This thesis is dedicated to my caring wife, family, and in-laws. Your love, support, and encouragement were more than I could have asked for, and helped me strive for excellence.
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<tr>
<td>A</td>
<td>inlet cross-sectional area, m²</td>
</tr>
<tr>
<td>A*</td>
<td>effective or throat cross-sectional area, m²</td>
</tr>
<tr>
<td>a_t</td>
<td>speed of sound at the throat, m/s</td>
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<tr>
<td>C_P</td>
<td>specific heat at constant pressure, kJ/kg K</td>
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<tr>
<td>E</td>
<td>total energy, W</td>
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<tr>
<td>h</td>
<td>specific enthalpy, kJ/kg</td>
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<tr>
<td>k</td>
<td>specific heat ratio, C_P/C_v</td>
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<td>k_t</td>
<td>thermal conductivity, W/m² K</td>
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<tr>
<td>L</td>
<td>tank-wall thickness, m</td>
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<tr>
<td>M</td>
<td>flow Mach number, dimensionless</td>
</tr>
<tr>
<td>m</td>
<td>mass, kg</td>
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<td>( \dot{m} )</td>
<td>mass flow Rate, kg/s</td>
</tr>
<tr>
<td>P</td>
<td>pressure, kPa</td>
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<tr>
<td>q''</td>
<td>heat flux, W/m²</td>
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<tr>
<td>Q</td>
<td>total heat transfer rate, W</td>
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<td>R</td>
<td>gas constant, kJ/kg K</td>
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<td>S</td>
<td>total entropy, kJ/K</td>
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<td>u</td>
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<td>( \dot{u} )</td>
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<td>V</td>
<td>velocity, m/s</td>
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<td>x</td>
<td>position from datum in cartesian coordinate system</td>
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Subscripts
A  discharging tank
B  charging tank
c, char  characteristic
t  throat conditions
i, o  initial, stagnation
s  surface or isentropic

Superscripts
*, bar  nondimensional
i  iterative counter
'  normalized

Greek Symbols
ρ  density, kg/m³
Δ  finite change in quantity
α  thermal diffusivity, cP
τ  nondimensional time
β_m  roots of transcendental equation
Efficient transfer of liquid hydrogen is critical for a successful transition to a hydrogen-based economy. The objective of this study is to model and quantify the amount of liquid para-hydrogen vaporized during a discharging/charging process in a cryogenic storage system. The effects that are included in this study include geometrical effects (storage tank volume), two-phase compressible flow, choking/unchoking, and wall-fluid heat transfer. A brief description of other physical boil-off mechanisms is also presented. This study provides a foundation for application-specific optimization. The storage system studied comprises two inter-connected tanks whose transfer line has a variation in flow area. This system models current liquid hydrogen storage and transportation systems. A computer program was written to track the temperature and pressure time history of liquid hydrogen as it flows between storage tanks, in both the choked and unchoked flow regimes. An iterative technique helps account for choking, which is likely in two-phase flow, at the throat. Cases of zero and infinite tank wall...
thermal mass are also discussed. By analyzing the behavior of fundamental variables
during the transient transfer of liquid hydrogen, boil-off losses may be minimized if the
variables with the greatest effect on boil-off losses are controlled. Basic models for the
transfer of supercritical gas are also developed and analyzed, using the ideal gas equation
of state. Directions for future work to provide a more comprehensive
discharging/charging vaporization model are indicated.
CHAPTER 1
INTRODUCTION

The major push to switch the world’s energy-hungry economies to the use of hydrogen is plagued by many issues of which the storage, transportation, and handling of hydrogen are major obstacles. Although hydrogen is the most abundant element on our planet, the processed form (diatomic hydrogen) has a low viscosity, low ignition energy, explosive potential, and high combustion velocity, and the low heat of vaporization in its liquid state make it very volatile, and extremely difficult to handle/store. Hydrogen may be stored in three states. The most common way of storing hydrogen is as gas. Hydrogen may also be stored as liquid or as solid combined with a metal hydride. This study does not analyze the storage and transfer of solid hydrogen.

The most common state of storing and transferring hydrogen is in its gaseous state. A drawback of this simple way of storing hydrogen is the fact that its low density makes the storage volume associated with it very large, and thus uneconomical. Many different studies try to tackle this problem by pressurizing the hydrogen. Both the type of application and the economics involved ultimately determine if gaseous hydrogen can be used.

According to many studies, liquid hydrogen has the greatest potential of all, as a fuel. The properties of liquid hydrogen (as well as associated problems with this method of storage and transportation) are briefly discussed in the next sections. Inefficiencies such as heat gains incurred during storage and transportation could result in large amounts of liquid hydrogen boil-off. Boil-off losses associated with the storage,
transportation, and handling of liquid hydrogen can consume up to 70% of the available combustion energy [1]. One method of avoiding this boil-off is to substitute gaseous hydrogen for liquid hydrogen. The major drawback of this simple way of storing hydrogen has been discussed previously. A more promising alternative is to understand the several mechanisms that contribute to these large losses. Only a thorough understanding of these mechanisms and a minimization of the boil-off losses associated with them will lead us to a quicker transition to a liquid-hydrogen based economy. If the production of diatomic hydrogen may be generated by using renewable technologies this may lessen dependency on soon-to-be depleted fossil fuels both as a primary energy source and as the resource from which diatomic hydrogen is produced. This study concentrates on developing a model that will aid in understanding time-varying properties (such as pressure and temperature) during the transfer of liquid and gaseous hydrogen. This will aid in optimizing current cryogenic storage systems, and help quantify the amount of liquid-hydrogen vaporized during a discharging/charging process in a cryogenic storage system. The ability to quantify the amount of liquid vaporized is also desirable in space applications, where limited amounts of liquid will be available to replenish boil-off.

**Modeling of Storage System**

Figure 1 shows a schematic of a cryogenic storage and transfer system. At t>0, the valve connecting the two storage tanks will open, creating a change in the cross-sectional area of the flow. This change in cross-sectional area can be modeled as a convergent nozzle. Gravitational potential energy has been neglected, and therefore only a pressure differential between the charging and discharging tanks is the driving force behind the transfer of either gaseous or liquid hydrogen.
Flow Regimes

During high-speed fluid flow, the pressure applied at the nozzle discharge region (i.e., the back pressure), plays a significant role in determining the flow regime that the flow is experiencing. For all back pressures in the charging tank less than the pressure at the throat region, choked flow (flow Mach number is unity) is observed where the flow rate is maximum. The flow becomes unchoked when the back pressure and throat pressures have reached equilibrium and the fluid velocity is less than the speed of sound (i.e., subsonic).

Literature Survey and Current Applications of this Study

In most current literature and textbooks, the discharging and charging analyses have been the basis of many different studies. These studies share a common goal: to describe key variables (pressure, temperature, etc.) as a function of time. These theoretical solutions have found a wide range of practical applications. These applications include, but are not limited to, predicting the time required to fill or vent a storage vessel, fill an airbag in the case of an accident, and fill an aircraft’s evacuation slide in case of an emergency.

The study of discharging and charging processes in space applications is also of significance. A number of space missions have been identified that will require, or could benefit from resupply of cryogenic liquids in orbit [2]. Before charging aircraft in space
with cryogenic propellants, coolant fluids and other liquids, many operational challenges must be overcome. Aydelott et al. [2] and Taylor et al. [3] described some of the challenges that low-gravity conditions pose to charging cryogenic liquids in space, and present a summary of the results obtained to date. According to Aydelott et al. [2], in order to charge a tank without venting, the assumption made in this study, a thermodynamic (or no-vent) filling technique must be utilized in order to minimize low liquid-transfer rates. Conceptually, the thermodynamic filling technique is the process of alternately and repeatedly charging cryogenic storage tanks with a liquid cryogen, allowing the liquid to vaporize and therefore cool the storage tank, then venting the vapor until the charging tank is cold enough to be filled without venting.

Aydelott et al. [2] also discussed the importance of efficiently transferring cryogenic propellants and liquids to and from in-space storage tanks (aboard the Space Station, for example), to help reduce operational costs associated with transporting propellants to orbit. This may be done by scavenging unused propellants from space vehicles, and the propellants may be replenished on an as-available basis.

