The 6th International Chemical Engineering Congress & Exhibition
16 - 20 November, 2009 Kish Island, I.R. Iran (ICHEC 2009)

Design of cryogenic system for liquefaction of hydrogen

J. Sargolzaei[*,1] Saghatoleslami[1]
[*, 1] Department of Chemical Engineering, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran

Abstract
Recently, hydrogen known as an efficient source of energy is used for long distances. One of the most suitable ways of liquefying hydrogen is Linde-Hampson process which has a pre cooler. In this research, selection of the most efficient equipments is discussed. We will also read about the details of the process. This article presents thermodynamic terms and main structure of different parts like compressor or heat exchange, purifier, and dryer unit and catalytic reactor for converting of para hydrogen to ortho hydrogen with expansion valve and storage tank and design details have presented. The fastest flow that this system can bear in optimum hydrogen flow is 300 lit/hr.

Keywords: Energy, Cryogenic, Hydrogen, liquefaction, Linde-Hampson

1 Introduction

Cryogenics is the science of producing and studying low-temperature conditions. The word cryogenics comes from the Greek word cryos, meaning "cold", combined with a shortened form of the English verb "to generate". It has come to mean the generation of temperatures well below those of normal human experience. More specifically, a low-temperature environment is termed a cryogenic environment when the temperature range is below the point at which permanent gases begin to liquefy. Permanent gases are elements that normally exist in the gaseous state and were once believed impossible to liquefy. Among others, they include oxygen, nitrogen, hydrogen, and helium [1, 2, 3]. Nowadays producing energy plays an important role. Lack of fossil fuels and increasing need to energy has made us to pay a special attention to replacing fossil fuels with renewable resources. Also the fossil fuels and their combustion products were causing global environment problems [4]. These resources of energy are clean and do not pollute the environment. One these sources are hydrogenic energy. Hydrogen derived from renewable energies eventually will contribute to the sustainable development of such countries [4]. Hydrogen combustion produces water vapor that does not make any pollution. Hydrogen is gas form, occupies a large volume and has low density (0.0897 kg/m^3) and high pressure [5]. Thus we need to liquefy hydrogen for an easier transportation and safety [6]. After 1951, when hydrogen was produced in industrial scale, it was used in many different areas. Besides the United States other countries like France, England, Germany, Netherlands, and Russia tried to improve in this field.
In this research hydrogen liquefaction in small scale designed.

2 Process of liquefaction

Hydrogen liquefaction consists of several processes. In this research, Linde-Hampson process is discussed since it is one of the simplest methods [7].
Figure 1 shows diagram of this process. G_i (kg) is mass of hydrogen that enters the compressor at T=300 K. Compression heat (q_k) is transferred to coolers. Compressed gas enters the two silica beds which are floating in liquid nitrogen temperature decreases when gas compresses.

* To whom correspondence should be addressed.
Email : sargolzaei@um.ac.ir , Tel : +98 915 512 4591, Fax : +98 511 8816840

