

## Basic Design of Hydrogen Liquefier Precooled by Cryogenic Refrigerator

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Key Words : Cryogenic refrigerator, Liquid hydrogen, Hydrogen, Liquefier, Ortho-to-para conversion

### Abstract

A thermodynamic cycle analysis is performed for refrigerator-precooled Linde-Hampson hydrogen liquefiers, including catalysts for the ortho-to-para conversion. Three different configurations of the liquefying system, depending upon the method of the o-p conversion, are selected for the analysis. After some simplifying and justifiable assumptions are made, a general analysis program to predict the liquid yield and the figure of merit (FOM) is developed with incorporating the commercial computer code for the thermodynamic properties of hydrogen. The discussion is focused on the effect of the two primary design parameters - the precooling temperature and the high pressure of the cycle. When the precooling temperature is in a range between 45 and 60 K, the optimal high pressure for the maximal liquid yield is found to be about 100 to 140 bar, regardless of the ortho-to-para conversion. However, the FOM can be maximized at slightly lower high pressures, 75 to 130 bar. It is concluded that the good performance of the precooling refrigerator is significant in the liquefiers, because at low precooling temperatures, high values of the liquid yield and the FOM can be achieved without compression of gas to a very high pressure.

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### Nomenclature

$COP$ : Coefficient of performance of refrigerator	$h$ : Specific enthalpy [J/g]
$FOM$ : Figure of merit of liquefier or refrigerator	$\dot{m}$ : Mass flow rate [g/s]
	$P$ : Pressure [bar]
	$\dot{Q}$ : Heat transfer rate [W]
	$s$ : Specific entropy [J/g-K]

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$T$	: Temperature [K]
$\dot{W}$	: Power input [W]
$x$	: Fraction of para-hydrogen
$x_e$	: Fraction of para-hydrogen at equilibrium
$y$	: Liquid yield

### Greek letters

$\varepsilon$	: Heat exchanger effectiveness
$\eta$	: Adiabatic efficiency of compressor

### Subscripts

0	: Room temperature, Atmospheric pressure
1,2,...	: State in liquefier
<i>comp</i>	: Compressor
<i>f</i>	: Liquid
<i>g</i>	: Vapor
<i>in</i>	: Input
<i>pc</i>	: Precooling
<i>ref</i>	: Refrigerator
<i>rev</i>	: Reversible
<i>out</i>	: Output

## 1. Introduction

As an effort to reduce the air pollution and the global warming due to the excessive usage of fossil fuels, a number of research works have been performed to utilize the hydrogen energy. Hydrogen is called an environment-friendly fuel, since it does not generate carbon dioxide when it is combusted. The enthalpy of combustion per unit volume of hydrogen gas at standard condition is only 1/5 of that of diesel, but the enthalpy of combustion per unit mass of liquid hydrogen is 3 times greater than that of diesel.<sup>(1)</sup>

Hydrogen has been used as a fuel for the propulsion of rockets or spaceships since 1950's, but has recently drawn attention as a fuel for

automobiles mainly because the hydrogen engines emit no or little air-pollutants. A recent state-of-the-art report<sup>(2)</sup> predicted that in the next century a significant part of the liquid fuel would be replaced by gas fuels such as methane (natural gas) or hydrogen and that hydrogen could cover almost 90% of the entire fuel consumption at the end of 21st century.

Hydrogen can be stored as a fuel in three different forms: the cryogenic liquid at atmospheric pressure, the compressed gas at room temperature, and the metal hydride. While each of these storage methods has both advantages and disadvantages, the cryogenic liquid has been evaluated best by the German car manufacturer BMW<sup>(3)</sup> from the point of the energy storage density per unit volume or unit mass. The Los Alamos National Laboratory in U.S.A.<sup>(4-5)</sup> also reported the favors of the liquid storage of hydrogen fuel in overall energy-efficiency at least for 20 years from now on.

Since the maximum inversion temperature of hydrogen is lower than the room temperature<sup>(6)</sup>, hydrogen can not be liquefied with the simple method of Joule-Thomson expansion. At the beginning of this century, hydrogen was liquefied by a classical method called the cascade system.<sup>(6)</sup> In the system, a standard vapor-compression refrigeration cycle with ammonia pre-cools a nitrogen refrigeration cycle, which again pre-cools the compressed hydrogen before its Joule-Thomson expansion. This system is not relevant in commercial liquefaction because of low liquefaction efficiency. Most of large scale liquefaction of hydrogen has been achieved by Claude cycles.<sup>(6)</sup> The Claude system should employ an expander or an expansion engine that extracts work from the compressed hydrogen.

