Hydrogen Liquefaction Process with Mixed Refrigerant Pre-cooling

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Abstract. A novel hydrogen liquefaction process based on precooled mixed refrigerant is proposed in this paper. The specific energy and the exergy loss are also analyzed. The feed gas with a temperature of 302K and a pressure of 2.012MPa is first precooled to 81K with mixed refrigerant. Three refrigerant cycles with hydrogen expanders and one with throttling valves are adopted to cool the gaseous hydrogen to 21K. The proportion of para-hydrogen of the product is 99%. The specific energy consumption of the process is 9.28 kW-h/kgLH2 and the exergy efficiency is 24.3%. Furthermore, the exergy analysis indicates that the exergy loss caused by heat exchangers, compressors and expanders weights the most.

1. Introduction

Hydrogen is the "energy of the future" for human beings because of its wide source, high energy density, and environmental friendliness [1]. With the increasing global climate change, countries around the world are paying more and more attention to hydrogen as a zero-carbon energy source. Liquid hydrogen, as a highly efficient means of storing hydrogen, has a hydrogen storage density that is 2.8 times that of high-pressure hydrogen at 35 MPa and 1.7 times that of high-pressure hydrogen at 70 MPa. Meanwhile, compared with high-pressure hydrogen storage, liquid hydrogen has low storage pressure and high purity of vaporized hydrogen. Therefore, liquid hydrogen is an important means of hydrogen transportation and large-scale energy storage in the future. However, due to the extremely low liquefaction temperature of hydrogen, it is the most difficult gas to liquefy besides helium, and the high energy consumption of hydrogen liquefaction is an important factor restricting the application of liquid hydrogen. Currently, the main hydrogen liquefaction processes commonly used in industry are the liquefaction process using reverse Brayton cycle as well as Claude cycle [2]. The former is mainly used for small and medium-sized hydrogen liquefaction plants with a production capacity of less than 5 tpd (tons per day), with a typical energy consumption of 17 kW-h/kgLH2. The Claude cycle process has lower energy consumption and is suitable for large-scale hydrogen liquefaction equipment. The 5tpd hydrogen liquefaction equipment in operation in Ingolstadt and Luena, Germany, adopts this process, with energy consumption of 13.6 and 11.9 kW-h/kgLH2 (kilowatt-hour per kilogram of liquid hydrogen), respectively [3][4]. All of the above hydrogen liquefaction plants use liquid nitrogen pre-cooling.

The concept of mixed refrigerant refrigeration was first proposed by Podbielniak in 1936 [5], and has been widely used in natural gas liquefaction plants since the 1970s. Currently, 95% of the natural gas liquefaction plants around the world use mixed refrigerant refrigeration [6]. Since the natural gas liquefaction temperature (110 K) is closer to the liquid nitrogen temperature (80 K), researchers have developed a hydrogen liquefaction process that utilizes mixed refrigerant pre-cooling, which is typically around 80 K. Compared to the natural gas liquefaction process, the hydrogen liquefaction pre-cooling mixing reagent has a lower boiling point of neon added to keep the cooling temperature lower than 110 K. In 2010, David Berstad [7] et al. simulated a hydrogen liquefaction cycle with hybrid refrigerant pre-cooling, using a four-stage heat exchanger to pre-cool the feed hydrogen from ambient temperature to 75 K. Compared to the hydrogen liquefaction cycle proposed by Quack [8], the hybrid refrigerant efficiency was increased to 47.1% and the power consumption was reduced by 2.9%. Although its hydrogen liquefaction energy consumption is as low as 6.15 kW-h/kgLH2, the process employs a liquid expander, an immature process equipment, as well as a compressor adiabatic efficiency of up to 85% and an expander efficiency of up to 90%, which are values also difficult to achieve in industrial applications. Krasae et al. [9] proposed a hydrogen liquefaction process for a production rate of 100 tpd with a hybrid refrigerant to precool the feed hydrogen to -193°C. The refrigerant mixture consists of hydrogen, methane, ethane, and butane, and the expansion refrigeration is also used in the pre-cooling process, and the overall power consumption of the hydrogen liquefaction process is 5.91 kW-h/kgLH2. Asadnia et al. [10] proposed a hybrid refrigerant pre-cooled hydrogen liquefaction process for a production rate of 100 tpd of liquid hydrogen, and the pre-cooling
temperature is -198.2°C. The pre-cooling temperature is -198.2°C. The pre-cooling temperature is -198.2°C, and the pre-cooling cycle is refrigerated by an expander, and below the temperature zone of liquid nitrogen, a 6-stage cascade cycle is used, which is a complicated process with a final energy consumption of 7.69 kW-h/kgLH2. Yujing Bi et al. [11] proposed a hydrogen liquefaction cycle using methane, ethane, propane, isobutane, R14, and nitrogen as the mixed refrigerant pre-cooling, with a production rate of 5 tpd, and the energy consumption is 9.703 kW-h/kgLH2.

