IV.E.1 System Level Analysis of Hydrogen Storage Options

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Objective

The overall objective of this effort is to support DOE with independent system level analyses of various H_2 storage approaches, to help to assess and down-select options, and to determine the feasibility of meeting DOE targets.

Fiscal Year (FY) 2012 Objectives

- Model various developmental hydrogen storage systems.
- Provide results to Hydrogen Storage Engineering Center of Excellence for assessment of performance targets and goals.
- Develop models to "reverse-engineer" particular approaches.
- Identify interface issues, opportunities, and data needs for technology development.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(B) System Cost
(C) Efficiency
(E) Charging/Discharging Rates
(J) Thermal Management
(K) System Life Cycle Assessments

Technical Targets

This project is conducting system level analyses to address the DOE 2015 technical targets for onboard hydrogen storage systems:

- System gravimetric capacity: 1.8 kWh/kg
- System volumetric capacity: 1.3 kWh/L
- Minimum H_2 delivery pressure: 5 bar
- Refueling rate: 1.5 kg/min
- Minimum full flow rate of H_2: 0.02 g/s/kW

FY 2012 Accomplishments

- Analyzed the carbon fiber (CF) requirement using ABAQUS for Type-4 700-bar compressed hydrogen tank. Developed the integrated end cap vessel (IECV) concept to reduce CF usage and cost. Optimized the hoop winding angle layer by layer to reduce the total amount of filament windings.
- Simulated 700-bar fast fill scenario using ANSYS CFX for a Type-4 tank with an enhanced thermal conductivity liner.
- Updated the onboard analyses of the metal-organic framework (MOF-5) system (powder and pellets) with adiabatic para LH_2 refueling. Determined the intrinsic capacities, thermodynamics, dormancy, H_2 refueling dynamics, and discharge dynamics with the potential benefits of para-to-ortho conversion in the onboard storage tank.
- Developed a model of the onboard hydrogen discharge reactor for the single-component liquid carbon-boron-nitrogen (CBN) hydrogen storage material that is being investigated as a potential H_2 storage medium at the University of Oregon.
- Performed off-board analysis of ammonia-borane (AB) regeneration using hydrazine that is produced via the benzophenone process to close the fuel cycle.

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Introduction

Several different approaches are being pursued to develop onboard hydrogen storage systems with the goal of meeting the DOE targets for light-duty vehicle applications. Each approach has unique characteristics, such as the thermal energy and temperature of charge and discharge, kinetics of the physical and chemical process steps involved, and requirements for the materials and energy interfaces

between the storage system and the fuel supply system on the one hand, and the fuel user on the other. Other storage system design and operating parameters influence the projected system costs as well. We are developing models to understand the characteristics of storage systems based on the various approaches, and to evaluate their potential to meet the DOE targets for onboard applications, including the off-board targets for energy efficiency.

Approach

Our approach is to develop thermodynamic, kinetic, and engineering models of the various hydrogen storage systems being developed under DOE sponsorship. We then use these models to identify significant component and performance issues, and to assist DOE and its contractors in evaluating alternative system configurations and design and operating parameters. We establish performance criteria that may be used, for example, in developing storage system cost models. We refine and validate the models as data become available from the various developers. We work with the Hydrogen Storage Systems Analysis Working Group to coordinate our research activities with other analysis projects to assure consistency and to avoid duplication. An important aspect of our work is to develop overall systems models that include the interfaces between hydrogen production and delivery, hydrogen storage, and the fuel cell or internal combustion engine hydrogen user.

