

STATE OF THE ART IN HYDROGEN LIQUEFACTION

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Abstract

Hydrogen is a potential option to replace fossil fuels considering the increasing demand of energy applications. It is naturally abundant and is regarded as a suitable energy carrier. There has been extensive research to improve the efficiency of storing hydrogen with different methods, including gas compression, liquefaction and sorption in metal hydrides or carbon nanotubes. A comparison of the storage methods shows that liquefaction of hydrogen is more beneficial than compression of hydrogen in terms of higher volumetric capacity, and it is more technologically mature than sorption technologies. This makes it more plausible for long distance distribution. On the other hand, the obstacles in full exploitation of the method are low energy efficiency of the liquefaction process and associated high cost. The recent research has been focusing on increasing the energy efficiency of the storage process. This paper provides, with regard to the conventional methods, a state of the art review of the novel and modified liquefaction process and the latest developments in increasing the efficiency of the energy intensive process. Furthermore, the developments in combining the hydrogen liquefaction plants with renewable energy sources are covered and reviewed. Finally, the ongoing development of hydrogen liquefaction is highlighted.

Keywords: Hydrogen, Liquefaction, Energy Storage, Efficiency, Exergy

1. Introduction

The increasing trend of the world energy demand requires a sustainable source of energy with a lower environmental impact than the conventional energy resources. Energy generated from the renewable resources, as alternative to the conventional ones, including wind and solar energy, needs to be stored through a storage medium. Hydrogen (H₂) is an interesting energy carrier. It is an abundant source of energy throughout the world and can be harnessed in different ways. It can be produced through many processes of fuel processing including hydrocarbon and ammonia reforming, desulfurization, and pyrolysis among others. In these processes, hydrogen is extracted through converting fuels containing hydrogen. It can be also produced from water through electrolysis or thermolysis processes at which hydrogen and oxygen are split apart using electricity in a relatively wide range of operating temperature range (Nikolaidis and Poullikkas, 2017; Satyapal et al., 2007).

Hydrogen is stored and transported in different methods. It can be compressed and stored in special high pressure withstanding containers, or be liquefied and maintained under certain temperature and pressure condition. It can be adsorbed in carbonic structures or can be distributed in metallic structures forming metal hydrides.

The highly compressed hydrogen is currently the most common way to store hydrogen, however, the compression is an energy intensive process, consuming about 15% of its low heat value (LHV) per unit mass (Jensen et al., 2007). The drawback with gas compression is its low volumetric capacity. To increase the volumetric capacity the compression needs to be increased, leading to a higher energy demand process.

Storing hydrogen with adsorption in carbon materials or by forming of hydrides in metals such as magnesium and iron, composing complex metal hydrides including nitrogen-containing and boron-containing hydrides is associated with major drawbacks as well. Storing and releasing of hydrogen in most of the hydrides are highly endothermic or exothermic reactions, occurring at extreme temperatures, demanding significant cooling and heating (Umegaki et al., 2009). In addition, metal hydrides suffer from low gravimetric capacity (wt %) and low volumetric capacity (g L⁻¹), making them unappealing to be used extensively in industrial scale (Durbin

and Malardier-Jugroot, 2013).

Liquefaction of hydrogen is an alternative to the aforementioned methods. However, the boiling temperature of hydrogen is about $-253\text{ }^{\circ}\text{C}$ and liquefying through reaching to such low temperature can be highly energy consuming. Liquefied hydrogen has some advantages over the other hydrogen storage solutions. As shown in **Fig. 1**, it can have as high gravimetric capacity as compressed hydrogen gas and as high volumetric capacity as the best of the chemical hydrides or even higher. The cost of liquefaction is reported to be lower than the compressed hydrogen and competitively low relative to hydrides (Satyapal, 2006). As compared to other techniques, liquefaction of hydrogen is closer to the demanding conditions imposed and capacity announced by the U.S. Department of Energy (DOE) in terms of gravimetric and volumetric capacities, as shown in **Fig. 1**.

