperature sensors.

A hydrogen-methane mixture with hydrogen concentration of 0.1 was fed into the reactor at absolute pressure of 9.5 bar, and the thermostat temperature was set 0°C for absorption. Setpoints for mixture mass flow at the inlet and outlet flow meters/controllers were 2 st.L/min. For desorption the reactor was heated up to 80°C and hydrogen was released to the atmosphere.

Desorption isotherms for the intermetallic compound LaNi_{4.8}Mn_{0.3}Fe_{0.1} were measured by the Sieverts method [9] and fitted with Lengmuir-like function [10]:
\[
\frac{C}{C_{\text{max}}} = 0.849 \frac{0.810 (p / p_s(T))^{1/0.201}}{1 + 0.810 (p / p_s(T))^{1/0.201}} + 0.150 \frac{0.276 (p / p_s(T))^{1/1.38}}{1 + 0.276 (p / p_s(T))^{1/1.38}}
\]

(1)

Properties of the alloy are presented in Table 1.

| Property                              | Value       |
|---------------------------------------|-------------|
| Desorption enthalpy \( \Delta H_{\text{MT}} \), kJ/mole H\(_2\) | 34.0        |
| Desorption entropy \( \Delta S_{\text{MT}} \), J/mole H\(_2\) | 108         |
| Hysteresis \( \ln(p_{\text{abs}} / p_{\text{des}}) \) | 0.13        |
| \( C_{\text{max}}, \% \) wt.     | 1.35        |

3. Thermodynamic model

Overall exergy balance is determined by inputs and outputs from the main process points (see figure 1).

At the feed (point 1) the molar flow balance is:

\[
n_i = n_1^{H_2} + n_1^{CH_4}, \quad \frac{n_1^{H_2}}{y_1^{H_2}} = \frac{n_1^{CH_4}}{y_1^{CH_4}}
\]

(2)

where \( n \) is the molar flow, \( y \) is the molar concentration, subscripts indicate points at the process diagram and superscripts indicate substances.

The following assumptions have been made for the analysis:

- selective absorption of hydrogen:
  \[
  n_1^{CH_4} = n_2^{CH_4} \quad \text{and} \quad y_3^{H_2} = 1
  \]

(3)

- all gases are ideal and have ambient temperature outside the reactor:
  \[
  T_1 = T_2 = T_3 = T_0
  \]

(4)

- equilibrium pressure is given by the van’t Hoff equation with no slope and hysteresis:
  \[
  \frac{p_i(T)}{p_0} = \exp\left[ \frac{\Delta S_{\text{MT}}}{R} \right]
  \]

(5)

- heat exchange with coolant, reactor is isobaric and isothermal:
  \[
  p_3 y_2^{H_2} = p_5(T_{\text{cold}}) \quad \text{and} \quad p_5 = p_3(T_{\text{hot}})
  \]

(6)

A thermodynamic efficiency of the separation process can be defined as [11]:

\[
\eta = \frac{P_{\text{sep}}}{\Delta E_{\text{exp}}} = \frac{\Delta E_{v}^{H_2} + \Delta E_{p}^{H_2} + \Delta E_{t}^{H_2}}{\Delta E_{v} + \Delta E_{Q} + \Delta E_{p} + \Delta E_{t}^{\text{exp}}}
\]

(7)

where \( P_{\text{sep}} \) is the power of separation equal to the rise in chemical exergy rate of separated products over feed, and \( \Delta E_{\text{exp}} \) is the exergy expenditure rate due to the transformation of work into heat.

Following the exergy calculation method for hydrogen purification by absorption [12], we can define an exergy gain for purified hydrogen as a sum of exergy generation due to an increase of hydrogen concentration, pressure and temperature. Exergy losses are due to expenditures of electricity during the process \( \Delta E_{e} \), exergy losses for cooling and heating of the MH bed \( \Delta E_{Q} \), and decrease of partial pressure and temperature of methane and hydrogen in the outflow mixture. We neglect the electricity expenditures, and due to (4) we neglect all the temperature terms, and thus:

\[
\Delta E_{v}^{H_2} = n_3^{H_2} R T_0 \ln\left( \frac{y_3^{H_2}}{y_1^{H_2}} \right); \quad \Delta E_{p}^{H_2} = n_3^{H_2} R T_0 \ln\left( \frac{p_3 y_3^{H_2}}{p_1 y_1^{H_2}} \right); \quad \Delta E_{t}^{H_2} = 0
\]