Results

Physical Storage

We analyzed the 5.6-kg 700-bar compressed hydrogen Type-4 tank to determine the amount of T700S CF needed to meet the 2.25 safety factor. We first constructed the dome shape based on a geodesic path along the isotensoid in a cylindrical tank for a given length-to-diameter ratio. We then performed netting analyses to estimate the needed helical and hoop layer thicknesses. Finally, we performed three-dimensional finite element analyses using ABAQUS with the Wound Composite Modeler extension. A 5° azimuthal strip was modeled with the proper axisymmetric and cyclic boundary conditions. The helical layer thickness and winding angle were varied element by element in the dome section. Changing the helical layer thickness had little effect on hoop stress because the helical winding angle was small ($\alpha_c = 15°$) in the cylindrical section. It was found that the minimum helical and hoop thicknesses were 10.4 mm and 14.8 mm, respectively.

We developed and analyzed the IECV concept (Figure 1) for Type-4 compressed hydrogen storage tanks. The end caps are first fabricated separately by resin transfer molding and are made of the same CF (T700S) and resin material that is used in the tank overwrap. The end caps are then integrated
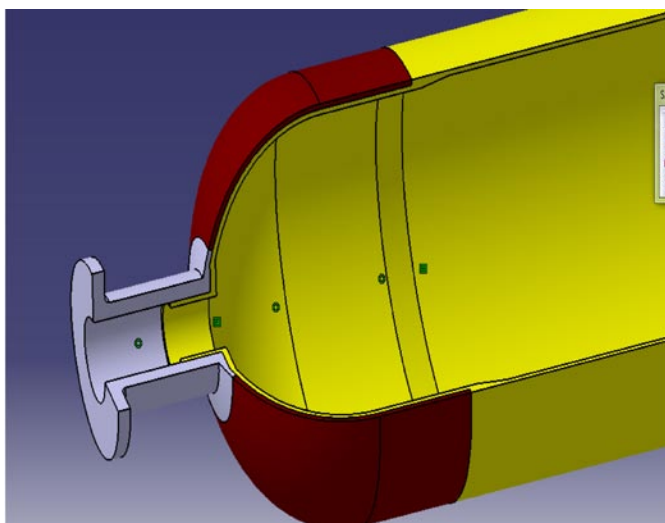

FIGURE 1. The integrated end cap vessel concept for Type-4 tanks

with the high-density polyethylene (HDPE) liner and the aluminum boss using the blow molding method. Finally, the tank is reinforced by conventional helical and hoop winding of the fibers. In this design, the end caps absorb a significant portion of the axial stress in the dome, so that the amount of helical windings needed is substantially less than that in a conventional tank that is reinforced by filament wound fibers only. For the 5.6-kg 700-bar compressed hydrogen tank, our finite element analysis showed that the required helical thickness in the IECV is 5.5 cm, about half the 10.4-cm thickness needed in the baseline design, thereby reducing the needed total CF-composite weight by 18%. Further improvements in the end cap design could result in additional weight reduction. In addition to reducing helical winding using the IECV concept, we also investigated means to reduce the amount of hoop winding material. This can be accomplished by varying the hoop fiber winding angle. In the baseline design where the hoop angle is 90°, the stress at the innermost layer is ~15% higher than that in the outermost layer. Our analysis showed that the stress distribution could be made more uniform across the layers by changing the fiber angle in the layers, which would result in smaller helical and hoop layer thicknesses. This suggests that the amount of filament windings could be reduced by an additional 10% by optimizing the hoop winding angles.

700-bar Fast-Fill Simulation

We investigated the effect of the thermal conductivities of the liner and the carbon fiber on the tank temperature (gas, liner, and CF) during fast fill for 700-bar nominal operating pressure. We used the commercial code ANSYS CFX 13.0 to simulate the thermal hydraulic behavior of the H_2 gas tank filling at 1.5 kg/min at 20°C and −40°C inlet temperatures. The Type-4 tank in our model has a 5-mm thick HDPE liner and a 2.6-cm thick T700S CF overwrap.

We assumed 5 W/m^2·K external heat transfer coefficient and 20°C ambient temperature. It was found that a five- to ten-fold increase in the HDPE thermal conductivity would have the potential to reduce the liner temperature by up to 20°C. A similar increase in CF thermal conductivity (which is already ~20 times that of HDPE) has little impact. Figure 2a shows the time variation of the average gas temperature during and after refueling. The peak liner temperature was below 85°C with a five-fold increase in the liner thermal conductivity, even with the fuel initially at ambient temperature (20°C), as shown in Figure 2b.