Contemporary Claude systems have attained reasonably high liquefaction efficiency especially in large-scale plants. In order to use the liquid hydrogen effectively as a fuel for automobiles, the liquid should be liquefied locally at the fueling station in a relatively small scale so that the thermal loss through the transfer might be minimized.<sup>(1)</sup>

One of the simple methods for small-scale hydrogen liquefaction is to use a closed-cycle cryogenic refrigerator. Hydrogen can be liquefied by a contact with a cryogenic refrigerator whose cold head temperature is lower than the liquid temperature.<sup>(8-9)</sup> This system has, however, a very low liquefaction efficiency, because the room-temperature hydrogen should be cooled by the cryogenic refrigerator and the large temperature difference between hydrogen and the cold head of the refrigerator results in a great thermodynamic irreversibility.

A refrigerator-precooled Linde-Hampson system has been proposed to meet both the simplicity and the efficiency for the small scale liquefaction of hydrogen. This system has the same configuration as the conventional precooled Linde-Hampson systems except the precooling cycle is the compact regenerative gas cycle in stead of the large Joule-Thomson cycle. While any type of small or medium-sized cryocoolers including GM (Gifford-McMahon) refrigerators, Stirling refrigerators or pulse tube refrigerators can be good candidates for the precoolers, single-stage or two-stage GM refrigerators are readily available from more than 20 manufactures worldwide.

The present authors see that the technology for the small-scale liquefaction of hydrogen has not been developed as much as the large-scale liquefaction<sup>(10-12)</sup> but is worth

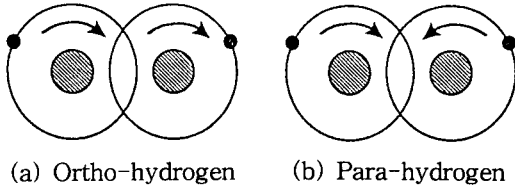
while to investigate for the potential application in near future. As a beginning step of the investigation, this study aims at the determination of the basic design parameters in the small refrigerator-precooled Linde-Hampson liquefaction systems through a thermodynamic cycle analysis. In this paper, the thermodynamic properties of hydrogen, the performance parameters of the liquefaction cycle, and the possible configurations of the systems are briefly introduced from existing literatures. After some reasonable analysis models are made, the cycle analysis program is written and incorporated with the commercial codes for the thermodynamic properties of hydrogen. The optimal values for the precooling temperature and the high pressure are sought for various ortho-to-para conversion schemes.

## 2. Liquefaction Systems

### 2.1 Thermodynamic properties of hydrogen

The critical temperature, the triple point temperature and the normal boiling temperature of hydrogen are 33K, 13K, and 20K, respectively. A unique feature of hydrogen as a biatomic molecule is that it has two molecular forms, ortho-hydrogen and para-hydrogen, depending upon the angular momentum. Figure 1 shows schematically the directions of the angular momentum of two molecules for ortho-hydrogen and para-hydrogen.

At room temperature, the equilibrium hydrogen is a mixture of 75% of ortho-hydrogen and 25% of para-hydrogen, which is called normal-hydrogen. As temperature decreases, the equilibrium concentration of para-hydrogen increases and at the liquid temperature, 20K, it is 99.9% of para-hydrogen.<sup>(6)</sup> Since the ortho-hydrogen has a greater energy than the para-hydrogen at the same tempe-



**Fig.1** Schematic representation of angular momentums in ortho-hydrogen and para-hydrogen

ature, the ortho-to-para conversion is an exothermic reaction. In general, the rate of the ortho-to-para conversion is very slow, so the liquid obtained from the liquefier has almost the same para-concentration as the normal hydrogen. However the most of the liquid will evaporate in a storage vessel because of the heat of conversion as it reaches an equilibrium, even though the vessel may be well-insulated.<sup>(7)</sup> In order to reduce the loss of liquid due to the ortho-to-para conversion, the proper catalyst is needed to augment the para-concentration during the liquefaction process.<sup>(6,13)</sup>

## 2.2 Performance parameters of liquefier

Liquefier is an open cycle from the thermodynamic point of view and may have two different performance parameters. The first is the liquid yield and the second is the FOM (figure of merit). The liquid yield is defined as the ratio of the liquefied mass to the total compressed mass.

$$y = \frac{\text{mass liquefied}}{\text{mass compressed}} = \frac{\dot{m}_f}{\dot{m}} \quad (1)$$

The FOM is defined as the ratio of the minimum work required to liquefy gas to the actual work.

