

2.3 Liquid Hydrogen Storage

2.3.1 Cryogenic Refrigerators and Cost of Manufacturing CryoFuels. Manufacturing of cryofuels such as liquid hydrogen (LH_2) and methane (LCH_4) requires costly liquefaction plants and large amounts of energy. The cost of a cryofuel is dependent on the cost of gaseous feedstock plus a cost for its liquefaction. In the following sections, we review the state of the art of liquefaction technology and manufacturing costs associated with production of liquid hydrogen and methane. The liquefaction constitutes a major fraction of the overall fuel production cost (especially for LH_2). Furthermore, other obstacles to general acceptance of cryofuels like LH_2 include the bulkiness of storage and handling systems, high cost of cryogenic devices needed, and problems with the evaporation losses. All of these issues are important and need to be addressed. The liquefaction costs constitute both energy and nonenergy (capital cost, operating and maintenance, supplies, administration, etc.) costs. The capital cost of liquefaction is generally high since most commercial processes use expensive machinery to accomplish liquefaction. The nonenergy costs of producing cryofuels are a direct function of the plant size or capacity. The energy related costs, on the other hand, are primarily a function of the overall efficiency (and therefore the method of liquefaction used) and the level of desired refrigeration temperature of the cycle. The energy demand of liquefaction is generally expressed as a fraction of energy (high heating value, HHV) contained in a unit mass of cryofuel produced, $10^6\text{Btu}/10^6\text{Btu}$. This ratio, hereafter called specific energy consumption (SEC), is a strong function of the normal boiling point temperature of the product. Selected thermophysical properties of relevance to liquefaction of hydrogen and methane are given in Table IV. For the sake of comparison, the property values for gasoline are also included in this table.

The minimum power required to produce a unit of refrigeration under ideal conditions is given by (38)

$$\left(\frac{\dot{W}_c}{\dot{Q}}\right)_{\text{carnot}} = \frac{T_o - T}{T}$$

where \dot{W}_c is the net input power required (power required for compression less the power produced by expanders), \dot{Q} is the refrigeration produced, T_o is the ambient temperature (usually taken to be 300 K), and T is the desired refrigeration temperature level. The specific power requirement increases rapidly as an inverse function of T (taken to be the normal boiling temperature of the fluid) as seen in Table V.

Table IV
Selected Thermophysical Properties of Hydrogen,
Methane and Gasoline (37)

Property	Hydrogen	Methane	Gasoline
Molecular weight	2.016	16.043	~107.0
Triple point pressure, atm	0.0695	0.1159	—
Triple point temperature, K	13.803	90.680	180 to 220 ^a
Normal boiling point (NBP) temperature, K	20.268	111.632	310 to 478
Critical pressure, atm	12.759	45.387	24.5 to 27
Critical temperature, K	32.976	190.56	540 to 569
Density at critical point, g/ml	0.0314	0.1604	0.23
Density of liquid at NBP, g/ml	0.0708	0.4226	~.70 ^b
Density of vapor at NBP, g/ml	0.00134	0.00182	~0.0045 ^b
Density of gas at NTP, g/ml	83.764	651.19	~4400
Density ratio: NBP liquid-to-NTP gas	845	649	156 ^c
Heat of vaporization, J/g	445.59	509.88	309
Heat of combustion (low), J/g	119,930	50,020	44,500
Heat of combustion (high), J/g	141,860	55,530	48,000
Specific heat (C_p) of NTP gas, J/g-K	14.89	2.22	1.62 ^b
Specific heat (C_p) of NBP liquid, J/g-K	9.69	3.50	2.20 ^b
Specific heat ratio (C_p/C_v) of NTP gas	1.383	1.308	1.05 ^b
Specific heat ratio (C_p/C_v) of NBP liquid	1.688	1.676	—
Compressibility factor (Z) in NTP gas	1.0006	1.0243	1.0069
Compressibility factor (Z) in NBP liquid	0.01712	0.004145	0.00643 ^b
Gas constant (R), J/g-K	4.1243	0.51825	0.078
Isothermal bulk modulus (α) of NBP liquid, MN/m ²	50.13	456.16	763 ^d
Volume expansivity (β) of NBP liquid, K ⁻¹	0.01658	0.00346	0.0012 ^b

NBP = Normal boiling point

NTP = 1 atm and 20°C (293.15K)

Note: Thermophysical properties listed are those of para hydrogen. Gasoline property values are the arithmetic average of normal heptane and octane in those cases where "gasoline" values could not be found (unless otherwise noted).

a) Freezing temperature for gasoline at 1 atm

b) at 1 atm and 15.5°C

c) Density ratio at 1 atm and 15.5°C

d) at 1 atm and 25°C

Table V

Reversible Power Requirements (38)

Fluid	T, (°K)	Refrigeration, (W/W)	Liquefaction, (J/L)
Helium	4.2	70.4	849,600
Hydrogen	20.4	13.7	1,000,800
Neon	27.1	10.1	1,609,200
Nitrogen	77.4	2.88	622,800
Fluorine	85.0	2.53	896,800
Argon	87.3	2.44	666,000
Oxygen	90.2	2.33	702,000
Methane	111.5	1.69	464,400

The ideal work of liquefaction is determined by means of availability function of the product (39);

$$\psi = h - h_o - T_o(s - s_o)$$

where;

- ψ = availability function associated with the minimum work of formation, also maximum work recoverable from a fluid at a defined state
- h, s = specific enthalpy and entropy of liquid product at 1 atmosphere,
- h_o, s_o = specific enthalpy and entropy of fluid at ambient conditions.

For a perfect gas system, the ideal (reversible) liquefaction power can be determined as a sum of:

- (1) the ideal (reversible) power required to precool the product stream (\dot{W}_1), and
- (2) the ideal (reversible) power required to condense the product (\dot{W}_2) at the normal boiling temperature of the fluid (T).

The precooling of the product stream occurs over a range of temperature for which the ideal precooling power is readily calculated from Carnot refrigeration cycle to be;

$$\dot{W}_1 = \frac{T_o - T_m}{T_m} \dot{Q}_1 = \frac{T_o - T_m}{T_m} \dot{w} C_p (T_o - T)$$

where

$$T_m = (T_o - T) / \ln (T_o / T)$$

$$\dot{Q}_1 = \dot{\omega} C_p (T_o - T),$$

$$C_p = \text{constant pressure specific heat}$$

The ideal power needed to condense a fluid isothermally at saturation temperature of T is;

$$\dot{W}_2 = \dot{Q}_2 \left(\frac{T_o - T}{T} \right) = \dot{\omega} h_{fg} \left(\frac{T_o}{T} \right)$$

where

$$\dot{Q}_2 = \dot{\omega} h_{fg}, \text{ and } h_{fg} = \text{latent heat vaporization}$$

Thus, the total reversible liquefaction power required, \dot{W}_1 (watts), will be;

$$\dot{W}_1 = \dot{W}_1 + \dot{W}_2 = \dot{\omega} (T_o - T) \left\{ \left(\frac{T_o - T_m}{T_m} \right) C_p + \frac{h_{fg}}{T} \right\} \quad (1)$$

Using the equation above, the ideal liquefaction power required per unit mass flow rate of the liquid product (i.e. $\dot{W}_1 / \dot{\omega}$, J/l) is given by

$$\frac{\dot{W}_1}{\dot{\omega}} = (T_o - T) \left\{ \left(\frac{T_o - T_m}{T_m} \right) C_p + \frac{h_{fg}}{T} \right\}$$

This quantity is evaluated for several different cryogenic fluids and given in Table V.