Hydrogen Storage in MOF-5

We updated an analysis of onboard hydrogen storage in MOF-5 (Basolite Z 100-H) powder (130 kg·m^{-3}) and pellets (310 and 510 kg·m^{-3}). We extended the H$_2$ equation of state in REFPROP to account for para/ortho conversion. We

validated the extended equation of state against the available tabulated values of H$_2$ properties (enthalpy, density, etc.) as a function of pressure and temperature for ortho and para hydrogen. Figure 3 shows the principal components of the reference onboard hydrogen storage system with adiabatic refueling, in which the MOF tank is evaporatively cooled during refueling with LH$_2$. During discharge, the heat of desorption and any temperature swing in the sorbent bed is provided by recirculating the hydrogen through a small external heat exchanger. The composite pressure vessel consists of T700S CF (2,550 MPa tensile strength) wound on an Al 6061-T6 alloy liner, and it is thermally insulated with multi-layer vacuum super insulation in a 3-mm thick Al 6061-T6 alloy vacuum shell. We conducted fatigue analyses to estimate the required liner thickness to meet the target life of 5,500 pressure cycles (SAE J2579 requirement). The thickness of the insulation was determined so as to limit the heat transfer rate from the ambient to 5 W.

We analyzed the MOF-5 system performance assuming that the system is charged with liquid para H$_2$, which converts to the equilibrium para-ortho composition solely as a function of the prevailing pressure and temperature (i.e., without any kinetic limitations). The analysis showed that the endothermic heat of para-ortho conversion (~700 J/g-H$_2$ converted at 20–40 K) sufficiently increases the allowable temperature swing such that the recoverable fraction of sorbed H$_2$ approaches unity for temperatures above about 80 K. The system can reach lower temperatures with equilibrium H$_2$ than with normal H$_2$. We concluded that additional external cooling would not be needed for the system to reach the theoretical gravimetric and volumetric
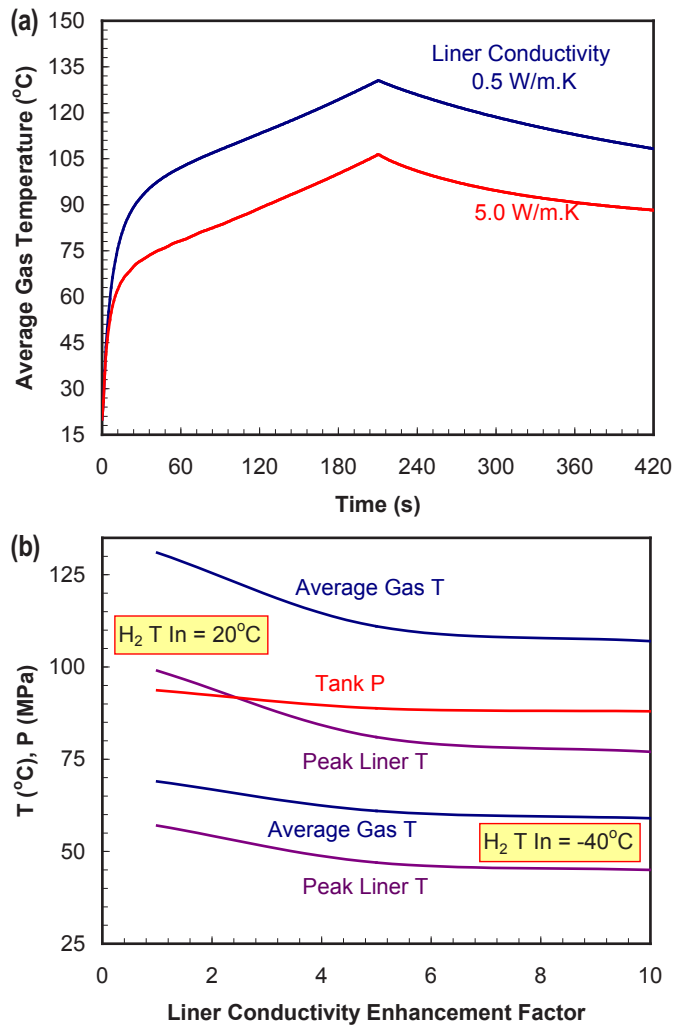