The importance of quantifying the amount of liquid hydrogen vaporized during a discharging/charging process has also been given much attention in current literature. Sherif et al. [4] proposed a research program that will address issues that affect boil-off losses during the storage and transport of cryogens. Among the issues discussed, they emphasized boil-off losses associated with the transfer of liquid hydrogen among storage tanks with an initial pressure differential. Sherif et al. [4] also proposed that if the transfer of liquid hydrogen is carried out at atmospheric pressures, a reduction in the amount of boil-off will be realized.
To my knowledge, the transient analysis of transfer of both gaseous and liquid hydrogen in both the choked and unchoked flow regimes, and the quantifying of resultant boil-off, have not been presented in one unifying resource.

**Mechanisms of Boil-off**

This section introduces the mechanisms of boil-off, and states all necessary assumptions relevant to this study, dealing with them. Assumptions that deal directly with the transfer conditions or the equations used are stated when relevant.

**Ortho-para Conversion**

Room temperature hydrogen, in its natural state, is 75% ortho and 25% para. The difference between the two forms of hydrogen is in their relative spin of the particles that constitute the hydrogen molecule. Ortho-hydrogen is at the higher energy level. Ortho-hydrogen is slowly converted to the lower energy state (para-hydrogen), in an exothermic reaction. The heat of conversion between the two energy levels is 702 kJ/kg. Boil-off is induced since the heat of conversion exceeds the heat of vaporization of normal liquid hydrogen (which is 443 kJ/kg at atmospheric pressure). Many different studies and procedures have been used to reduce the boil-off associated with the ortho-para hydrogen conversion. Gursu et al. [1] showed that the fraction of mass remaining in a storage tank is greatly dependent on the initial ortho-para concentration, as storage times vary. The present study assumes that the liquid hydrogen stored and transferred is pure para-hydrogen and that the effects of conversion between the two states are neglected. This assumption is appropriate since at the normal boiling point of hydrogen, 20.4 K, hydrogen has a composition of approximately 99.8% para-hydrogen.
Sloshing

A challenge to any cryogenic engineer is to build an apparatus for storage and/or transportation that, among other things, takes into account the effects of environmental conditions. The device must be designed to withstand shocks, vibrations, and accelerations encountered during road, sea or air transportation. These vibrations or accelerations cause sloshing. Sloshing is any fluid motion that may result from vibrations, impacts and shocks. Several types of fluid motions have been observed by Abramson [5] such as lateral, vertical and dome sloshing. Lateral sloshing occurs when the liquid moves in response to translational or pitching motions of the tank. Vertical sloshing results from liquid motions that occur in response to motions of the tank normal to the liquid-vapor interface. Dome sloshing results from liquid motions that result from a sudden change in the motion of the vehicle and the impact of the liquid against the opposing tank wall. These types of fluid motion all increase the kinetic energy of the liquid hydrogen and thus greatly influence boil-off [5]. The mechanism of heat transfer also increases with the increase in turbulence caused by sloshing. Different approaches have been researched to minimize the effects of sloshing. The most common of which, is the isolation of the inner tank form vibrations by designing appropriate suspension systems. Welt and Modi [6] encourage, rather than suppress, sloshing to control structural oscillations. Hara and Shibata [7] propose that by introducing timed injections of air bubbles into the liquid, sloshing may be restrained. The present study assumes that the storage system is stationary and that sloshing has neither an effect on boil-off nor an increase in heat transfer.
**Heat Leaks**

Heat leaks are usually the largest cause of boil-off losses. This is due to the fact that cryogenic liquids in general have a relatively small heat of vaporization. Liquid hydrogen has a heat of vaporization of 443 kJ/kg (190.5 Btu/lbm) at a pressure of 1 atm. Poorly insulated storage tanks of liquid hydrogen would require substantial amounts of needed make-up liquid hydrogen. Due to these constraints special high-performance insulations have been developed to reduce the evaporation rate of cryogenic liquids in storage vessels. Barron [8] has discussed and evaluated the most common high-performance insulations. The present study does not account for the heat losses that may arise from imperfections in the exterior insulation or the effect that various types of insulations may have on heat losses.

**Thermal Stratification**

Another obstacle in the way of minimizing boil-off losses is thermal stratification. This phenomenon occurs when heat leaks initiate convection currents. These heat leaks are generally associated with the sidewalls. The heat warms the fluid near the sidewalls and causes the fluid to be more buoyant and gradually rise to the top. A warm layer develops across the liquid-vapor interface and a temperature gradient then exists across the depth of the liquid [9]. Gursu et al. [10] have suggested that for some cryogenic fluids, including liquid hydrogen, the total vertical temperature difference across the liquid might be in the range from 1 to 15 K. This study neglects heat losses from the sidewalls and therefore the thermal stratification associated with those losses is neglected.

Chapter 2 presents the assumptions and derivation of fundamental equations of the transfer of gaseous hydrogen in both adiabatic and isothermal transfer conditions. This section will enable the reader to understand the fundamentals of transfer in the choked
and unchoked flow regimes before moving on to the transfer of liquid. Chapter 3 presents the models used to develop the computer program written to analyze the transfer of liquid hydrogen in both the choked and unchoked flow regimes. Many additional complexities that arise during this transfer process are also discussed. Chapter 4 presents and discusses the results obtained for both the transfer of liquid and gaseous hydrogen. This section discusses how key parameters (geometrical, flow regime, etc.) affect the behavior of fundamental variables (temperature and pressure) and their subsequent influence on boil-off. Chapter 5 presents conclusions that may be formed from the previous chapter pertaining to the variation of temperature, pressure and boil-off. This section also provides recommendations for future research in order to derive more comprehensive discharging/charging vaporization models.
CHAPTER 2
TRANSFER OF GASEOUS HYDROGEN

This study models the time dependent characteristics associated with the transfer of gaseous hydrogen in both the choked and un-choked flow regimes for isothermal and adiabatic cases. Many assumptions are made in order to obtain essential elementary results. Spatial gradients of pressure and temperature are neglected. The gaseous hydrogen is treated as an ideal gas since it is assumed to be both thermally and calorically perfect. The variation in cross sectional flow area is modeled by a converging nozzle. The flow to the throat is one-dimensional, compressible and isentropic. Both the discharging and charging tanks are at the same ground level, therefore gravitational potential energy is neglected. The velocity of the gaseous hydrogen in both the discharging and charging tanks is zero at any instant in time.

Isothermal Case

This assumption is appropriate when the discharging tank undergoes a slow discharge allowing for sufficient time for heat transfer to keep the temperature of the gas constant in the storage system.

Analysis of Discharging Tank

At low densities all gases are considered ideal and follow this equation of state,

\[ P_A V_A = m_A R T_A \]  

Writing the integral continuity equation for the discharging tank,

\[ -\int_{CS} \rho \rho dA \frac{\partial}{\partial t} \int_{CS} \rho dV = \int_{CS} \rho \rho dA \frac{\partial}{\partial t} \int_{CS} \rho dV \]

and simplifying we find,
\[
\frac{dm}{dt} = -\dot{m}
\]  

(3)

Since isothermal storage conditions have been assumed, the pressure in tank A is the only parameter that is a function of time and therefore we can write,

\[
\left( \frac{dP}{dt} \right) \frac{V}{RT_A} = -\dot{m}
\]

(4)

Initially, the flow is in the choked flow regime and the mass flow rate, which is a maximum, is

\[\dot{m} = CP_A\]

(5)

where

\[C = \frac{A'}{\sqrt{RT_{A,i}}} \sqrt{k \left( \frac{2}{k+1} \right)^{\frac{k+1}{k-1}}}\]

(6)

where \(k\) in Equation (6) is the specific heat ratio. Substituting Equation (4) into (3) and simplifying we find

\[
\frac{dP}{dt} = -DP_A
\]

(7)

where

\[D = \frac{RT_A}{V_A} C\]

(8)

Setting up the integral for the pressure in the discharging tank, \(P_A\),

\[
\int_{P_{A,i}}^{P_A} \frac{dP}{P_A} = -D\int_0^t dt
\]

(9)

Integrating and simplifying we find

\[
P_A = e^{-Dt}
\]

(10)

by introducing the nondimensional parameters,

\[
p_m = \frac{P}{P_{m,i}}, \quad \bar{T}_m = \frac{T}{T_{m,i}}, \quad \text{and} \quad \tau = \frac{t}{t_{char}}, \quad \text{where} \quad t_{char} = \frac{V_m}{A' \sqrt{kRT_{m,i}}}
\]
where the subscript \( m \) denotes that these nondimensional parameters may be used for either the discharging or charging tanks, A and B respectively. By applying these nondimensional parameters to Equation (10) we find

\[
\overline{P}_A = e^{-\left(\frac{2}{(k+1)}\right)\frac{M}{RT_A}}
\]  