The liquefaction cost of a gaseous fuel constitutes a large portion of the cost of liquid cryofuel produced. The liquefaction costs are a function of the liquefier efficiency which is a fraction of Carnot for most present-day, large-scale liquefaction and refrigeration systems (40). Fig. 2 depicts the efficiency of refrigerators versus refrigeration capacity. To convert the refrigeration capacity to an equivalent liquefier capacity, the refrigerator capacity from the graph is multiplied by the ideal work of compression per unit of refrigeration at the liquefaction temperature of interest and divided by the total ideal work of liquefaction per unit of liquid product produced, i.e.,

$$\left(\frac{T_o - T}{T} / \frac{\dot{W}_1}{\dot{\omega}} \right).$$

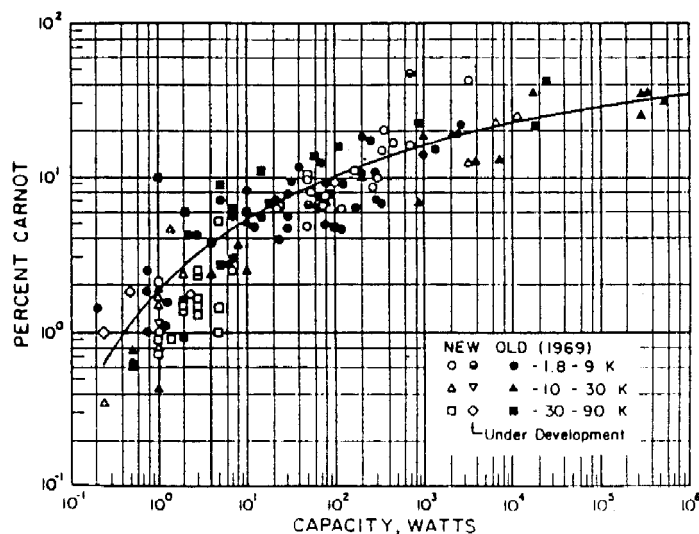


Figure 2. Efficiency of low temperature refrigerators and liquefiers as a function of refrigeration capacity (56).

Although the Carnot cycle work is a good basis for comparing the efficiencies of various cryogenic systems operating under vastly different conditions, it is not amenable to provide insights into the effects of practical component efficiencies on the overall liquefaction cycle efficiency (41). A real liquefaction cycle is a complex thermodynamic system which involves the use of many subcomponents (Joule-Thomson valves, wet expanders, compressors, heat exchangers, catalytic converters, etc.) each having their own efficiencies. The analysis of the process is further complicated by the temperature and pressure dependent thermophysical properties of the cryogen and the fact that a very large number of liquefaction cycles may be conceived and are possible. The analysis of real liquefaction systems are normally carried out numerically and by means of using powerful computers. It is possible, however, to define a cycle that permits evaluation and optimization of overall cycle efficiency which incorporates practical liquefaction components, and effects due to heat exchanger temperature differences and variable system pressure drop. This approach makes it possible to estimate the maximum attainable cycle efficiency with components of given efficiencies. Another advantage of using such a defined cycle is that it provides a closed form solution for the overall cycle efficiency, η_{cy} , defined as:

$$\eta_{cy} = \frac{\text{Ideal power requirements}}{\text{Actual net power requirements}} = \frac{\dot{W}_i}{\dot{W}_c - \dot{W}_E}$$

The net power required by the cycle is the required compressor power (\dot{W}_c) less the recoverable power from the expanders (\dot{W}_E).

In Appendix B the relationships for calculating overall cycle efficiency of a defined cycle (Modified Collins Cycle) are developed and used to evaluate the specific energy consumption of two cryofuels of interest (LH_2 and LCH_4). Table VI depicts results of performance calculations assuming realistic efficiencies for the LH_2 and LCH_4 liquefaction cycle subcomponents as discussed in Appendix B.

Table VI			
Performance of the Defined Cycle for Liquefaction of Hydrogen and Methane			
Cryofuel	Cycle Efficiency (%)	$\frac{\text{mass of fluid recycled}}{\text{mass of liquid product}}$ (-)	SEC (-)
hydrogen	32.13	9.64	0.308
methane	23.53	18.72	0.084

As would be expected, the specific energy requirement for liquefaction of methane (0.084 from Table VI) is far less than that of hydrogen (approximately 0.308). This is in part due to methane's higher normal boiling point temperature (111.6 K) compared to that of hydrogen (20.27 K). Results of Table B-1 also indicate that the compressor and expanders are the major sources of inefficiency, no major improvement of the cycle efficiency is possible without a corresponding increase in the compressor or expander efficiencies. This is difficult since both compressors and expanding turbines are highly developed. Therefore it is hard to envision higher conventional (mechanical) liquefaction system efficiencies than those calculated here in the near future. This point will be further elaborated upon in the next section when we discuss real liquefaction systems.

2.3.2 Real Liquefaction Cycles. In a real liquefaction cycle, real properties of the fluid need to be used instead of ideal fluid equations. This presents many variables not considered previously in the Collins cycle. For example, the specific heat of hydrogen is a function of T at low temperatures. Furthermore, hydrogen has a positive Joule-Thomson coefficient at low temperatures. This provides an opportunity to use a Joule-Thomson valve or other advanced devices (such as a wet expander) as the final expansion method in the liquefaction system. We recall that the Collins cycle was limited to the use of an isothermal expanding turbine to provide final liquefaction step. Another complexity introduced by using real hydrogen properties is the need for the ortho-para conversion devices. The effects introduced by the use of real fluid properties, etc. and associated component losses in a real liquefaction system result in the

possibility of heat exchanger temperature "pinches". Further, the analysis of many different hydrogen liquefaction cycles has indicated that the compressors and turbine expanders are responsible for the most of the losses incurred in the liquefier. The system losses due to the inefficiencies of the J-T valve or heat exchangers are by comparison very small and insignificant. Since the current technology provides for highly developed and optimized compression and expansion devices, it is highly unlikely that any major improvement in the overall efficiency of the conventional mechanical liquefiers can be realized soon. However, it is important to elaborate on the techniques that have been used to optimize and achieve the current status of the hydrogen liquefiers since in a way these systems provide the ultimate challenge to the liquefaction of any potential cryofuel.