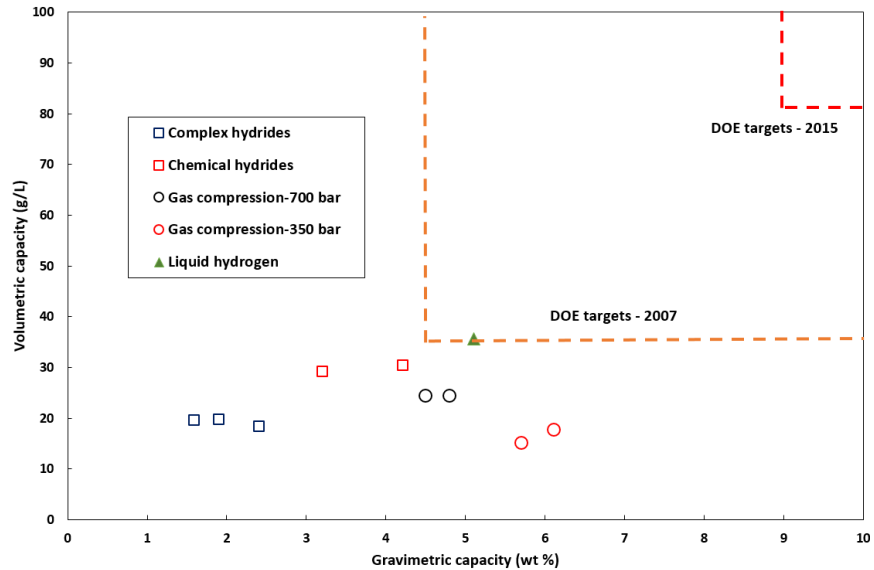


Fig. 1: Gravimetric and volumetric capacity of hydrogen storage technique, illustrated based on (Satyapal, 2006)

2. Liquefaction principles and existing plants

To liquefy hydrogen it needs to be cooled down in an isobaric process to the proximity of its critical temperature, and in a process of expansion through a throttling valve would be entered into the two-phase region.

Hydrogen naturally exists in two forms of ortho and para depending on the spinning axis of the neutrons. If the neutrons rotate symmetrically, the hydrogen molecule is denoted as ortho and if the spinning is asymmetric, it is referred to as para. In ambient temperature, 75% of naturally existing hydrogen is ortho and 25 % is para (Weitzel et al., 1958). In the liquefaction process of hydrogen the ortho type needs to be converted to para using some catalyzers embedded in catalyst beds. Ortho hydrogen converts to para hydrogen naturally and slowly as it is being cooled down to the boiling temperature. Since the reaction is an exothermic and causing vaporization of some part of the liquid hydrogen, the conversion needs to be conducted and accelerated in multistage catalyst beds embedded in the liquefaction plant (Baker and Shaner, 1978).

The liquefaction process initially began with collaboration of Carl von Linde and William Hampson in 1895, devising a simple thermodynamic cycle used to liquefy air (Barron, 1972). The Linde-Hampson cycle, as shown schematically in **Fig. 2**, was comprised of an isothermal compression process, heat exchange in a constant pressure and a Joule-Thomson effect through an expansion valve. After an isobaric regenerative cooling by the return line, the highly compressed air was expanded to a pressure close to the atmospheric pressure through a throttling valve followed with a reduction in the temperature in a constant enthalpy process.