In this paper, a novel hydrogen liquefaction process based on precooled mixed refrigerant is proposed, and the specific energy and the exergy loss are also analyzed.

2. Hydrogen liquefaction process design

2.1 Simulation methods
In this paper, the MBWR equation is chosen for the physical equation of hydrogen in the hydrogen liquefaction process, and the PR equation is chosen for the physical equation of mixed refrigerant. Since the simulation software cannot directly simulate the continuous hydrogen conversion process, a normal hydrogen flow unit with the same temperature as the inlet and outlet of the feedstock hydrogen (normal hydrogen) is added to the heat exchanger to simulate the heat released from the continuous hydrogen conversion, and the flow rate of the additional hydrogen flow unit is determined by the enthalpy change caused by the conversion of the ortho-neutral hydrogen. The following assumptions are also made in the simulation:
1. the pressure drop in the heat exchanger is 5kPa for the mixed refrigerant stream and 2kPa for the hydrogen stream
2. the adiabatic efficiency of all compressors, pumps and expanders is 80%.
The refrigerant mix is 12.9% methane, 20.2% ethylene, 7.4% propane, 8.3% isopentane, 47.1% nitrogen and 4.1% neon.

2.2 Methods of analysis
SEC (Specific Energy Consumption) for hydrogen liquefaction is defined as:

\[ SEC = \frac{W_{\text{total}}}{m_{\text{product}}} \]

\[ W_{\text{total}} \text{ is the total power of compressors and pumps in the process, and } m_{\text{product}} \text{ is the liquid hydrogen flow rate.} \]

The energy efficiency ratio is defined as

\[ COP = \frac{m_{\text{feed}} \times (h_{\text{feed}} - h_{\text{product}})}{W_{\text{total}}} \]

where \( m_{\text{feed}} \) is the mass flow rate of feed gas, \( h_{\text{feed}} \) is the specific enthalpy of feed gas, and \( h_{\text{product}} \) is the specific enthalpy of liquid hydrogen.

Equipment exergy loss is defined as:

\[ \Delta E_x = W + \sum m_{\text{in},i} \cdot e_{\text{in},i} - \sum m_{\text{out},i} \cdot e_{\text{out},i} \]

\( W \) is the input work of the device, \( m_{\text{in},i} \) and \( e_{\text{in},i} \) are the mass flow rate and mass exergy of the inlet flow of the device, \( m_{\text{out},i} \) and \( e_{\text{out},i} \) are the mass exergy of the outlet flow of the device, respectively.

The system exergy efficiency is defined as:

\[ \eta = \frac{e_{\text{product}} - e_{\text{feed}}}{\text{SEC}} \]

\( e_{\text{feed}} \) is the mass exergy of feed hydrogen and \( e_{\text{product}} \) is the mass exergy of liquid hydrogen.

3. Result and Discussion

3.1 Hydrogen liquefaction process
Figure 1 shows the schematic diagram of the hydrogen liquefaction process in this study. The hydrogen liquefaction process can be divided into three parts: the feed hydrogen path, the refrigerant mixing pre-cooling path, and the deep-cooling liquefaction path. The temperature of feed hydrogen is 302K, the pressure is 2.012MPa, the flow rate is 347.2g/s (30tpd), the feed hydrogen is cooled down to 21K through 6-stage heat exchanger in turn, and then throttled down to 0.15MPa to enter the liquid hydrogen storage tank, the ortho-to-para conversion process occurs in the last four heat exchangers, and the final proportion of para-hydrogen is 99%, and the liquefaction rate is 97.6%, and the flash gas is refluxed to recover the cooling capacity.

