

Thermodynamic (energy-exergy) analysis of hydrogen liquefaction system

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Abstract

Hydrogen system is a unique design system for liquefaction of hydrogen gas. It comprises as liquid nitrogen chamber which helps the system to attain critical temperature point of hydrogen. From the exergy analysis study of hydrogen system it observed that System output does not deteriorate during off design condition when operated in selected operated range of PR 20-52 bar. Exergetic efficiency of the low temperature heat exchanger (HXD) at the lowest temperature of a hydrogen liquefier improved by increasing the pressure ratio because the mass imbalance gets compensated by the specific heat imbalance. Initial feasible range of pressure ratio 20 to 87 bar, COP of the system decrease at very rapidly.

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Keywords: Hydrogen liquefaction System, Thermodynamic Analysis, Energy-Exergy Analysis

1. Introduction

Hydrogen system is a unique design system for liquefaction of hydrogen gas. It comprises as liquid nitrogen chamber which helps the system to attain critical temperature point of hydrogen. Hydrogen derived from renewable energies eventually will contribute to meet the energy demand of world and help in sustainable development of countries [1]. Hydrogen combustion produces water vapor that does not make any pollution. Hydrogen is in gas form occupies a large volume, having low density (0.0897 kg/m^3) and high pressure, thus need to liquefy hydrogen for an easier transportation and safety. Production of liquefy hydrogen is a challenging task due to its very low cryo-temperature of liquefaction. The major components of liquefaction cycle are: compressor powered by external energy source, four heat exchanger including nitrogen fill chamber, Joule Thomson valve and separator, which are shown in the Fig.1 Various important properties of H_2 are represented in Table 1. Saturated temperature and pressure at (STP) condition is denoted by T_0 and P_0 , respectively. Exergy is consumed or destroyed due to entropy generation based upon related processes, exergy destruction in various components of the system are not same. Thermodynamic analysis is to be made to identify the exergy losses in the system.