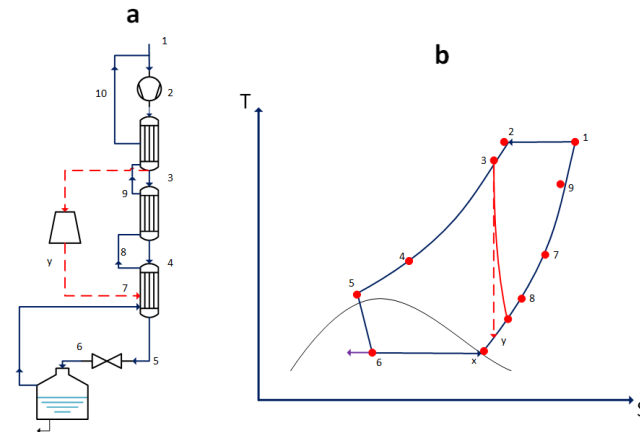


Fig. 4: a) Schematic layout of the Claude cycle, b) T-S diagram of Claude cycle

Another alternative was to provide external cooling via cascade heat exchangers, instead of regenerative cooling. Nandi and Sarangi (1993) made a comparison of Linde-Hampson and Claude cycles, both pre-cooled by liquid nitrogen, and a hydrogen-helium cascade system, shown schematically in Fig. 5. In the cascade hydrogen-helium design, the helium cycle was a Linde-Hampson system worked as a refrigerator for the hydrogen cycle. The throttling valve in the helium Linde-Hampson cycle was replaced by an isentropic expander to ensure that the helium reached down to a temperature below 20K needed for the hydrogen liquefaction. This helped the hydrogen cycle to be operated at a pressure below the critical pressure. They found the pre-cooled Claude cycle more efficient than the other two systems and the helium-hydrogen cascade system more efficient than the pre-cooled Linde-Hampson system. This can be attributed to the inferior thermos-physical heat transfer properties of helium as compared to hydrogen, leading to a higher exergy destruction and a lower energy efficiency.

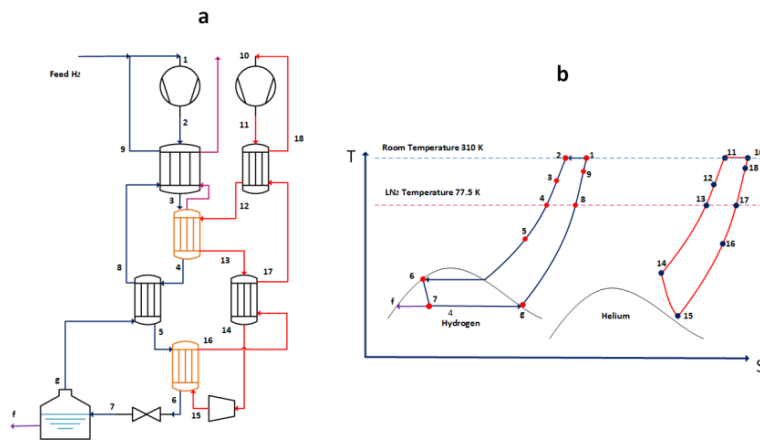


Fig. 5: a) Schematic layout of the H₂-He cascade system, b) T-S diagram of Claude cycle

Current large-scale production systems have so far been using the Claude cycle pre-cooled by nitrogen. The industrial-scale hydrogen liquefaction plant at Ingolstadt near Munich works based on the Claude cycle and liquefies about 4.4 tons of hydrogen a day. The electrical energy demand of the plant is about 13.8 kWh kg_{LH₂}⁻¹ with cycle efficiency of 22% (Bracha et al., 1994). In the following section, the recent development in conceptual designs of liquefaction systems with higher efficiency are described and analyzed.

3. Conceptual design and potential for improvement

Conceptual design have been proposed with modifications to improve the efficiency of the current large-scale industrial plants. Shimko and Gardiner (2008) proposed a cascade Joule-Brayton system. A simplified schematic layout of the cascade helium Joule-Brayton system coupled with Claude cycle is shown in Fig. 6.

Their theoretical analysis showed that the energy demand reduced to $7.4 \text{ kWh kg}_{\text{LH}_2}^{-1}$ and the efficiency increased to 44%. Working on a rather similar system, Quack (2002) claimed that the energy demand could be lowered down to $7 \text{ kWh kg}_{\text{LH}_2}^{-1}$. Valenti and Macchi (2008) simulated a system of four cascade Joule-Brayton cycles working with helium, refrigerating hydrogen from 25°C down to -253°C with multi stage intercooled compression system. It was revealed that the electrical energy consumed for the refrigeration plant could be lowered to $6 \text{ kWh kg}_{\text{LH}_2}^{-1}$.