(11)

Equation (5) is derived from Equation (12) by setting the Mach number equal to unity and represents the mass flow rate in the unchoked flow regime.

\[
\dot{m} = \frac{P_d A^* \sqrt{k}}{\sqrt{RT_d}} \frac{M}{M^2} \left[ 1 + \left(\frac{k-1}{2}\right)M^2 \right]^{\frac{k+1}{2(k-1)}}
\]  

(12)

Adopting a similar procedure to that described above, the pressure time history of the discharging tank in the unchoked flow regime is found to be

\[
\overline{P}_A = e^{-\left(\frac{M}{\left[1 + \left(\frac{k-1}{2}\right)M^2\right]^{\frac{k+1}{2(k-1)}}}\right)\tau}
\]  

(13)

where the Mach number may be determined iteratively for a given variation of the flow area relative to the throat area of the nozzle (\( A/A^* \)), for the same mass flow rate and stagnation properties from Equation 14.

\[
\frac{A}{A^*} = \frac{1}{M} \left[ \frac{2}{k+1} \left(1 + \frac{k-1}{2}M^2\right) \right]^{\frac{k+1}{2(k-1)}}
\]  

(14)

There is a unique value of \( A/A^* \) for each value of the flow Mach number, but there are two possible values of the flow Mach number for each value of \( A/A^* \). The values obtained represent the flow Mach numbers for subsonic and supersonic flows respectively. To determine the conditions where the flow becomes unchoked, the known
ratio of the stagnation to static pressure in the discharging and charging tanks respectively allows for solution for the flow Mach number from Equation (15),

\[
\frac{P_o}{P} = \left[ 1 + \left( \frac{k-1}{2} \right) M^2 \right]^{\frac{k}{k-1}}
\]

(15)

which is 1.8929 for gaseous hydrogen with a flow Mach number equal to unity and whose specific heat ratio is 1.4.

**Analysis of Charging Tank**

The gas in the charging tank can also be modeled with the ideal gas equation of state

\[
P_B V_B = m_B R T_B
\]

and the accumulated mass in the charging tank varies with time and may be written as

\[
m_B = m_{B,i} + \int_0^t m dt
\]

(16)

where

\[
m_{B,i} = \frac{P_{B,i} V_B}{R T_{B,i}}
\]

(17)

Solving for the pressure in charging tank

\[
P_B = \frac{R T_B}{V_B} \left( m_{B,i} + \int_0^t C P_i dt \right)
\]

(18)

Simplifying and substituting Equation (10) to account for the pressure variation in the discharging tank, we find

\[
P_B = P_{B,i} + \frac{R T_B}{V_B} CP_{A,i} \int_0^t e^{-D_i} dt
\]

(19)
After dividing Equation (19) through by $P_{b,j}$, integrating, and evaluating the limits, Equation (19) reduces to

$$\frac{P_{b}}{P_{b,j}} = 1 + \frac{P_{A,j}}{P_{b,j}} \left(1 - e^{-\frac{D_{j}}{t}}\right)$$

(20)

which may be simplified to Equation (21) in a nondimensional form

$$\bar{P}_{b} = 1 + \frac{P_{A,j}}{P_{b,j}} \left(1 - e^{-\left(\frac{\kappa_{A}}{\kappa_{b}}\right)^{\frac{3}{2}} t} \right)$$

(21)

Adopting a similar procedure to that described above, the pressure time history of the charging tank in the unchoked flow regime is found to be

$$\bar{P}_{b} = 1 + \frac{P_{A,j}}{P_{b,j}} \left(1 - e^{-\left(\frac{M}{\kappa_{A}^{\frac{2}{3}}} t\right)^{\frac{3}{2}}} \right)$$

(22)

Adiabatic Case

The adiabatic assumption is ideal for a case of rapid discharging/charging. It is an appropriate assumption since little or no time is allotted for any heat transfer between the tank-wall and the gas.

Analysis of Discharging Tank

Initially, the mass flow rate at the throat for choked flow is

$$\dot{m} = X \frac{P_{A}A^{*}}{\sqrt{RT_{A}}}$$

(23)

where

$$X = \sqrt{k} \left(\frac{2}{k+1}\right)^{\frac{k+1}{2(k-1)}}$$

Applying the above definition to the continuity equation, Equation (3), we find
Nondimensionalizing Equation (24) we find

\[
\frac{dm_{Ai}}{dt} = -\frac{P_{Ai}A^*}{\sqrt{RT_{Ai}}} \tag{25}
\]

By applying ideal gas relationships between the mass in the discharging tank initially and in the next time-step, we find an expression for \( \frac{m_{Ai}}{m_{Ai,j}} \) in Equation (25)

\[
\frac{m_{Ai}}{m_{Ai,j}} = \frac{P_{Ai}T_{Ai,j}}{P_{Ai,j}T_{Ai}} = \frac{P_{Ai}}{\overline{T}_{Ai}} \tag{26}
\]

but from the definition of an isentropic process we know,

\[
\overline{T}_{Ai} = \overline{P}_{Ai}^{\frac{k-1}{k}} \tag{27}
\]

therefore Equation (26) reduces to

\[
\frac{m_{Ai}}{m_{Ai,j}} = \overline{P}_{Ai}^{\frac{1}{k}} \tag{28}
\]

Deriving an expression for \( \overline{P}_{Ai} \) in Equation (25) we find

\[
\frac{\overline{P}_{Ai}}{\sqrt{\overline{T}_{Ai}}} = \frac{\overline{P}_{Ai}}{\sqrt{\overline{P}_{Ai}^{\frac{k-1}{k}}}} = \overline{P}_{Ai}^{\frac{k+1}{2k}} \tag{29}
\]

Substituting Equations (27) and (28) into (25) we find

\[
\frac{d}{d\tau} \left( \frac{1}{\sqrt{T_{Ai}}} \right) \frac{m_{Ai,j}}{m_{Ai}} = -\frac{P_{Ai}A^*}{\sqrt{RT_{Ai,j}}} \overline{P}_{Ai}^{\frac{k+1}{2k}} \tag{30}
\]
Let

\[ \Omega = X \frac{P_{A,i} A^*}{\sqrt{RT_{A,i}} m_{A,i}} \]  

(31)

which reduces to the following after simplifying,

\[ \Omega = \left( \frac{2}{k+1} \right)^{\frac{k+1}{2(k-1)}} \]  

(32)

Equation (30) then reduces to

\[ \frac{d\Omega^{\frac{1}{k}}}{d\tau} = -\Omega \Omega^{\frac{k+1}{2k}} \]  

(33)

Simplifying Equation (33) and setting up the integral we find

\[ \int_{\frac{P_1}{P_i}}^{1-\frac{1}{k}} \frac{dP_i}{P_i^{\frac{1}{2k}}} dP_i = -k\Omega \int_0^\tau d\tau \]  

(34)

Integrating, evaluating the limits and substituting \( \Omega \) from Equation (32) we find

\[ \bar{P}_i = \left[ 1 + \frac{(k-1)}{2} \left( \frac{2}{k+1} \right)^{\frac{k+1}{2(k-1)}} \tau \right]^{\frac{2k}{1-k}} \]  

(35)

Substituting Equation (35) into Equation (27) and simplifying, we find the nondimensional temperature variation in the discharging tank, \( \bar{T}_i \), to be

\[ \bar{T}_i = \left[ 1 + \frac{(k-1)}{2} \left( \frac{2}{k+1} \right)^{\frac{k+1}{2(k-1)}} \tau \right]^{-2} \]  

(36)

Equations (35) and (36) may be modified to represent the pressure and temperature distribution in the choked flow regime by modifying Equation (32) by introducing the effect of the flow Mach number from Equation (12).
Analysis of Charging Tank

Applying the first law of thermodynamics we find that

\[ \dot{Q} - \dot{W} = \Delta E \]

Since \( U_B = 0 \) and assuming that the diameter of the charging tank is much larger than the diameter of the throat (i.e., throat velocity), is negligible and this is an isentropic charging process, we may write the following,

\[ \frac{dU_B}{dt} - \dot{m}h_A = 0 \]

which reduces to the following for an ideal gas,

\[ C_v T_B \frac{dm_B}{dt} = \dot{m}C_p T_A \]  \hspace{1cm} (37)

where the mass flow rate is expressed by Equation (23). Nondimensionalizing and simplifying Equation (37) we find

\[ \frac{d\bar{P}_B}{d\tau} = kX \frac{P_{A,i}^{k-1}RT_{A,i}P_{char}}{P_{B,i}^{k-1}RT_A} \sqrt{\bar{P}_A \bar{T}_A} \]  \hspace{1cm} (38)