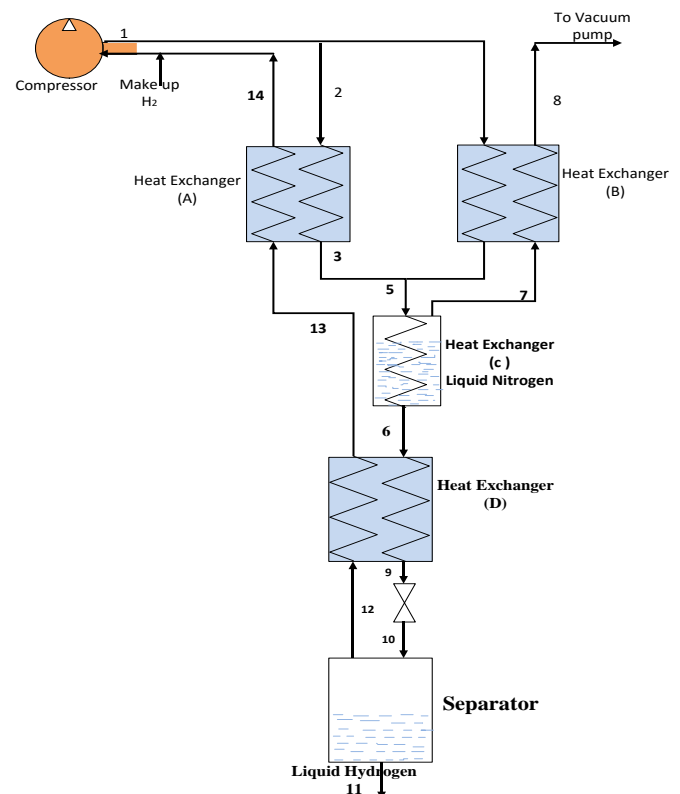


Figure 1: Block diagram of hydrogen liquefaction system

2. Literature Review

Ibrahim Dincer et.al [1] carried out Exergy Analysis of Cryogenic and Liquefaction Systems and compared the numerical results with experimental measurements while M.T. Syed, [2] carried out the economic analysis of three hydrogen liquefaction systems, Akihiro Nakano, et.al.[3], analyzed Small-scale hydrogen liquefaction with a two-stage Gifford–McMahon cycle refrigerator. David O. et.al [4], also considered Large-scale hydrogen liquefier utilizing mixed-refrigerant pre-cooling”, David O. Berstadet.al [5], carried out Comparison for large-scale hydrogen liquefaction processes. Gianluca Valenti and Ennio Macchi [6] proposed innovative, high-efficiency, large-scale hydrogen liquefier Neksa, [7] carried out Simulation on a proposed large-scale liquid hydrogen plant using a multi-component refrigerator refrigeration system. Gianluca Valenti [8], developed thermodynamic model of equilibrium-hydrogen on the simulation of its liquefaction

3. Thermodynamic (Energy-Exergy) Model hydrogen liquefaction system [1]

Following assumptions are made in the exergy analysis:

1. Steady state conditions are remained in all the components.
2. Pressure loses in the pipelines are neglected.
3. Heat gains and heat loses from the system or to the system are not considered.
4. Kinetic and potential energy and exergy losses are not considered.
5. With reference to cited literatures, it is assumed that mechanical efficiency of the compressor is 90% and the electrical efficiency of the motor is 90%.

Energy and exergy analyses need some mathematical formulations for the hydrogen liquefaction cycle. Mathematical formulation for exergy analysis in different components can be arranged in the following way: The equations for exergy balance of Hydrogen Liquefaction systems are written as

3.1 Compressor analysis

$$Q = m_2 * (h_2 - h_1)$$

Specific exergy in any state is expressed as

$$Ex_{state} = (h_{state} - h_0) - T_0 * (s_{state} - s_0)$$

Where ‘Q’ is the rate of heat transfer across boundary, T2 and T0 is the temperature after the compression and reference state temperature. Exergy transfer accompanying the work interaction equals the electrical or mechanical work W (kW) itself. The exergy transfer accompanying mass crossing the boundaries at the inlet and outlet of the Compressor is expressed as

$$Ex_{comp} = \left(m * ((h_2 - h_0) - (h_1 - h_0)) - ((s_2 - s_0) - (s_1 - s_0)) \right)$$

Where ‘m’ represents the mass flow rate, (kg/s), ‘Ex’

represents the exergy per unit mass, ‘h’ and ‘s’ correspond to the enthalpy and entropy of the fluid, h0 and s0 represent the enthalpy and entropy at the reference state (T0, P0) respectively. For this analysis, the atmospheric condition is taken as the reference state (T0 = 300K and P0 = 1.01325bar).

$$W_{comp} = (m_2 * ((h_2 - h_1)) - T_2 * (s_2 - s_1))$$

$$COP = \frac{m_2 * (h_1 - h_{11})}{W_{comp}}$$

$$Ed_{comp} = \left(m_2 * T_1 * (s_1 - s_2) - \left(Q * \left(\frac{T_0}{T_1} \right) \right) \right)$$

Unlike energy, exergy would be destroyed due to irreversibility associated with the processes. The term ‘Ed’ of Eq. (1) accounts for the destruction of exergy and according to Gouy Stodola theorem it is expressed as

$$Ed = T_0 * \Delta S_{gen}$$

Where ‘ ΔS_{gen} ’ represent the rate of entropy generation during the process.

$$Ed_{comp\%} = \left(\frac{Ed_{comp}}{Ed_{HLsys}} \right) * 100$$

$$Eta_{2nd\%} = \left(\frac{m_f * ((h_{11} - h_1) - T_0 * (s_{11} - s_1))}{(h_2 - h_1) - T_1 * (s_2 - s_1)} * m_2 \right) * 100$$

3.2 Heat Exchanger (HX) analysis

The function of heat exchanger is to exchange heat between two moving fluid streams without mixing; the hot fluid is releasing heat to the cold and the changes of kinetic and potential energy negligible.