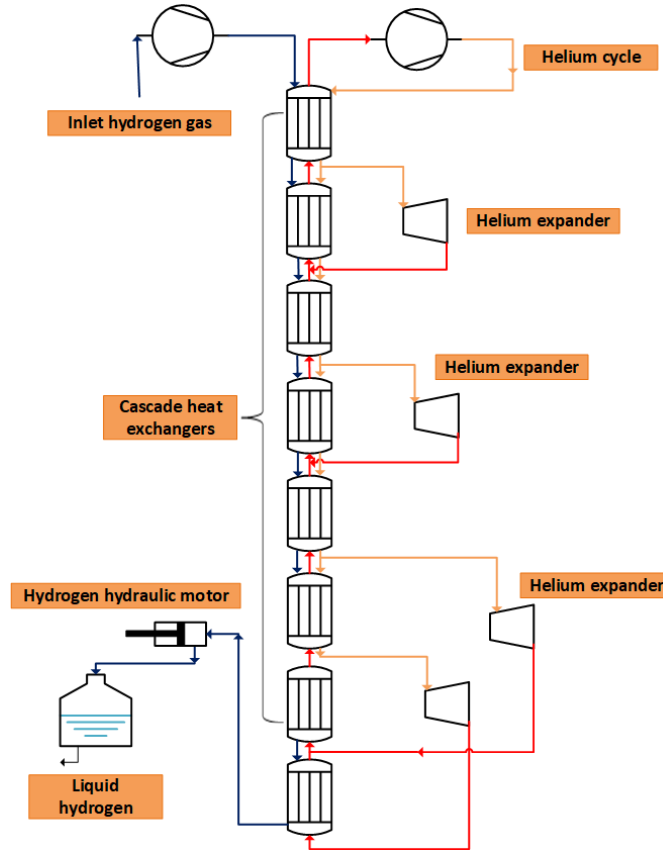


Fig. 6: Liquefaction of hydrogen with a cascade Joule-Brayton system working with helium, illustrated based on Shimko and Gardiner (2008)

To improve the heat transfer through the cryogenic liquefaction, a process mixture of refrigerants in the refrigerating vapor compression cycles has been suggested. The idea is to use materials with different boiling temperature to be used in the cascade heat exchangers in the Claude or Linde-Hampson cycle. The concept of pre-cooling hydrogen with mixed refrigerants is shown to have a lower energy demand, as compared to previous designs, due to higher heat transfer coefficients associated with the boiling of the refrigerants. The refrigerating vapor compression cycle is comprised of multiple receiver vessels along the supply line of hydrogen to separate and accumulate the evaporated refrigerants. The refrigerants boil at different temperature providing cooling for different temperature level of the cycle. The potential refrigerants can be listed as neon, nitrogen, methane, ethylene, ethane, propene, propane, I-butane, butane, I-pentane, and pentane. Careful considerations need to be taken into account in designing the refrigerants composition to ensure that there would be enough flow of each refrigerant at each temperature level to meet the cooling demand at each desired temperature (Krasae-in et al., 2011).

Krasae-In et al. (2010) proposed and simulated the performance of a large-scale mixed refrigerants design coupled with the Joule-Brayton cycle working with hydrogen at extreme low temperatures. A simplified schematic layout of the design is shown in Fig. 7.

