Use of methane-hydrogen mixtures for energy accumulation

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Abstract. Hydrogen-methane mixtures draw attention due to an idea of injection of hydrogen into natural gas network, thus lowering the need of huge investing in development of hydrogen infrastructure. Extraction of hydrogen from dilute mixtures with natural gas differs from traditional separations, since hydrogen concentration is low. Due to selective absorption of hydrogen from the feed, metal hydrides purification achieves high values of separation efficiency. We have experimentally demonstrated successful separation of the hydrogen (10\%) – methane (90\%) mixture at inlet pressure 9.5 bar by the LaNi\textsubscript{4.8}Mn\textsubscript{0.3}Fe\textsubscript{0.1} intermetallic compound in one step with roundtrip (absorption/desorption) hydrogen recovery 74\% and absorption hydrogen recovery 76\%.

1. Introduction

Hydrogen is a clean and effective energy carrier suitable for a long term storage of renewable energy. Pipelines are preferred for transmission and distribution of large amounts hydrogen in a future energy system, but the pipeline costs scale strongly with both distance and flow rate, and capital cost is the largest single factor that contribute to delivery cost [1]. Hydrogen-methane mixtures draw attention due to an idea of injection of hydrogen into natural gas network, thus lowering the need of huge investing in development of hydrogen infrastructure. The injection of hydrogen is limited by standards and regulations, which are country specific. For example, in European Union according to local laws and EU Directives the amount of hydrogen vary from almost 0\% to 12\% [2]. In Russia the standard GOST 5542-2014 does not regulate components of natural fuel gases, and possible hydrogen content is only restricted by requirements for Wobbe index and low heating value (not less than 31.8 MJ/m\textsuperscript{3}).

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\textsubscript{4} via methanation [3]. Several technological and economic barriers exist, and currently operation of power-to-gas plants is not economically viable under current market conditions [4]. The key challenge today is to identify concrete short-term investment opportunities, initial business cases will likely be based on producing green hydrogen and supplying it to industry and mobility [5].

Extraction of hydrogen from dilute mixtures with natural gas differs from traditional separations [6], since hydrogen concentration is low. Production of pure hydrogen from a gas mixture containing 60–90 mol\% H\textsubscript{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\textsubscript{2} is a minor component [7]. 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 [8].

Metal hydrides are known to selectively absorb hydrogen, and hydrogen separation is one of their applications [9]. A number of process developments utilizing MH for separation and purification of
hydrogen were undertaken since 1970s [10-12]. One of the key performance indicators of a separation process is its separation efficiency (recovery), which is defined as the ratio of concentration that has been removed from the feed stream to the initial concentration in the feed stream. Due to selective absorption of hydrogen from the feed, metal hydrides purification achieves high values of separation efficiency. Generally, LaNi5-type alloys are used for hydrogen purification due to their good cyclic stability and increased tolerance to impurities [13], other metal hydride type are also in use [12]. Two main purification techniques are implemented: batch operation and continuous operation (running-flow, flow-through). During the batch operation a metal hydride reactor is periodically filled with mixture, hydrogen is absorbed by the metal hydride bed and later impurities are blown off from the reactor. At continuous operation a mixture flows through the metal hydride bed, which absorbs hydrogen. Process performance can be increased by adjusting the ratio between inlet and outlet gas streams [14, 15]. Investigations show that hydride technologies can be more efficient than conventional ones [16] for low temperature applications. Isothermal operation of metal hydride reactors [17], heat recovery and use of ambient temperature [18] are considered as promising ways to increase efficiency.

The goal of the present study is to perform experimental investigation on separation of a lean mixture of hydrogen (10%) and methane, and formulate optimization strategy for scale up of the technology.

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), absorption enthalpy is removed by cooling (point 4). Purified hydrogen (point 3) is obtained by heating of the reactor (point 5).

For experiments, we use an experimental metal hydride reactor for hydrogen purification and storage RSP-8e [14]. A reaction chamber consist from coaxial steel tubes with outer diameters 40 mm and 18 mm and length 400 mm, a space between the tubes if filled with 1 kg of LaNi5.8Mn0.3Fe0.1 intermetallic alloy, the inner tube is cooled or heated 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, simplified scheme of experiments is presented at the right in figure 1. Gas supply (hydrogen, mixture, nitrogen and helium for purge) is provided from cylinders.

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.
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 $T_1$ – $T_3$ and in gas space over the bed $T_4$, 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.

A hydrogen-methane mixture with hydrogen concentration 0.1 was fed into the reactor at absolute pressure 9.5 bar, 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.

3. Results and conclusions
Total amount of the mixture fed to the reactor is $1237\pm12$ s.tL and $1150\pm20$ st.L of mixture left the reactor. Direct calculation of the recovery ratio is useless due to the loss of precision from subtraction of two close values. Amount of absorbed hydrogen was measured during desorption.

For desorption inlet coolant temperature was $T_{in} = 80.0\pm0.05^\circ$C and outlet temperature $T_{out} = 79.5\pm0.05^\circ$C, and average temperature inside the reactor was around 70°C. There were desorbed 91±1 st.L of hydrogen, which corresponds to roundtrip hydrogen recovery 0.74±0.02, also ca. 3 st.L of hydrogen were not desorbed, resulting in recovery ratio during absorption 0.76±0.02.

Exergy balance for the experiment is presented in the Sankey diagram in Fig. 2. Exergy flows are calculated with the use of REFPROP software [19]. Outlet pressure is supposed to be 5 bar (nearly average for the process). The diagram confirms that the main contributors to the exergy gain are chemical exergy due to increase of hydrogen concentration (22 kJ) and pressure (14.5 kJ), while the losses are due to decrease of mixture pressure (from 300 kJ to 199 kJ) and compensation of the reaction enthalpy (143 kJ at absorption and 138 kJ at desorption). When all the heat of hydride formation is obtained by electric energy, the exergy efficiency is 11%. Efficiency is higher with the use of low potential heat for cooling and heating. Taking into account dependence of heat qualification coefficients on temperature, the exergy efficiency increases to 34%.

![Figure 2. Sankey diagram for the hydrogen purification experiment.](image-url)
Our experiments show that metal hydrides absorb hydrogen selectively and can be used for purification. For lean mixtures the metal hydride purification has the advantage over conventional PSA technology, since a metal hydride bed absorbs the minor fraction of the mixture, while PSA units have to adsorb the major part. Optimization strategy for metal hydride separation of hydrogen from lean mixtures with methane should include the increase of permeability of the bed to decrease methane pressure losses, decrease absorption equilibrium pressure to increase hydrogen recovery, use ambient temperature for cooling and low potential heating of the metal hydride bed. Ensuring efficient separation of hydrogen from lean mixtures with methane opens the way to accumulation of energy from variable renewable sources by blending renewable electrolytic hydrogen with natural gas.

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