

UNDERSTANDING THE PHYSICAL PHENOMENA THAT OCCUR INSIDE HEAT EXCHANGERS FOR LIQUEFACTION OF HYDROGEN

**Wilhelmsen Øivind,^(a,b) Skaugen Geir,^(a) Berstad David,^(a) Aasen Ailo,^(a)
Nekså Petter^(a,b)**

^(a) SINTEF Energy Research, Trondheim, 7034, Norway, oivind.wilhelmsen@sintef.no

^(b) Norwegian University of Science and Technology, Trondheim, 7491, Norway

ABSTRACT

Liquid hydrogen is an attractive solution for long-range distribution. The largest barriers for implementing large-scale hydrogen liquefaction plants are currently their high energy consumption and cost. The heat exchangers are among the most important equipment in these plants. It has been shown that it may be beneficial to use a mixture of helium-neon ("Nelium") as refrigerant in the cryogenic cooling cycle, because this gives the possibility to utilize highly efficient turbocompressor equipment. In this work, we discuss the physical phenomena that are expected to occur inside cryogenic heat exchangers if Nelium is used as refrigerant for low temperature cooling and liquefaction of hydrogen. We present a detailed heat exchanger model for a simple heat exchanger geometry and study phenomena such as nonequilibrium ortho-para conversion, possible solid-formation of neon and boiling/condensation of Nelium at the lowest temperatures. We elaborate how the physical phenomena can be exploited in the design of more energy- and space-efficient heat exchanger equipment for hydrogen liquefaction processes.

Keywords: Hydrogen, Liquefaction, Heat exchanger, mathematical modelling, geometry, Nelium, Helium, Neon, Cryogenic.

1. INTRODUCTION

Hydrogen represents a zero-emission fuel when used, for instance, in fuel cells for mobility or electricity generation. The only components emitted from such fuel cells are heat and water. The most common way to produce hydrogen is by steam reforming of natural gas (48%), but a relative large portion is also produced from oil (30%) and by coal gasification (18%) (Voldsund et al., 2016). When steam reforming is combined with pre-combustion CO₂ capture and storage, the processes can be used to provide a clean energy carrier for transportation or for generating electricity. On a long-term, a gradual conversion to a hydrogen-based society can be a way of mitigating one of the world's greatest challenges today, the threat of global warming from greenhouse gas emissions.

Some of the largest technological challenges with the transition into a hydrogen-based society are associated with the transport and storage of the hydrogen. The hydrogen can either be liquefied (e.g. at 1.3 bar and 21 K), or compressed (typically in the range 200–700 bar and 298 K). The preferred method of transportation depends on different circumstances such as the quantity of hydrogen and the distance of transportation. The advantage with liquefied hydrogen is that the energy density is almost 4.5 times larger than for compressed hydrogen (at 200 bar). This reduces the necessary volume and weight of storage-facilities, which becomes particularly attractive if large quantities of hydrogen are going to be transported from remote locations and for distribution to filling stations in cities.

How beneficial liquefaction of hydrogen will be in comparison to compressed hydrogen depends to a large extent on how energy and cost efficient the hydrogen liquefaction process can be realized. One of the current barriers for implementing large-scale plants for liquefaction of hydrogen is the large energy consumption. The exergy efficiency of existing liquefaction plants is relatively low (20–30% when factoring in the penalty for externally supplied liquid nitrogen for pre-cooling) and there is a large potential for improvement (Berstad et al., 2009). Several concepts for hydrogen liquefaction have been proposed in the literature. They are usually characterized by the nature of the refrigeration cycle that has been used in the cryogenic refrigeration section, i.e. whether a Claude cycle or a reverse Brayton cycle has been employed. Several works have recently proposed novel process concepts for liquefaction of hydrogen, e.g. the work by Quack (2002), Valenti and Macchi (2008), Shimko (2008) and Berstad et al. (2010).