$$\begin{aligned} FOM &= \frac{\dot{W}_{rev} / \dot{m}_f}{\dot{W} / \dot{m}_f} \\ &= \frac{(h_f - h_g) - T_0(s_f - s_g)}{\dot{W} / \dot{m}_f} \end{aligned} \quad (2)$$

The liquid yield is associated only with the amount of liquid fraction that can be obtained through compression and cooldown of gas, while the FOM can be considered as a kind of efficiency involving the thermodynamic availability of the gas and the liquid. The minimum work required to liquefy unit mass of gas in Equation (2) is the difference in flow availability of the gas at standard condition and the saturated liquid at atmospheric pressure. The minimum work per unit mass is 11.62MJ/kg for normal-hydrogen and 18.83MJ/kg for equilibrium-hydrogen.<sup>(7)</sup> It should be noted that the enthalpy and the entropy of hydrogen are functions of the fraction of para-hydrogen as well as temperature and pressure.

## 2.3 Refrigerator-precooled L-H(Linde-Hampson) system

The basic refrigerator-precooled L-H liquefaction system consists of precooling refrigerator, compressor, counterflow heat exchangers, JT(Joule-Thomson) valve, and flash chamber, as shown in Fig.2(a).<sup>(6-7)</sup> The gas at atmospheric pressure and room temperature is compressed to a high pressure and then cooled to room temperature. The high pressure gas is cooled further by a heat exchange with the cold and low pressure gas in counterflow heat exchangers and with the precooling refrigerator. The cold high pressure gas expands through JT valve to a saturated fluid at atmospheric pressure and the liquid is extracted from the bottom of the flash chamber. In this system without catalysts, the ortho-to-para conversion process is very slow and the liquid would have the same fraction of para-hydrogen as normal hydrogen.

Among various methods to install the ca-

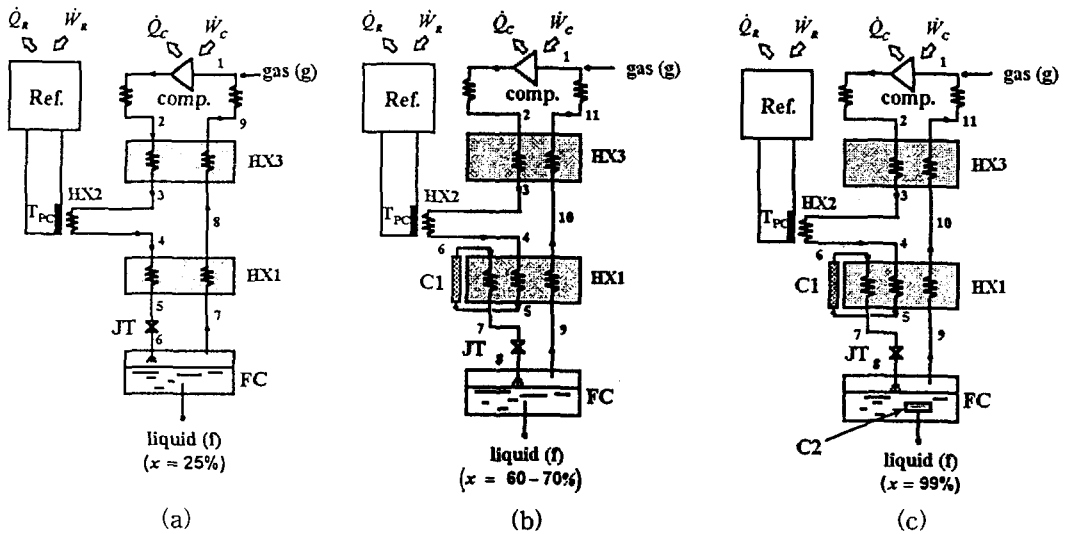


Fig.2 Schematic diagram of L-H liquefier pre-cooled by cryogenic refrigerator (a) without catalyst, (b) with one adiabatic catalyst, (c) with adiabatic and isothermal catalysts (HX : heat exchanger, JT : Joule-Thomson valve, Comp : compressor, Ref. : refrigerator, C : catalyst, FC : flash chamber)

talysts to accelerate the ortho-to-para conversion in refrigerator-precooled L-H system, two efficient configurations are considered in this study as shown in Fig.2 (b) and (c). As the high pressure gas (state 5) passes through an adiabatic catalyst, some of ortho-hydrogen is converted to para-hydrogen and the temperature of gas increases because of the heat of conversion. The warmer gas (state 6) should be cooled again in the cold heat exchanger before it expands at JT valve. In case of (b), the fraction of p-hydrogen in liquid will be the same as the equilibrium concentration at the temperature of state 6, which is about 60 or 70 % for the most of typical operating conditions as discussed later. In case of (c), an isothermal catalyst is added in flash chamber so that the extracted liquid may have the equilibrium concentration at the liquid temperature, 99.9 %.