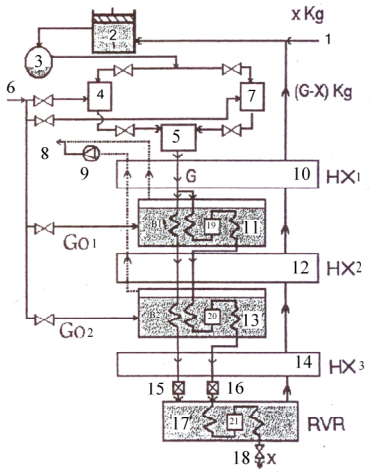

Figure 1. Schematic flow of hydrogen liquefaction system

In Fig. 1 accounts are hydrogen input gas (1), compressor (2), separation of gas and oil (3), purification units (4,7), cooler (5), liquid nitrogen (6), discharge to liquid nitrogen unit (8), vacuum pump (9), heat exchangers (10, 12, 14), liquid nitrogen tanks (11, 13), expansion valves (15, 16), Para-hydrogen (18), catalytic beds (19, 20, 21). After passing the first heat exchanger (HX1) some heat is transferred to liquid nitrogen and hydrogen temperature decrease from T to T_3. Then the gas passes the second heat exchanger and its temperature decreases again from T_3 to T_4. After that the gas enters nitrogen vessel in vacuum and one more time its temperature reduces from T_4 to T_5. Nitrogen which flow in B1 and B2 vessel are respectively Go_1 and Go_2. Compressed gas is cooled in the third heat exchanger (HX3) and its temperature decreases to lower than the inversion temperature (T_{inv}=200 K). Then the gas enters the expansion valve and some of it will be stored in liquid form in a RVR tank. The rest of the gas returns to system as a cooling fluid in coolers. Liquid nitrogen in B1 and B2 vessels goes out through a vacuum pump and enters an other nitrogen liquefier hydrogen is separated in two equal portion before entering B1 vessel. One of these parts is sent to catalytic bed for convergence of ortho-hydrogen to para-hydrogen and the other portion is liquefied after passing B1 vessel. Finally the net liquefied portion (X) of hydrogen is consisted of 99.98 percent of para-hydrogen. Using energy balance laws in tanks and heat exchangers, we can obtain the amount of heat (q_o) and the amount of liquid nitrogen. The work of cycle is considered as the compressor work (W_k) and excessive work for producing of liquid nitrogen, therefore liquefaction work (W_o) is defined as follow [8]:

$$W_o = \frac{W_k + W_{exc}}{X} = \frac{R'T\ln(P_k/P_1)}{\eta_t . X} + \frac{\beta_o G_o W_{o,p}}{X} \qquad (1)$$

$W_{o,p}$ is the required work for producing liquid nitrogen, β_o is weight coefficient and η_t is thermodynamic performance. With attention to T-S diagrams for hydrogen and nitrogen, thermodynamic equations, mass and energy balances around the tanks and heat exchangers, we can perform required calculations. The results are shown in table 1.

Table 1. Results from mass and energy balance calculations

As calculated	signs	value	unit
Amount of nitrogen required in tank B1	Go1	0.516	$\frac{KgN2}{KgH2}$
Amount of nitrogen required in tank B2	Go2	0.34	$\frac{KgN2}{KgH2}$
Total amount of heat transferred	q	1047.5	Kj/Kg
Additional work required	W_{exc}	4815	Kj/Kg
Heat by the cooler	q_k	1673	Kj/Kg
Actual compressor work	W_k	5407	Kj/Kg

Work required special	W_o	222.22	$^{Mj}/_{Kg}$
Thermodynamic efficiency	η_t	0.0544	
Component liquid hydrogen	x	0.046	Percent, (%)

Note that G_i in table 1 is equal to 0.53 kg/hr, therefore we can write:

$$\text{System capacity} = \frac{0.046 \times 0.53(^{kg}/_{hr}) \times 1000(\text{lit})}{0.089(\text{kg})} = 300\,^{lit}/_{hr} \qquad (2)$$

With changing G_i, it is found new capacity and results. As shown in table 1, thermodynamic performance (η_t) is low due to existing of nitrogen pre coolers [6].

3 Design

3.1 Compressor

One of the most important equipments in liquefying systems is compressor. As usual, in cryogenic systems two kinds of compressors have been used, reciprocating and rotary compressors since the reciprocating compressors are used for high pressures (greater than 0.12 MPa) and low mass flows [8], therefore in this design due to high pressure (4 MPa), reciprocating compressors have been used. Because of high pressure and temperature in this compressors, it is necessary to use carbon steel 304 in construction, also since the steel with low carbon has high stability and resistance, then we can use this type of steel too [2]. Also we can construct compressor piston from aluminum, cast iron or stainless steel 304. Mechanical performance of these types of compressors is high. The cylinder of compressor has been cooled with cold gas that surrounded the cylinder. Since compressing process is isothermal, therefore isothermal performance of these compressors is 80 to 85 percent and evaluated required power is 28 kw.

3.2 Purification and dryer unit

Impurities in feed are comes from hydrogen generating unit. The main impurities are oxygen, water in vapor form and Potassium hydroxide. For purification in this system, we used fixed bed silica gel that floated in liquid nitrogen. Fixed bed filled with silica gel particles with 25 mm diameter and porosity of 30 percent. We can calculate diameter and height of bed with using of break through curve for silica gel. With attention to impurities concentration (0.01 volumetric percent) results are shown in Fig. 2.