The mass low rate of hot fluids and cold fluid should be constant. Energy balance equation can be expressed as follows: $Ex_{inHX} - Ex_{outHX} - Ed_{HX} = \Delta E_{xHX} = 0 \Rightarrow$ steady

$$Ex_{HX} = m_i * ((h_{in} - h_{out}) - (T_0 * (s_{in} - s_{out})))$$

$$Ed_{HX} = ((Ex_{inHX}) - (Ex_{outHX}))$$

$$m_{hHX} * (h_{h,i} - h_{h,o}) = m_{cHX} * (h_{c,o} - h_{c,i}) + q$$

Considering the heat transfer rate is the function of fluid mass flow rate and the inlet and outlet temperature different, the function can be written as:

$$q=f(m,T)$$

The heat transfer rates from the hot fluid to cold fluid are calculated by using following

$$q_{HX} = C_{h,HX} * (T_{h_i} - T_{h_o})$$

The rate of heat received by the cold fluid can be calculated:

$$q_{HX} = C_{c,HX} * (T_{c_o} - T_{c_i})$$

In the heat exchanger, maximum heat exchange is occurred when the fluid temperature will be in a constant mass flow rate of the fluids.

$$T_{h_i} = T_{c_o}; T_{h_o} = T_{c_i}$$

Maximum heat transfer rate capacity $q_{max\ HX}$ can be calculated by using the following equation:

$$q_{max\ HX} = C_{min\ HX} * (T_{h_i} - T_{c_i})$$

The expression of heat energy effectiveness (epsilon) of the heat exchanger considered in the present study are based on the

following definition.

$$\epsilon = q_{HX}/q_{max_{HX}} = \left(\frac{\frac{\text{Actual heat}}{\text{actual energy transfer}}}{\frac{\text{Maximum heat possible}}{\text{Maximum energy transfer}}} \right)$$

$$N_{tu_{HX}} = (G_{HX})/C_{min_{HX}}$$

As the heat transfer is from the hot stream to cold stream in heat exchanger, the entropy of the hot stream decreases. This decrease in entropy is achieved by supplying exergy from the cold stream to the hot stream. In the case of heat exchangers employed in a refrigeration/ liquefaction system, the objective is to increase the exergy of the high pressure hot stream such that finally it is capable enough to absorb heat from the given external load. So the rational exergetic efficiency of the heat exchanger is defined as

$$\eta_{HX} = (m_h * (Ex_{h,out_{HX}} - Ex_{h,in_{HX}})) / (m_c * (Ex_{c,out_{HX}} - Ex_{c,in_{HX}}))$$

In the considered case the changes of kinetic and potential energy are neglected so change of exergy destruction of each stream can be written in the following form