In order to maximize the hydrogen liquefier efficiency, it is important to remove the enthalpy of conversion of normal to pure hydrogen at the highest temperature possible. It is also important to arrange the precooling expanders in such a way to minimize heat exchanger temperature differences. Most real liquefaction systems consist of a collection of one or more of the following components; compressors, Claude and Brayton modules and J-T valves, arranged in such a way to give an optimum cycle efficiency. Other liquefaction cycle modifications (such as Cascade cycle) do not actually increase the optimum cycle efficiency, rather simplify and provide the best pressure ratios and inlet temperatures for the compressors and expanders (39).

2.3.2.1 Exergy Analysis Of The Real Liquefaction Cycles. The actual power to produce a quantity of liquid is given by

$$\dot{W}_a = \frac{L_T + \dot{W}_i}{\eta_c} - \dot{W}_E$$

where \dot{W}_a = actual liquefaction power required, and L_T = total liquefier power losses. Overall liquefier efficiency is expressed as

$$\eta_{cy} = \frac{\dot{W}_i}{\dot{W}_a} = \frac{\dot{W}_i}{\frac{1}{\eta_c}(L_T + \dot{W}_i) - \dot{W}_E}$$

In these equations the losses for all components are determined using an availability balance around the component. It is further assumed that the expanders' output power is considered as a loss because the room temperature compressor supplies the total expander power plus the ideal power needed to liquefy the fluid (39).

The ideal power required to compress a real fluid is given by;

$$\dot{W}_{ci} = \dot{m}(\psi_{out} - \psi_{in})$$

where \dot{W}_{ci} = isothermal compression power = $\eta_c \dot{W}_{ac}$, \dot{W}_{ac} = actual compression power, and ψ = the availability function.

The compressor losses are determined by (39):

$$L_c = \dot{m} \left\{ \frac{1 - \eta_c}{\eta_c} (\psi_{out} - \psi_{in}) \right\}$$

where L_c = compression power losses.

Isothermal compressor efficiency depends on the compression ratio and is about 60% for most commercial systems. However, for very large compressors this value may approach 70%.

The isentropic expander efficiency, η_{pe} , is defined as (39)

$$\eta_{pe} = \Delta h_a / \Delta h_s$$

where Δh_a , Δh_s = actual and isentropic specific enthalpy charges across the turbine respectively.

Expander losses are related to the difference in availability across the turbine or;

$$L_{pe} = \dot{m}(\psi_{in} - \psi_{out})$$

Based on the current state of technology of expanders, a maximum expander efficiency of about 80% is possible if care is taken to match operating pressure ratios and inlet temperatures to the characteristics of the expander (39).

The losses due to the Joule-Thomson device are normally high because of the zero efficiency and are given by

$$L_{JT} = \dot{m}(\psi_{in} - \psi_{out})$$

It is possible to reduce and minimize these losses by optimizing the operating conditions.

The counterflow heat exchangers constitute a substantial cost of any liquefaction system. In design of a heat exchanger it is important to consider the capital cost of the unit and the cost of energy to manufacture the liquid. An ideal heat exchanger provides a very large surface area for heat transfer, minimizing the heat exchanger temperature difference, improving the overall liquefaction cycle efficiency. The size of a heat exchanger may be determined using a method given by Daney (42) and described by Voth (39) as

$$\frac{AU}{\dot{m}} = \frac{dh}{(\Delta T_l)d\alpha}$$

where;

A = heat transfer area on one side of the counterflow heat exchanger,

U = overall heat transfer coefficient,

\dot{m} = mass flow rate on one side of the HE,

dh = change in specific enthalpy on one side of the HE,

ΔT_l = local HE temperature difference,

$d\alpha$ = dA/A .

and the heat exchanger size should be optimized to provide a good balance between the capital costs and heat exchanger losses.

2.3.2.2 A Real Hydrogen Liquefier Cycle. Many cycles have been conceived for the liquefaction of hydrogen and many detailed thermodynamics and exergo-economical analysis of liquefiers exists, Voth and Daney (41), Gutowski and Wanner (43), Dini and Martorano (44), Baker and Shaner (45), Newton (46-48), Baker (49-51), and Smith (52). However, in our case, we examined a hydrogen liquefaction cycle similar to that given by Gutowski and Wanner (43). A schematic representation of the cycle is shown in Fig. 3 and the corresponding input parameters for the base case simulation are given in Table VII. The plant is characterized by a hydrogen-liquefaction line, containing the product stream and a hydrogen-circuit, which provides the necessary cooling by means of compressors, precooling expanders and a Joule-Thomson valve. The cycle includes several ortho-para catalyst systems and adsorbent loop for product purifications. The liquefier utilizes a series of counter current heat exchangers in three Claude modules to cool the product stream to well below the maximum inversion temperature of hydrogen (~204 K) prior to the final expansion in a Joule-Thomson device. In many hydrogen liquefaction systems, the final cooling through the J-T valve takes place from the fluid at the supercritical state.

Table VII
Design Parameters for the Base Case

MASSFLOW TO BE LIQUEFIED (kg/s)	0.21
PRESSURE BEFORE COMPRESSOR (bar)	1
PRESSURE AFTER COMPRESSOR (bar)	25
NUMBER OF COMPRESSOR STAGES (-)	2
COMPRESSOR EFFICIENCY (-)	0.7
H2 INLET TEMPERATURE (K)	293
COMPRESSOR COOLING TEMPERATURE (K)	293
PRESSURE OF LIQUID H2 (bar)	4
MIXTURE OF LIQUID H2 (%)	98
1. CONVERSION TEMPERATURE (K)	60
1. CONVERSION MIXTURE (%)	60
2. CONVERSION TEMPERATURE (K)	32
2. CONVERSION MIXTURE (%)	90
VAPOR CONTENT AFTER THROTTLE (-)	0.145
HEAT LOSS FACTOR COLD-BOX (-)	0
MASSFLOW OF CIRCUIT H2 (kg/s)	2.55
MASSFLOW OF TURBINE 1 (kg/s)	2.48
MASSFLOW OF TURBINE 2 (kg/s)	1.09
HIGH PRESSURE LEVEL (bar)	25
MEDIUM PRESSURE LEVEL (bar)	12
LOW PRESSURE LEVEL (bar)	3
NUMBER OF COMPRESSOR STAGES (-)	2
COMPRESSOR EFFICIENCY (-)	0.7
COMPRESSOR COOLING TEMPERATURE (K)	293
TEMPERATURE DIFFERENCE HOT END (K)	3.5
1. TURBINE END-TEMPERATURE (K)	111
1. TURBINE EFFICIENCY (-)	0.7
2. TURBINE END-TEMPERATURE (K)	59
2. TURBINE EFFICIENCY (-)	0.6
3. TURBINE END-TEMPERATURE (K)	28
3. TURBINE EFFICIENCY (-)	0.7

In precooling the high pressure stream below its inversion temperature against colder returning vapor, it is important to ensure that heat transfer takes place with minimal temperature difference between the two fluids at all points. However, this is not easy to achieve since the high pressure fluid is just above its critical pressure and is being cooled past its critical temperature by a second fluid at lowest system pressure and temperature conditions (52). The critical pressure of hydrogen is 12.76 bar, and the problem discussed above is avoided by choosing to operate with high and low pressure streams at 25 and 3 bars.

