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Development and validation of a slurry model for chemical hydrogen storage in fuel cell vehicle applications

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HIGHLIGHTS

- Chemical H_2 storage (CHS) materials evaluated for fuel cell-based vehicles.
- Simulink® transient model developed for slurry-based storage system.
- Models validated with reactor and radiator prototype experiments.
- Models predict systems can meet four DOE-selected drive cycles.
- Models identified acceptable ranges of reaction enthalpy and H_2 capacity.

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ABSTRACT

The U.S. Department of Energy's (DOE) Hydrogen Storage Engineering Center of Excellence (HSECoE) is developing models for hydrogen storage systems for fuel cell-based light duty vehicle applications for a variety of promising materials. These transient models simulate the performance of the storage system for comparison to the DOE's Technical Targets and a set of four drive cycles. PNNL developed models to simulate the performance and suitability of slurry-based chemical hydrogen storage materials. The storage systems of both a representative exothermic system based on ammonia borane and an endothermic system based on alane were developed and modeled in Simulink®. Once complete, the reactor and radiator components of the model were validated with experimental data. The system design parameters were adjusted to allow the model to successfully meet a highway cycle, an aggressive cycle, a cold–start cycle, and a hot drive cycle. Finally, a sensitivity analysis was performed to identify the range of material properties where these DOE targets and drive cycles could be met. Materials with a heat of reaction >11 kJ mol^{-1} H_2 generated and a slurry hydrogen capacity of >11.4% will meet the on-board efficiency and gravimetric capacity targets, respectively.

1. Introduction

Engineering of onboard hydrogen storage materials for fuel cell applications is one of the key objectives of the U.S. Department of Energy's (DOE) Hydrogen Storage Engineering Center of Excellence (HSECoE) program. The goal is to model and optimize the necessary hardware required to build hydrogen storage systems for light duty vehicle applications [1]. On the basis of their promising H_2 storage capacity, ammonia borane (AB) and alane have been chosen by HSECoE for the initial chemical hydride simulation studies. Several studies on the science and material properties of AB and alane have been reported in the literature. Autrey and co-workers studied hydrogen release from AB, its thermal stability, and other engineering aspects [2,3], while Aardahl et al. discuss system issues, such as heat management and reactor design, that need to be considered for vehicular storage system designs [4]. Several researchers have studied the decomposition kinetics of alane and developed kinetic expressions for hydrogen generation [5–7]. Alane also has been studied for vehicle applications [8–10], although a significant concern is its regeneration [11]. Our work at HSECoE focuses on designing, developing, and evaluating reactor systems. We use a modeling approach based on scientific knowledge for chemical hydrogen storage materials reported in the literature.

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While there have been a large number of models for metal hydride storage systems reported in the literature, Pacific Northwest National Laboratory (PNNL) was the first to develop systems models of various chemical hydrogen storage materials (solid AB, solvated AB, and alane) for engineering analysis and development [12–16]. Chemical hydrogen storage materials differ from metal-hydride storage systems in that they must be removed from the vehicle before they can be regenerated by chemical processing. Metal-hydride storage materials allow direct addition of hydrogen onboard a vehicle for regeneration.

Previous studies using PNNL-developed systems assumed that the chemical hydrogen storage materials were a pelletized solid that was reacted either in place or by moving through the system using auger or pneumatic transport [12–14]. Because of the challenge of moving solid pellets through a pressurized system while preventing hydrogen loss to the environment, the use of solids has been rejected in the HSECoE. Alternatively, pure liquid systems would be ideal in terms of transport both within and outside the vehicle. Studies also have been performed assuming AB is dissolved in an ionic liquid [15,16]. However, successfully developing a solvated fluid at high concentration that remains a liquid both pre- and post-reaction has been elusive. As a result, the focus of the research for the HSECoE has been the development of these materials in a slurry form. This ongoing development work has demonstrated AB slurries in silicone oil at solids concentrations up to 45 wt% [17] and alane in either silicone oil or mechanical pump fluid at solids concentration up to 60 wt%. This paper focuses on the development of a system and a model describing the transient behavior of a slurry-based hydrogen storage system. The model will include both AB and alane. Experimental validation of these models has been performed for two key system components. The experimental work associated with this testing will be described.