The necessary fraction of para-hydrogen in

liquid is dependent upon the period of storage. For example, if the liquid is to be stored for only several hours, the liquid of normal hydrogen could be enough and the best liquefaction system should be Fig.2(a). If it is to be stored for about a week, the optimal fraction of para-hydrogen would be approximately 60 or 70 % and the system should be Fig.2(b). If it is to be stored more than a month, the liquid should be almost para and the system should be Fig.2(c). A more quantitative relationship between the fraction of para-hydrogen and the storage period is described in the published literature.<sup>(7)</sup>

### 3. Cycle Analysis

#### 3.1 Analysis model

Some simplifying and justifiable assumptions are made for the cycle analysis. For the precooling refrigerator, the  $FOM_{ref}$  (figure of

merit) is assumed to be given as a function of the precooling temperature. The  $FOM_{ref}$  of a refrigerator is the ratio of the actual COP (coefficient of performance) to the COP of a reversible refrigerator operating between the same temperatures. In general, the  $FOM_{ref}$ 's of commercial refrigerators are dependent on the type of thermodynamic cycle, the size and the refrigeration capacity or the operating temperature range. A simple and reasonable function for the  $FOM_{ref}$  can be derived from the refrigeration characteristics provided by the manufacturer of the actual refrigerators. For a given function, the required work to operate the precooling refrigerator can be calculated as

$$\dot{W}_{ref} = \frac{\dot{Q}}{FOM_{ref}(T_{pc})} \times \left( \frac{T_0}{T_{pc}} - 1 \right) \quad (3)$$

For the compressor in the L-H liquefier, the adiabatic efficiency is assumed to be given and the gas is compressed in multi-stage with intercoolings to room temperature such that the pressure ratio of each stage does not exceed 5. For the heat exchangers, the heat leak from the surroundings and the pressure drop in the passage are neglected, and the effectiveness is assumed to be given. Since the specific heat of the high pressure gas varies very much in the heat exchangers, the effectiveness of heat exchanger should be based on the amount of heat transfer via enthalpy of gas instead of the temperature. For example, in case of the cold heat exchanger HX1 in Fig.2(a), the effectiveness can be expressed as

$$\epsilon_1 = \frac{h(T_7, P_L, x_7) - h(T_6, P_L, x_6)}{h(T_3, P_L, x_3) - h(T_6, P_L, x_6)} \quad (4)$$

The cold heat exchanger HX1 in Fig.2 (b) and (c) is a triple-pass counterflow heat

exchanger, where the cold and low pressure gas exchanges heat simultaneously with two high pressure gases. The published effectiveness-NTU method for triple-pass counterflow heat exchangers<sup>(14)</sup> is included in this analysis. The expansion process through JT valve is assumed to be isenthalpic and the saturated hydrogen in flash chamber is assumed to be completely separated into saturated liquid and saturated vapor.

### 3.2 Ortho-to-para conversion

As mentioned above, the equilibrium concentration of para-hydrogen increases as the hydrogen gas is cooled, but the ortho-to-para conversion is a very slow process. A conservative assumption is made that the concentration of para hydrogen does not vary at all unless the gas passes through catalyst. It is further assumed that the surface area of the catalyst is enough and the hydrogen gas reaches its equilibrium concentration of para-hydrogen at the exit. For an adiabatic catalyst as in Fig.3(a), the enthalpy should remain constant.

$$h_{in}(T_{in}, P_{in}, x_{in}) = h_{out}(T_{out}, P_{out}, x_e(T_{out})) \quad (5)$$

For a given inlet state of the adiabatic catalyst, the exit state can be determined by the same method as so-called adiabatic saturation process in air-water vapor mixture. On the other hand, for an isothermal catalyst as in Fig.3(b), the heat should be removed by the amount equal to the difference in enthalpy between at inlet and at exit.

### 3.3 Cycle analysis

Table 1 is the list of the input parameters, the unknowns and the equations in the cycle analysis for three different systems in Fig.2.