The recent works by Berstad et al. (2010) and Cardella et al. (2016), present processes that have very high overall energy efficiencies. In some of these processes, either helium/neon or hydrogen/neon mixtures are used as refrigerants in the cryogenic cycle while a mixed refrigerant consisting of nitrogen and light hydrocarbons is used in the precooling cycle. Cardella et al. (2016) optimized the process parameters to minimize either the energy demand, or alternatively the capital and operational cost. The two processes proposed by Cardella et al. (2016) that were optimized with respect to energy demand yielded energy requirements for liquefying hydrogen of 5.91 and 5.95 kWh/kgLH₂, which is almost half of the energy demand in existing plants. A common denominator for the most efficient hydrogen liquefaction processes is



Figure 1: Illustration of the heat exchanger geometry.

that they use a mixed refrigerant in the precooling cycle and a mixture with neon in the cryogenic cooling cycle, so that efficient turbo compressor equipment can be employed. There are currently knowledge gaps that need to be closed, both to realize the novel concepts proposed by Berstad et al. (2010) and Cardella et al. (2016), and to develop even more energy efficient processes for hydrogen liquefaction. For instance, it is crucial to have a tight thermal match between the hydrogen and the refrigerant, in particular at the lowest temperatures due to the otherwise high entropy production. An additional necessity in the hydrogen liquefaction process is that one must include a catalyst to convert ortho- to para-hydrogen (the protons in the H₂ molecule spin in the same (ortho) or in opposite directions (para)). Otherwise, the heat that is generated when liquefied ortho-hydrogen converts to para-hydrogen in e.g. storage tanks will lead to full evaporation, since the enthalpy difference of ortho-para conversion exceeds the latent heat of evaporation at low temperatures. The ortho to para conversion requires energy demanding refrigeration, and the exergy destruction increases at decreasing temperature. In the cryogenic refrigeration cycle that brings the hydrogen from 80–100 K down to 20–30 K, the use of helium-neon or hydrogen-neon as refrigerants can contribute to increase the energy efficiency of the process significantly. Challenges that arise when these refrigerants are used are possible flow maldistributions, boiling/condensation and possible formation of solid neon. In further development of such novel concepts, it is crucial to enhance the understanding of the physical phenomena that occur inside the heat exchangers.

2. MATHEMATICAL MODEL OF THE HEAT EXCHANGER

In this work we investigate a simplified model of the main cryogenic heat exchanger that is located after the precooling section in the hydrogen liquefaction process. The purpose of the main cryogenic heat exchanger(s) is to bring the temperature of the hydrogen from 110 K to about 25–28 K, and simultaneously convert ortho-hydrogen to para-hydrogen. A simplified geometry has been considered, however, the same physical phenomena are expected to occur as in a more sophisticated plate-fin heat exchanger. The simplified heat exchanger model is displayed in Figure 1, where hydrogen is cooled within a pipe filled with catalyst for ortho-para conversion (Tube 1). A low pressure helium-neon mixture (Helium) is used as refrigerant in the outer shell and cools both high pressure Helium (Tube 2) and hydrogen. We shall next formulate the mathematical model for such a heat exchanger. The inlet is located at $z=0$ and we assume that a mixture of ortho- and para-hydrogen enters the pipe with a total molar flowrate of F_{0,H_2} . With catalyst present, the following (reversible) reaction occurs inside the pipes:



which gives the following balance equation for the mass flow rate of para-hydrogen:

$$dm_{H_{2,para}}/dz = A_1 r, \quad \text{Eq. (2)}$$

where A_1 is the cross section area of Tube 1 where hydrogen flows and r is the reaction rate for the conversion of ortho to para-hydrogen (the forward reaction in Eq. (1)) per total volume. The formula and associated parameters to obtain the reaction rate were obtained from Maegher (2008). The equation of state (EoS) by (Leachman et al., 2009) was used to describe ortho- and para-hydrogen. The Peng-Robinson (PR) cubic EoS (Peng and Robinson, 1976), was used to describe Nelium. The steady-state energy balances in the shell (subscript s) and the tubes (subscripts 1 and 2) are:

$$dh_s / dz = \pi(D_1 J_{q,1} + D_2 J_{q,2}) / m_{s,tot}, \quad \text{Eq. (3)}$$

$$dh_1 / dz = -\pi D_1 J_{q,1} / m_{1,tot}, \quad \text{Eq. (4)}$$

$$dh_2 / dz = -\pi D_2 J_{q,2} / m_{2,tot}, \quad \text{Eq. (5)}$$

where h is the specific enthalpy, D is diameter of the tube, m_{tot} is the total mass flow rate, $J_{q,1}$ is the heat flux out of Tube 1 and $J_{q,2}$ is the heat flux out of Tube 2. The advantage of such a formulation of the energy balances is that any enthalpy change that comes from phase-changes or reactions is automatically taken into account and does not have to be explicitly modelled, in contrast to when the energy balance is formulated in terms of differential equations for the temperature. The temperature in the shell is found by use of Eq. (2) and simultaneously requiring the same temperature and pressure for ortho- and para-hydrogen. The nonequilibrium mixture of the two isomers is described as an ideal mixture, which agrees well with the EoS for normal hydrogen presented by Leachman et al. (2009). The temperatures in Tube 1 and 2 are found by performing enthalpy-pressure phase-equilibrium calculations, assuming at all times equilibrium between the vapour-phase and the liquid-phase. The momentum balances of all sections can be simplified in terms of differential equations for the pressure:

$$dp_s / dz = -f_s m_{s,tot}^2 / (2A_s^2 \rho_s D_{h,s}), \quad \text{Eq. (6)}$$

$$dp_1 / dz = -f_1 m_{1,tot}^2 / (2A_1^2 \rho_1 D_1), \quad \text{Eq. (7)}$$

$$dp_2 / dz = -f_2 m_{2,tot}^2 / (2A_2^2 \rho_2 D_2), \quad \text{Eq. (8)}$$

where p is the pressure, f is the Darcy-Weisbach friction factor, ρ is the density and $D_{h,s}$ is the hydraulic diameter of the shell side. The heat flux further depends on the heat transfer coefficients of both the tube and the shell side according to standard correlations. The heat transfer coefficients and the friction factors depend on physical properties such as the thermal conductivity, the viscosity, the surface tension, the heat capacity and whether the fluid involved is in the single-phase or the two-phase regime. In this work, we have used the same correlations as Skaugen et al., (2013) for Tube 2 and the shell-side. For Tube 1 where catalyst pellets are present, we used the correlations given by Maegher (2008) for the friction factor, and the correlation presented by Peters et al. (1998) to describe the wall heat transfer coefficient inside a packed catalyst bed.

Table 1. The inlet conditions and geometrical specifications of the streams in the heat exchanger

	Shell-side	Tube 1	Tube 2
Mixture:	Low pressure Nelium	Hydrogen	High Pressure Nelium
Temperature (K)	26	110	110
Pressure (bar)	1 or 5	50	30
Molar flow rates (mol/s)	0.5	0.1	0.02
Mole fraction hydrogen	0.0	1.0	0.0
Mole fraction helium	0.5	0.0	0.5
Mole fraction neon	0.5	0.0	0.5
Diameter (mm)	28	8	6

3. RESULTS AND DISCUSSION

The inlet conditions of the heat exchanger are presented in Table 1. The length (L) of the heat exchanger is 10 m, and Nelium has been used as refrigerant. The catalyst pellets located inside Tube 1 are assumed perfectly spherical with an average diameter of 0.5 mm. We assume that no conversion of ortho- to para-hydrogen has taken place prior to the hydrogen entering the heat exchanger, and the inlet mole-fraction of para-hydrogen is therefore $x_{0,Ne} = 0.25$, where subscript Ne refers to Nelium. Figure 2 shows the phase diagram of Nelium as predicted by the PR EoS. The PR EoS has displayed a very good ability to predict the

phase behaviour of non-polar mixtures, but a required input parameter for mixtures is the binary interaction coefficient between helium and neon, k_{ij} , which is usually between -0.1 and 0.1.