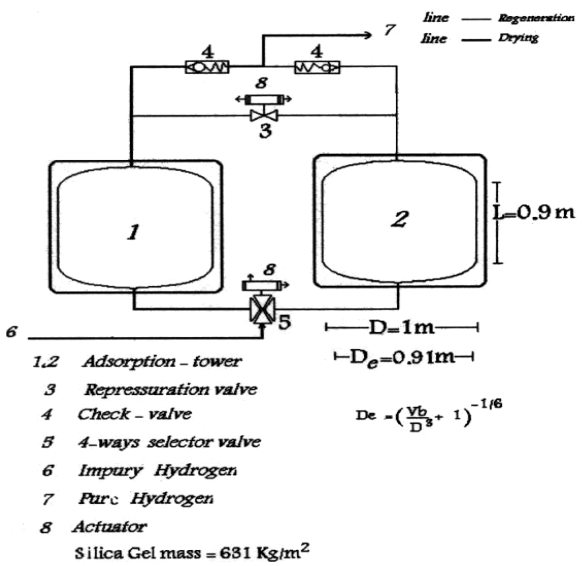

Figure 2. Purification and dryer unit

As usual, for pressure drop of bed, the Ergun equation [9], given below is for a no spherical particle:

$$\Delta P = 1.75 \frac{1-\varepsilon}{\varepsilon^3} \frac{G^2 h}{\rho de} + 150 \frac{G\mu}{\rho de^2} \frac{(1-\varepsilon)^2}{\varepsilon^3} h \qquad (3)$$

ρ is gas density, h is height of bed, ε is porosity coefficient (0.3), de is equal diameter of silica gel particles (25 mm), G is mass flow of gas and μ is gas viscosity. Pressure drop for this bed is calculated and its value is 1 MPa. Also for calculated height of bed (0.9m) we required 631Kg/m^2 of silica gel.

3.3 Heat exchanger

Several changes of specific heat in heat exchanger, effect on temperature profile and forming temperature pinch [10]. Since the system temperature is very low and we require high performance and also the very pure gas is entered the exchanger, therefore we used the aluminum plate-fin heat exchanger in this design [11]. Material of this exchanger is brazed aluminum [12].

For this design the selected heat exchanger is the best selection low weight, low heat capacity, high compression, and good malleability, high stability in low temperature, high heat surface area, low pressure drop and low holdup [2].

In this design, heat exchangers were designed with LMTD procedure. Intensity of heat flow is $Q = U.A.\Delta T_m$ those ΔT_m is the logarithmic difference and obtain from below equation [11]:

$$\Delta T_m = \frac{\Delta T_{max} - \Delta T_{min}}{Ln(\Delta T_{max} / \Delta T_{min})} \quad (4)$$

That ΔT_{max} and ΔT_{min} are $(T_{h1} - T_{C2})$ and $(T_{h2} - T_{C1})$, respectively. Also T_{h1}, T_{h2}, T_{C1}, T_{C2} are temperature of hot inlet, hot outlet, cold inlet, and cold outlet stream, respectively. Since we can specify inlets and outlets mass flows with respect to figure 1, therefore we can write:

$$Q = \dot{m}_h.C_{Ph}(T_{h1} - T_{h2}) = \dot{m}_C.C_{PC}(T_{C2} - T_{C1}) \quad (5)$$

That $\dot{m}_h$ and $\dot{m}_C$ are mass flows of hot and cold streams, respectively. With using equation 5 we can obtain temperature of outlet hot flow and Q. Therefore we can calculate ΔT_m and then with using below equation, surface area of each exchanger is obtained:

$$A = \frac{Q}{U.\Delta T_m} \quad (6)$$

Results are brought in Fig. 4. With attention to results, we used three heat exchangers and surface area of HX1, HX2, and HX3 are 101.7 m^2, 0.3072 m^2, and 10.865 m^2, respectively. Also we used 12.5 blades in each 0.02m of exchangers. Several changes of heat capacity and inversion of the temperature in middle of exchangers can be solved with controlling of mass flows, therefore mass flow hydrogen is calculated and its value is 0.53 Kg/hr.