The feed hydrogen requires a high purity (at least 99.9%) and is cooled at 85 K over a silica gel adsorbent to remove residual impurities. The conversion of normal to para hydrogen is effected catalytically in three temperature levels (60, 30, and 25 K).

Table VIII depicts the corresponding fluid states for the base-case hydrogen liquefier considered here. The most recent thermodynamic property values for hydrogen (normal, ortho, and para) given in reference (38) was used in these calculations. For the base-case simulation, we utilized both the feed and circuit compressors in a two-stage configuration. Table VIII also gives the fluid states for the two compressor systems. An estimate of the cycle efficiency and the specific energy required for liquefaction of hydrogen were made using exergy method (ability to do work), described earlier, and the results are summarized in Table IX. The exergy of the liquid hydrogen produced is equal to the minimum work required to liquefy the fluid in a reversible process. This is only possible if the ortho-para conversion takes place continuously as the temperature of the fluid changes. Due to many system inefficiencies and thermodynamic losses, the actual work required for the liquefaction is much greater than the exergy of the liquid hydrogen produced. These losses are attributed to the irreversibilities in the heat exchangers, compressors, expanders, Joule-Thomson devices, etc. and were discussed earlier. The results of Table IX indicate that the hydrogen compressors constitute the majority of the irreversibility of the whole process (a little less than 60% total exergy loss). The precooling expanders (turbines) and heat exchangers, collectively, contribute the remaining (approximately) 40% of the total exergy loss of the system.

The loss of exergy due to the J-T valves is very small in accord with our previous statements. The greatest opportunity for improving the overall cycle efficiency therefore lies in the compressors and expanders. To amplify this point, the cycle efficiency and specific energy consumption were recalculated for the liquefaction system being considered here, assuming 100% thermodynamic efficiencies for all of the compressors and expanders, and found to be 54.53% and 0.224, respectively. Unfortunately, the assumed efficiencies for the compressors and expanders in the base-case example are already typical of the

state-of-the-art large-scale heavy-duty compression and expansion systems currently available and it is difficult to imagine the possibility of much improvement in the efficiencies of these machines in the near future. Nevertheless, it was possible to make a considerable improvement in the overall liquefaction cycle efficiency (more than 9% increase over the η_{cy} of the base-case considered) by doubling the number of compressor stages from two to four. The cycle efficiency and the specific energy consumption for the cycle with four stages of compression (otherwise identical to the base-case cycle) were calculated to be approximately 26.4% and 0.346, respectively. Clearly, selecting the proper compressor configuration and the number of stages required involves a balance between the cost of energy to produce the product and the capital cost of the compression system.

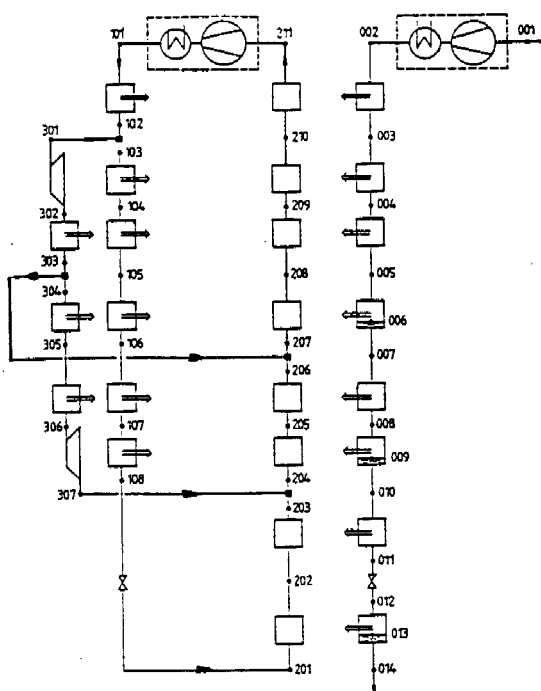


Figure 3. Schematic representation of hydrogen liquefier.

It is customary to analyze systems involving heat exchangers by means of Q-T diagrams. Fig. 4 depicts the Q-T diagrams for the base-case liquefaction cycle considered here. Fig. 4 also shows heat transfer and temperatures in both warm and cool stream side of the cycle showing the locations of the temperature "pinch" points. The difference in the fluid temperature between the warm and cool stream is indicative of irreversibilities and associated exergy losses in the system. To increase the overall cycle efficiency, it is important to minimize the area between the two curves (warm and cool side streams). In an

ideal reversible liquefaction cycle, both curves overlap, resulting in a zero area on the Q-T diagram. It might be possible to reduce the size of this area on the Q-T diagram of a real liquefaction cycle for hydrogen by incorporating an intermediate heat exchange loop using a second refrigerant fluid such as liquid nitrogen.

Table VIII
Fluidstates for the Base Case

STATE	P (bar)	T (K)	VOL (m ³ /kg)	H (kj/kg)	S (kj/kg-k)	% para in mixture
001	1.000	293.000	12.09162	4126.9	70.292	25.
002	25.000	293.000	.49079	4138.5	56.996	25.
006	25.000	60.000	.08894	1049.2	36.487	25.
007	25.000	60.000	.08894	804.0	33.786	60.
009	25.000	32.000	.01737	194.0	19.434	60.
010	25.000	32.000	.01737	-16.9	15.280	90.
011	25.000	29.332	.01598	-59.8	13.882	90.
012	4.000	25.963	.04332	-59.8	15.224	90.
013	4.000	25.963	.01589	-116.4	13.044	90.
014	4.000	25.963	.01589	-172.6	11.382	98.
101	25.000	293.000	.49079	4138.5	56.996	25.
108	25.000	29.012	.01585	392.5	20.593	25.
201	3.000	24.576	.06030	392.5	22.115	25.
202	3.000	24.576	.27241	731.0	35.888	25.
211	3.000	289.500	3.98734	4077.9	65.588	25.
301	25.000	134.058	.22431	1956.5	46.351	25.
302	12.000	111.000	.38238	1685.5	47.185	25.
306	12.000	44.686	.13190	910.8	36.480	25.
307	3.000	28.000	.33538	778.3	37.690	25.
308	12.000	85.558	.29106	1391.0	44.175	25.
309	3.000	59.000	.79931	1123.9	46.082	25.
First Compressor						
001	1.000	293.000	12.09162	4126.9	70.292	25.
001	5.000	537.432	4.44121	7665.3	72.422	25.
001	5.000	293.000	2.42426	4128.8	63.651	25.
002	5.000	293.000	2.42426	4128.8	63.651	25.
002	25.000	537.706	.89521	7685.4	65.791	25.
002	25.000	293.000	.49079	4138.5	56.996	25.
Second Compressor						
001	3.000	289.500	3.98734	4077.9	65.588	25.
001	8.660	436.324	2.08598	6200.5	67.131	25.
001	8.660	293.000	1.40279	4130.6	61.382	25.
002	8.660	293.000	1.40279	4130.6	61.382	25.
002	25.000	441.715	.73677	6290.7	62.934	25.
002	25.000	293.000	.49079	4138.5	56.996	25.