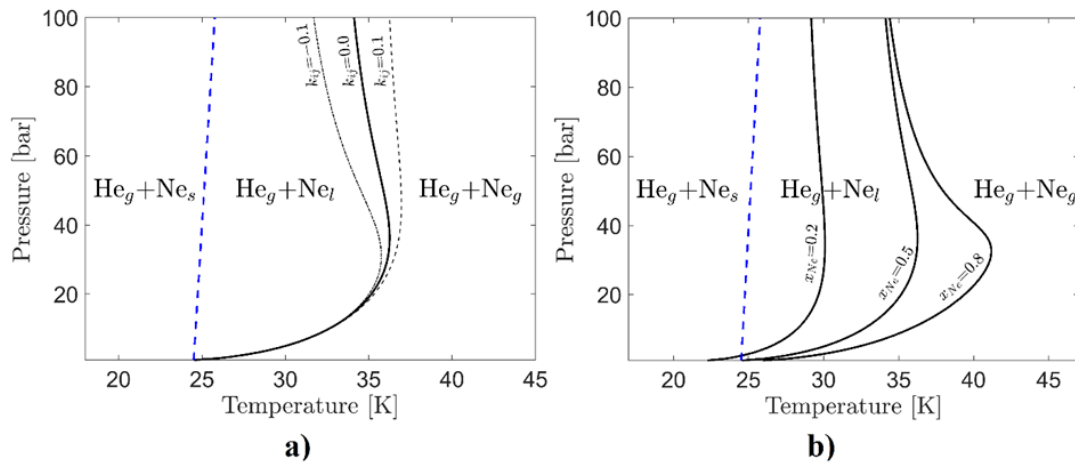


Figure 2: Phase diagram of the helium-neon mixture as predicted by the PR EoS with a) Different choices of the binary interaction parameter between helium and neon, $k_{ij} = -0.1, 0, 0.1$ with $x_{Ne} = 0.5$ and b) Different mole fractions of neon, $x_{Ne} = 0.2, 0.5$ and 0.8 . The blue dashed line represents the solid formation line of pure Neon and subscripts g, s, l refer to gas, solid and liquid.

Figure 2a shows that the choice of binary interaction parameter influences the predicted behaviour of the fluid mainly for pressures that exceed 20 bar. There is quite some uncertainty in the prediction of the phase boundary of Nelium at high pressures, and more work is thus needed to characterize the thermodynamic properties of Nelium. For pure neon, the solid formation line is located at about 25 K (blue dashed line). The solid formation line of Nelium is likely to be at lower temperatures than pure neon due to freezing point depression. This is beneficial, because it means that Nelium can be used as refrigerant at even lower temperatures than 25 K, but future work should address solid-formation in Nelium. Figure 2b shows that the temperature where the two-phase region starts, shifts towards higher temperatures when the overall mole fraction of neon in the mixture increases. Boiling refrigerant usually leads to a higher heat transfer coefficients in comparison to forced convection of gases. This means that it may be beneficial that the refrigerant enters the heat exchanger close to the two-phase regime. Consequently, it may be beneficial to have a higher mole fraction of neon to shift the phase boundary towards higher temperatures. With an overall mole fraction of neon of 0.8, the predicted onset of the two-phase regime at 30 bar exceeds 40 K. However, the dew-point temperature drops quickly at lower pressures, where it passes below 25 K at 1 bar (see Figure 2b at $x_{Ne} = 0.2$). To study the heat exchanger, Eqs. (2)–(8) were solved simultaneously as elaborated in Sec. 2, with the inlet conditions from Table 1 and with input from correlations for both single- and two-phase heat transfer coefficients and friction factors. For comparison, we considered two cases:

Case 1: The inlet pressure of low pressure (LP) Nelium on the shell side was 1 bar and in the single-phase regime according to Fig 2a.

Case 2: The inlet pressure of LP Nelium on the shell side was 5 bar and in the two-phase regime.

The resulting temperatures and conversion of hydrogen along the heat exchanger are displayed in Figure 3a and 3b respectively, where the thin-lines are from Case 1 and the thick lines are from Case 2. With an inlet pressure of 1 bar for LP-Nelium, all fluids in the heat exchanger are in the single-phase regime, similar to the heat exchangers used in commercial hydrogen liquefaction plants. For Case 1, the outlet temperature of hydrogen is 87 K, and there has been little conversion from ortho- to para-hydrogen. The reason for this is that the equilibrium mole fraction of para-hydrogen is below 0.5 at 87 K. The figure shows that for Case 1, the present heat exchanger configuration has too short thermal length to achieve a sufficient cooling of the hydrogen, as 87 K is far from the desired outlet temperature.

Both the evolution of the temperatures and the mole fraction of para-hydrogen are substantially different in Case 1 and Case 2, even if the only parameter that has been modified is the inlet pressure of LP-Nelium. LP-Nelium enters the heat exchanger at $z=L$ and flows counter-currently with the two other streams at the shell-side. In Case 2, LP-Nelium starts to boil at the inlet ($z=L$) and continues to boil until about $z=1.7$. High pressure (HP)-Nelium enters at $z=0$ and starts to condense at $z=4.7$ m. Boiling and condensation typically

enhances the heat transfer coefficient in comparison to heat transfer from single-phase gas. This enhancement is also predicted by the correlations that we have used in this work, described in Skaugen et al. (2013). For LP-Nelium, the heat transfer coefficient increases by about three orders of magnitude in the boiling regime, while the heat transfer coefficient of condensing HP-Nelium is more similar to that of single-phase gas. It can be seen that the temperature of HP-Nelium and hydrogen for Case 1 and Case 2 follow each other closely until $z=1.7$, beyond which the thick lines from Case 2 start to drop quickly due to the enhanced heat transfer from boiling of LP-Nelium at the shell-side. For Case 2, the exit temperature of the hydrogen is 28 K and the hydrogen consists of 98% para-hydrogen. This is a remarkable improvement in performance in comparison to Case 1, which is achieved, only by increasing the inlet pressure of LP-Nelium by 4 bar.