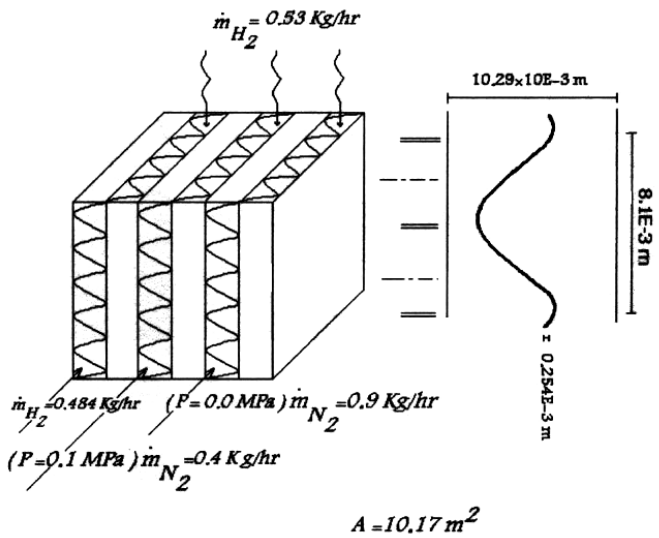

Figure 4. Heat exchanger with plate-fin type

3.4 Catalytic beds and preparation of catalysts

We have to produce the special catalyst for converting the hydrogen in ortho-hydrogen to para-hydrogen. A hydrogen molecule exists in two forms of ortho-hydrogen and para-hydrogen. Nuclear of hydrogen atoms only has one proton. Except in high temperature, hydrogen molecule has not vibratory energy and only has energy. Rotational move of

nuclear can be in two forms parallel and nonparallel. If the rotations are parallel, the molecule is ortho, other wise molecule is para [13, 14, 10]. Energy level of para is lower than ortho, therefore usually in industrial uses such as rocket fuel and storage of liquid hydrogen, its better that para hydrogen is used [15]. Three different models are used for fixed bed reactors among which the reactor with pseudo homogenous types is adopted in this work. The assumptions used for this model are as follows: i) external resistances to heat and mass transfer are neglected ii) thermal equilibrium exists between the gas and the catalyst iii) the reactor is assumed to behave as plug flow (PFR)
Therefore, the reactor is assumed to be tubular and in order to maintain the reactor at constant temperature, a vessel of small diameter which is submerged in a nitrogen bath is chosen. Considering the above assumption, we can write the following material and energy balances, respectively:

$$\frac{d}{dz}(VC_A) - r_{Ao}\alpha = 0 \qquad \text{mass balance} \qquad (7)$$

$$V\rho C_P \frac{dT}{dz} + (-\Delta H_r) r_{Ao}\alpha + UA_n (T - T_j) = 0 \qquad \text{energy balance} \qquad (8)$$

Where r_{Ao} is the initial reaction rate when the catalyst is used and the activity of catalyst (i.e., α) is defined as the ratio of reaction rate at time t=0 to t.

3.5 Expansion valve

One of the most important of the equipment in the liquefaction cycle is the expansion valve, because as a result of pressure filling, a portion of gas is liquefied. For using expansion valve, the gas must be reach to inversion temperature, therefore we have to use pre cooler with liquid nitrogen, Freon, and etc. as a working fluid. Therefore in this design we use liquid nitrogen tank (Fig. 5) with volume 0.125 cubic meters with insulated wall that the walls made from epoxy and fiberglass.

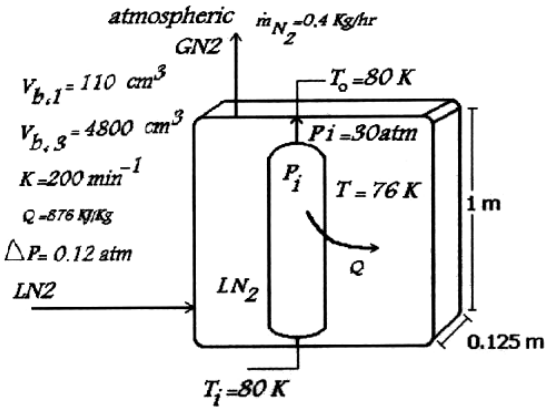

Figure 5. Liquid nitrogen tank for catalytic reaction

Nitrogen works in isenthalpic process and Joule-Thamson effect occurs in the expansion valve. Joule-Thamson coefficient defined as follow [16, 17]:

$$\mu = \left(\frac{T_2 - T_1}{P_2 - P_1}\right)_h \qquad (16)$$

Since the inversion temperature of hydrogen is 200 K, therefore in the pressure 3 MPa and inlet temperature 40 K, when the outlet pressure is reach to 0.1 MPa, temperature of outlet gas is reach to critical temperature of hydrogen (20.23 K). Material of this kind of valves is stainless steel. For insulation valves, vacuum jacket is use. Length to diameter ratio in these valves is 3.5 [12]. As we shown in figure 6, for calculated fluid flow 22.14 m^3/sec, allowable diameter of the valve is calculated and its valve is 5.047×10^{-3} m .