FIGURE 2. (a) Time variation of gas temperature during fast-fill of 700-bar tanks; (b) Changes in gas/liner temperatures with changing liner thermal conductivity
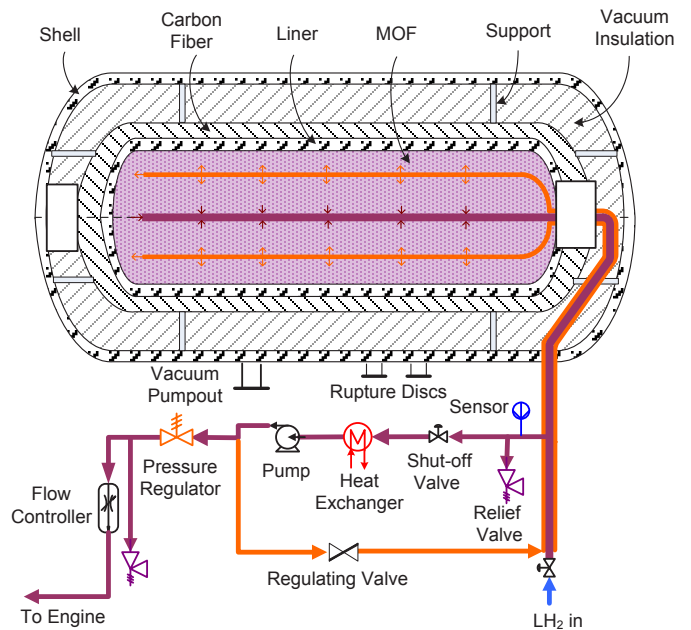

FIGURE 3. Onboard MOF-5 storage system with para LH$_2$ refueling

capacities if the para-to-ortho conversion occurs inside the MOF bed. The analysis showed that for MOF-5 powder at 150 atm storage pressure, without para-to-ortho conversion, the allowable temperature swing at 60 K nominal storage temperature is 18 K, whereas with equilibrium H_2, the endothermic conversion allows a temperature swing of 36 K at a 10 K lower storage temperature. At a storage pressure of 150 atm, the system gravimetric capacity increases from 6.5 wt% without conversion to 7.1 wt% with conversion to equilibrium. The corresponding volumetric capacity increases from 34.9 kg·m⁻³ to 40.9 kg·m⁻³. With MOF-5 pelletized to a bulk density of 310 kg·m⁻³, the corresponding storage capacities increase from 4.6 wt% to 5.5 wt% and from 29.5 kg·m⁻³ to 37.6 kg·m⁻³. With further compaction of the MOF-5 to a bulk density of 510 kg·m⁻³, the H_2 storage capacities increase from 3.3 wt% to 4.1 wt%, and from 24.1 kg·m⁻³ to 32.9 kg·m⁻³.

We also evaluated the kinetics of the para-to-ortho conversion. We found that the gas phase kinetics is too slow for any significant conversion during the refueling process (3–5 min duration). We also determined that the kinetics is sufficiently rapid on a commercially available catalyst (APACHI–1) that the equilibrium conversion can be achieved in 3–5 minutes. There is some literature data that suggests that para-to-ortho conversion occurs within minutes on MOF-74 [1]; however, the kinetics on MOF-5 is largely unknown.