Since the volumes of the discharging and charging tanks are identical, Equation (38) reduces to

\[ \frac{d\bar{P}_B}{d\tau} = \beta \bar{P}_A \sqrt{\bar{T}_A} \]  \hspace{1cm} (39)

where

\[ \beta = k \left( \frac{2}{k+1} \right)^{\frac{k+1}{2(k-1)}} P_{A,i} \]

Using the isentropic relations, we find

\[ \bar{P}_A \sqrt{\bar{T}_A} = \bar{P}_A \bar{P}_A^{\frac{k-1}{k}} \]
Substituting Equation (35) for any nondimensional pressure terms that appear, and simplifying, Equation (39) reduces to

\[
\frac{d\bar{P}_B}{d\tau} = \beta \left[ 1 + \frac{(k-1)}{2} \left( \frac{2}{k+1} \right)^{\frac{k+1}{2(k-1)}} \tau \right]^{\frac{3k-1}{1-k}}
\]

(40)

A change of variables is needed in order to integrate Equation (40). Let

\[
\varphi = 1 + \frac{(k-1)}{2} \left( \frac{2}{k+1} \right)^{\frac{k+1}{2(k-1)}} \tau
\]

Applying the change of variables, simplifying and setting up the integral of Equation (40) the following equation may be written

\[
\int_{\tau_1}^{\tau_2} d\bar{P}_B = \frac{2k}{(k-1)} \frac{P_{A,i}}{P_{B,i}} \frac{\varphi^{\frac{3k-1}{1-k}}}{\varphi^{\frac{1}{1-k}}} d\varphi
\]

(41)

By integrating, applying the limits, and changing back the variables we find that the nondimensional pressure in the charging tank to be

\[
\bar{P}_B = 1 + \frac{P_{A,i}}{P_{B,i}} \left[ 1 - \left( 1 + \frac{(k-1)}{2} \left( \frac{2}{k+1} \right)^{\frac{k+1}{2(k-1)}} \tau \right)^{\frac{2k}{1-k}} \right]^{\frac{1}{1-k}}
\]

(42)

From the definition of the mass flow rate in the charging tank, tank B, we may find the nondimensional temperature variation (\(\bar{T}_B\)). By Nondimensionalizing the definition of pressure in the charging tank from the ideal gas equation of state the following may be written

\[
\bar{P}_B = \bar{T}_B \frac{RT}{\bar{P}_{B,i}} m_B
\]

(43)

An expression for the total mass that accumulates in the charging tank may be written as
where $\bar{m}$ is the nondimensional mass flow rate. The nondimensional mass flow rate may be written as

$$\bar{m} = \left( \frac{2}{k+1} \right)^{\frac{k+1}{2(k-1)}} \frac{P_{A,i}V_p - P_A}{RT_i \sqrt{T_A}}$$

(45)

Substituting Equation (45) into the expression of the mass flow rate in Equation (44) we find

$$m_B = \frac{P_{A,i}V_p}{RT_i} + \left( \frac{2}{k+1} \right)^{\frac{k+1}{2(k-1)}} \frac{P_{A,i}V_p}{RT_i} \int_0^\tau \frac{\bar{P}_d}{\sqrt{T_A}} d\tau$$

(46)

Finding an appropriate form of $\frac{\bar{P}_d}{\sqrt{T_A}}$ will enable us to solve the integral. By substituting Equation (35) into Equation (29) we may write

$$\frac{\bar{P}_d}{\sqrt{T_A}} = \left[ 1 + \lambda \tau \right]^{\frac{k+1}{1-k}}$$

(47)

where

$$\lambda = \frac{k-1}{2} \left( \frac{2}{k+1} \right)^{\frac{k+1}{2(k-1)}}$$

Substituting Equation (47) into Equation (46) we find

$$m_B = \frac{P_{A,i}V_p}{RT_i} + \left( \frac{2}{k+1} \right)^{\frac{k+1}{2(k-1)}} \frac{P_{A,i}V_p}{RT_i} \int_0^\tau \left[ 1 + \lambda \tau \right]^{\frac{k+1}{1-k}} d\tau$$

By introducing a change of variables

$$\sigma = 1 + \lambda \tau$$

the mass in the charging tank reduces to
\[ m_B = \frac{P_{B,i} \nu}{RT_i} + \left( \frac{2}{k+1} \right)^{\frac{k+1}{2(k-1)}} \frac{P_{A,i} \nu}{RT_i} 1^\frac{k+1}{\lambda} \ \int_\omega^{1-k} d\omega \]  

Integrating and simplifying Equation (48) yields,

\[ m_B = \frac{P_{B,i} \nu}{RT_i} + \frac{P_{A,i} \nu}{RT_i} \left(1 - \omega^{\frac{2}{1-k}}\right) \]  

(49)

By substituting Equation (49) into Equation (43) we find

\[ \bar{T}_B \left[ 1 + \frac{P_{A,i}}{P_{B,i}} \left(1 - \omega^{\frac{2}{1-k}}\right) \right] = \bar{P}_B \]  

(50)

Simplifying Equation (50) we find the dimensionless variation of temperature in the charging tank to be

\[ \bar{T}_B = \frac{\bar{P}_B}{1 + \frac{P_{A,i}}{P_{B,i}} \left[1 - \left(1 + \frac{k-1}{2} \left(\frac{2}{k+1}\right)^{\frac{k+1}{2(k-1)}} \right)^{\frac{2}{1-k}}\right]} \]  

(51)

Similar expressions may be derived for the pressure and temperature distributions in the charging tank during the unchoked flow regime by modifying Equation (42) with the flow Mach number expression of Equation (12).
CHAPTER 3
TRANSFER OF LIQUID HYDROGEN

As mentioned previously, the storage and transportation of liquid hydrogen is hindered by several issues. These issues include the fact that additional complexities arise from the fact that liquid hydrogen’s heat of vaporization is extremely low. The slightest change in the cross-sectional flow area (i.e., the resulting throat area) will result in a pressure drop that will take the saturated liquid into the two-phase region. This makes the slightest change in properties a key factor in determining the amount of liquid hydrogen that boils off. The assumptions and equations used in the analysis of the transfer process are briefly discussed below.

Heat Transfer Model

This section explains the transient model that was used to describe the heat transfer to the liquid in both the discharging and charging tanks. As stated earlier in the Introduction, this study does not account for the heat losses that may arise from imperfections in the exterior insulation or the effects that various types of insulation may have on heat loss. In fact, this section is devoted to the heat transfer that occurs internally from the thermal mass of the storage tank wall to the fluid. This assumption may be of significance since the heat gain from the thermal mass of the storage tank walls may have a greater contribution to boil-off losses than the losses associated with heat gains from imperfections in the exterior insulation.

An analytical closed form solution was used to model the heat transfer to the liquid hydrogen. The assumption that has been made is that the thickness of the storage tank
wall is much smaller than the radius of the storage tank. This assumption allows for the use of the cartesian conduction equation, Equation (52), which is solved along with the boundary and initial conditions [11] for either the discharging or charging tanks:

\[
\frac{\partial^2 T}{\partial x^2} = \frac{1}{\alpha} \frac{\partial T}{\partial t} \tag{52}
\]

\[
\frac{\partial T}{\partial x} \bigg|_{x=0} = 0 \tag{53}
\]

\[
T(x = L) = T_{A,B}(r) \tag{54}
\]

\[
T(x, t = 0) = T_0 \tag{55}
\]

where \(T_{A,B}(r)\) is the bulk temperature of the fluid in the storage tank. The subscript \(A,B\) denotes that it applies to both the discharging and charging tanks respectively. \(T_{A,B}(r)\) is also the temperature of the surface that is in contact with the fluid. The model analyzes the limiting case of an infinitely large heat transfer coefficient.