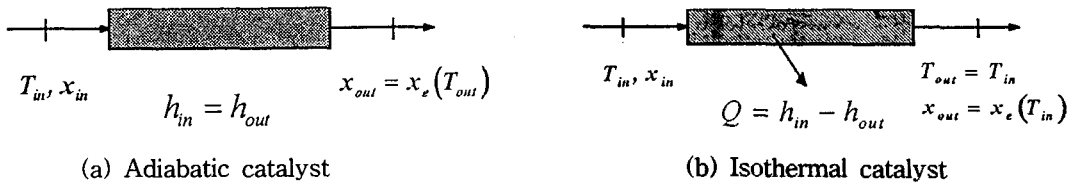


Fig.3 Two different models of catalyst for ortho-to-para conversion

Table 1 Unknowns and equations for analysis of the three models(HX : heat exchanger, JT : Joule-Thomson valve, Comp : compressor,Ref. : refrigerator, C : catalyst, FC : flash chamber)

		model (a)	model (b)	model (c)
given values	temperature	T <sub>2</sub> , T <sub>7</sub>	T <sub>2</sub> , T <sub>9</sub>	T <sub>2</sub> , T <sub>9</sub>
	x (para %)	x <sub>2</sub>	x <sub>2</sub>	x <sub>2</sub>
unknowns	temperature	T <sub>3</sub> , T <sub>4</sub> , T <sub>5</sub> , T <sub>6</sub> , T <sub>7</sub> , T <sub>8</sub> , T <sub>9</sub>	T <sub>3</sub> , T <sub>4</sub> , T <sub>5</sub> , T <sub>6</sub> , T <sub>7</sub> , T <sub>8</sub> , T <sub>10</sub> , T <sub>11</sub>	T <sub>3</sub> , T <sub>4</sub> , T <sub>5</sub> , T <sub>6</sub> , T <sub>7</sub> , U <sub>8</sub> , T <sub>10</sub> , T <sub>11</sub>
	x (para %)	x <sub>3</sub> , x <sub>4</sub> , x <sub>5</sub> , x <sub>6</sub> , x <sub>7</sub> , x <sub>8</sub> , x <sub>9</sub>	x <sub>3</sub> , x <sub>4</sub> , x <sub>5</sub> , x <sub>6</sub> , x <sub>7</sub> , x <sub>8</sub> , x <sub>9</sub> , x <sub>10</sub> , x <sub>11</sub>	x <sub>3</sub> , x <sub>4</sub> , x <sub>5</sub> , x <sub>6</sub> , x <sub>7</sub> , x <sub>8</sub> , x <sub>9</sub> , x <sub>10</sub> , x <sub>11</sub> , x <sub>f</sub>
	work	W <sub>comp</sub> , W <sub>ref</sub>	W <sub>comp</sub> , W <sub>ref</sub>	W <sub>comp</sub> , W <sub>ref</sub>
	total number	16	19	20
equations	energy balance	HX <sub>1</sub> , HX <sub>3</sub> , JT, Comp., Ref.(HX <sub>2</sub> ), FC	HX <sub>1</sub> , HX <sub>3</sub> , JT, Comp., Ref.(HX <sub>2</sub> ), FC, C <sub>1</sub>	HX <sub>1</sub> , HX <sub>3</sub> , JT, Comp., Ref.(HX <sub>2</sub> ), FC, C <sub>1</sub> , C <sub>2</sub>
	HX effectiveness	ε <sub>1</sub> , ε <sub>2</sub> , ε <sub>3</sub>	ε <sub>1</sub> , ε <sub>2</sub> , ε <sub>3</sub>	ε <sub>1</sub> , ε <sub>2</sub> , ε <sub>3</sub>
	x relation	x <sub>2</sub> =x <sub>3</sub> =x <sub>4</sub> =x <sub>5</sub> =x <sub>6</sub> =x <sub>7</sub> = x <sub>8</sub> =x <sub>9</sub>	x <sub>2</sub> =x <sub>3</sub> =x <sub>4</sub> =x <sub>5</sub> , x <sub>6</sub> =x <sub>7</sub> =x <sub>8</sub> =x <sub>9</sub> =x <sub>10</sub> =x <sub>11</sub>	x <sub>2</sub> =x <sub>3</sub> =x <sub>4</sub> =x <sub>5</sub> , x <sub>6</sub> =x <sub>7</sub> =x <sub>8</sub> =x <sub>9</sub> =x <sub>10</sub> =x <sub>11</sub>
	catalyst, x=x <sub>e</sub> (T)		x <sub>6</sub>	x <sub>6</sub> , x <sub>f</sub>
	total number	16	19	20
y (liquid yield)		$\frac{(h_7 - h_3)}{(h_7 - h_f)}$	$\frac{(h_9 - h_7)}{(h_9 - h_f)}$	$\frac{(h_9 - h_7)}{(h_9 - h_f)}$

The numbers of the knowns are 16, 19, and 20 for the cases of Fig.2 (a), (b) and (c), respectively. The same numbers of equations are provided by the energy balance, the effectiveness of heat exchangers and the models for the concentration of para-hydrogen.