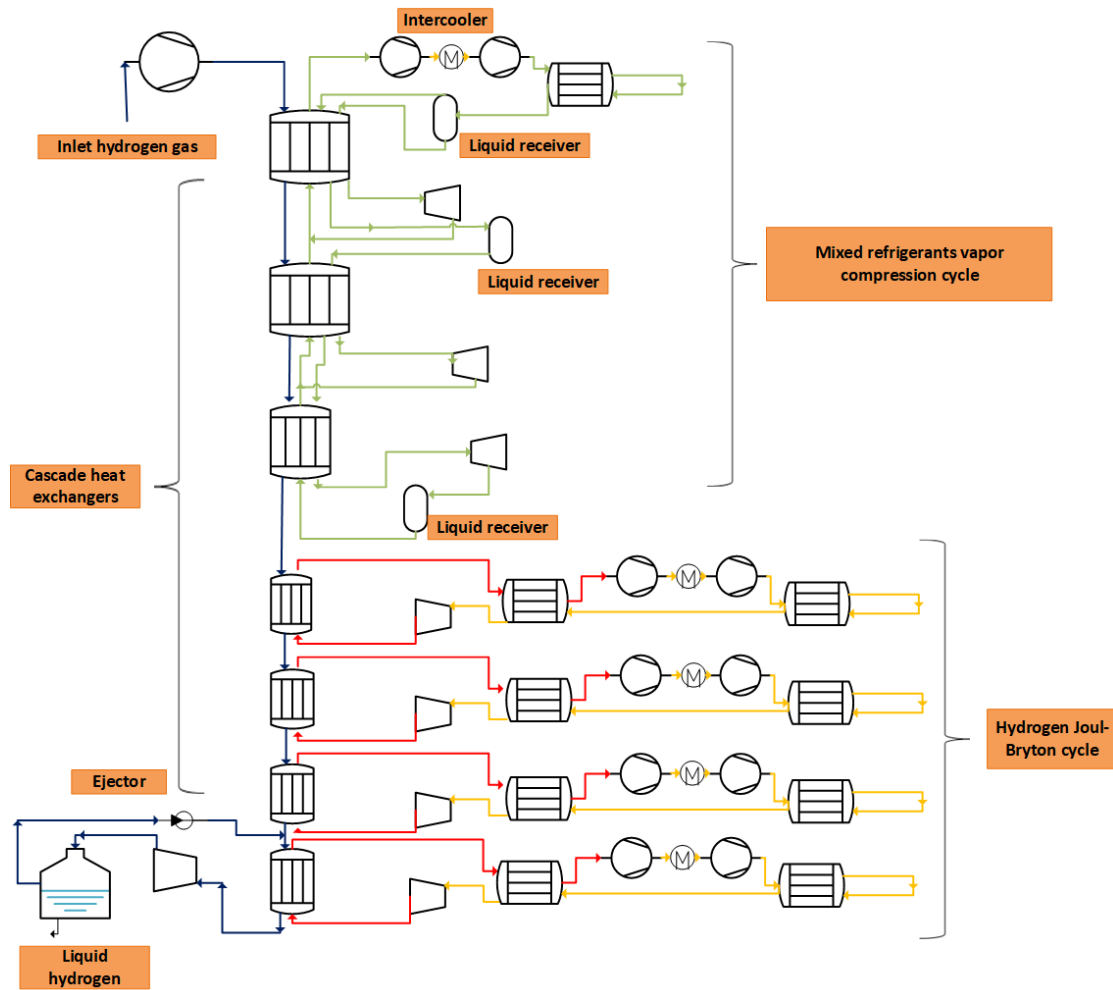


Fig. 7: Schematic layout of large-scale liquefaction plant working with mixed refrigerant vapor compression and hydrogen Joule-Brayton cycles, illustrated based on Krasae-In et al. (2010a)

In this conceptual design, the mixed refrigerant vapor compression cascade cycle and the Joule-Brayton cascade cycles were aimed to cover the cooling demand for the temperature range of 25°C to -193°C and -193°C to -253°C, respectively. The used refrigerant were listed as neon, nitrogen, methane, R14, ethylene, ethane, propane, ibutane, butane, ipentane, pentane and hydrogen. In the Joule-Brayton cascade cycles helium was replaced by hydrogen as working fluid due to its superior heat transfer properties. An ejector was used to recover and return the hydrogen gas to the supply line. The system was reported to have energy demand of 5.35 kWh kg_{LH2}⁻¹, at which 1.36 kWh kg_{LH2}⁻¹ and 3.99 kWh kg_{LH2}⁻¹ were accounted for the mixed refrigerant cycle and the Joule-Brayton cycle, respectively. The total conceptual plant efficiency was calculated to be about 54%.

To evaluate the performance of the concept mixed refrigerant design in real conditions, Krasae-in et al. (2011) conducted an experiment of running a small-scale lab facility at which a mixed refrigerant vapor compression cycle was dedicated to refrigerate hydrogen from 18°C to -158°C. The mixture was comprised of 1% neon, 10% nitrogen, 33% methane, 38% ethane and 18% butane. The energy demand was measured to be 1.76 kWh kg_{LH2}⁻¹, which showed a superior performance as compared to the Ingolstadt large-scale liquefaction facilities in Germany consuming about 4.86 kWh kg_{LH2}⁻¹ for the same temperature range. Another conceptual plant, similar to the one illustrated in Fig. 7, was simulated and analyzed by Krasae-in (2014). The energy demand was found to be 5.91 which was about half that of the Ingolstadt plant.

Sadaghiani et al. (2018) worked on a conceptual design consisted of mixed refrigerant vapor compression system and Joule-Brayton cycles using mixed refrigerants as well as working medium. In the Joule-Brayton cycles a mixture of 10% neon, 6.5% hydrogen and 83.5% helium was used. The system was reported to have

energy demand of $1.36 \text{ kWh kg}_{\text{LH}_2}^{-1}$ and $3.99 \text{ kWh kg}_{\text{LH}_2}^{-1}$ for the mixed refrigerant and Joule-Brayton cycles, respectively.