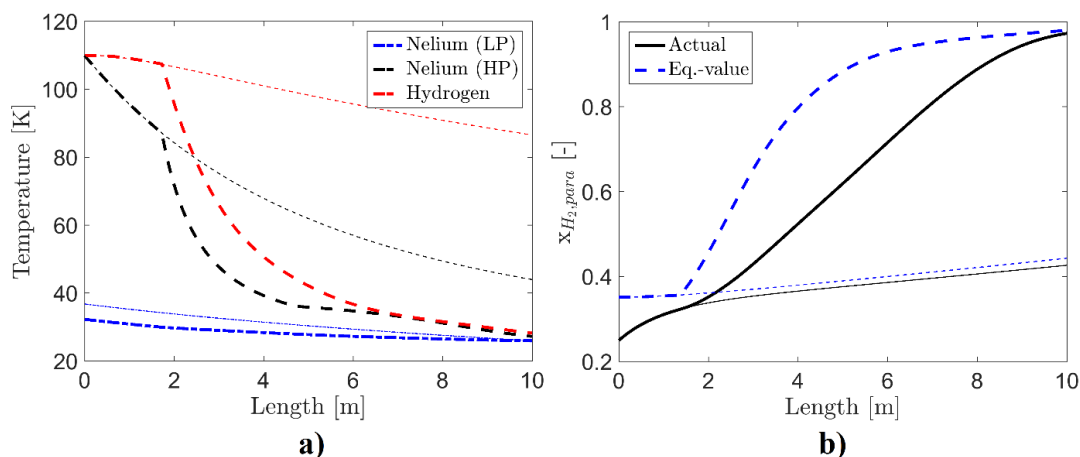


Figure 3: a) Temperatures of Nelium (low pressure (LP), and high pressure (HP)) and hydrogen, and b) mole-fractions of para-hydrogen throughout the heat exchanger, where the fat lines are from a simulation with an inlet pressure of the HP-Nelium of 5 bar, and the thin lines are with an inlet pressure of 1 bar.

An interesting physical phenomenon that occurs when catalyst is placed inside the cryogenic heat exchanger is the strongly exothermic conversion of ortho-hydrogen to para-hydrogen. More heat needs to be transferred from hydrogen to LP-Nelium to compensate for this. The mole fraction of para-hydrogen is shown throughout the heat exchanger in Figure 3b. The blue dashed lines show the equilibrium mole fraction of para-hydrogen, which is a function of the hydrogen temperature. The solid lines show the actual mole fraction of para-hydrogen, which lags behind the equilibrium-mole fraction of para-hydrogen due to the finite reaction rate (see Eq. (2)).

The main purpose of the present work was to investigate the physical phenomena that occur inside heat exchangers for hydrogen liquefaction. It is evident from Figure 3 that the simple heat exchanger geometry depicted in Figure 1 with a total length of 10 m does not allow for a feasible thermal match between the cold and the hot side, since the maximum temperature difference is almost 80 K. However, the figure elucidates that Nelium has much potential as refrigerant in the hydrogen-liquefaction process and can reduce the necessary heat exchanger surface area in comparison to more commonly used refrigerants. The main reason for this is that LP-Nelium boils and HP-Nelium condenses at the lowest temperatures if sufficiently high pressures are used, where boiling and condensation enhances the heat transfer.

The models we have employed have significant uncertainties, since many of the properties of Nelium have never been measured. Examples include the transport properties, the surface tension, and the appropriate correlation to use to describe boiling and condensation. There is a high potential to obtain a tighter thermal match between the cold and the hot-sides of the heat exchanger than what we have presented in Figure 3, both by modifying geometry, the inlet conditions of Nelium, as well as the ratio between neon and helium in the mixture, where we in this work have used a 50-50 mixture.