Dormancy in MOF-5 H_2 storage systems is a function of the amount of H_2 and the pressure and temperature at the start of the dormancy event. The effect of the para-to-ortho conversion is to extend dormancy by about 20% if the tank is initially more than 75% full, with shorter dormancy increases for smaller initial amounts of H_2 (because of the lower thermal mass of the system).

Chemical Storage

We developed an onboard hydrogen discharge reactor model for the single-component liquid CBN material (BN-methylcyclopentane) being investigated as a potential hydrogen storage material at the University of Oregon [2]. The material is liquid at ambient conditions and does not undergo a phase charge upon dehydrogenation. We analyzed the H_2 release data and formulated a 2-step, self-inhibited catalytic reaction model described by the reactions,

$$2R_1 = R_2 + 2\alpha_1 H_2$$
$$3R_2 = 2R_3 + 2\alpha_2 H_2$$
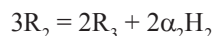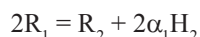
where $\alpha_1 = 1$, and $\alpha_2 = 3$. Figure 4a compares the model prediction of H_2 release rate with the data at 80°C and 5-mol% $FeCl_2$ catalyst loading. Both the model and data exhibit a double peak in reaction rate that is consistent with self-inhibited catalytic behavior. Figure 4b shows the good
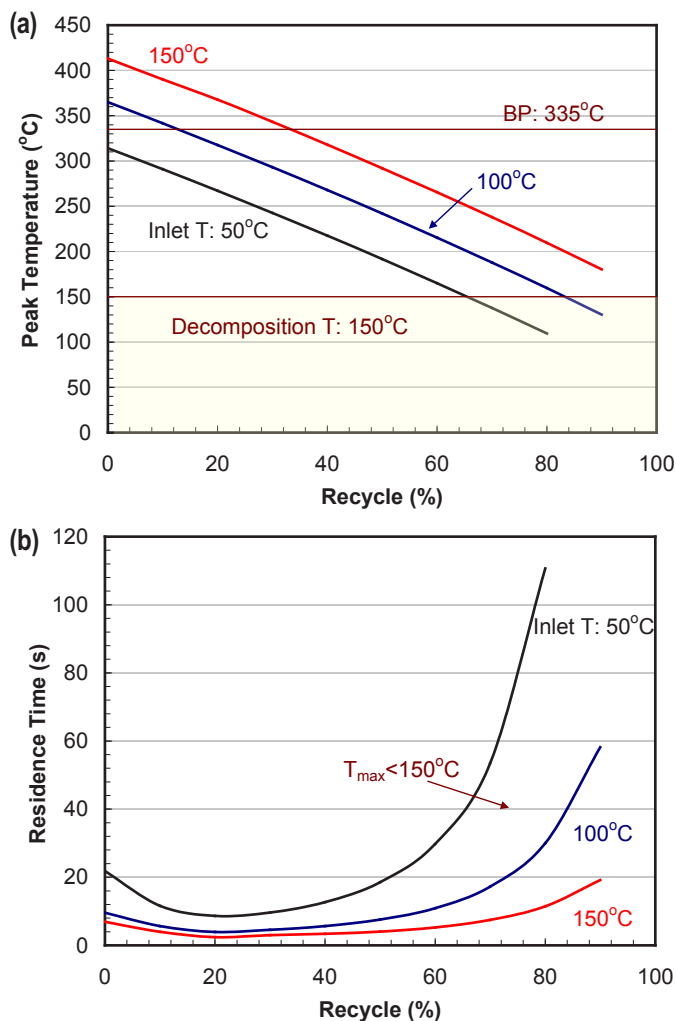
FIGURE 4. (a) Peak reactor temperature for CBN in the hydrogen discharge reactor; (b) Residence time for CBN in the hydrogen discharge reactor as a function of the fraction of spent fuel recycled to the hydrogen discharge reactor

fit between the model results and the experimental data for cumulative hydrogen release.