The liquefaction process suffers from a significant exergy destructions but significant potential has been found to lower the losses and improve the cycle performance. **Fig. 8** shows the history of exergy reduction and efficiency improvement for some of the real and conceptual plants. The exergy losses mostly happen in compressors, heat exchangers and expansion valves (Krasae-In et al., 2010b). As can be seen, the most recent studies have been able to reach to an exergy efficiency of about 55% and energy demand of about $5 \text{ kWh kg}_{\text{LH}_2}^{-1}$.

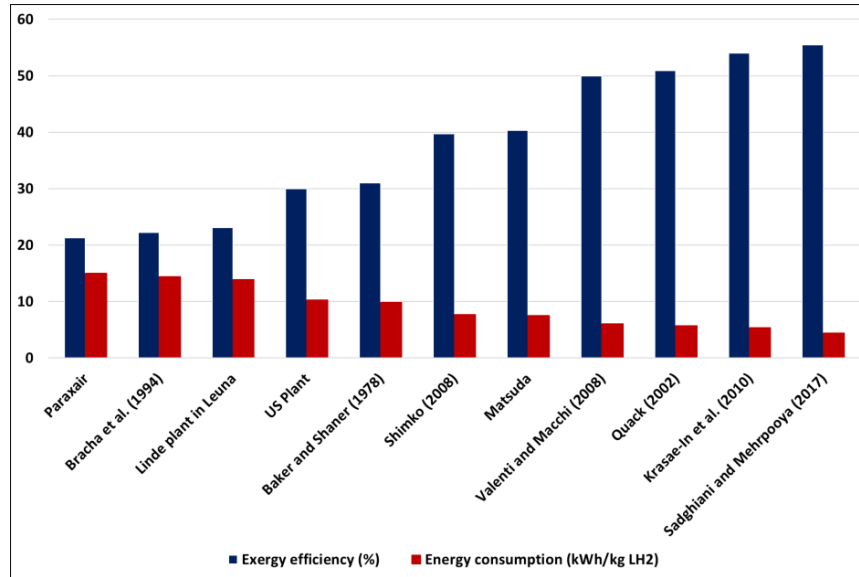


Fig. 8: Recent development in exergy efficiency and energy demand of real and conceptual plants

The largest loss is related to the compressors in the mixed refrigerant vapor compressor and Joule-Brayton cycles. Yuksel et al. (2017) analyzed the performance of a liquefaction plant with cascade Joule-Brayton cycles working with helium and reached to the conclusion that by reducing the pressure ratio over the compressors significant exergy losses can be avoided and the exergy efficiency would be improved to 57%.

One other measure for reducing the loss is lowering the suction temperature to the compressors. This means that the mixture needs to have high enough share of low temperature boiling refrigerants like neon and methane to ensure there would be boiling instead of sensible heat transfer down the cooling cascade line. This helps to reduce the corrosion and fatigue in the compressors and increase their lifetime. In addition, the compression process is associated with significant heat loss to the ambient from the compressor, resulting in a non-efficient compression process. It is recommended to cool down the compressor by having a cooling system around it, or to use multi-stage compression process with intercooling processes in between (Krasae-In et al., 2010b).

To reduce the exergy loss in the heat exchangers the heat transfer needs to be enhanced further so that the matching of the temperature profiles between the hydrogen and the mixed refrigerants is improved. This could be achieved by having enhancement techniques in the heat exchangers or by pre-cooling the hydrogen on the supply line prior to the cascade heat exchangers. In addition, it needs to be ensured that boiling is happening in all the cascade heat exchangers.

Improving the exergy efficiency in the expansion device could be accomplished with having a lower pressure difference of over the expansion valves in vapor compression cycles. In the cycles, the difference of the suction pressure and the discharge pressure needs to be as low as possible. In the expander used on the hydrogen line it is suggested to have a higher pressure ratio which leads to a lower destruction of exergy, while it is suggested to have a lower pressure ratio in the compressors (Ansarinassab et al., 2017).

There is also the potential to increase the efficiency; however, this is likely to require more efficient and more expensive components in the cycle. Nevertheless, developing components with improved thermal performance and higher efficiency.

4. Conceptual liquefaction scenarios coupled with geothermal energy

Conceptual couplings of liquefaction plants with renewable energy resources including geothermal energy have been proposed and studied. Kanoglu et al. (2007) evaluated the feasibility of coupling a geothermal energy source to a liquefaction plant. Two schemes of connecting the geothermal heat source to an absorption chiller, used to pre-cool hydrogen, and using the electrical energy generated in geothermal plants in the liquefaction plants were assessed. It was concluded that using the geothermal heat as generator source in an absorption chiller could be more advantageous and can have significant savings.