(8)
\[ \Delta E_p^{\text{exp}} = \Delta E_p^{\text{exp},\text{CH}_4} = n_2^{\text{CH}_4} RT_0 \ln\frac{p_1 y_1^{\text{CH}_4}}{p_2 y_2^{\text{CH}_4}} \] 
\[ \Delta E_p^{\text{ref}} = 0 \quad \Delta E_e = 0 \] 

Exergy losses for heating and cooling depend on hydride formation enthalpy:

\[ \Delta E_Q = \alpha_Q n_i^{\text{H}_2} \Delta H_{\text{MH}} \]

where the heat exchange coefficients \( \alpha_{\text{cold}} \) and \( \alpha_{\text{hot}} \) represent exergy performance of heat exchange, and they are proportional to coefficients of performance (COP) of cooling and heating systems used in the process. We assume

\[ \alpha_i = 0 \quad \text{for} \quad T_i = T_0 \quad \text{and} \quad \alpha_i = 1 \quad \text{for} \quad T_i \neq T_0 \]

thus \( \alpha_0 = 1 \) if the ambient temperature is used for cooling or heating, and \( \alpha_0 = 2 \) in all other cases.

Hydrogen recovery ratio can be defined as:

\[ \beta = \frac{n_i^{\text{H}_2}}{n_i^{\text{H}_2}} = 1 - \frac{p_i y_i^{\text{H}_2}}{p_i y_i^{\text{H}_2}} \]

The main losses of exergy are due to heat transient processes and decrease of methane pressure. Taking into account that hydrogen concentration in the feed is supposed to be low and hydrogen recovery is supposed to be as high as possible, we can neglect the loss of hydrogen pressure in the outflow, and obtain the following equation for exergy efficiency of metal hydride separation:

\[ \eta = \eta_0 \frac{1}{\alpha_Q + \alpha_p} \quad \eta_0 = \frac{RT_0}{\Delta H_{\text{MH}}} \ln\frac{p_i y_i^{\text{H}_2}}{p_i y_i^{\text{H}_2}} \quad \alpha_p = \frac{RT_0}{\Delta H_{\text{MH}}} \frac{1 - y_i^{\text{H}_2}}{y_i^{\text{H}_2}} \ln\frac{p_i (1 - \beta y_i^{\text{H}_2})}{p_i y_i^{\text{H}_2}} \]

Here \( \eta_0 \) depends only on metal hydride properties and external parameters, and can be easily estimated without any knowledge of processes inside the reactor. The dimensionless coefficient \( \alpha_p \) represents exergy losses due to a decrease of methane pressure scaled by the reaction heat of metal hydride formation.

4. Results

During experiments to prevent significant heating of the MH bed during absorption, the process was conducted very slowly. It took two consecutive days to charge the reactor. Coolant temperature was within \( T_{\text{cold}} \) = 0.35-0.55°C and average temperature inside the reactor was within 3-7°C. During the night, the process was stopped and the reactor heated to room temperature, and on the second day the process was restarted. Pressures and gas flows are presented in figure 2 (left), the break of the time axis indicates the night break during the experiment. Discontinuities due to the break have a little effect on integral characteristics of the absorption reaction.

Total amount of the mixture fed to the reactor is 1237±12 s.t.L and off-flow mixture is 1150±20 s.t.L. Direct calculation of the recovery ratio is useless due to the loss of precision in subtraction of two close values. Amount of absorbed hydrogen was measured during desorption at coolant temperature \( T_{\text{hot}} = 80°C \) with average temperature inside the reactor ca. 70°C. 91±1 s.t.L of hydrogen was desorbed, which corresponds to roundtrip hydrogen recovery of 0.74±0.02; also ca. 3 s.t.L of hydrogen was not desorbed, resulting in recovery ratio during absorption \( \beta = 0.76±0.02 \).