Table IX

Summary of the Results for the Base Case

TURBINE 1 POWER (kW)	-672.0724
TURBINE 2 POWER (kW)	-291.1319
TURBINE 3 POWER (kW)	-184.1571
COMPRESSOR POWER LIQ. H2 (kW)	1489.922
COMPRESSOR POWER CIR. H2 (kW)	10921.01
HEAT HOT SIDE (kW)	-7976.775
HEAT COLD SIDE (kW)	8064.201
HEAT REMOVED TO SURROUNDING (kW)	12253.9
PENETRATION OF HEAT (kW)	87.42578
MINIMUM REQUIRED POWER (kW)	2721.836
PROCESS EFFICIENCY	24.16496
EXERGY INPUT FLOWS:	
EXERGY FLOW STREAM 001 (kW)	0
EXERGY FLOW COMPRESSOR LIQ (kW)	1489.922
EXERGY FLOW COMPRESSOR CIR (kW)	10921.01
TOTAL INPUT	12410.93
EXERGY OUTPUT FLOWS:	
EXERGY FLOW STREAM 014 (kW)	-2721.836
EXERGY FLOW TURBINE 1 (kW)	-672.0724
EXERGY FLOW TURBINE 2 (kW)	-291.1319
EXERGY FLOW TURBINE 3 (kW)	-184.1571
TOTAL OUTPUT	-3869.198
EXERGY LOSSES:	
EXERGY LOSS COMPRESSOR LIQ (kW)	262.6871
EXERGY LOSS COMPRESSOR CIR (kW)	2312.613
EXERGY LOSS COMP-COOLER LIQ (kW)	406.6449
EXERGY LOSS COMP-COOLER CIR (kW)	2033.735
EXERGY LOSS TURBINE 1 (kW)	605.5407
EXERGY LOSS TURBINE 2 (kW)	608.7625
EXERGY LOSS TURBINE 3 (kW)	492.5431
EXERGY LOSS THROTTLE LIQ (kW)	82.57103
EXERGY LOSS THROTTLE CIR (kW)	31.20687
EXERGY LOSS COLD BOX (kW)	46.09603
EXERGY LOSS HEAT EXCHANGERS (kW)	1659.331
	TOTAL 8541.731
Specific Energy Consumption (SEC)	0.38

There have been many attempts to improve the overall hydrogen liquefaction cycle efficiency by primarily focusing on the modifications related to the cycle's compression system. One such attempt was made by Parrish (39) who proposed the use of a hydride compressor with no moving parts. The thermodynamic analysis of a LH₂ cycle incorporating a variety of metal hydride systems for compressing hydrogen has been described by Parrish and showed no significant improvement in η_{cy} at the pressure range of his study. It was found that the chemical nature of hydrides and their limitation to effect a rapid change in pressure with temperature renders all hydrides ineffective to be used as viable compression systems in liquefaction cycles.

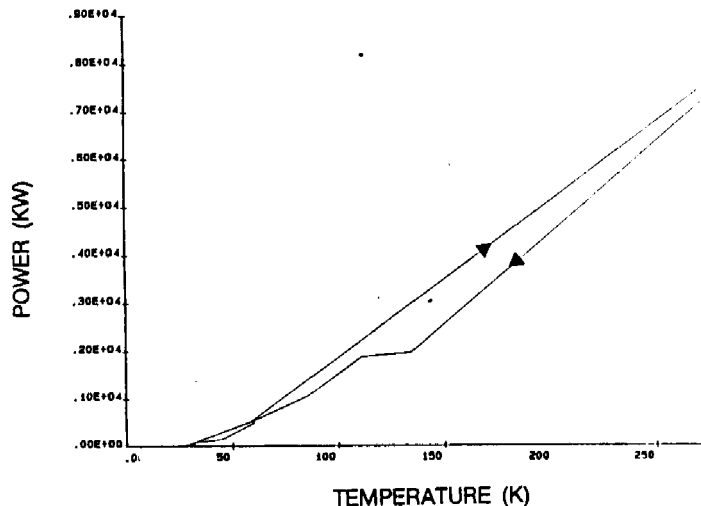


Figure 4. Q-T diagram for base case liquefaction cycle.

Another attempt to improve the conventional (mechanical) cycle efficiency by effecting the compression techniques is described by Baker (49-51). According to Baker, centrifugal compressors could be used instead of the traditional reciprocating compressors if the problems with the low molecular weight of hydrogen (which results in low pressure rise upon compression) were solved. Centrifugal compressors are more compact and less costly to operate and maintain than large and complex compression systems which utilize reciprocating devices. An admixture of a high molecular weight compound with suitable thermodynamic characteristics in hydrogen was suggested by Baker. Propane was identified as a viable candidate due to low cost, wide liquid range (easily condensable), and low vapor pressure at cryogenic temperatures and used in 15% propane to 85% hydrogen proportions in the recycle stream (circuit stream) to liquefy hydrogen. A detailed comparative analysis of propane/hydrogen and conventional all hydrogen processes indicated that the propane/hydrogen system required somewhat greater

power input than conventional liquefier. Nevertheless, due to reduced investment and maintenance costs, an estimated 8 to 12% reduction in the cost of liquid hydrogen produced was realized.

Another technique which is commonly utilized is using an auxiliary refrigerating fluid from a source external to the hydrogen liquefaction plant. Most such systems utilize liquid nitrogen to precool the product stream (in a Cascade cycle) below the inversion temperature of hydrogen (-204 K) to permit liquefaction of the hydrogen via Joule-Thomson expansion. The liquefaction plant for hydrogen may, in turn, employ other auxiliary refrigerants such as halogenated hydrocarbons, etc. Examples of Cascade cycles are given by Dini and Martorano (44) and Smith (52). A detailed comparative analysis of a nitrogen Cascade cycle and all-hydrogen liquefaction cycle has been made by Voth (39). According to Voth, when expanding turbines with efficiencies below about 75% are available, the best overall liquefier efficiency would be achieved with a Cascade cycle. Other more practical reasons regarding the advantages of liquid nitrogen precooling include:

- (1) It is possible to obtain higher efficiency expanders and compressors for nitrogen than hydrogen.
- (2) Liquid nitrogen is normally required in most hydrogen liquefaction systems to purify the gaseous hydrogen supply.