Mixed refrigerant pre-cooling circuit provides 302K~80K cooling capacity. After compression, cooling refrigerant goes into the first-stage heat exchanger and the gas-liquid separator, the gas continues to enter the second-stage heat exchanger, the liquid throttled back to the first-stage heat exchanger to provide cold energy after mixing with the reflux refrigerant. The gas cooled by the secondary heat exchanger is throttled and returned to the secondary heat exchanger to provide cold energy for the secondary heat exchanger.

The deep-cooling liquefaction circuit includes four independent refrigeration cycles, three of which use expander refrigeration to provide cold energy in the temperature zones of 80K~55K, 55K~36K, and 36K~28K, respectively, and the last refrigeration cycle uses throttling refrigeration to provide cooling in the temperature zones of 28K~21K, and the refrigerants of the four refrigeration cycles are all hydrogen.
3.2 Energy consumption analysis
Since the expander energy recovery device will increase the system complexity, the output power of the expander is not considered. The operating parameters of compression for the hydrogen liquefaction process are given in Table 1. The power consumption of the mixed refrigerant pre-cooling process is 3202.2 kW, and the specific energy consumption (SEC) is 2.62 kW-h/kgLH2, and the power consumption of the deep-cooling liquefaction process is 8125.1 kW, and the SEC is 6.66 kW-h/kgLH2, and the SEC of the whole hydrogen liquefaction process is 9.28 kW-h/kgLH2, which is 31.8 kW-h/kgLH2 lower compared with the energy consumption of the hydrogen liquefaction plants in Ingolstadt and Luena, Germany, respectively. Compared with the hydrogen liquefaction plants in Ingolstadt and Luena, Germany, the energy consumption of the plant has been reduced by 31.8% and 22%, respectively.

Table 1. Parameters of Compressors

<table>
<thead>
<tr>
<th>Compressor</th>
<th>Pressure ratio</th>
<th>Power/kW</th>
<th>Compressor</th>
<th>Pressure ratio</th>
<th>Power/kW</th>
</tr>
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<tbody>
<tr>
<td>COM-C1-1</td>
<td>2.287</td>
<td>126.5</td>
<td>COM-C4-1</td>
<td>2.07</td>
<td>862.3</td>
</tr>
<tr>
<td>COM-C1-2</td>
<td>2.41</td>
<td>135.7</td>
<td>COM-C4-2</td>
<td>2</td>
<td>816.5</td>
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<tr>
<td>COM-C1-13</td>
<td>2.33</td>
<td>130.4</td>
<td>COM-MR1</td>
<td>1.3</td>
<td>1337.1</td>
</tr>
<tr>
<td>COM-C2-1</td>
<td>2.56</td>
<td>3020</td>
<td>COM-MR2</td>
<td>1.44</td>
<td>1865.1</td>
</tr>
<tr>
<td>COM-C3-1</td>
<td>2.17</td>
<td>1553</td>
<td>PUP-MR1</td>
<td>-</td>
<td>-</td>
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<tr>
<td>COM-C3-2</td>
<td>2.1</td>
<td>1485.8</td>
<td>PUP-MR2</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

3.3 Energy efficiency analysis
From Eq. (2) and Eq. (4), the energy efficiency ratio and exergy efficiency of the hydrogen liquefaction process are 0.122 and 24.3%, respectively. Table 2 gives the hydrogen liquefaction equipment's losses and the proportion of the losses to the load of this equipment, the compressor loss is 1887.3kW, the heat exchanger loss is 2362.2kW, the throttle valve loss is 414.5kW, and the expander loss is 1046.3kW. The heat exchanger, compressor, and expander losses account for more than 92% of the total losses of the equipment. From the viewpoint of equipment, the fluctuation of the percentage of loss of different compressors and expanders is small; the percentage of loss of different heat exchangers has a big difference, and the percentage of loss of the heat exchanger of mixed refrigerant cycle is smaller than that of the heat exchanger of hydrogen refrigeration cycle, while the first-stage heat exchanger, though with the highest load, has the smallest percentage of loss of loss.
Table 2. Exergy Loss of Different Equipments