$$Ex_{in_{HXD}} = m_2 * ((h_6 - h_9) - (T_0 * (s_6 - s_9)))$$

$$Ex_{out_{HXD}} = m_g * ((h_{12} - h_{13}) - (T_0 * (s_{12} - s_{13})))$$

$$Ed_{HXD} = \text{abs}((Ex_{in_{HXD}}) - (Ex_{out_{HXD}}))$$

$$Ed_{HXD} \% = \left(\frac{Ed_{HXD}}{Ed_{HLsys}} \right) * 100$$

$$T_6 = T_7 = -77^\circ\text{C} (\text{Liq Nitrogen temp})$$

$$T_{hi} = T_6; T_{co} = T_{13}$$

$$m_{h_{HXD}} = m_2, m_{c_{HXD}} = m_g$$

$$T_{ho} = T_9; T_{ci} = T_{12}$$

$$C_{h_{HXD}} = m_{h_{HX}} * cp_{fluid_{hot_{HXD}}}$$

$$C_{c_{HXD}} = m_{c_{HX}} * cp_{fluid_{cold_{HXD}}}$$

3.3 Heat Exchanger 'C' Analysis

$$m_2 * h_5 + m_{LN} * HF_N = m_{LN_{evop}} * h_7 + m_2 * h_6 \quad (32)$$

$$m_{LN} = m_{LN_{evop}}$$

$$T_5 * m_2 = m_a * T_3 + m_b * T_4$$

3.4 Expansion Valve Analysis

$$h_9 = h_{10}; T_{10} = T_{12}$$

$$x_{10} = \frac{m_f}{m_f + m_g}$$

$$Ex_{in_{val}} = m_2 * ((h_9 - h_0) - T_0 * (s_9 - s_0))$$

$$Ex_{out_{val}} = m_2 * ((h_{10} - h_0) - T_0 * (s_{10} - s_0))$$

$$Ed_{val} = \text{abs}(Ex_{in_{val}} - Ex_{out_{val}})$$

$$Ed_{val} \% = \left(\frac{Ed_{val}}{Ed_{HLsys}} \right) * 100$$

3.5 Separator Analysis

$$m_2 * h_{10} = m_f * h_{11} + m_g * h_{12}$$

$$x_{11} = 0; x_{12} = 1$$

$$Ed_{sep} = T_0 * \left((m_g * s_{12} - m_2 * s_{10}) + \left(\frac{m_g * h_{12} - m_f * h_{11}}{T_0} \right) \right)$$

$$Ed_{sep} \% = \left(\frac{Ed_{sep}}{Ed_{HLsys}} \right) * 100$$

$$Ed_{HLsys} = Ed_{comp} + Ed_{HXC} + Ed_{HXA} + Ed_{HXD} + Ed_{val} + Ed_{sep} + Ed_{HXB}$$

4. Results and Discussions

Thermodynamic model for hydrogen liquefaction cycle has been developed using numerical computational technique. In the thermodynamic analysis of cycle, considered parameters like COP, liquefaction rate, compressor work and exergy destruction etc. with the cyclic pressure ratio, which have direct relationship with the performance of cycle have been varied. The effect of these parameters on the performance of the cycle is computed. In order to understand the individual effect of cycle parameters on the performance of the cycle, when varying a cycle parameter, other parameters are kept constant. The efficiency of the compressor (COMP) is kept constant at 85% and for all heat exchangers the effectiveness is kept at 0.85. The liquefaction temperature of liquid nitrogen (LN) is taken as 196 K (Liquefaction temperature of nitrogen). The above parameters have been chosen on the basis of the practical data available in open literature. An illustrative example is presented for the Hydrogen liquefaction cycle shown in fig.1 at 20 bar outlet pressure of compressor. Apart from above constant terms following other assumption are also considered while working on cycle like the compression is isothermal; expansion valve is isenthalpic and there is no heat leakage to the cycle. Furthermore the gas is taken is pure hydrogen at the inlet of compressor at 300 K and 1 bar. With all these assumption and constant parameters each of system component is studied and various performance parameters at every state is listed in Table-1&2. The properties of Hydrogen gas are obtained using computation software.

Table.1: various performance parameters

$COP = 1.064$	$m_{LN_{evop}} = 0.4 \text{ [Kg/s]}$	$m_b = 0.5 \text{ [Kg/s]}$
$\eta_{2nd\%} = 53.79$	$m_2 = 1 \text{ [Kg/s]}$	$\epsilon_{HXA} = 0.85$
$P_1 = 1 \text{ [bar]}$	$m_a = 0.5 \text{ [Kg/s]}$	$\epsilon_{HXB} = 0.85$
$P_2 = 20 \text{ [bar]}$	$m_b = 0.5 \text{ [Kg/s]}$	$\epsilon_{HXD} = 0.85$
$m_f = 0.166 \text{ [Kg/s]}$	$m_{HXD} = 1 \text{ [Kg/s]}$	$NTU_{HXA} = 3.886$
$m_g = 0.833 \text{ [Kg/s]}$	$HF_N = 25.35 \text{ [kJ/kg]}$	$NTU_{HXB} = 4.363$
$m_{LN} = 0.49 \text{ [Kg/s]}$	$W_c = 5770 \text{ kJ/kg}$	$NTU_{HXD} = 3.943$