The present study assumes the initial temperature of the discharging tank wall to be the saturation temperature of \(H_2\) at the initial pressure. The initial temperature of the charging tank wall was varied between 30 K and 100 K to emphasize the importance of pre-cooling as discussed earlier in Chapter 1. For the special case of a constant initial temperature, \(T_0=\text{constant}\), the solution of the general differential equation yields the temperature distribution within the tank-walls which is found to be

\[
T(x, t) = T_s(r) + \frac{2T_s}{L} \sum_{m=1}^{\infty} e^{-\alpha \beta m} \frac{\cos(\beta_n x)}{\beta_n} \cdot \sin(\beta_n L) \tag{56}
\]

which implies that the heat flux at the surface of the storage tanks is,

\[
q_s(x, t) = \frac{kT_s}{L} \sum_{m=1}^{\infty} e^{-\alpha \beta m} \sin(\beta_n x) \cdot \sin(\beta_n L) \tag{57}
\]
where $\beta_m$ are the roots that satisfy the equation

$$\cos(\beta_m L) = 0$$

(58)

Various complexities arise when modeling the heat transfer process in the storage tanks. These issues include but are not limited to nucleate pool boiling of the liquid, the heat transfer induced by free convection, radial conduction in the storage tank-walls, and the heat of condensation of the vapor in the charging tank. These effects have been neglected in the present study.

**Thermophysical Properties**

In this model the storage tanks were assumed to be constructed from 304 stainless steel. This material is among the most extensively used for tank and vessel construction. Although current literature contains a great deal of data concerning cryogenic material properties, convenient forms of this data are unavailable and would not be suitable for modeling purposes. Marquardt et al. [12] have collected, compiled and correlated thermal conductivity ($k_t$) and specific heat ($C_p$) data for numerous materials, which include 304 stainless steel. These correlations introduce errors of 2 and 5% in $k_t$ and $C_p$ respectively and are useful for temperature ranges of 4 to 300 K.

**Means of Storage**

In this study, the effect of storage size was also studied. Flynn [13] lists some of the typical storage systems that are currently used to store liquid hydrogen. Table 1 is a modified adaptation of what Flynn [13] has listed.
Table 1. Summary of current liquid-hydrogen storage and transportation means

<table>
<thead>
<tr>
<th>Container</th>
<th>Capacity (m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transportation</td>
<td></td>
</tr>
<tr>
<td>Over-the-road tankers*</td>
<td>53</td>
</tr>
<tr>
<td>Seagoing containers</td>
<td>42</td>
</tr>
<tr>
<td>Inland waterway barges</td>
<td>946</td>
</tr>
<tr>
<td>Railcars*</td>
<td>117</td>
</tr>
<tr>
<td>Storage</td>
<td></td>
</tr>
<tr>
<td>Large tanks</td>
<td></td>
</tr>
<tr>
<td>Spheres at Kennedy Space Center</td>
<td>3,142</td>
</tr>
<tr>
<td>Spheres at Air Products' New Orleans Plant</td>
<td>1,893</td>
</tr>
<tr>
<td>Horizontal cylinders at Air Products' Sacramento Plant</td>
<td>265</td>
</tr>
<tr>
<td>Customer tanks</td>
<td></td>
</tr>
<tr>
<td>Horizontal/vertical cylinder*</td>
<td>20</td>
</tr>
<tr>
<td>Horizontal cylinder*</td>
<td>55</td>
</tr>
<tr>
<td>* Average Capacity</td>
<td></td>
</tr>
</tbody>
</table>

Barbir et al. [14] discussed the contribution of tank volume and shape to boil-off. They reported that the most favorable storage vessel shape that minimizes boil-off losses associated with heat leaks is that of a sphere. This is due to the fact that losses are proportional to the ratio of surface area to the volume of the storage vessel. Spherical storage vessels are favored for their low surface to volume ratio as well as their excellent mechanical strength. Ewe and Selbach [15] found that the boil-off rate associated with heat leaks will decrease as the storage vessel size is increased. They have reported boil-off rates ranging from 0.06 to 0.5 percent per day for various vessels ranging in volume from 50 m³ to 19000 m³. Taylor et al. [16] reported that the spherical storage dewars that the National Aeronautics and Space Administration (NASA) use, usually have a boil-off rate of approximately 600,000 liters per year. Barbir et al. [14] have also noted that the rate of boil-off does not greatly decrease with an increase in the size of a
cylindrical vessel of constant diameter. For the purpose of this study, the discharging and the charging storage vessels are assumed to be spherical.

**Modeling of the Transfer Process**

The computer program calculates the transient conditions in the storage tanks. It includes both the choked and unchoked flow regimes. The properties of liquid hydrogen were obtained from NIST REFPROP 7.0 [17], a commercially available software package that was interfaced with the program. The heat transfer rate $\dot{Q}$, in either tank, is obtained by multiplying the result of Equation (57) by the internal surface area of the storage tank being analyzed.

**Analysis in the Choked-Flow Regime**

By neglecting the initial mass of vapor in the discharging tank and knowing the initial tank pressure, the initial state of the throat may be calculated. To obtain the state properties, we initially estimate that $P_t = P_A$ and $s_t = s_A$. The speed of sound at the throat is found by employing Equation (59). The ‘s’ in Equation (59) denotes an isentropic process. The velocity in the discharging tank is zero and therefore the energy balance between the discharging tank and the throat reduces to Equation (60).

$$a_t = \sqrt{(\frac{\partial P}{\partial \rho})_s}$$

(59)

$$V_t = \sqrt{2(h_d - h_i)}$$

(60)

$$M_t = \frac{V_t}{a_t}$$

(61)

Using Equations (59), (60) and (61), an iterative procedure changes the pressure of the throat $P_t$, and calculates the speed of sound and velocity at the throat for this choked
flow until a Mach number equal to unity is obtained. It is noted that heat transfer is neglected in the transfer line.

By solving the continuity and energy equations, Equations (62) and (63) simultaneously

\[
\begin{align*}
\frac{dm_A}{dt} &= -\dot{m} \\
\dot{Q}_A - \dot{m}h_A &= \frac{dU_A}{dt}
\end{align*}
\]  

(62)

(63)

the state properties of the discharging tank at the new time step can be found. In Equation (63) \( h_A \) is assumed to be the enthalpy of the saturated liquid that is being discharged. A check may be made by computing the entropy obtained at this new time step by the state relations and the entropy obtained from equating, Equation (64), the second law.

\[
\frac{\dot{Q}_A}{T_A} - \dot{m}S_A = \frac{dS_A}{dt}
\]  

(64)

Spatial gradients of pressure and temperature are neglected in the analysis of both the discharging and charging tanks.

Assuming that the charging tank has an initial mass (all saturated vapor) at a known pressure, the initial state properties in the charging tank can then be found. To find the state properties at the next time step, the continuity and energy equations, Equations (65) and (66),

\[
\begin{align*}
\frac{dm_B}{dt} &= \dot{m} \\
\dot{Q}_B + \dot{m}(h_B + \frac{V_B^2}{2}) &= \frac{dU_B}{dt}
\end{align*}
\]  

(65)

(66)
are solved simultaneously. In Equation (65), $h_t$ and $V_t$, are, respectively, the enthalpy and velocity of the two-phase flow exiting the throat that correspond to a Mach number equal to unity.

To solve and obtain useful data, Equations (62) thru (66), must first be written in a finite difference notation and nondimensionalized. All the variables in Equations (59) thru (66) contain the three basic dimensions $m$, $L$, $V$, except the second law, Equation (64). Since entropy and temperature are of importance to this analysis we introduce a fourth basic dimension, $T$. The reference constants, denoted by the letter $c$, which might be characteristic of the fluid flow and heat transfer processes are

Reference mass = $m_c$ 
Reference velocity = $V_c$
Reference length = $L_c$ 
Reference temperature = $T_c$

These reference constants are usually defined depending on the type of application worked on and the type of analysis that is required. In this study, for example, the reference length was chosen as the diameter of the largest discharging tank analyzed (6.2035 m), the reference mass as the approximate total mass that has been transferred to the charging tank (2300 kg), the reference temperature as the boiling point of para-hydrogen at the initial pressure in the discharging tank and the reference velocity being the initial speed of sound at the throat (138.5 m/s).

Defining all the relevant dimensionless variables, and denoting them by an asterisk we find

$$m^* = \frac{m}{m_c}, \quad t^* = \frac{tV}{L_c}, \quad \dot{m}^* = \frac{\dot{m}}{m_c}, \quad h^* = \frac{h}{L^2_c}, \quad \dot{Q}^* = \frac{\dot{Q}L^3_c}{L^2_c m_c}, \quad P^* = \frac{P L_c^3}{m_c V^2_c},$$

$$T^* = \frac{T}{T_c}, \quad \rho^* = \frac{\rho L_c^3}{m_c}, \quad s^* = \frac{s L_c^2}{t_c \rho}, \quad V^* = \frac{V}{V_c}, \quad D^* = \frac{D}{L_c}, \quad \nu^* = \frac{\nu}{L_c}$$
where $V$ denotes the volume of the storage tank.