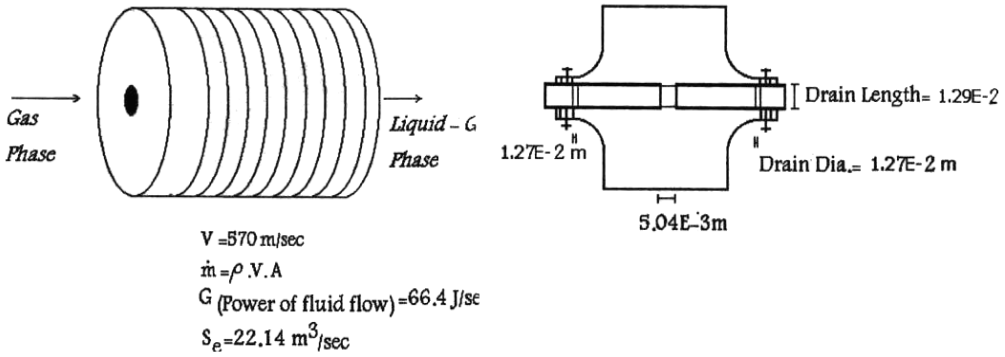

Figure 6. Expansion valve

3.6 Storage tank

Another part of cycle that have special importance, is liquid hydrogen storage tank. Storage tank is constructing in different forms such as cylindrical, spherical or conical and most of the have two wall. One of the economical forms is cylindrical form that has very advantages such as: easy construction, less heat leak with compare spherical type, suitability for transportation with trailer or rail way, there for in this design storage tank is cylindrical. Calculation results shown that the thickness of inner and outer wall is too low about 0.9mm. One of the important problems in design of tanks is selecting of construction materials. Since this storage tank has two inner and outer tanks, inner tank build from stainless steel, aluminum, and some of copper alloys because the outer tank is not in cryogenic temperatures and its in atmospheric pressure, this tank is build from carbon steel. Furthermore multilayer insulations (MLI) are the best types of insulations for storage tank [18].

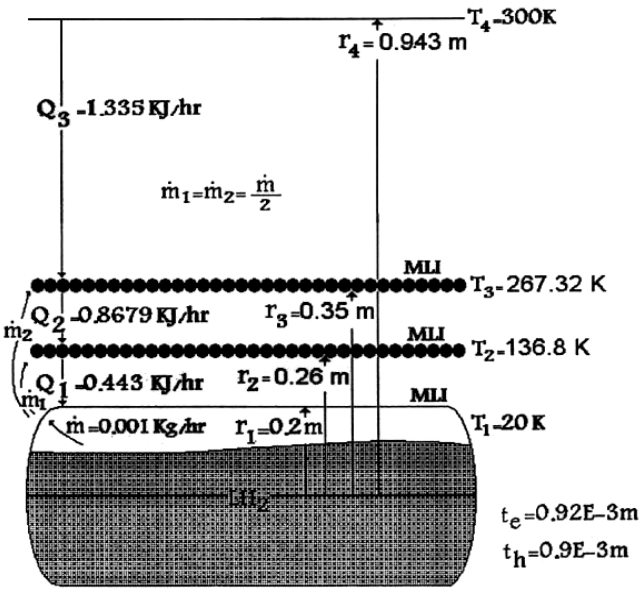

Figure 7. Storage tank for liquid hydrogen

In this tank vaporization of liquid hydrogen with rate 0.001 Kg/hr, supplying the coldness of tanks, although we have some heat leak from surrounding to tank, this heat leaks calculated for three insulation layer and results are 0.443, 0.8679, and 1.3354 Kg/hr, respectively (Fig. 7). Furthermore with trial and error procedure for cylinder with 0.2m diameter, radius of three insulation layer are 0.26, 0.35, and 0.943m from inner to outer, respectively, and temperatures between to layer of insulations are 136.8, 267.32 K from inner to outer respectively.

3.7 Piping and insulation

One of the important problems in this design is selecting the materials that selection of each material depends on characters such as: volume, quantity of substance, heat transfer problems, construction technology, and economic problems [18]. Due to this fat that the liquid hydrogen is evaporate with least of heat leak, therefore for optimizing the system, hydrogen gas is in circulation in chilling system. Transportation lines materials selected so that to have good

resistance in liquefaction process. Therefore it's better to manufactory the transportation lines with U form and from aluminum and its alloys (9% Nickel) with vacuum system due to low penetration of hydrogen in this materials and high stability towards heat stresses and low radiation. Pipes diameters are calculated with respect to pressure and fluid flow. For pipes flow of 0.53Kg/hr and pressure 3-4 MPa, we pipes 18mm diameter and pipes 4mm diameter are used for flow 0.484 Kg/hr and 0.1 MPa pressure.

