Compressor-Less Hydrogen Refueling Station Using Thermal Compression

Kenneth Kriha
Gas Technology Institute
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Project ID: PD126

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Overview

Timeline
• Start: August 2015
• End: August 2017
• Progress: 30% Complete

Barriers
A. Lack of Hydrogen/Carrier and Infrastructure Options Analysis
B. Reliability and Cost of Hydrogen Compression
   I. Other Fueling Site/Terminal Operations

Budget
• Total Project Funding: $625k
  o Federal Funds - $500k
  o Cost Share - $125k
• Total DOE Funds Spent*: $117,000
• Cost Share Percentage: 15%
  * as of 3/31/2016

Partners
• GTI: Lead, fueling station design, BOP specification
• LLNL: Thermodynamic modeling, experimental proof of concept
• ORNL: Cost-effective stationary storage
• Shell: Refueling station operator perspective
Objective - Demonstrate the technical and economic feasibility of the thermal compression concept for 700 bar H2 fueling stations.

Impact on DOE Barriers

A  Minimize energy loss in LH2 to GH2 refueling stations
B  Eliminate use of compressor(s)
I  Remove need of refrigeration chiller
Approach
Thermal Compression Refueling Station
Budget Period #1 (08/03/15 – 11/03/16)

Model
Transient thermodynamic station modeling
- Milestone - 02/03/16 Proof of concept
- Milestone - 05/03/16 Complete Model for Optimization
- Optimize - Minimize Capital Cost
- Minimize H2 Boil Off Losses

Evaluate
Evaluate cryogenic pressure vessel options
- Existing pressure vessel designs and innovative alternatives
- Optimize - Minimize Capital Cost
- Milestone – 11/03/16 Complete Pressure Vessel Study

Design
Establish design concept for full scale station
- Process Flow Diagram
- Balance of Plant, Heat Exchangers
- Milestone – 08/03/16 Complete PFD

Compare
Compare cost of conventional LH2 station to proposed thermal compression station.
- Go/No-Go Decision Point – 11/03/16
  Demonstrate a reduction in total (capital and operating) cost of 15%.
Approach
Thermal Compression Refueling Station
Budget Period #2 (11/03/16 – 8/03/17)

Demonstrate

Build and operate a small scale thermal compression test loop.
- Single pressure vessel (163L, 700bar, Type 3)
- 9 kg LH2 to 700 bar in < 3hrs
- Dispense at 1.5 kg/min for at least 1 minute
- Extrapolate thermodynamic system data from test loop to full-scale system
- Milestone – 05/03/17 Complete Demonstration Testing
Approach
Identification of 5 Steps of Thermal Compression Refueling

Step #1 – Fill CV with LH2

Step #2 – Heat to Increase CV Pressure

Step #3 – Vehicle Fueling

Step #4 – Recycle H2 to Dewar

Step #5 – Vent H2
Project Accomplishments
Developed strategy for thermodynamic modeling approach

Station Design
- Capacity: 400kg/24hr day
- Vehicle Capacity: 5.6 kg
- Amount Dispensed: 4.6 kg per car
- Fueling Temp: down to -40 C
- Pressure Class: H70
- Fueling Profile: from ANL (Summer, Friday)

Model Input Variables

Model Output
# and size of Cryogenic Vessels (CV)
% vented per kg H₂ delivered

Optimize
Minimize Overall Dispensing cost (Capital Cost and % Vented)
Project Accomplishments
Identified modeling framework with advantageous features for the required thermodynamic modeling

Preliminary model built on Excel (Visual Basic)
To make sure physics well captured

New modeling framework: Fortran 90

Advantages:
• Easy to manipulate (parameters sweep...)
• Same language as REFPROP
• Short computation time
• Free compilers are available

Drawbacks:
• GUI not as friendly as Excel
• Stiffer learning curve
• Debugging not straight forward

Drawbacks:
• Large file: 17280 x 180 spreadsheet for 20 CV over 24 hours, only for “Step 3”
• Long computation time per case, including “freezing”...
Project Accomplishments
Programmed, debugged, and evaluated the performance of the thermodynamic model