By introducing the nondimensional variables into Equations (62) thru (64) and writing the equations in a finite difference notation we obtain the following

$$V_A^* \left( \rho_A^{n+1} - \rho_A^n \right) \Delta t^* = -\dot{m}_A^n$$ \hspace{1cm} (67)

$$\dot{Q}_A^n - \dot{m}_A^n h_A^n = \rho_A^n V_A^* \left( \frac{u_A^{n+1} - u_A^n}{\Delta t^*} \right) + u_A^n V_A^* \left( \frac{\rho_A^{n+1} - \rho_A^n}{\Delta t^*} \right)$$ \hspace{1cm} (68)

$$\frac{\dot{Q}_A^n}{T_A^n} - \dot{m}_A^n s_A^n = \rho_A^n V_A^* \left( \frac{s_A^{n+1} - s_A^n}{\Delta t^*} \right) + s_A^n V_A^* \left( \frac{\rho_A^{n+1} - \rho_A^n}{\Delta t^*} \right)$$ \hspace{1cm} (69)

The governing equations for the analysis of the charging tank, Equations (65) and (66), can be written in a similar fashion and are found to be as follows:

$$\rho_B^n V_B^* \left( \frac{u_B^{n+1} - u_B^n}{\Delta t^*} \right) = \dot{m}_B^n$$ \hspace{1cm} (70)

$$\dot{Q}_B^n + \dot{m}_B^n \left( h_B^n + V_B^n \right) = \rho_B^n V_B^* \left( \frac{u_B^{n+1} - u_B^n}{\Delta t^*} \right) + u_B^n V_B^* \left( \frac{\rho_B^{n+1} - \rho_B^n}{\Delta t^*} \right)$$ \hspace{1cm} (71)

A similar method of solution is utilized as described above when describing the solution to the nondimensional forms of the governing equations. Equations (52) to (55) may be nondimensionalized in a similar fashion.

The program switches the analysis from a choked flow regime to an unchoked flow regime when the throat pressure is equal to the rising back-pressure of the charging tank. To ensure accurate results, an extra fine convergence criterion and time differential were used in the computer code.
Analysis of the Unchoked-Flow Regime

In this regime, the state at the throat can be calculated at every time step. In the calculation procedure the transfer of liquid from the discharging tank to the throat condition is assumed to be an isentropic process and the throat pressure to be equal to the pressure in the charging tank (back-pressure). Equations (67), (68), (70), and (71) are solved to find the state properties at the new time step for both the charging and discharging tanks, respectively.
CHAPTER 4
RESULTS AND DISCUSSION

In this chapter, the impact of the variation of several key parameters on system variables, namely pressure and temperature time histories, will be discussed in great detail for the transfer of liquid hydrogen and in brief for the transfer of gaseous hydrogen. In addition, the effects of initial pressure, storage volumes and the thermal capacity of the storage tank walls on the percent boil-off of liquid hydrogen will also be discussed.

Transfer of Liquid Hydrogen

The understanding of how boil-off losses arise from the change in system variables is of extreme importance. To understand those variables that have the greatest effect on boil-off losses of liquid hydrogen during a transfer process, the state points during the transfer process must be calculated on a transient basis in both the choked and unchoked flow regimes. For all simulations the system specifications were assumed to be invariant, unless otherwise stated. The values of the key system inputs, namely the throat diameter, storage tank volumes, as well as initial pressures in both the discharging and charging tanks are summarized below each figure. The nondimensional forms of the key system inputs are also shown for quick reference.

Figure 2 shows the variation of temperature in the discharging and charging tanks as well as the throat area with respect to time for adiabatic storage conditions. The bulk temperature observed in the charging tank at which the fluid undergoes a change in flow regime, which is at approximately \( t^* = 362 \), is 0.66 of the maximum temperature observed.
which is about 25 K. The bulk temperature increases to a nondimensional equilibrium temperature of 0.704 (26.2 K), at the end of the transfer process.

Figure 3 shows the pressure-time history for spherical discharging and charging tanks of nondimensional volume of 0.314 (75 m$^3$) and a nondimensional throat diameter of 0.0242 (0.15 m or 6 inches). For this adiabatic transfer, one sees a transition from a choked to an unchoked flow regime after approximately $t^*=362$. This occurs when the pressure at the throat is equal to the backpressure in the charging tank. Pressure equilibrium in the discharging and charging tanks occurs at a nondimensional pressure of 0.41. The variation of the pressure at the end of the fluid transfer process can be seen to be almost negligible (slope of zero). The nondimensional pressure in the charging tank increases by 0.056 (55.6 kPa) during the final 43% of the time where the flow is unchoked. This contrasts with a nondimensional pressure increase of 0.33 (359 kPa) during the initial 57% of the time where the flow is in the choked flow regime. This is due to the fact that theoretically it would take an infinite amount of time to reach pressure equilibrium between the discharging and charging tanks. The curves in Figure 2 also follow the same general trends including the approximate slope of zero towards the end of the transfer process.

A comparison of the pressure variations in the discharging tank for various storage tank volumes is shown in Figure 4. Again, the volumes of both tanks are identical. It can be seen that the time needed to reach pressure equilibrium for a storage tank whose nondimensional volume is 0.524 (125 m$^3$) is approximately 28 times that required for a storage tank whose nondimensional volume is 0.02 (5 m$^3$). It can also be seen that the
equilibrium nondimensional pressure is approximately 0.41 for all the various storage
volumes considered, with the exception of the smaller tanks.

Figure 5 compares the nondimensional pressure distribution as a function of
nondimensional time in the adiabatic charging tank for various nondimensional charging
tank volumes. The charging tanks are assumed to be at an initial nondimensional
pressure of zero (vacuum) and contain an insignificant initial mass of vaporized
hydrogen. It can be seen that as the volume of the charging tank increases, (a) the time it
takes to reach pressure equilibrium also increases, (b) the linear trend in the unchoked
flow regime becomes more evident, and (c) the nondimensional equilibrium pressure is
0.41 for larger nondimensional storage volumes but is about 2-5% higher for the smaller
ones.

Figure 6 shows the variation of nondimensional mass transferred to the adiabatic
charging tank whose nondimensional volume is 0.25 (60 m$^3$) with respect to
nondimensional time. The mass transferred is nondimensionalized by dividing it by the
maximum mass that is transferred to the charging tank. It can be seen that the final mass
of vapor levels off at approximately m*=0.21 (233 kg). It should be noted that the vapor
mass curve is horizontal after approximately t*=290. Competing effects cause this trend.
The drop in pressure causes some of the incoming liquid to flash, but the increasing
pressure in the charging tank re-condenses some of the vapor. Both the liquid and total
mass transferred to the charging tank increase linearly until about 85% of the total time of
transfer. At that point the increase in accumulated mass is seen to start decreasing. This
is due to the fact that as the pressure differential in the discharging and charging tanks
decreases and approaches zero, the velocity and mass flow rate decreases as pressure equilibrium approaches.

Figure 7 shows the variation of the boil-off percentage as a function of nondimensional time for various adiabatic storage volumes. The discharging tank is initially at a nondimensional pressure equal to unity (1000 kPa) in all cases. It can be seen that the percentage boil-off is higher at the beginning of the fluid transfer process (as much as 37%), and can be seen to decrease to about 21% for the larger tanks and about 23-27% for the smaller tanks at the end of the fluid transfer process. Other figures similar to Figure 7 may be generated for different levels of initial discharging tank pressure. This figure could help select the appropriate discharging tank volume to meet constraints dealing with the time allotted for discharging. These results agree with the reasoning of Sherif et al. [4] and the obvious advantage of transferring and storing liquid hydrogen in large tanks. This is also advantageous since the cost per unit volume of stored hydrogen in a larger storage tank is lower than that of hydrogen stored in smaller storage tanks.

In some cases, the percentage boil-off curves may appear to be irregular (i.e., not smooth). This is apparent in Figure 7’s percent boil-off curve associated with the nondimensional storage tank volume of 0.17. This irregularity occurs at the point of unchoking. The change in rate of boil-off is lower in the unchoked flow regime than in the choked flow regime since the pressure differential between the two tanks is smaller, the velocity of the transfer fluid is lower and therefore the mass flow rate of the liquid is smaller. These changes result in the decrease of the amount of saturated liquid that
undergoes phase change while being transferred from the discharging tank to the charging tank.