Kanoglu et al. (2016) investigated performance of a Claude liquefaction cycle with pre-cooled feed of hydrogen by an absorption chiller at which the geothermal heat was used as heat source in its generator. They reached to the conclusion that the consumption work of the pre-cooled liquefaction cycle by the geothermal absorption chiller could be reduced by 25%. Ratlamwala et al. (2012) conducted parametric studies of hydrogen liquefaction pre-cooled by a geothermal absorption chiller. They found that, given a constant capacity of condenser in the absorption chiller, increasing the geothermal source temperature results in a lower capacity of the evaporator and consequently a lower cooling of the hydrogen gas.

In a broader concept, Yilmaz et al. (2012) looked into different possibilities of hybrid coupling of geothermal energy to production and liquefaction of hydrogen. As shown in **Fig. 9** the schemes included coupling of generated power in geothermal plants to electrolysis of water, coupling the geothermal work and heat for the liquefaction process and devising hybrid connections of geothermal power to electrolysis of water and liquefaction process.

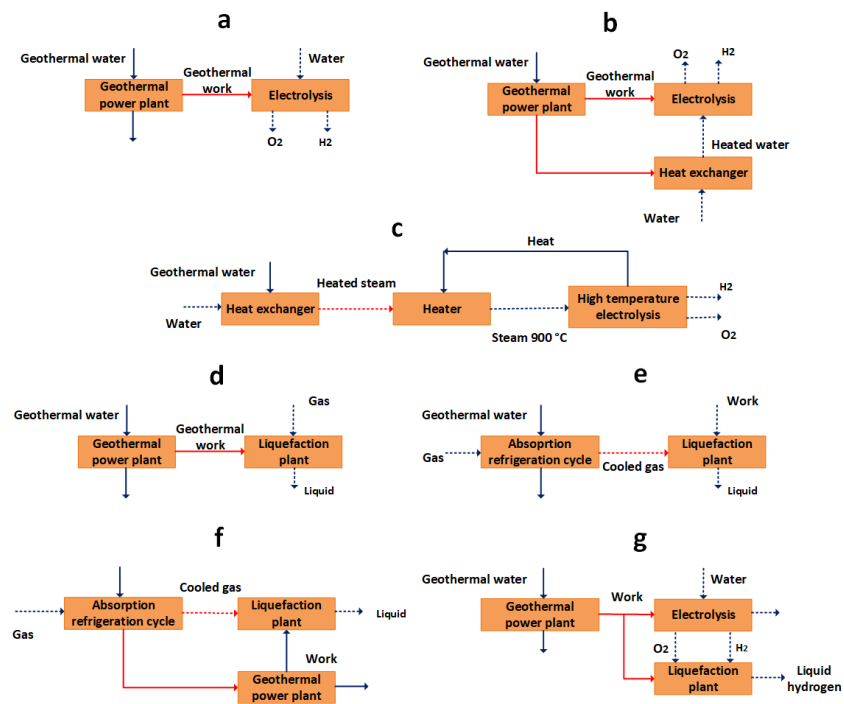


Fig. 9: Different scenarios of coupling geothermal energy resource with production and liquefaction of hydrogen

It was concluded that dual use of the geothermal source can be more beneficial than the single use. For instance, the option (a) was superior over the case (b) since the waste heat could have been used in the pre-heating of the production through electrolysis. Analysis on the scenarios of liquefaction including options (d-f) showed that it is more advantageous to use the geothermal resource for the pre-cooling purposes instead of using the generated power in liquefaction plants.

5. Concluding remarks

The liquefaction process of hydrogen and its basic principles are explained and reviewed. The recent studies on innovative and efficient cryogenic solutions, including the concept of mixed refrigerants and the Joule-Brayton cycles, are described and their influence on the liquefaction process in terms of efficiency are studied. Couplings of renewable geothermal resources with the liquefaction is shown to be a promising coupling. It is found that still there is significant potential to avoid exergy losses in the systems and improve the efficiency to high extent. The review shows that exergy losses are primarily related to the components used in the refrigerating cycles including compressors, expanders and heat exchangers.

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