Finally, an entirely new refrigeration concept, based on magnetic or magneto-caloric effect, has been proposed for liquefaction of hydrogen, Barclay (53-56). Many theoretical analyses published to date suggest that the magnetic refrigerator can make a significant improvement in the thermodynamic performance of hydrogen liquefiers. Efficiencies which are in order of double those attainable via gas compression and expansion cycles are foreseen. This could reduce the specific energy consumption of the process significantly lowering the cost of liquid hydrogen product. Since no actual working device of appropriate size has been built and operated, it is difficult to truly evaluate the viability of the magnetic liquefaction system. In a very recent presentation, Barclay (56) proposed and evaluated the preliminary characteristics of a (20/300 K) magnetic liquefier capable of producing 10 to 20 l/hr of LH_2 . An efficiency of 40 to 50% of Carnot and capital costs of about \$100,000 were estimated for a 15 l/hr system. For a magnetic refrigeration unit operating between $T_c = 20$ K and $T_H = 275$ K and having a cycle efficiency of 40 to 50%, the specific energy consumption is calculated to be 0.178 to 0.222. Table X summarizes the characteristics of several current and future hydrogen liquefaction systems.

Table X
Hydrogen Liquefaction Cycle Summary

Ref	Capacity (ton/day)	Cycle efficiency (%)	$\tilde{m}_{H_2}^1$ (-)	$\tilde{m}_{N_2}^2$ (-)	SEC ³ (-)	Comments
44	4	17	3.85	10.84	0.49	simple conceptual LH ₂ plant with single J-T valve, LN ₂ precooling
44	-	23	2.78	9.03	0.35	U.S. Air Force closed cycle LH ₂ plant "papa Bear"
44	-	28	5.26	-	0.287	maximum H ₂ pressure of 5.07 MPa
44	2644	~31.5	3.17	48.7	0.2535	an estimate of a well designed and optimized large scale LH ₂ plant
52	95.24	38.4	3.23	30.72	0.226	no heat leaks, hypothetical plant LN ₂ precooling, J-T valves, 95% PH ₂
57	110	N.A. ⁵	N.A.	N.A.	0.37	Air Products and Chemicals LH ₂ plant
47	2-5	N.A.	N.A.	10	0.483	complex J-T cycle
47	3-60	N.A.	N.A.	N.A.	0.281	expander cycle
58	20	N.A.	N.A.	N.A.	0.32	Cascade type, conceptual
45	250	36	4.84	15.85	0.275	Union Carbide Corp., liquefaction plant, conceptual
50	250	39.3	N.A.	N.A.	0.252	improved compressor and expander efficiencies, partial ortho/para conversion, H ₂ recovery in the purge gas, (1985-2000) technologies
24	250	N.A.	N.A.	N.A.	0.317	a realistic estimate given by Union Carbide Corp.
43	20	23.7	12.14	-	0.397	Claude type with J-T valves, conceptual
39	-	~30	12.78	-	0.305	a realistic estimate, Claude type LH ₂ plant, real cycle analysis
This study	-	32.13	9.64	-	0.308	based on the Modified Collins Cycle
This study	-	26.4	12.14	-	0.346	4 stage compressor, Claude type cycle with J-T valves, actual fluid properties
57	0.03	40-50	-	-	0.18-0.22	magnetic liquefier

¹ Mass flow rate of recycled hydrogen/mass flow rate of liquid hydrogen.

² Mass flow rate of nitrogen/mass flow rate of liquid hydrogen.

³ Specific energy consumption.

⁴ Not applicable.

⁵ Not given.

2.3.2.3 Summary of the Liquefaction Techniques. The calculated efficiencies of the practical hydrogen liquefiers compare favorably with the efficiencies derived earlier for Modified Collins Cycle (see Table X). This is important since the final expansion device for the MCC (using a theoretical isothermal expander) and the real cycles (using Joule-Thomson device) were quite different. It is therefore possible to study liquefaction systems for hydrogen and other cryofuels using the simple relationships developed for a Modified Collins Cycle rather than resorting to a detailed numerical analysis of a real cycle (similar to one described in the previous section). The method was applied to a liquefaction unit for production of methane and indicated a substantially lower specific energy requirement than that calculated for hydrogen (see Table VI).

The type of mechanical liquefaction cycle (Claude, Cascade, etc.) does not appear to affect the overall efficiency of a hydrogen liquefier. However, it is important to tailor a given liquefaction cycle concept to match the requirements imposed by the size and characteristics of the available compressors, expanders, heat exchangers, etc.

The efficiency of a mechanical liquefaction cycle is primarily a function of the efficiencies of the compressors and expanders used in the system. The state-of-the-art efficiencies and the specific energy consumptions for LH₂ plants are estimated and given in Table X. It is apparent that the hydrogen liquefaction energy requirements are very near their minimum practical value which may be expected from a conventional liquefaction system. When other actual losses (not accounted for in the theoretical cycles discussed here) such as those due to (1) heat leak to the cold portion of the liquefier, (2) consumed energy to purify hydrogen supply, (3) noncontinuous ortho-para conversion, (4) hydrogen leakage from various components in the cycle, and etc. are taken into account, a practical specific energy requirement greater than those predicted from theoretical cycles is obtained. According to Table X results, the current position with regard to the practical liquefaction cycle efficiency and the specific energy consumption (for production of 95% para-LH₂) lies around 23 to 30% and 0.3 to 0.37, respectively. Future efficiencies for liquefaction of hydrogen might be further increased from 42.5 (51) to 50% (56) resulting in a specific energy consumption as low as approximately 0.2.

2.3.3 Liquefaction Costs Of Hydrogen and Methane. The liquefaction costs of a cryofuel such as hydrogen or methane can be separated into the energy and nonenergy costs. The energy cost is determined directly from the specific energy consumption of the liquefaction complex and the cost of electricity (power). A realistic estimate of the energy cost of liquefaction can be made using the information presented in Table X. Since the energy cost is the larger cost component, the cost of liquefying a cryofuel (especially hydrogen) is very

sensitive to the method of liquefaction. The energy cost then varies widely from source to source and could be very low once the new technologies (such as magnetic cooling) are fully developed. The nonenergy costs of producing LH₂ include the capital cost of the plant, operation and maintenance, supplies, administration, cost of feedstock, etc. Other nonenergy related expenses include owner invested costs (start-up, interest before start-up, engineering, working capital, etc.) which are directly estimated from the cost of the liquefaction unit. It should be noted that the nonenergy costs are particularly sensitive to the method of financing used, e.g. utility or industrial type (such as discounted cash flow), etc.