Figure 8 shows the variation of the percent boil-off as a function of the percent of mass transferred to the adiabatic charging tank for various storage volumes. During the initial stages of transfer a large percentage of the mass transferred is boiled-off. As the percent of mass transferred to the charging tank increases, the percent boil-off is seen to decrease linearly. It can also be seen that as the storage tank volume decreases the amount of boil-off for the various curves become identical throughout the later stages of the fluid transfer process. The minimum and maximum boil-off percentages (21 and 71%), correspond to 0 and 100% of the total mass transferred, respectively. Depending upon the quantity of mass to be transferred it may be concluded that any storage tank volume may be selected in order to minimize boil-off losses.

Variation of the initial pressure in the discharging tank while keeping the charging tank at a constant initial pressure and mass seems to have a significant effect on the pressure variation in both the discharging and charging tanks and the amount of liquid hydrogen that boils off as a result. For reference, the critical pressure of para-hydrogen is 1268 kPa.

In Figure 9 it can be seen that the nondimensional pressure variation in the adiabatic discharging tank as function of time varies significantly for different initial pressures in the adiabatic discharging tank. The initial pressures have been nondimensionalized by the highest pressure analyzed (the near critical pressure of 1250 kPa). It can be seen that the rate of decrease of pressure increases as the initial pressure in the discharging tank increases. High rates of pressure reduction are not desired since
the resultant percent boil-off may be larger. The time needed to reach pressure
equilibrium can also be seen to be substantially longer for lower initial pressures in the
discharging tank.

Figure 10 shows the variation of nondimensional pressure in the adiabatic charging
tank as a function of time for various initial pressures in the adiabatic discharging tank.
A higher rate of increase in pressure in the charging tank and a longer time needed to
reach pressure equilibrium can be observed.

As stated earlier, the trends observed in Figures 9 and 10 have a significant effect
on the amount of liquid hydrogen that boils off. Figure 11 presents the variation of
percent boil-off in the charging tank as a function of nondimensional time for various
initial pressures in the discharging tank. Both storage tanks are assumed to be adiabatic.
The maximum amount of boil-off initially is 77% and corresponds to a near critical
pressure of 1250 kPa. The maximum amount of boil-off for the various initial pressure
curves occurs in the initial stages of transfer. This result signifies the fact that as the
pressure differential between the discharging and charging tank decreases, the liquid
transferred is mostly vaporized in the initial stages of transfer. It can also be seen that as
the initial pressure increases in the discharging tank, the boil-off rate will increase in the
initial stages of transfer. This is the result of the increasing percentage of liquid
vaporizing almost instantaneously as it meets a lower pressure in the charging tank. The
minimum amount of boil-off corresponds to $P^* = 0.2$ and is about 4.6% at the end of the
fluid transfer process. The trends from Figure 11 agree with the recommendation made
by Sherif et al. [4] that, in order to minimize boil-off losses due to flashing, or the sudden
vaporization of liquid due to the pressure differential between the storage tanks, the transfer of liquid should be carried out at atmospheric or near atmospheric pressures.

The variation of the percent boil-off as a function of the percent of total mass transferred to the adiabatic charging tank for various initial nondimensional discharging tank pressures is shown in Figure 12. It is evident that the maximum and minimum percent boil-off occur when the percent of mass transferred ranges form 0 to 100 percent for nondimensional pressures of 0.2 and 1.2, respectively. These general trends also support the conclusions made by Sherif et al. [4] and supported by the discussion of Figure 11 found in the preceding paragraph.

It was found that by accounting for the heat flux that resulted from the thermal mass of the tank wall, the pressure equilibrium between the two storage tanks would be reached at a faster rate than when compared with the adiabatic case. This can be seen in Figure 13, which shows the pressure variation as a function of time for both adiabatic and nonadiabatic storage conditions in the charging tank. Both storage tanks were assumed to be spherical tanks with a nondimensional volume of 0.314 (75 m$^3$) and a nondimensional shell thickness of 0.081 (0.048 m or 1.9 inches). Initially, the temperature of the storage tank-wall in the discharging tank was assumed to be the saturation temperature of para-$\text{H}_2$ at the initial pressure 1 MPa (which is 31.268 K). The initial temperature was varied in the charging tank between 30 K and 100 K to show how crucial the “thermodynamic” filling technique discussed in Chapter 1 is. It can be seen from Figure 13 that if the initial temperature in the charging tank was 30 K, the time needed for the storage tanks to reach an equilibrium nondimensional pressure of 0.435 would be $t^*=485$. This is 5.8% less than the time required for the adiabatic case whose equilibrium nondimensional pressure
is 0.41. In the case of a high initial tank-wall temperature, 100 K, the equilibrium nondimensional pressure of 0.471 would be reached in 15% less time than the adiabatic case. This rapid increase in pressure is undesirable due to substantially larger resulting boil-off losses which can be seen in Figures 14 and 15.

Figure 14 shows the variation of the percent boil-off with respect to time for both the adiabatic and nonadiabatic cases in the charging tank. The range of difference in percent boil-off between the adiabatic and the nonadiabatic curve (T₀ =30 K) is 1-5% corresponding to the end of the fluid transfer process and during the initial stages, respectively. The transition point between the choked and unchoked flow regimes is apparent for the all three cases. The apparent advantage of pre-cooling the tank-wall is evident by comparing the minimum and maximum percent boil-off differences between the two nonadiabatic cases. There is a continuous 10-20% boil-off difference throughout the fluid transfer processes of the two fluids. The time needed for the tanks in the T₀=100 K nonadiabatic case to reach pressure equilibrium is about 15% and 5.8% less than the times needed for the adiabatic and T₀=30 K nonadiabatic cases, respectively. This is attributed to the fact that as the heat addition from the thermal mass of the tank-wall increases, the higher the rate of pressure increase in the charging tank becomes. This may also be concluded from examining Figure 13.

Similar conclusions can be made about Figure 15. Figure 15 shows the variation of the percent boil-off as a function of the percent mass that is transferred to the charging tank for both adiabatic and nonadiabatic storage conditions. A 4-5% continuous difference exists between the pre-cooled and adiabatic cases.
Figure 16 shows the amount of mass transferred to the charging tank as a function of time for both adiabatic and nonadiabatic storage conditions. In the nonadiabatic case where the initial tank-wall temperature is 100 K it takes about 17% less time to reach pressure equilibrium between the two storage tanks than the adiabatic case. In this time, only about 87% of the mass (965 kg) is transferred to the charging tank when compared with the adiabatic case. Of the mass transferred, it can be seen that up to 26% has boiled-off and is vapor, in contrast to the 21% boil-off in the adiabatic case. The liquid mass that is transferred can be seen to increase dramatically as the mass of the vapor transferred nears a maximum. This maximum occurs after approximately 54% of the total transfer time in the nonadiabatic ($T_o=100$ K) case. The comparison of the results obtained for the pre-cooled nonadiabatic and adiabatic cases show that only minor differences exist in the quantities of mass transferred.

Similar figures, for the nonadiabatic cases, may be plotted for the variation of pressure, temperature, percent boil-off and amounts of liquid/vapor transferred as a function of time and percent of mass transferred. They may be analyzed for various initial pressures, storage tank volumes, and throat-to-inlet area ratios. Similar trends to those obtained in the adiabatic case are expected.

There exists a possibility for analyzing different cryogens or storage systems since the computer program written has no restriction to the type of fluid, storage tank geometry or storage tank-wall material that may be used. This is because the properties of para-hydrogen and 304 stainless-steel have not been hard-coded into the model.

**Transfer of Gaseous Hydrogen**

In the case of the transfer of gaseous hydrogen it was found that the pressure and temperature time histories are greatly dependent upon the specific heat ratio in the
isothermal case. In the adiabatic case it was found that along with the specific heat ratio, the inlet-to-throat area ratio as well as the flow Mach number had a big effect on the temperature and pressure variation during the unchoked flow regime. The nonadiabatic analysis was not included in this study since Dutton and Coverdill [18] have found experimentally that the pressure and temperature distributions of the nonadiabatic case had very good agreement with both the isothermal and adiabatic cases. They have shown experimentally that for a small tank (4,920 cm$^3$) with a large throat diameter (fast discharge and filling) the adiabatic assumption is valid. They have also shown that for a large tank (29,100 cm$^3$) with a small throat diameter (slow discharge and filling) the isothermal assumption is valid. These results are expected to be valid for the larger storage tanks (up to 4,300 times larger) analyzed in this study.