Table 2: Various performance parameters

Temperature [K]	Enthalpy [kJ/kg]	Entropy [kJ/kg – K]	Specific Heat [kJ/kg – K]
T ₀ = 298	h ₀ = 3929	s ₀ = 53.42	cp _{c_fHXA} = 10.55
T ₁ = 300	h ₁ = 3958	s ₁ = 53.52	cp _{c_fHXB} = 10.68
T ₂ = 300	h ₂ = 3966	s ₂ = 41.14	cp _{c_fHXD} = 11.71
T ₃ = 103.2	h ₃ = 1316	s ₃ = 27.02	-----
T ₄ = 132.3	h ₄ = 1669	s ₄ = 30.03	----
T ₅ = 117.7	h ₅ = 1490	s ₅ = 28.6	-----
T ₆ = 77	h ₆ = 1007	s ₆ = 23.57	-----
T ₇ = 77	h ₇ = 1007	s ₇ = 36.4	-----
T ₈ = 266.5	h ₈ = 3488	s ₈ = 51.83	-----
T ₉ = 44.87	h ₉ = 373.5	s ₉ = 11.12	-----
T ₁₀ = 20.32	h ₁₀ = 373.5	s ₁₀ = 3.664	-----
T ₁₁ = 20.32	h ₁₁ = 0.4445	s ₁₁ = 0.02093	-----
T ₁₂ = 20.32	h ₁₂ = 448.4	s ₁₂ = 22.06	-----
T ₁₃ = 68.5	h ₁₃ = 962.9	s ₁₃ = 35.16	-----
T ₁₄ = 229.2	h ₁₄ = 2958	s ₁₄ = 49.72	-----

The pressure ratio which is defined as the ratio of outlet pressure (P2) to inlet pressure (P1) at the compressor side put marked effect upon the performance and energy required in a liquefaction cycle. The inlet pressure (P1) is kept constant at 1.0133 bar where as for study, the cyclic pressure ratio is varied by changing the outlet pressure between the low pressures to high pressure range to analyze the behavior of hydrogen liquefaction system. Detroit of performance largely depend upon the pressure range in which they are designed to function whereas inlet pressure also depend upon the lower temperature required by the application and other operating condition so inlet pressure also have to be choose carefully. The Fig.2 depicts that when the cycle pressure ratio PR is in between 35 and 60, there is condition when system give maximum output with less compressor work input. There is a particular pressure ratio within this range for which the cycle output is at its maximum for the given configuration and operating conditions, this corresponds to PR = 55. Fig.2 shows that the work requirement for the cycle is increasing proportionally with the compressor pressure corresponding to its input pressure, whereas there is decrease in output of the system (liquefaction mass) with increase of pressure ratio. However, the actual energy input to the system is the exergy supplied to it (kW), and is expressed as:

$$Ex_{system} = m * (Ex_{system,in} - Ex_{system,out})$$

Where ‘Ex_{system,in}’ and ‘Ex_{system,out}’ are the flow exergies of the high pressure stream out of the after cooler and the low pressure stream input to the compressor respectively.

A part of the work input to the compressor is destroyed inside various components of the cycle. But as discussed above at right hand side of Fig.2. ,the maximum output at the approx. PR=55,at this PR the exergy destruction is more contributed by heat exchanger HXD, Separator and compressor while other components HXA,HXB and HXC is showing less destruction and minimum in JT valve of system. Exergy destruction in HXD, HXA, HXB and HXC decreases with increasing

pressure ratio, this trend is reverse for the rest of the components of the system. The exergy destruction of each heat exchanger in the cycle with increasing cycle pressure ratio is shown in Fig.3 It shows that for all heat exchanger except HXD, the trend of decreasing the destruction with increasing pressure ratio is same in all, destruction is first increases up to PR=70 then start decreasing with increasing compressor pressure while in HXD this trend is from the initial stage, destruction start decreasing from initial point of increasing compressor pressure. It shows that appropriate care should be taken for HXD which also a JT-heat exchanger (Heat exchanger connected to Joule Thomson valve) and separator while designing the cycle. It also notice that all the heat exchangers in a liquefaction cycle are not equally balanced primarily due to reasons:

- (1) As the liquid is drawn out of the system, the return stream flow is less than the high pressure forward stream.
- (2) At temperatures below 20 K, there is considerable mismatch in their specific heats due to the pressure difference between the forward and return streams. For all the heat exchangers in the cycle, the specific heat capacity of the hot forward stream is plotted as a function of cycle pressure ratio (Fig.3).

For hydrogen at very low temperatures, the higher pressure stream has a lower specific heat than low pressure stream. In Fig.4 shows the heat exchanger HXD, which is working at the lowest temperature level, there is a large variation in specific heat (Cphf) with compression pressure ratio. The specific heat at high pressure side is maximum at PR=105 for HXD, and then there is significant drop in the Cp with increase in compressor pressure, other side the heat exchanger HXA and HXB having same inlet but still showing the different trend of variation in their respective specific heat, this variation is due to difference in the cold side inlet. Heat exchanger HXA have inlet of residual mass of which is not liquefy while HXB have vapors of LN which is form when hot Hydrogen is passes from LN chamber (HXC).

In optimization of system the first and second law analysis play a very important role carefully study relation between these two help in identifying the losses of the system which degrade the performance of system. Fig.5. show the effect of pressure ratio upon the COP and second law of system From the graph study it determined that there is high reduction in COP of system with increase of pressure ratio between 20- 87 bar but after that the reduction start stable and showing very less effect on COP with increases in pressure whereas right hand side second law show continuous decrease with high slop with increase of compressor pressure. At 262.5 bar the COP and Second law efficiency intersect each other. From the Fig. 5 it notice that; low compressor pressure in feasible range show high performance characteristics. NTU is very important term defining the number of transfer unit and very useful estimating the surface area of HX under design condition. In our Hydrogen liquefaction process we required three HX and one liquefy nitrogen chamber, NTU help us in estimating the size of all heat exchanger at various range of pressure ratio. Fig.6 show variation in dimensionless NTU at different pressure

ratio, from fig. 6 it depicted that the lowest temperature heat exchanger HXD show NTU decrement upto 70 bar then it became constant upto 105 bar but after this pressure range it increase at a very fast rate, which show gradually increase in size of heat exchanger while NTU trend of HXB is reverse of HXD and its value start decreasing after 105 bar. The variation in HXA NTU is very less. The mass vapour fraction ratio after J-T valve effect gives an idea how much mass can be liquefied. By using right technique the maximum output is can gathered e.g. three column separator is more efficient than two column separator. Fig.7 follow the same trend of liquefy mass as in above fig. 2 and show highest mass vapour fraction between 35 bar to 70 bar. The analysis is repeated at different pressure ratio and as a part of analysis, exergy destructions of each component is computed and various results of these studies are discussed in Fig 2 to 7.

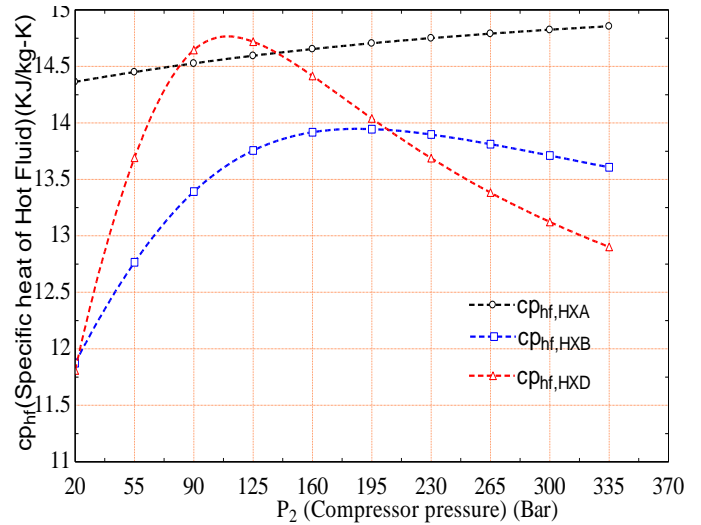


Figure 4: Variation in Cp_{hf} (specific heat of hot fluid) versus compressor pressure