Hydrogen recovery ratio during the absorption process using experimental data on gas flow, temperature and pressure was calculated as:

\[ \beta(t) = 1 - \int_0^t \frac{p_i (T(t'))}{p_i y_i^{\text{H}_2}} q_i^{\text{H}_2} (t') dt' \]

\[ \int_0^t q_i^{\text{H}_2} (t') dt' \]
Figure 2. Absorption results: pressures at the reactor inlet and outlet (top left), and mass flow of mixture at the reactor inlet and flow difference between inlet and outlet (bottom left); and calculation of hydrogen recovery ratio at absorption (right) by (14) using van't Hoff equation (5) and approximation of experimental isotherm by (1).

While the mixture flow at inlet remains almost constant during the process, the outlet pressure drops significantly from 8 bar at the start of absorption to less than 3 bar at the end, thus efficiency of purification decreases with an increase of hydrogen concentration. Surprisingly recalculation of experimental results using van't Hoff equation gives the opposite result (figure 2 at right). The van't Hoff equation does not take into account the slope of pressure-composition isotherms and thus overestimates equilibrium pressure at low hydrogen concentrations in alloy, which results in apparent minimum of hydrogen recovery at low $C$. Calculation using real isotherms by approximation (1) gives the correct result for hydrogen recovery, which steadily decreases during the process (figure 2 to the right). Since isotherms are almost symmetrical, the integral results are the same for both curves giving $\beta = 0.77$, which is very close to the experimental value obtained by desorption of purified hydrogen.

Results for exergy efficiency are presented in figure 3. Exergy efficiency has clear maximum in the range of hydrogen concentrations from 0.05 to 0.15 depending on the outlet pressure and coolant temperature. Efficiency of purification can be increased by the use of ambient temperature for cooling as it is seen from the right part of figure 3. Indeed, transient heat transfer processes between two temperature levels require a large amount of heat energy and substantially restrain efficiency of metal hydride systems, being the main source of efficiency losses [13]. Thus, recovery of waste heat is a direct way to increase efficiency.

Conclusion
Metal hydrides absorb hydrogen selectively and can be used for purification. Second law thermodynamic analysis shows that the exergy efficiency of hydrogen extraction has the clear maximum at hydrogen concentrations around 5-15%.

We have experimentally demonstrated successful separation of the hydrogen (10%) – methane (90%) mixture at inlet pressure of 9.5 bar by the LaNi$_{4.8}$Mn$_{0.3}$Fe$_{0.1}$ intermetallic compound in one step with
roundtrip (absorption/desorption) hydrogen recovery of 74% and absorption hydrogen recovery of 76%, which is close to the value of 77% calculated based on the thermodynamic analysis.

The advantage of the metal hydride purification is absorption of the minor fraction from the feed, thus it is preferable for dilute mixtures, and the highest selectivity of metal hydride beds makes practical applications of the proposed method possible.

![Graph](image)

**Figure 3.** Exergy efficiency of metal hydride purification for several outlet pressures and absorption temperatures.

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**References**

[1] Götz M, Lefebvre J, Mörs F, McDaniel Koch A, Graf F, Bajohr S, Reimert R and Kolb T 2016 *Renew Energy* 85 1371–90
[2] van Leeuwen C and Mulder M 2018 *Appl Energ* 232 258–72
[3] Melaina M W, Antonia O and Penev M. 2013 *National Renewable Energy Laboratory. Technical Report NREL/TP-5600-51995*.
[4] Sircar S and Golden T C 2000 *Sep Sci Technol* 35 667–87
[5] Ritter J A and Ebner A D 2007 *Sep Sci Technol* 42 1123–93
[6] Sandrock G 1999 *J Alloy Compd* 293-295 877–88
[7] Muthukumar P, Kumar A, Raju N N, Malleswararao K and Rahman M M 2018 *Int J Hydrogen Energ* 43 17753–79
[8] Dunikov D, Borzenko V, Blinov D, Kazakov A, Lin C Y, Wu S Y and Chu C Y 2016 *Int J Hydrogen Energ* 41 21787–94
[9] Malyshenko S P and Romanov I A 2014 *High Temp+* 52 403–10
[10] Bjurström H, Suda S and Lewis D 1987 *Journal of the Less Common Metals* 130 365–70
[11] Sorin M and Rheault F 2007 *Appl Therm Eng* 27 1191–7
[12] Leites I L, Sama D A and Lior N 2003 *Energy* 28 55–97
[13] Lototskyy M V, Yartys V A, Pollet B G and Bowman Jr R C 2014 *Int J Hydrogen Energ* 39 5818–51