Two Fortran 90 sub-routines written (>2,000 lines each) to simulate:
(1) Transient cascading design to meet station demand
(2) H₂ boil-off during cryogenic vessel filling and recycling
(aka “Steps 1, 4 & 5”)

Computation time on 1 processor:
1 to 8 minutes for transient cascading
< 2 minutes for H₂ boil-off sub-routine

Screenshot of the input file for the transient cascading sub-routine
Project Accomplishments
Identified optimal size and quantity of type 3 cryogenic vessels necessary for 400kg/day hydrogen refueling station

Influence of switch pressure, time off-line and vessel volume on numbers and size of cryogenic vessels, thus material cost

- “Smaller & more vessels” designs reduce material cost, by enabling more refilling/emptying cycles per vessel
- Optimal: ~200-300 Liters, ~30 vessels
Project Accomplishment

Developed model to quantify the amount of hydrogen lost to boil off during the thermal compression process.

Boil-off occurs during Dewar/cryogenic vessel interactions due to temperature differences.
Project Accomplishment
Defined the limits of the refueling station’s design and operating parameters

- Tested 1000’s of combinations of the 10 input parameters to explore best design and operating conditions that minimize boil-off, using a quasi Monte Carlo low discrepancy screening method (Sobol sequence)

<table>
<thead>
<tr>
<th>#</th>
<th>Design parameters</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CV rated pressure [bara]</td>
<td>700</td>
<td>900</td>
</tr>
<tr>
<td>2</td>
<td>CV volume [Liters]</td>
<td>100</td>
<td>1,000</td>
</tr>
<tr>
<td>3</td>
<td>CV L/D ratio [-]</td>
<td>1</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>Dewar rated pressure [bara]</td>
<td>1.5</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>Dewar volume [m³]</td>
<td>10</td>
<td>40</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>#</th>
<th>Operating parameters</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>%full (step1)</td>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td>7</td>
<td>%full (step 4)</td>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td>8</td>
<td>Liquid Temperature (step 1) [K]</td>
<td>20.3</td>
<td>24</td>
</tr>
<tr>
<td>9</td>
<td>Vapor Pressure (step 4) [bara]</td>
<td>1.5</td>
<td>6</td>
</tr>
<tr>
<td>10</td>
<td>Switch pressure [bara]</td>
<td>100</td>
<td>250</td>
</tr>
</tbody>
</table>

“CV”=Cryogenic Vessel

- Results can then be analyzed using machine learning techniques, such as High Dimensionality Model Representation (HDMR), to sort out most sensitive input parameters, including single and interaction effects
Project Accomplishment
Using thermodynamic model to identify parameters with most impact on the amount of hydrogen boil off

2,300 combinations of 10 parameters

Controlling (most sensitive) parameters difficult to single-handedly identify due to rather large distribution of the boil-off estimates, especially in Step 5

<table>
<thead>
<tr>
<th></th>
<th>Mean</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>%boil-off Step 1</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>%boil-off Step 5</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>%boil-off Total</td>
<td>18</td>
<td>42</td>
</tr>
</tbody>
</table>
Project Accomplishment
Evaluating the impact of variables on hydrogen boil off using Sobol indices

- High Sobol Indice (up to 1) = Large influence of parameter on output
- If Total Sobol Indice close to 1: very good polynomial fit
- Interaction between 2 parameters shown in black

Screening for “mock-up” Type 3 vessels only. Will repeat when more precise pressure vessel designs become available

Preliminary analysis of the parameter screening using High Dimensionality Model Representation shows major single effect contributions (P_CV max, Volume CV, liquid temperature Dewar, P_Dewar) but fails to adequately characterize boil-off from Step 5
Approach
Cryogenic Vessel (CV) Design

> Drivers for CV Pressure Vessel Design
  – Capable of sustaining high pressure cyclic loading and transient thermal loading over extreme temperature swing
  – Thermal mass considerations for CV operational efficiency
  – Economic and cost competitive

> Challenging CV pressure vessel operation conditions
  – Operation pressure and temperature window
    
    \[ 3\text{bar @ 25K} \rightarrow 900\text{ bar @ 200K} \quad 15-30 \text{ cycles/day} \]
  – 60,000 to 110,000 cyclic loading over 10 years of service life. This is an order of magnitude higher than the life cycles for on-board cryogenic storage vessels
  – Limiting material selections and design options for cost
**Project Accomplishment**