We modeled the performance of an onboard CBN tube-in-shell reactor for hydrogen discharge. We considered a one-dimensional, steady flow of CBN inside the heat exchanger tubes, and ethylene glycol heat transfer fluid on the shell side. A single-tube, multi-pass tube arrangement was selected to further enhance the tube-side heat transfer coefficient by maintaining a high Reynolds number and a stable two-phase flow. The model results indicated that heat transfer alone was not sufficient to control the peak temperature of the exothermic dehydrogenation reaction. The peak temperature can be controlled, however, by partial recycling of the spent liquid fuel back to reactor. The higher the recycle ratio, the lower is the peak temperature, as shown in Figure 4a for various inlet temperatures. A 65% to 85% recycle of spent CBN is needed, however, to keep the maximum reactor temperature below 150°C, the decomposition temperature of

fresh fuel. Figure 4b shows the residence time of the fuel in the reactor as a function of the spent fuel recycle ratio. For 65% to 85% recycle and inlet temperatures of 50 to 100°C, the residence time is about 40 s. The residence time can be reduced with the use of more active and/or dispersed catalyst, a topic currently being investigated at the University of Oregon.
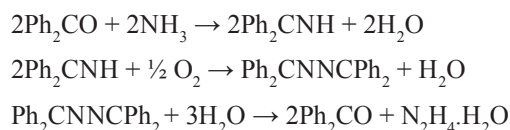
Off-Board Regeneration of AB using Hydrazine

We analyzed the off-board regeneration process for ammonia borane in a single-pot scheme, in which the spent AB is reacted with hydrazine (N_2H_4, limiting reagent) in liquid ammonia [2].

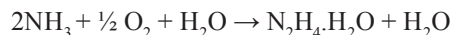$$BNH_2 + N_2H_4 \rightarrow BH_3NH_3 + N_2$$
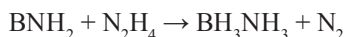
Previously, two flow sheets were constructed to close the cycles by considering the commercial processes (Bayer Ketazine and PCUK) for producing hydrazine. The Bayer Ketazine process requires large amounts of electricity to produce NaOH and Cl_2, which are the feed materials for hydrazine production. The PCUK process consumes a large amount of steam in making hydrogen peroxide. We constructed a third flowsheet for hydrazine production using benzophenone (Figure 5). This process [3,4] requires only ammonia as a feed material for the production of hydrazine. All reagents and catalysts are recycled in a closed loop. Although this process has been thoroughly reviewed, it has

not yet been commercialized. All reagents and catalysts are recycled in a closed loop. A mixture of ammonia and air ($NH_3:O_2 = 4:1$) is passed through benzophenone under pressure (~1-8 atm) in the presence of zinc chloride and cuprous chloride catalysts at 200°C. The reaction produces benzophenone azine; the reaction mixture is diluted with ethanol to precipitate azine and the catalysts. Unreacted benzophenone and some of the catalysts remain in the ethanol solution, from which the ethanol is subsequently distilled off to return the unreacted benzophenone and catalysts to the reaction step. The precipitated catalysts are recovered by washing with benzene to dissolve the azine. The solution is distilled to remove benzene, and the azine is hydrolyzed in the presence of a strong acid, such as sulfuric acid, to yield hydrazine and benzophenone, which is recycled. The reactions are as follows:

$$2Ph_2CO + 2NH_3 \rightarrow 2Ph_2CNH + 2H_2O$$
$$2Ph_2CNH + \tfrac{1}{2} O_2 \rightarrow Ph_2CNNCPh_2 + H_2O$$
$$Ph_2CNNCPh_2 + 3H_2O \rightarrow 2Ph_2CO + N_2H_4.H_2O$$