Many estimates for the liquefaction costs of hydrogen are available in literature (24, 38, 40, 49, 57-61). Strobridge (38) and Parrish and Voth (40) give a detailed cost analysis of hydrogen production and liquefaction. The capital investment required for liquefaction is related to the installed compressor power and is given by Strobridge (38) to be:

$$C_c = 6000\dot{W}_c^{0.7}$$

where \dot{W}_c refers to the installed compressor power (kW) and C_c is cost in dollars (1973). One can adjust to 1985 dollars by applying the 2.254, 1985/1973 GNP price deflator:

$$C_c = 13526\dot{W}_c^{0.7}$$

The power required is a simple function of the ideal liquefaction power and conversion efficiency, then;

$$C_c = 13526 \left(\frac{\dot{W}_i}{\eta_{cy}} \right)^{0.7} = 557.2 \left(\frac{\dot{m} w_i}{\rho \eta_{cy}} \right)^{0.7}$$

where w_i (kJ/m³) refers to the reversible volumetric energy requirement and is given in Table V for a number of cryogenic compounds. η_{cy} is the liquefaction cycle efficiency and is depicted in Table X. ρ (kg/m³) denotes the density of cryofuel obtained from Table VII, and \dot{m} (ton/day) refers to liquefaction plant capacity.

Alternatively, we have:

$$C_c = 557.2 \{ \dot{m} (\text{SEC}) (HHV) \}^{0.7} \quad (1)$$

where (SEC) denotes the specific energy consumption of liquefaction process and is depicted in Table X, and (HHV), in kj/kg, refers to the higher heating value of the liquid fuel obtained from Table IV.

By substituting for (HHV) from Table VII and assuming (SEC) = 0.37 (see Table X), the following relationship is obtained for the capital costs of liquefying hydrogen;

$$C_c = 1.12 \times 10^6 \cdot m^{0.7} \quad (2)$$

Recently, an estimate of the capital costs of hydrogen liquefaction (excluding reforming equipment for natural gas, pretreatment, storage and loading) is given by Air Products and Chemicals (57). The estimate is expressed below and is valid for the plant capacities from 6 to 110 ton/day;

$$C_c(1985\$) = 3.45 \times 10^6 \cdot m^{0.6} \quad (3)$$

where m (ton/day) denotes liquefaction unit capacity. The estimates of capital costs made using equations (2) and (3) are found to differ as much as 100%. Equation (2) was developed in the early 1970s whereas equation (3) is a very recent formula and is more likely to be closer to the actual costs.

In order to determine the cost of manufacturing LH₂, the cost of the required power, the operating and maintenance costs (O&M), and fixed charges on the capital investment must be determined. The fixed charges are calculated based on operation of the plant 90% of the time and include interest on the capital and debt retirement. The O&M costs include maintenance, operating and labor costs and do not usually include the cost of feedstock (e.g. natural gas, etc.).

The energy or power cost (C_e) of the liquefaction plant is simply

$$C_e = 2.778 \times 10^{-6} \frac{E}{(SEC)}$$

where C_e = \$/kj of liquid fuel, higher heating value, and E denotes the cost of electricity in cents/kWh. This equation can also be represented in the following form:

$$C_e (\$/10^6 \text{Btu, higher heating value}) = 2.931 \times 10^{-6} E / (SEC)$$

where E is again in cents/kw-hr.

Operating and maintenance costs (O&M) per unit weight of liquid product can be calculated by (40):

$$\tilde{C}_{O\&M}(1985\$/kg) = 0.70175 \left(\frac{w_i}{\rho \eta_{cy}} \right)^{0.65} \dot{m}^{-0.35}$$

or;

$$\tilde{C}_{O\&M}(1985\$/kg) = 0.70175 \{(\text{SEC})(\text{HHV})\}^{0.65} \dot{m}^{-0.35}$$

The fixed charges on the capital investment/unit liquid produced may be determined from (40):

$$\tilde{C}_{FC}(1985\$/kg) = (\text{FCR}) \frac{C_c}{0.9(\text{production rate})(\text{hours/year})}$$

where;

(FCR) = $i(1+i)^n / ((1+i)^n - 1)$, i = interest rate (15%), and n = liquefaction plant life (25 years).

The cost of liquefaction is sensitive to the assumptions made regarding the method of financing and economic models used to arrive at the total cost of the liquid product. For example, the following formula was developed by the Union Carbide Corporation (24) for determining the cost of hydrogen liquefaction;

$$C (\$/10^6\text{Btu of LH}_2, \text{ higher heating value}) = 1.73 + 0.761 E$$

This equation may be adjusted to give liquefaction costs in 1985 dollars by applying 1.117, 1985/1982 GNP price deflator (62):

$$C (1985\$/10^6\text{Btu of LH}_2, \text{ HHV}) = 1.93 + 0.761E$$

or,

$$C (1985\$/10^9\text{j of LH}_2, \text{ HHV}) = 1.831 + 0.7218E$$

This cost equation has been developed for an optimum and large scale (250 ton/day) hydrogen liquefier, based on utility-type financing. The equation also incorporates improvements in hydrogen liquefaction technology foreseen in the 1985 to 2000 time frame. The process economics were assumed to improve in this time frame by increased compressor and expander efficiencies, partial conversion of ortho- to para-hydrogen (for storage requirements less than a few days), and purge gas hydrogen recovery. If electricity costs 4 cents/kWh, the cost of liquefying hydrogen (excluding the cost of gaseous H₂ feedstock) is calculated from the equation above to be approximately \$4.80/10⁶Btu or \$4.55/10⁹J.

Table XI depicts a summary of the calculated costs of hydrogen liquefaction obtained from several recent estimates. The data of Table XI shows that nonenergy costs of LH₂ production currently range from \$3 to \$11/10⁶Btu of LH₂. The lower end of this estimate is indicative of the minimum which might be expected as a result of future liquefaction technology developments and optimizations. A \$2/10⁶Btu for the nonenergy costs of a large-scale, future LH₂ plant seems to be well justified. Based on the emerging new liquefaction technologies (as reflected in lower specific energy consumption figures), an energy cost portion of \$4.2 to \$8.8/10⁶Btu (assuming SEC = 0.2 and \$21-44/10⁶Btu cost of clean, delivered electrical power) may soon be realized. Therefore, the total costs of LH₂ product in upcoming years in the range of \$6.2 to \$16.8/10⁶Btu appear quite possible.