3.8 Cryogenic valves

The valves that used in this design are named cryogenic valves that are in two type of long body and valve with vacuum jacket [2]. The long body valves produce in the thin wall pipes with body 10 to 12 m. Also body of the valve is seal in surrounding temperature that this procedure reduces the sealing problems. In valves with vacuum jacket for reducing the heat leak, it is used from vacuum about 10^{-6} mmHg .

4 Conclusion

Various thermodynamic cycles exist for liquefying of hydrogen and selection of each cycle depending on important factors such as heat transfer, thermodynamic problems, manufacturing technology, and economic aspects. Because the Linde-Hampson cycle is one of the bests and simplest of thermodynamic cycles that we use this cycle in this design. Therefore for optimization of the system, hydrogen must be in cycle with chilling cycle. One of the important problems in this design is selecting of materials that carbon steel 304 used. Also, although multilayer insulations are expansive but since liquefaction of hydrogen is so expansive, therefore we used this insulation. Also mass and energy balance shows that the amount of produced liquid hydrogen is 10 percent of feed gas.

Reference

1. Radebaugh, R., Cryogenics: Chemistry, Foundations and Applications, Macmillan Reference USA (2004).
2. Randall, F. B.,Cryogenic Systems, second edition, Oxford University Press, Oxford (1985).
3. Van Sciver, S. W., Helium Cryogenics, Plenum Press, New York (1986).
4. Veziroglu, T.N., Sumer Sahin, 21st Century's energy: Hydrogen energy system, *Energy Conversion and Management*, 49 (7), p. 1820-1831 (2008).
5. Aceves, S.M. , Martinez-Frias, J., Garcia-Villazana, O., Analytical and experimental evaluation of insulated pressure vessels for cryogenic hydrogen storage, *International Journal of Hydrogen Energy*, 25 (11), p. 1075-1085 (2000).
6. Ludwig, E.E., Applied Process design for chemical and petrochemical plants, Gulf Publishing Company, 4 edition (2007).
7. Kanoglu, M., Dincer, I. , Rosen, M.A., Geothermal energy use in hydrogen liquefaction, *International Journal of Hydrogen Energy*, 32 (17) (2007).
8. Miller, F.K., Brisson, J.G., Development of a low-dissipation valve for use in a cold cycle dilution refrigerator, *Cryogenics Journal*, 39, p. 859–863 (1999).
9. Basu, P. , Butler, J., Studies on the operation of loop-seal in circulating fluidized bed boilers, *Applied Energy Journal*, 86 (9), p. 1723-1731 (2009).
10. Arkharou, A., Martenina, I., Mikulin, Ye., Theory and design of cryogenic systems, Mir Publishers (1981).
11. Hands, B.A., Cryogenic engineering, Academic Press Inc., London, Ltd. (1986).
12. K. Mendelssohn, The quest of absolute zero, second edition, Taylor and Franceis Ltd. (1977).
13. Charignon, T., Celik, D., Hemmati, A., Van Sciver, S.W., Dielectric coefficient and density of subcooled liquid hydrogen, *Cryogenic Journal*, 47, p. 252-256 (2007).
14. Celik, D. Van Sciver, S.W., Dielectric coefficient and density of subcooled liquid oxygen. *Cryogenics Journal*, 45 (5), p. 356–61 (2005).
15. Saunders, E.A.D. , Heat exchanger selection design and application, Longman scientific and Technical (1988).
16. Brisson, J.G., Superfluid Joule-Thomson refrigeration, a new concept for cooling below 2 Kelvin, *Journal of low temperature physics*, 120 (1-2), p. 151-168 (2000).
17. Yurum, Y., Taralp, A., Veziroglu, T.N., Storage of hydrogen in nanostructured carbon materials, *International Journal of Hydrogen Energy*, 34 (9), p. 3784-3798 (2009).
18. Plachta, D.W., Christie, R.J., Jurns, J.M., Kittel, P., Passive ZBO storage of liquid hydrogen and liquid oxygen applied to space science mission concepts, *Cryogenics Journal*, 46 (2-3), p. 89-97 (2006).