The net reaction is

$$2NH_3 + \tfrac{1}{2} O_2 + H_2O \rightarrow N_2H_4.H_2O + H_2O$$

We analyzed the AB regeneration process using hydrazine produced via the benzophenone pathway. Results of the analysis showed a well-to-tank (WTT) efficiency of ~18%, a notable increase over the ~8% and ~12% WTT
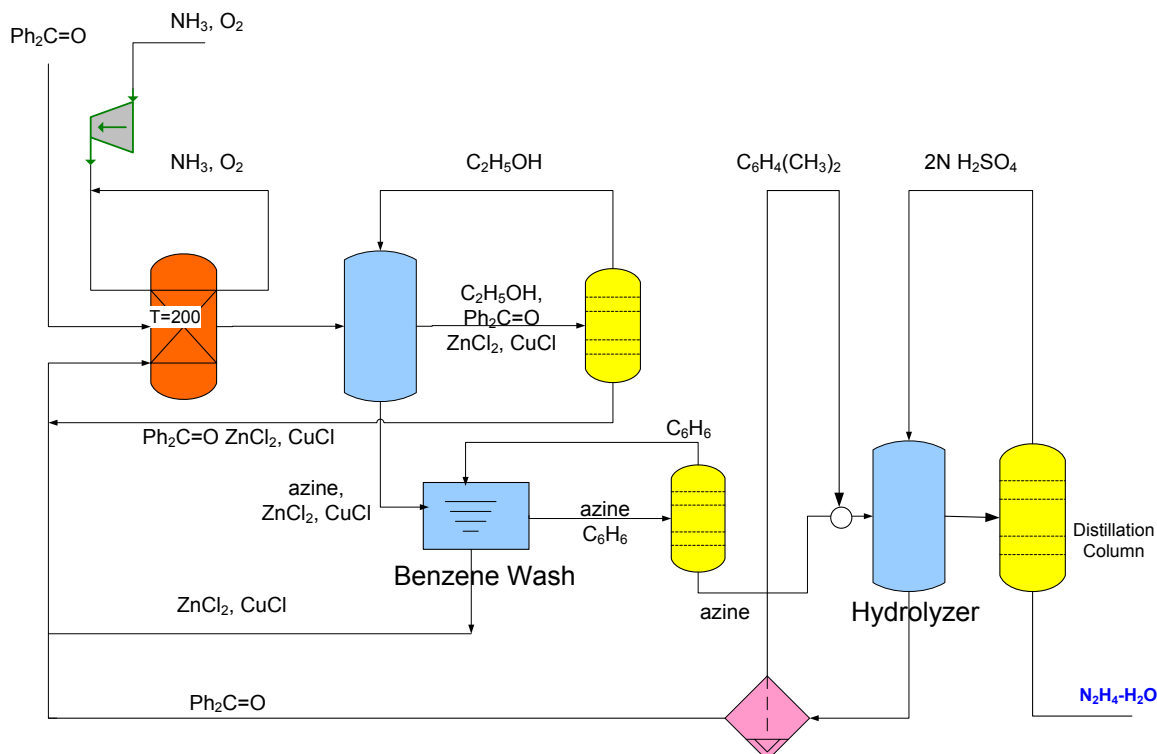

FIGURE 5. The benzophenone process for hydrazine production

efficiencies using the Bayer Ketazine and the PCUK pathways, respectively, for producing hydrazine.

Conclusions and Future Directions

- We project that an onboard MOF-5 system with adiabatic liquid para H_2 refueling and 5.6 kg recoverable H_2 can achieve 7.1 wt% gravimetric capacity and 40.9 g/L volumetric capacity at 150 atm. The loss-free time and hydrogen loss rate are functions of the amount of hydrogen stored and the pressure and temperature at the start of the dormancy event.

- We estimate that the IECV design for Type-4 tanks has the potential to reduce the amount of CF composite usage by ~18% for 700-bar hydrogen storage. We further estimate that optimizing the hoop winding angle layer by layer can bring about an additional 10% savings in the amount of filament windings.

- We estimate that partial recycling of the spent CBN liquid fuel back to reactor is needed to control the peak reactor temperature. A 65% to 85% recycle of the spent fuel would keep the maximum reactor temperature below 150°C, the decomposition temperature of fresh fuel. We estimate that for 65% to 85% recycle and inlet temperatures of 50 to 100°C, the needed residence time is about 40 s.