Ref.	Capacity (ton/day)	(SEC) (-)	assumed cost of electricity (\$/10 ⁶ Btu) ¹	energy cost (\$/10 ⁶ Btu)	nonenergy cost (\$/10 ⁶ Btu)	liquefaction cost (\$/10 ⁶ Btu)
75	12	0.39	20.3	7.91	5.31	13.22
76	39.7	0.45	21-44	9-19	7-11	16-30
65	250	0.34	20	7	3-5	10-12
77	68 ²	0.3	NA	NA	NA	~25 ³
24,52,	250	0.26	21-43.5	5.5-11	1.9-2.23	7.4-13.23
73	110	0.37	20.5 ⁴	7.6	2.5	10.1

¹ Cost of delivered electricity from renewable, clean sources (62).
² Air Products and Chemicals, New Orleans plant.
³ Estimate, assuming 20 \$/10⁶Btu for the cost of gas (62), which appears to be too high.
⁴ Power at 0.07/kw-hr.

Similar estimates may also be made for the costs of liquefying methane as a transportation fuel. Many estimates are available from the natural gas industries. For example, DeLuchi et al. (62) quote from the Atlanta Light and Gas Company that their 210 ton/day liquid natural gas (LNG) facility currently under construction cost \$31 million (1987\$, about \$29 million 1985\$, or \$2856/10⁶Btu/day). The liquefaction plant will produce LNG at a cost of approximately \$0.48/10⁶Btu. This estimate includes O&M costs, administration, overhead, and other expenses. The \$0.48/10⁶Btu of LNG does not include the cost of gas nor does it take in to account the recovery of the capital expenditure. A 1984 estimate, Knowles (63), gives \$3058/10⁶Btu/day for the capital cost of LNG production. Colavincenzo's (64) estimate is \$2692/10⁶Btu/day. DeLuchi et al. (62) amortized the initial cost of the Atlanta plant at a 20-percent before-tax

return on investment (ROI) over 20 years and assumed operation at 90% capacity. Their calculation produced a capital charge cost of about \$1.80/10⁶Btu of LNG. The Atlanta plant uses 0.15 x 10⁶Btu of gas to produce one million Btu of LNG. Assuming the input gas at an industrial cost of \$6 to \$10/10⁶Btu, the energy cost would be approximately \$1.30/10⁶Btu of LNG. The total liquefaction cost of the LNG plant would then be about \$3.60/10⁶Btu, significantly lower than that of hydrogen.

2.3.4 Boil-Off Losses. Boil-off losses constitute a practical problem with almost all cryogenic fuel storage systems (especially LH₂). This is so because most cryogenic tanks would allow a certain amount of heat leak into the cryofuel causing evaporation and the gradual loss of the liquid. To reduce the boil-off losses, cryogenic containers are slightly pressurized. As the liquid continues to vaporize and pressurize the vessel, the gas must be released to prevent excessive internal pressure build up. The vented gas is combustible and must be recondensed or burned for safety reasons. Burning the vented gas has been suggested as an inexpensive and safe method of dealing with the boil-off problem in motor vehicles. The pilot lights similar to those used in the methane burning stoves may be incorporated into the vehicular storage systems. Several catalysts are currently available (62) which minimize boil-off loss for liquid methane and hydrogen. The system for methane vehicles costs no more than \$50 (1987\$). Catalyst systems for LH₂ vehicles are also available but their reliability in continuous use remains questionable (65).

A major problem with the vented boil-off gases is the irreversible loss of cryofuel. Most liquid methane tanks are designed to vent boil-off gases when the vessel pressure exceeds 60 to 85 psi (62). The length of time required for the cryogenic tank to vent off all of its content when left idle is termed "lock-up time" and depends on the vent pressure and the heat transfer characteristics of the vessel. The lock-up time for LCH₄ vehicle storage tanks varies between 7 to 13 days for the vessel vent pressures of 60 to 85 psi (66) and may be increased to about 20 days with minor modifications to the tank. This modification of the LCH₄ tank would add \$75 to \$100 to the cost of the tank (62) but virtually eliminates the boil-off problems with the LCH₄ vehicles entirely (unless the car is left idle for longer than 20 days). The lock-up time for a typical liquid methane vehicle is approximately 42 days (62). A typical LH₂ vehicle, on the other hand, vents at 44 to 74 psi (65, 67), which is reached after two to five days, a substantially shorter time than LCH₄ vehicles. A full 75-liter LH₂ tank venting at a rate of 6.2 L/day would be depleted to 1.22 liters (87g) of liquid in 12 days, after venting began. The remaining cold vapors would provide an approximate five-mile range. Managing boil-off problems with LH₂ vehicles is a formidable task since there is essentially no way to entirely eliminate the heat transfer to the liquid and furthermore, small-scale GH₂ capture and

reliquefaction is impractical and extremely expensive. Measures similar to those suggested for increasing the lock-up time of LCH₄ vehicles (such as increasing vent pressure) are not very useful and cost-effective in the case of LH₂ vehicles.

The boil-off problem with liquid hydrogen cars is much more severe than with LCH₄ vehicles. This is primarily due to the fact that the lock-up time for LH₂ tanks is much shorter and the fuel and storage system costs are much higher and more expensive. It is clear that this particular area (especially with LH₂ systems) requires further research to identify promising systems, approaches, and equipments for optimal use and management of the boil-off gases in vehicular storage systems.

It is advantageous to make cryogenic tanks stronger and increase the vent pressure. This approach can significantly improve and increase the range of the vehicle on residual gases. In the case of LCH₄, if the vent pressure were increased to 500 psi, the vehicle range after complete vaporization of the fuel would be approximately 40 to 50 miles (62). This modification increases the time between fill-up and venting (lock-up time) as much as ten times to 70 to 80 days (if the pressure were 500 psi and the boil-off rate remained constant) (62). There appears to be a need to analyze and design an optimum LCH₄ storage tank which satisfies an array of requirements, some of which were discussed above. It is known that the cost of LCH₄ tanks is very sensitive to the designed vent-period of the system. The state of the art of the design and manufacture of the advanced LCH₄ storage systems has been discussed by Colavincenzo (64) and Fischer (66). In 1982, the Aerospace Corporation simulated for the Department of Energy an LCH₄ vehicle that was more thermally efficient and more powerful than a "comparable" gasoline vehicle (62). The vehicle weighed only 26 pounds more than a "comparable" gasoline car and had the same 350-mile range. It was noted that Beech Aircraft Company reportedly had an aluminum tank design which resulted in a total storage system weight which was actually lower than that of the gasoline system it replaced (62). These data indicate that the difference in weight between dedicated liquid methane and a "comparable" gasoline vehicle with a similar range need not be significant at all if not in favor of LCH₄ vehicle.

Currently the most compact LCH₄ tanks are about twice as bulky as gasoline tanks holding an equivalent amount of energy (62). We might point out that LCH₄ storage system is significantly more energy dense than compressed methane storage. The liquid methane storage is in general comparable to methanol storage in terms of displacement and weight i.e. (comparable installed gravimetric and volumetric energy densities). This point will be further discussed in Section 2.6.