A cycle analysis program has been written by incorporating a commercial code for the real properties of normal- and para-hydrogens, to determine the state of each location

in the cycles and calculate the liquid yield and the FOM of liquefier. There are two significant design parameters in the liquefaction cycles; the precooling temperature and the high pressure. The input parameters in the program include the characteristics of the components such as the effectiveness of heat exchanger, the adiabatic efficiency of compressor or FOM<sub>ref</sub>, in addition to the two design parameters.

The cycle analysis requires a numerical method to solve the systems of equations simultaneously. A step-by-step iterative method has been adopted in this study, as can be briefly described below. The temperature at the exit of precooling heat exchanger (HX2) is assumed to start an iteration. Then the exit temperatures of the cold heat exchanger (HX1) and the liquid yield are determined by solving the energy balance equations for the heat exchanger, the JT valve and the flash chamber with the relation for the given heat exchanger effectiveness. Next, the exit temperatures of the warm heat exchanger (HX3) are determined by the energy balance and the given effectiveness. Finally, the exit temperature of precooling heat exchanger (HX2) is calculated by the given precooling temperature and the effectiveness. The iteration is repeated until the calculated exit temperature of precooling heat exchanger is same as the assumed value at the beginning.

The real properties of hydrogen are calculated by the code developed by the U.S. NIST<sup>(15)</sup>, which provides the subprograms for normal- and para-hydrogens. The liquid yield can be calculated by the equations listed in Table 1 and the FOM can be calculated as

$$FOM = \frac{(h_f - h_g) - T_0 (s_f - s_g)}{(\dot{W}_{comp} + \dot{W}_{ref}) / \dot{m}_f} \quad (6)$$

where  $h_f$  and  $s_f$  are dependent on the concentration of para-hydrogen at liquid,  $x_f$  and the required work is the sum of the compressor work and the work for the precooling refrigerator.

#### 4. Results and Discussion

The input conditions to the developed cycle analysis program are summarized in Table 1.  $FOM_{ref}$  of the precooling refrigerator is a linear function of the precooling temperature, which is based on the characteristics of several commercial cryogenic refrigerators for a temperature range between 40 K and 100 K, manufactured by Cryogenic Technology Inc., Cryomech, Air Product Inc., CVI, Leybold or Balzers. The adiabatic efficiency of compressor and the heat exchanger effectiveness are also selected as typical values for the cryogenic liquefaction systems.

Figures 4 and 5 show the liquid yield and the FOM as functions of the precooling temperature and the high pressure for a simple refrigerator-precooled L-H liquefier without

**Table 2** Input conditions for sample calculation

L-H cycle	temperature where heat is rejected	$T_0$	300 K
	low pressure (liquid temperature)	$P_L$ ( $T_L$ )	1 bar (20.39 K)
refrigerator	figure of merit	$FOM_{ref} = \frac{COP}{COP_{rev}}$	$\frac{1}{5} + \frac{2}{15} \frac{(T_{PC} - 37)}{153}$
compressor	adiabatic efficiency	$\eta_{comp}$	0.8
	number of stages	-	6
heat exchangers	effectiveness	$\epsilon$	0.95



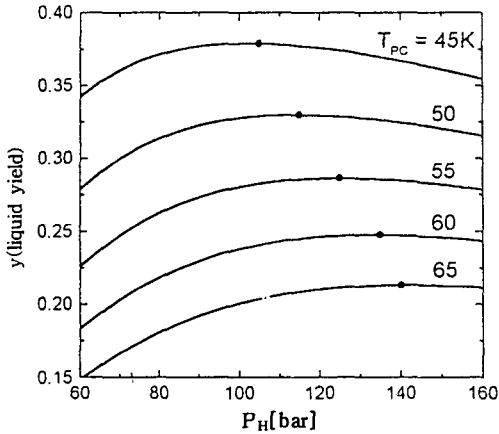


Fig.4 Liquid yield vs high pressure for various precooling temperatures for Fig.2 (a)