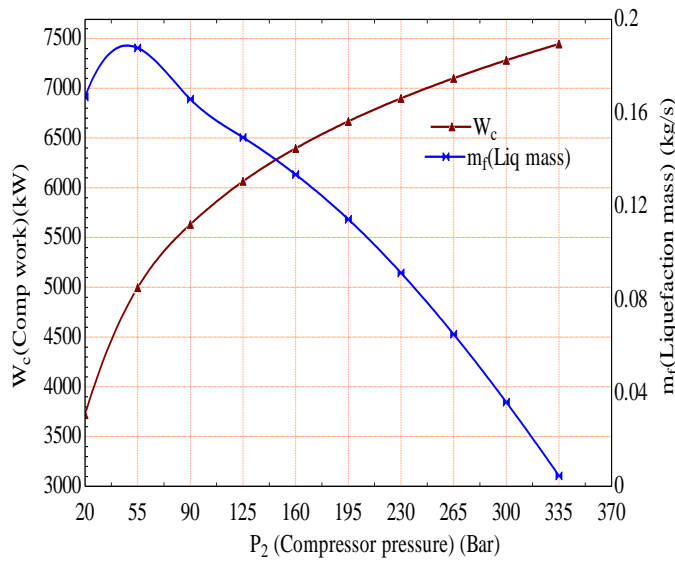


Figure 2: Work input (Compressor work W_c) and rate of liquefied mass m_f versus compressor pressure