- We estimate that a five- to ten-fold increase in the HDPE thermal conductivity has the potential to reduce the liner temperature by up to 20°C for 700-bar fast fill at 1.5 kg/min.

- We estimate WTT efficiency of ~18% for regenerating AB using hydrazine produced via the benzophenone process. This WTT efficiency is a notable increase over the ~8% and ~12% WTT efficiencies of AB regeneration using hydrazine produced by the Bayer Ketazine and the PCUK pathways, respectively.

- In FY 2013, we will extend our analysis of Type-4 tank to optimize the end cap design, analyze the effect of mismatch in the coefficient of thermal expansion between the resin and the CF at cold/cryo temperatures, investigate improvements in CF composite mechanical properties with tailored mechanical properties of the epoxy matrix, and investigate differences in tensile strength and translation efficiency for pre-preg versus wet winding.

- In FY 2013, we will analyze a complete CBN onboard system to determine the key performance metrics, and off-board regeneration of CBN for three different chemistries.

- Also in FY 2013, we will perform reverse engineering for onboard hydrogen storage systems based on metal hydrides or chemical hydrogen. The primary goal of the analyses will be to determine the range of materials properties that are needed for the systems to meet the DOE onboard performance targets.

FY 2012 Publications/Presentations

1. R.K. Ahluwalia, T.Q. Hua and J.K. Peng, "On-Board and Off-Board Performance of Hydrogen Storage Options," International Journal of Hydrogen Energy, 37 (2012) 2891-2910.

2. T.Q. Hua and R.K. Ahluwalia, "Alane Hydrogen Storage for Automotive Fuel Cells – Off-Board Regeneration Processes and Efficiencies," International Journal of Hydrogen Energy, 36 (2011) 15259-15265 .

3. R.K. Ahluwalia and T.Q. Hua, "Hydrogen Storage in Ammonia Borane Dissolved in an Ionic Liquid," International Journal of Hydrogen Energy, 36 (2011) 15689-15697.

4. T.Q. Hua and R.K. Ahluwalia, "Hydrogen Storage in Ammonia Borane – Off-board Regeneration Processes and Efficiencies," International Journal of Hydrogen Energy, 37 (2012) 14382-14392.

5. T.Q. Hua, R.K. Ahluwalia and J.K. Peng "Analysis of Hydrogen Storage Options for Automotive Fuel Cells," 12th China Hydrogen Energy Conference, Wuhan, China, October 2011.

6. T.Q. Hua, R.K. Ahluwalia and J.K. Peng "Analysis of Hydrogen Storage Options for Automotive Fuel Cells," Shanghai Jiao Tong University, Shanghai, October 2011.

7. R.K. Ahluwalia, J.K. Peng and T.Q. Hua, "Enhanced Cryogenic Hydrogen Storage in MOF-5 with Para-to-Ortho Conversion," Storage System Analysis Working Group Meeting, Argonne National laboratory, February 2012.

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1. S. FitzGerald et al., "Quantum dynamics of adsorbed normal- and para- H_2 , HD, and D_2 in the microporous framework MOF-74 analyzed using infrared spectroscopy," Physical Rev. B 2010 (81), 104305.

2. W. Luo, P.G. Campbell, L.N. Zakharov, S-Y Liu, "A single-component liquid phase hydrogen storage material," J. Am. Chem. Soc., 2011 (133) 19326 - 19329.

3. H. Hayashi, A. Kainoh, M. Katayama, K. Kawasaki, T. Okazaki. "Hydrazine production via azine," Ind. Eng. Chem. 1976; Pro. Res. Dev., 15 (4).

4. M. Hayashi, "Hydrazine synthesis: commercial routes, catalysis and intermediates," Res. Chem. Intermed., 1998; 24 (2): 183-196.