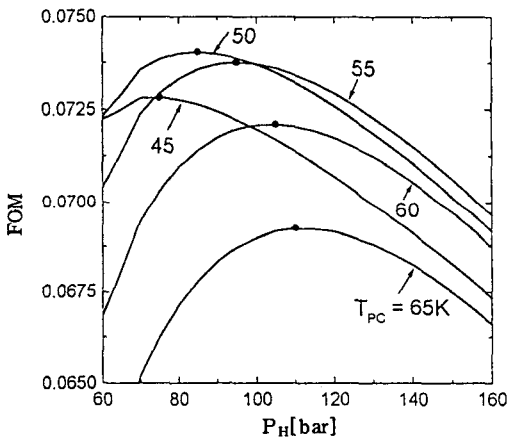


Fig.5 FOM vs high pressure for various precooling temperatures for Fig.2 (a)

catalyst as shown in Fig.2(a). For a constant precooling temperature, the liquid yield increases and then decreases as the high pressure increases so that there exists an optimal high pressure to maximize the liquid yield. This phenomenon is closely related with the thermodynamic properties of hydrogen. In order to produce a large fraction of liquid, the enthalpy of hydrogen should be small. The JT (Joule-Thomson) coefficient has a positive value at relatively low pressures but a negative value at higher pressures in the pre-

cooling temperature ranges. At a given temperature, the enthalpy has its minimum when the JT coefficient equals 0. As the precooling temperature decreases from 65 K to 45 K, the optimal high pressure to maximize the liquid yield varies from 140 bar to 105 bar and the corresponding maximum of the liquid yield increases from 0.20 to 0.38. This result coincides with the existing design data for large liquefaction plant that the high pressure is about 140 to 150 bar when the precooling temperature is about 63 to 66 K.<sup>(17)</sup>

It is also observed that there exist an optimal high pressure to maximize the FOM for a given precooling temperature, which is greater by 20 or 30 bar than the optimum to maximize the liquid yield. The main reason for this is that a more compressor work is required for a greater high pressure, but the liquid yield has nothing to do with the compressor work. As the precooling temperature decreases from 65 K to 50 K, the maximum in liquid yield increases from 0.069 to 0.074. However, if the precooling temperature decreases further to lower temperatures than 45 K, the maximum decreases to 0.073, because the  $FOM_{ref}$  of the precooling refrigerator has lower values. It could be stated that there exist the unique optimal values for the precooling temperature and the high pressure to maximize the FOM of simple L-H liquefier without catalyst.

Figures 6 and 7 show the liquid yield and the FOM as functions of the precooling temperature and the high pressure for a refrigerator-precooled L-H liquefier with adiabatic catalyst as shown in Fig.2(b). The effects of the precooling temperature and the high pressure on the liquid yield are qualitatively the same as the case without catalysts, even though the amount of liquid yield is smaller.

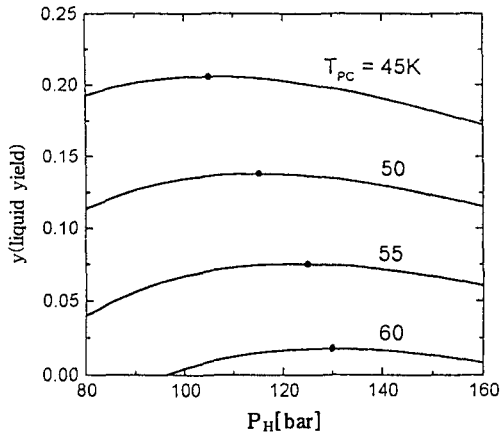


Fig.6 Liquid yield vs high pressure for various precooling temperatures for Fig.2 (b)

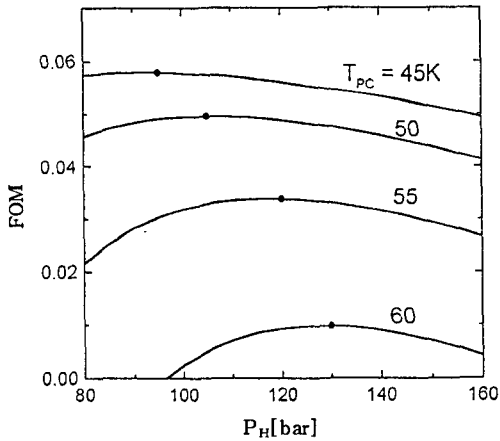


Fig.7 FOM vs high pressure for various precooling temperatures for Fig.2 (b)

The main reason for this is that the concentration of para-hydrogen in obtained liquid is higher. The para-concentration in liquid is identical to its equilibrium concentration at state 6 and thus it increase as the precooling temperature decreases. In the calculated conditions, the concentration has a value between 60 and 70 %. It is noted that if the precooling temperature is higher than 60 K, the liquid can not be obtained at any high pressures. The optimal high pressure decreases from 130

to 103 and the maximum liquid yield increases from 0.02 to 0.20, as the precooling temperature decreases from 60 K to 45 K.