4. CONCLUSIONS

In this work, we have studied the fundamental physical phenomena that occur inside heat exchangers for use in hydrogen liquefaction plants, where a mixture of helium and neon (Nelium) has been used as refrigerant. Nelium is beneficial for the energy efficiency because it gives the possibility to use highly efficient turbocompressor equipment in the hydrogen liquefaction process. A detailed mathematical heat exchanger model with a simple geometry was studied, including nonequilibrium ortho-para conversion and

boiling/condensation of Nelium at the lowest temperatures. The work showed that by using boiling/condensing Nelium, it was possible to significantly reduce the size of the heat exchanger equipment in comparison to conventional heat exchangers where all fluids are in the single-phase regime. In particular, evaporation of Nelium at the shell-side leads to a significant enhancement of the overall heat transfer coefficient. To further evaluate the potential of Nelium in hydrogen liquefaction processes, more work is needed to close present knowledge gaps related to the thermophysical properties of this mixture.

ACKNOWLEDGEMENTS

This publication is based on results from the research project Hyper, performed under the ENERGIX program. The authors acknowledge the following parties for financial support: Statoil, Shell, Kawasaki Heavy Industries, Linde Kryotechnik, Mitsubishi Corporation, Nel Hydrogen and the Research Council of Norway (255107/E20).

NOMENCLATURE

p	Pressure (Pa)	h	Specific enthalpy (H/kg)
J_q	Heat Flux (W/m ²)	z/L	Spatial coordinate/ Total length (m)
D	Diameter (m)	m	Mass flow rate (kg/s)
H_2	Hydrogen	A	Cross section area (m ²)
D_h	Hydraulic diameter (m)	r	Reaction rate (kg/m ³ catalyst per sec.)
ε	Catalyst bed void fraction	ρ	Density (kg/m ³)
x_{Ne}	Overall mole fraction of neon	k_{ij}	Binary interaction parameter
f	The Darcy-Weibach friction factor	$s_{,1,2}$	Shell, Tube 1 and Tube 2 respectively

REFERENCES

- Berstad, D. O., Stang, J. H., Neksa, P., 2009. Comparison criteria for large-scale hydrogen liquefaction processes. *International Journal of Hydrogen Energy* 34(3), 1560-1568.
- Berstad, D. O., Stang, J. H., Neksa, P., 2010. Large-scale hydrogen liquefier utilising mixed-refrigerant precooling. *International Journal of Hydrogen Energy* 35(10), 4512-4523.
- Cardella, U., Decker, L., Klein, H., 2016. Economically viable large-scale hydrogen liquefaction. *Proceedings of the 26th International Cryogenic Engineering Conference*. New Dehli, India.
- Leachman, J. W., Jacobsen, R. T., Penoncello, S. G., Lemmon, E. W., 2009. Fundamental Equations of State for Parahydrogen, Normal Hydrogen and Orthohydrogen. *Journal of Physical and Chemical Reference Data* 38(3), 721-748.
- Maegher, J. P., 2008. Modelling of hydrogen liquefiers with kinetic conversion of ortho to para hydrogen in plate-fin heat exchangers. Msc. Thesis. State University of New York.
- Peng, D. Y., Robinson, D. B., 1976. A new two-constant equation of state. *Industrial and Engineering Chemistry: Fundamentals* 15, 59-64.
- Peters, P.E., Schiffino, R.S., Harriott, P., 1988. Heat Transfer in Packed-Tube Reactors. *Ind. Eng. Chem. Res* 27, 226-233.
- Quack, H., 2002. Conceptual design of a high efficiency large capacity hydrogen liquefier. *Proceedings of the cryogenic Engineering Conference - CEC. 2002, Madison, Wisconsin (USA)*, 613, 255.
- Shimko, M., 2008. Innovative Hydrogen Liquefaction Cycle. *Proceedings of the Annual Merit Review on Hydrogen Production and Delivery*. Washington, D.C., USA.
- Skaugen, G., Kolsaker, K., Walnum, H. T., Wilhelmsen, Ø., 2013. A flexible and robust modelling framework for multi-stream heat exchangers. *Computers & Chemical Engineering* 49, 95-104.
- Valenti, G., Macchi, E., 2008. Proposal of an innovative, high-efficiency, large-scale hydrogen liquefier. *International Journal of Hydrogen Energy* 33(12), 3116-3121.
- Voldsund, M., Jordal, K., Anantharaman, R. 2016. Hydrogen production with CO₂ capture. *Int. J. Hydrogen Energy* 41(9), 4969-4992.