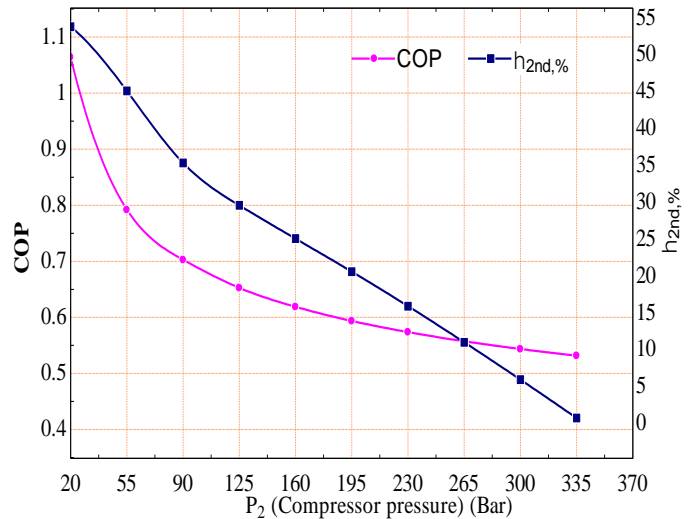


Figure 5: Variation in COP and Second law efficiency versus compressor pressure

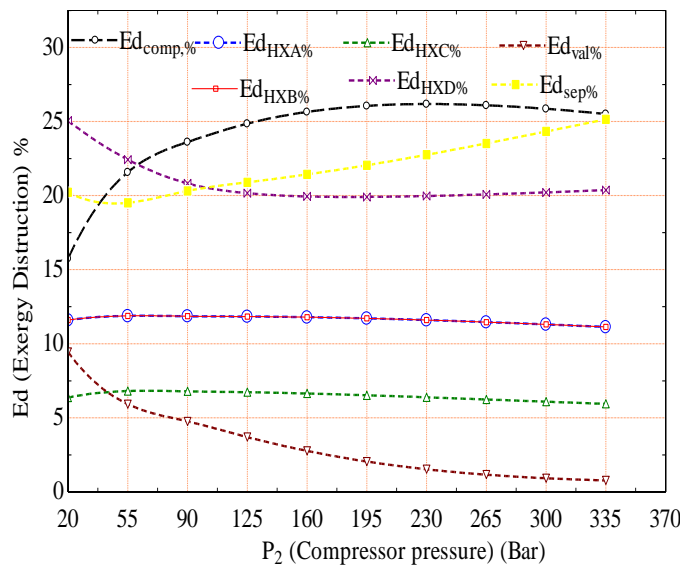


Figure 3: Variation in Ed (Exergy destruction) % versus compressor pressure

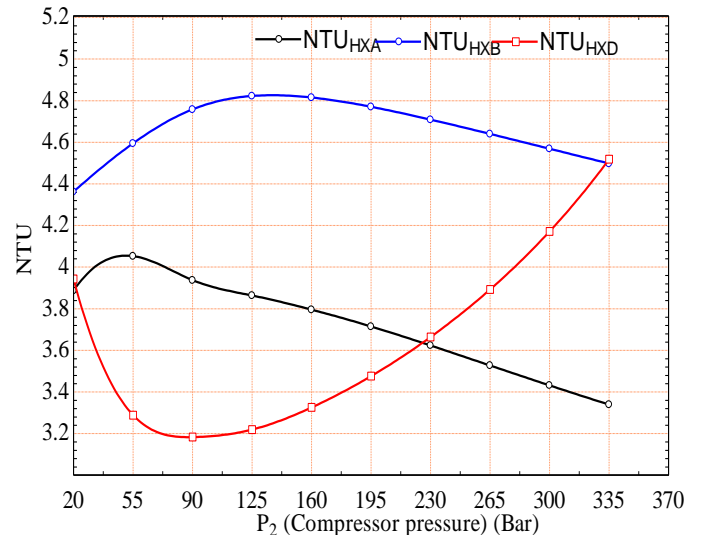


Figure 6: NTU vs Compressor Pressure

Using the above methodology, exergetic analysis of cycle design parameters on the performance of the hydrogen liquefaction cycle has been performed for obtaining optimum design guidelines. The observations and findings are described in the form of following graphic data mention below.

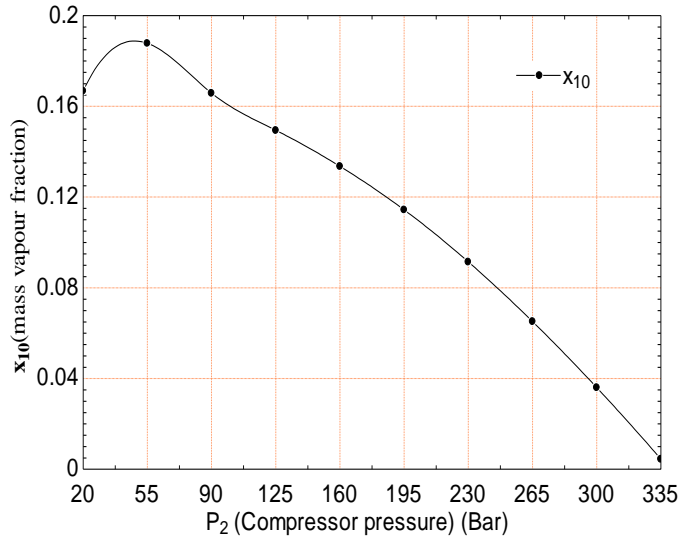


Figure 7: Mass Vapour fraction versus compressor pressure

5. Conclusion

- Second law efficiency in terms of Exergetic Efficiency of liquefaction in hydrogen system is 17.29 % and it start decreasing with further increases of compressor pressure
- COP of the liquefaction in hydrogen system is 0.8687 when input at ambient condition and compressor pressure is 15 bar and as like second like efficiency it also start decreasing with increases of compressor pressure.
- Liquefaction mass ratio and Total work done is increases with increase in compressor pressure in the hydrogen liquefaction system

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