There also exists an optimal high pressure for a given precooling temperature to maximize the FOM. The optimal high pressure to maximize the FOM is lower by about 10 bar than the optimum to maximize the liquid yield. The maximum FOM increases from 0.01 to 0.06 as the precooling temperature decreases from 60 K to 45 K. It should be noted that as the precooling temperature decreases, the concentration of para-hydrogen in liquid increases and therefore the minimum liquefaction work increases as shown in the numerator of Equation (6).

Figures 8 and 9 show the liquid yield and the FOM as functions of the precooling temperature and the high pressure for a refrigerator-precooled L-H liquefier with adiabatic catalyst and isothermal catalyst as shown in Fig.2(c). It should be reminded in this case that the extracted liquid is an equilibrium-hydrogen at the normal boiling temperature or the fraction of para-hydrogen is 99.9 %. Because of the high para concentration, the liquid yield and FOM has much lower values than the two previous cases.. As precooling temperature decreases from 60 K to 45 K, the maximum liquid yield increases from 0.008 to 0.105 and the corresponding optimum high pressure decreases from 130 to 95 bar. The effect of the precooling temperature and the high pressure on FOM is basically the same as in Fig.7, except that the maximum values of FOM are much lower.

Finally, it should be mentioned that the cycle analysis in the current study has been performed with an assumption that the para-hydrogen is converted back to ortho-hydrogen at room temperature so the state 2 in

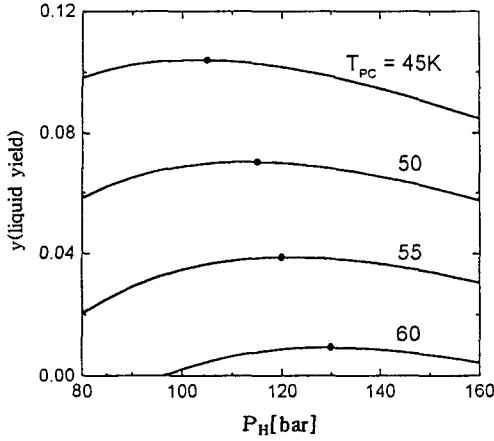


Fig.8 Liquid yield vs high pressure for various precooling temperatures for Fig.2 (c)

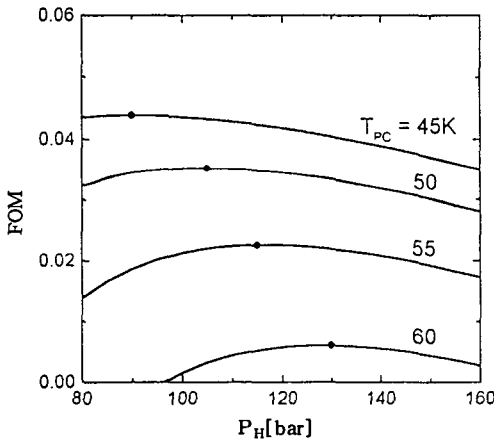


Fig.9 FOM vs high pressure for various precooling temperatures for Fig.2 (c)

Fig.2 is a normal hydrogen. Practically, the hydrogen gas remains at room temperature for a long time before it is cooled down, because of large surge volumes around the compressor. If the para-to-ortho conversion is not complete, the concentration of para-hydrogen at state 2 would be greater than normal hydrogen and a greater liquid yield and a greater FOM could be obtained. This assumption in the analysis is therefore a conser-

vative one in predicting the liquefaction performance.

## 5. Conclusions

A cycle analysis program has been developed to estimate the liquefying performance of three different configurations for the refrigerator-precooled Linde-Hampson liquefaction system. The analysis includes the ortho-to-para conversion, the characteristics of the components such as the precooling refrigerator, the heat exchangers or the compressors, and the real thermodynamic properties of hydrogen. The liquid yield and the FOM (Figure of Merit) have been calculated for various values of the input parameters and the following significant conclusions have been drawn.

1) The optimal high pressure to maximize the liquid yield is in a range between 100 and 140bar, when the precooling temperature is in a range between 45K and 60K. The optimal ratio is not strongly dependent on the employment of catalyst for the ortho-to-para conversion.

2) The optimal high pressure to maximize the FOM is in a range between 75 and 105 bar when the precooling temperature is in a range between 45K and 60K for a simple refrigerator-precooled L-H system. For the system with catalyst, the optimal ratio is as high as 100 to 130 bar for the same precooling temperature.

3) In general, both the liquid yield and the FOM increase and the optimal high pressure decreases, as the precooling temperature decreases. This suggests that a precooling refrigerator with sufficient cooling capacity at lower temperatures is very important to improve the liquefaction performance without

compressing hydrogen gas to a very high pressure.

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