The variation of nondimensional pressures in the discharging and charging tanks for both isothermal and adiabatic storage/transfer conditions can be seen in Figures 17 and 18, respectively. The unchoking points in Figures 17 and 18 are evident.
Figure 2. Variation of temperature as a function of time for the throat conditions, discharging and charging tank conditions for the adiabatic case. \( D_i^* = 0.0242, \quad P_A^* = 0.007942, \quad P_{B,i}^* = 0, \quad \nu_A^* = \nu_B^* = 0.314 \)
Figure 3. Variation of pressure as a function of time for the throat conditions, discharging and charging tank conditions for the adiabatic case. $D^*_i = 0.0242$, $P^*_{A,i} = 0.007942$, $P^*_{B,i} = 0$, $\nu^*_A = \nu^*_B = 0.314$, $P^*_* = \frac{PL^3}{mV_c^2}$.
Figure 4. Variation of pressure in the adiabatic discharging tank as a function of time for various storage volumes. $V_A^* = V_B^*$, $D_L = 0.0242$, $P_{A,i} = 0.007942$, $P_{B,i} = 0$, $p^* = \frac{PL_i}{m_V c_s^2}$
Figure 5. Variation of pressure in the adiabatic charging tank as a function of time for various storage volumes. $\frac{P^*}{P_{\text{max}}^*-P_{\text{min}}^*} = \Phi^*$, $D^* = 0.0242$, $P_{\text{t}^*} = 0.007942$, $P_{\text{b}^*} = 0$, $p^* = \frac{PL^3}{mV_c^2}$.
Figure 6. Variation of mass transferred to the adiabatic charging tank as a function of time. $t^* = t V_c/L_c$.

Total Mass
Liquid Mass
Vapor Mass

$\rho_{A}^* = \rho_{B}^* = 0.25, D_i^* = 0.0242, P_{A,i}^* = 0.007942, P_{B,i}^* = 0$
Figure 7. Variation of percent boil-off in the adiabatic charging tank as a function of time for various storage volumes. $V_A^* = V_B^*, D_1 = 0.0242, P_{A,j}^* = 0.007942, P_{B,j}^* = 0$
Figure 8. Variation of percent boil-off as a function of the mass transferred to the adiabatic charging tank for various storage volumes.

\( V_j^* = V_B^* \), \( D_j = 0.0242 \), \( P_{A,j} = 1 \), \( P_{B,j} = 0 \)
Figure 9. Variation of pressure in the discharging tank as a function of time for various initial pressures in the adiabatic discharging tank \( P^* \). \( \nabla_A^* = \nabla_B^* = 0.25, D_t = 0.0242, P^*_{B,t} = 0, P = \frac{P' - P_{\text{min}}}{P_{\text{max}} - P_{\text{min}}} \)
Figure 10. Variation of pressure in the charging tank as a function of time for various initial pressures in the adiabatic discharging tank $(P_{A,i}^*, P_{B,i}^*). \ V_A^* = V_B^* = 0.25, D_t^* = 0.0242, \ P_{B,i}^* = 0, \ p^* = \frac{p' - p_{\text{min}}'}{p_{\text{max}}' - p_{\text{min}}'}$
Figure 11. Variation of percent boil-off in the charging tank as a function of time for various initial pressures in the adiabatic discharging tank ($P_{\text{A},i}$). $\nu_A^* = \nu_B^* = 0.25$, $D_i^* = 0.0242$, $P_{B,i}^* = 0$
Figure 12. Variation of percent boil-off in the charging tank as a function of the percent of mass transferred to the charging tank for various initial pressures in the adiabatic discharging tank ($P_A^*$). $\mathcal{V}_A^* = \mathcal{V}_B^* = 0.25, D_i^* = 0.0242, P_{B,i}^* = 0$
Figure 13. Variation of pressure in the charging tank as a function of the time for adiabatic and nonadiabatic storage conditions.

$p^* = \frac{pL}{P_{A^*}} = 0.314, D_t = 0.0242, P_{A^*} = 0.007942, P_{B^*} = 0, \frac{P' - P_{in}}{P_{max} - P_{min}}$
Figure 14. Variation of pressure in the charging tank as a function of the time for adiabatic and nonadiabatic storage conditions.

\( \frac{V}{V_c} = 0.314, \; \frac{D}{D_c} = 0.0242, \; \frac{P}{P_A} = 0.007942, \; \frac{P}{P_B} = 0 \)
Figure 15. Variation of percent boil-off in the charging tank as a function of the percent of mass transferred for adiabatic and nonadiabatic storage conditions. \( \nu^*_A = \nu^*_B = 0.314, D^*_I = 0.0242, P^*_{A,i} = 0.007942, P^*_{B,i} = 0 \)
Figure 16. Variation of mass transferred to the charging tank as a function of time for adiabatic and nonadiabatic storage conditions.

\[ \frac{m}{m_c} = 0.314, \quad D_t = 0.0242, \quad P_{d,j} = 0.007942, \quad P_{b,j} = 0 \]
Figure 17. Variation of pressure in the discharging tank as a function of time for adiabatic and isothermal storage conditions during a gaseous hydrogen discharge, $p^* = \frac{p}{p_i}$, $t^* = \frac{t_A^* \sqrt{kR_t}}{\zeta}$.
Figure 18. Variation of pressure in the charging tank as a function of time for adiabatic and isothermal storage conditions during a gaseous hydrogen charge, \( \frac{P^*}{P_i}, t^* = \frac{t_A^*}{\sqrt{kR_i}} \)
The analysis presented in this study examined the transfer of liquid and gaseous hydrogen in storage and transportation mediums currently used, to determine the parameters that most significantly influence liquid hydrogen boil-off. The following conclusions may be drawn:

- The total fraction of boil-off is greatly dependent on the initial pressure in the discharging tank at a constant initial pressure in the charging tank.
- It can be seen that the total heat storage of the tank wall is considerable when the initial temperature of the storage tank wall is high for the range of parameters that have been analyzed in this study. Pre-cooling the tank wall is therefore vital in the reduction of boil-off losses and increasing the total fraction of liquid mass transferred.
- Smaller nondimensional tank volumes have a lower initial rate of boil-off losses. Initial boil-off losses may be reduced by 37% by utilizing a nondimensional tank volume of up to 20 times smaller. This is because a smaller nondimensional volume will correspond to a greater mass flow rate, which will result in a decrease in the initial fraction of the transferred mass that boils-off.
- The fraction of boil-off towards the end of the fluid transfer process remains constant due to competing effects that take place in the charging tank. This implies that the increase in vapor is proportional to the amount of mass transferred to the charging tank, which towards the end of the fluid transfer process also approaches zero. These competing effects are realized when a drop in pressure causes some of the incoming
liquid to vaporize (flashing) while the increase in pressure in the charging tank will re-
condense some of the vapor that has formed. These competing effects occur throughout
the fluid transfer process but towards the end of the process the flashing effect is no
longer dominant.

The analysis presented in this study will help optimize current liquid hydrogen
storage/transfer systems and therefore minimize resultant boil-off losses. Modifications
to key system variables, such as tank volumes, initial tank pressures and tank wall
temperature can then be made to satisfy time and/or quantitative constraints that may be
impinging on the specific application.

Additional complexities always arise and should be included in future models.

Future models should include:

- Investigating whether a more detailed model should be used to analyze both radial
  and axial conduction in the storage tank walls

- Modeling of the effective film coefficient by using nucleate or pool boiling
correlations (depending on the boiling regime that is experienced)

- Adding a model to analyze effects of free convection in both the discharging and
  charging tanks.

- Accounting for external heat leaks when modeling heat transfer into the tanks and the
  transfer lines

- Modeling the boundary layers that may arise from the internal flow in the transfer
  lines may also be addressed to provide more accurate results
• An approximate cost and economic optimization associated with the boil-off of liquid hydrogen. This may be an interesting and practical analysis that should be added to future studies.

• Common practices such as venting the charging tank while filling it will make the current model more flexible and realistic.

• A more detailed study of whether the pressure differential (between the two storage tanks), or the absolute value of the initial pressures (in the discharging and charging tanks), has the greatest effect on the fraction of mass that is boiled-off should be added.
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Ahmad M. Mahmoud was born in Canada and was then raised in the U.S.A and Kuwait. He received his BS from Kuwait University in 2002. While pursuing his Master of Science degree, he also worked at the University of Florida’s Industrial Assessment Center, where he gained valuable practical experience in the fields of manufacturing and energy management. The author plans to follow in his father’s footsteps and continue his on-going struggle for higher education by pursuing a Ph.D in mechanical engineering.