Performed initial figure of merit analysis of cryogenic pressure vessels (200L @ 900 bar, 13kg H2)

<table>
<thead>
<tr>
<th>Basic options</th>
<th>Material</th>
<th>Cost $/kg H2</th>
<th>Approx. Weight, lbs</th>
<th>Approx. Thermal mass, kJ/C</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type III</td>
<td>Aluminum/CF [1]</td>
<td>High</td>
<td>400</td>
<td>250</td>
<td>Durability for $10^5$ combined pressure and temperature loading cycles needs to be investigated for cryogenic applications [2]</td>
</tr>
<tr>
<td></td>
<td>Aluminum/Glass fiber</td>
<td>TBD</td>
<td>400</td>
<td>TBD</td>
<td></td>
</tr>
<tr>
<td>Type I</td>
<td>Aluminum alloy</td>
<td>High</td>
<td>4,000</td>
<td>1800</td>
<td>ASME code compliant</td>
</tr>
<tr>
<td></td>
<td>Stainless steel 304</td>
<td>High</td>
<td>5,000</td>
<td>1300</td>
<td>ASME code compliant</td>
</tr>
<tr>
<td></td>
<td>Alternative steel</td>
<td>Low</td>
<td>3,000</td>
<td>600</td>
<td>Material under ASME code case consideration</td>
</tr>
<tr>
<td></td>
<td>9% Ni. steel</td>
<td>High</td>
<td>2,500</td>
<td>500</td>
<td>ASME code compliant</td>
</tr>
<tr>
<td>SCCV (Type II)</td>
<td>Flexible</td>
<td>$600-800 [3]</td>
<td>2,500-3500</td>
<td>300</td>
<td>Design for cryogenic applications need to be refined/optimized</td>
</tr>
<tr>
<td>Type IV</td>
<td>Polymer liner/CF</td>
<td>$560-1100 @700bar [4]</td>
<td>TBD</td>
<td>TBD</td>
<td>Durability for $10^5$ combined pressure and temperature loading cycles has been shown to be inadequate.</td>
</tr>
</tbody>
</table>

[1] LLNL has vessel for small scale demonstration  
Project Accomplishment

Completed initial design analysis for Type 1 cryogenic pressure vessel (200L @ 900 bar, 13kg H2, 200K)

- Different materials are considered for Type 1 vessel
- Initial design shows the vessel cost is lower when length/diameter ratio is larger.
- The results for a representative case with **10in ID** are shown in the table below:
  - Balance with cost and the thermal mass, “low cost steel” is a potential candidate
  - Using ASME allowed material, Al6061, SS304 or 9%Ni, vessel cost will be above 2020 DOE cost target ($600/kg H2)
- This low cost steel is under ASME code approval process for cryogenic service.

<table>
<thead>
<tr>
<th>Material</th>
<th>Design Allowable, ksi</th>
<th>Relative raw material cost*</th>
<th>Relative total material cost*</th>
<th>Shell thickness, in</th>
<th>Total vessel weight, lbs</th>
<th>Approx. material cost, $/Kg H2</th>
<th>Total thermal mass, KJ/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al. 6061</td>
<td>22.08</td>
<td>1</td>
<td>1</td>
<td>4.4</td>
<td>4200</td>
<td>1,000</td>
<td>1,770</td>
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<tr>
<td>SS304</td>
<td>32.68</td>
<td>0.88</td>
<td>1.28</td>
<td>2.4</td>
<td>5750</td>
<td>1,770</td>
<td>1,300</td>
</tr>
<tr>
<td>Low cost steel</td>
<td>50</td>
<td>0.53</td>
<td>0.56</td>
<td>1.4</td>
<td>3000</td>
<td>400</td>
<td>600</td>
</tr>
<tr>
<td>9% Ni steel</td>
<td>58.3</td>
<td>1.14</td>
<td>2.05</td>
<td>1.2</td>
<td>2450</td>
<td>1,200</td>
<td>500</td>
</tr>
</tbody>
</table>