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Exergy loss/kW</th>
<th>Proportion</th>
<th>Equipment</th>
<th>Exergy loss/kW</th>
<th>Proportion</th>
</tr>
</thead>
<tbody>
<tr>
<td>COM-C1-1</td>
<td>18.8</td>
<td>0.149</td>
<td>E4</td>
<td>190.6</td>
<td>0.322</td>
</tr>
<tr>
<td>COM-C1-2</td>
<td>20.4</td>
<td>0.15</td>
<td>E5</td>
<td>117</td>
<td>1.02</td>
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<tr>
<td>COM-C1-3</td>
<td>19.8</td>
<td>0.152</td>
<td>E6</td>
<td>80</td>
<td>2.13</td>
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<tr>
<td>COM-C2-1</td>
<td>496.9</td>
<td>0.165</td>
<td>J1</td>
<td>125.8</td>
<td>-</td>
</tr>
<tr>
<td>COM-C3-1</td>
<td>241.7</td>
<td>0.156</td>
<td>J2</td>
<td>40.6</td>
<td>-</td>
</tr>
<tr>
<td>COM-C3-2</td>
<td>232.1</td>
<td>0.157</td>
<td>J3</td>
<td>106</td>
<td>-</td>
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<tr>
<td>COM-C4-1</td>
<td>135.8</td>
<td>0.157</td>
<td>J4</td>
<td>142.1</td>
<td>-</td>
</tr>
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<td>COM-C4-2</td>
<td>130</td>
<td>0.159</td>
<td>EXP1</td>
<td>375.2</td>
<td>2.75</td>
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<tr>
<td>COM-MR1</td>
<td>252.9</td>
<td>0.189</td>
<td>EXP2</td>
<td>239</td>
<td>2.17</td>
</tr>
<tr>
<td>COM-MR2</td>
<td>338.9</td>
<td>0.182</td>
<td>EXP3</td>
<td>187.7</td>
<td>1.68</td>
</tr>
<tr>
<td>E1</td>
<td>882.7</td>
<td>0.026</td>
<td>EXP4</td>
<td>133.1</td>
<td>1.42</td>
</tr>
<tr>
<td>E2</td>
<td>858.5</td>
<td>0.151</td>
<td>EXP5</td>
<td>111.2</td>
<td>1.14</td>
</tr>
<tr>
<td>E3</td>
<td>233.4</td>
<td>0.22</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For compressors and expanders, the means to reduce loss is to improve the efficiency of the equipment, and for heat exchangers, it can be realized by reducing the minimum heat exchanger temperature difference and reducing the overall heat exchanger temperature difference. The former can be achieved by increasing the heat transfer area, because the minimum heat transfer temperature difference can be achieved when the heat exchanger heat transfer area tends to be infinite, so the minimum heat transfer temperature difference and heat exchanger size should be balanced. The latter can be achieved by improving the process, such as the application of mixed refrigerants, the rational design of heat exchanger inlet and outlet temperatures and the pressure to realize loss reduction.

Figure 2 shows the temperature curves of heat exchanger E1 and E2. Cold and hot stream temperature distribution curve of E1 is basically parallel, with a large deviation only in the hot end, while for E2, the temperature difference above 90K is larger, which is caused by the E1 and E2 exergy loss. Improving the E2 temperature distribution curve can effectively reduce the power loss. Analogous to natural gas liquefaction, the main ways to reduce the energy loss are as follows:

1. increasing the number of heat exchanger stages and the number of refrigerant types
2. using multi-cycle mixed refrigerant refrigeration

The first method will increase the number of equipment (heat exchangers and control valves, etc.), while the increase in the number of refrigerants will increase the difficulty of system control. For the second method, with the increase of refrigeration cycles, the number of equipment will be greatly increased, while the increase in the number of compressors and other motion equipment will increase the operational risk of the system.

Figure 2. Temperature difference curve of E1 and E2

Figure 3 gives the heat exchanger temperature difference of each heat exchanger in the deep-cooling liquefaction cycle, E3 and E4 have a smaller overall heat exchanger temperature difference, and thus the percentage of exergy loss is relatively small, whereas the percentage of exergy loss is much higher than that of other heat exchangers due to the larger heat exchanger temperature difference of due to the existence of the phase change in E5 and E6.
4. Conclusion

This paper proposes a hydrogen liquefaction process based on mixed refrigerant pre-cooling, through the reasonable setting of equipment type and parameters. The final energy consumption of hydrogen liquefaction is 9.28 kW-h/kgLH2, the energy consumption is greatly reduced compared with the hydrogen liquefaction plant currently in operation. The results show that the heat exchanger and the compressor are the largest source of the loss of the loss of the heat exchanger and the compressor. The improvement of the efficiency of the equipment and the reasonable design of the process can effectively reduce the energy consumption of hydrogen liquefaction process.

References