* Based on private communications with material suppliers. Material cost should be further refined for current market value and for mass production.
## Collaborations

<table>
<thead>
<tr>
<th>Partner</th>
<th>Primary Investigator</th>
<th>Project Functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>GTI</td>
<td>Ken Kriha</td>
<td>Project Management, Station Design, Heat Exchanger Modeling, Cost Analysis</td>
</tr>
<tr>
<td>LLNL</td>
<td>Guillaume Petitpas</td>
<td>Transient Thermodynamic Modeling, Station Design, Cost Analysis, Lab Scale Demonstration</td>
</tr>
<tr>
<td>ORNL</td>
<td>Yanli Wang/Zhili Feng</td>
<td>Pressure Vessel Study, Cost Analysis</td>
</tr>
<tr>
<td>Shell</td>
<td>Herie Soto</td>
<td>Station Design, Cost Analysis</td>
</tr>
</tbody>
</table>
Remaining Barriers and Challenges

**Challenge:** Design heat exchanger capable of building cylinder pressure in the desired amount of time.

**Challenge:** Design station to minimize H2 boil off losses.

**Challenge:** Determine economic material capable of withstanding cryogenic pressure cycling.
## Proposed Future Work

### 2016 Milestones

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Description</th>
<th>Due Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1.2.1</td>
<td>Lock in station design and create process flow diagram</td>
<td>08/03/2016</td>
</tr>
<tr>
<td>M2.1.1</td>
<td>Complete analysis of vessels suitable for use in the thermal compression station</td>
<td>11/03/2016</td>
</tr>
</tbody>
</table>

### Go/No-Go

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Description</th>
<th>Due Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>GN2.2.1</td>
<td>Cost analysis showing 15% total reduction cost over a $8.72/kg levelized baseline</td>
<td>11/03/2016</td>
</tr>
</tbody>
</table>

### 2017 Milestones

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Description</th>
<th>Due Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>M2.3.1</td>
<td>Complete analysis of what technologies need to be advanced in order to implement and commercialize this concept</td>
<td>02/03/2017</td>
</tr>
<tr>
<td>M3.2.1</td>
<td>Complete demonstration testing</td>
<td>05/03/2017</td>
</tr>
</tbody>
</table>
Summary

**Objective** - Demonstrate the technical and economic feasibility of the thermal compression concept for 700 bar H2 fueling stations.

**Transient Thermodynamic Modeling used to size Station Components thus cost**
- Transient Cascade Model
  - Indicating cryogenic vessel size between 200-300L
  - Indicating need for 25-30 cryogenic vessels in the cascade
- H2 Boil–Off Model – over 1300 runs already performed
  - Investigating 10 station variables (design and operations)
  - Using machine learning to understand how each variable influences station design

**Cryogenic Vessel Study enables evaluation of cost-effective designs**
- Identified several material options with economic advantages over Type 3
- Researching material’s ability to withstand thermal compression cycles
- Exploring cycle data at cryogenic temperatures and high pressure (900bar)
Technical Back-Up Slides
Project Accomplishments

Thermodynamic Model-Transient Cascading Subroutine

**Inputs:**
- Refueling Station Capacity
- # of dispenser hoses
- Station demand profile
- CV Volume
- CV Liner Thickness
- ∆P needed for fueling
- Minimum P before venting
- Etc...

![Graph showing pressure in a vehicle and each vessel of the cascade](image)

- **Pressure in Vehicle**
- **Pressure in each vessel of the cascade (CV=“Cryogenic Vessel”)**

- **Chevron profile.**
- **Max demand: Friday in the summer**
Project Accomplishments

Thermodynamic Model-Transient Cascading Subroutine

Model Input
Station Size = 400kg/day
Fueling Profile = Chevron
# of Dispenser Hoses = 2
Vehicle: 5.6kg @700bar
Accomplishment

Thermodynamic Model - H2 Boil Off Subroutine

**Step 1**
- 65 kg delivered to cryogenic vessel
- 6 kg vented

**Steps 4 and 5**
- 45 kg delivered to vehicle (20 kg ullage at 90 bar)
- 9 kg vented (in Step 5)