2. Slurry system design

The slurry system design on which the modeling and experimental work is based is shown in Fig. 1. Details of this system and how components were selected are provided elsewhere [18], but a brief description of the process will be provided here. In this system, the slurry is transported on and off the vehicle between the filling station and a volume displacement tank. A volume displacement tank configuration minimizes the system components by requiring only one tank for both the feed and the product. A membrane separates the feed side of the tank from the product. As fresh slurry is loaded into the tank, the membrane forces spent slurry out of the tank and back to the filling station for eventual reprocessing.

During startup, electrical resistance heaters bring the reactor walls to reaction temperature. Meanwhile, the fresh feed in the volume displacement tank is mixed to ensure homogeneity before it is sent into the system. Once the reactor reaches the required temperature, the feed pump begins moving fresh feed into the reactor. As the slurry flows through the heated tubular reactor, hydrogen is generated in a non-catalytic thermolysis process. The hydrogen gas is separated from the three-phase mixture in a phase separator, cooled in a radiator, and then sent back to the volume exchange tank.

For the exothermic AB slurry, a fraction of the hot slurry product from the phase separator and/or cold product after the radiator can be recycled to the feed if needed. These two recycle streams preheat the feed stream to reaction temperatures while adding thermal mass to minimize the temperature excursions associated with the exothermic reaction. For the endothermic alane slurry, the feed is not recycled. Instead it passes through a recuperator to recover the heat of reaction before being cooled in the radiator.

Once the gases generated in the reactor are separated from the slurry, they pass through a coalescing filter, a radiator, and an impurities-adsorbent bed to condition the hydrogen feed prior to the fuel cell. The hydrogen must be cooled with a radiator to below 85 °C, and impurities must be removed to the levels required by SAE J2719 and ISO/PDTS 14687-2, which is >99.97% purity [19]. Rather than heat the system quickly to meet the stringent startup time required by the DOE technical targets, hydrogen gas is stored in a ballast tank. The ballast tank allows for immediate flow of hydrogen to the fuel cell during cold startup while the storage system is warming to the required temperature to initiate the thermolysis reaction. The ballast tank also provides hydrogen to accommodate the transients during operation.

3. Slurry system model

The mass and energy balances of the entire storage system described in the previous section were modeled using the Simulink® simulation software, which provides an understanding of the operational dynamics of the storage system under simulated drive-cycle scenarios. The components that are modeled are described below.

3.1. Reactor model

The reactor for both the AB and alane slurry is a tubular reactor with an internal stirrer or auger to prevent agglomeration of the solids during reaction while allowing the gas to flow through the reactor center. The parameters used for the reactor model are provided in Table 1. For the purposes of modeling, it is assumed that the slurry is pushed to the walls of the reactor while the gas flows down the reactor center.

The fractional conversion of the chemical hydrogen storage material (CH) to H_2 in the slurry through the length of the reactor is given by α and is calculated as shown in Eq. (1).

$$\frac{\partial \alpha_i}{\partial t} = -u_{\text{slurry}}\frac{\partial \alpha_i}{\partial z} + \left.\frac{\partial \alpha_i}{\partial t}\right|_{\text{kinetics}} \tag{1}$$

In the case of AB, Eq. (1) consists of two equations ($i = 2$) for the two separate polymerization reactions that correspond approximately to the first equivalent, and the second and a fraction of the third equivalent for a total H_2 production of 2.35 equivalents. In the case of alane, Eq. (1) is a single equation producing 1.5 equivalents. The velocity of the slurry (u_{slurry}) is calculated based on equation Eq. (2):

$$u_{\text{slurry}} = \frac{\dot{m}_{\text{slurry}}}{\rho_{\text{slurry}} A_{\text{slurry}}} + Z_{\text{auger}}\upsilon_{\text{auger}} \tag{2}$$

where Z_{auger} is the axial displacement of the auger per rotation, υ_{auger} is the rotational speed, and A_{slurry} is the area of the gas/slurry interface in the reactor where the slurry channel is estimated to be 75% of the total area of the reactor calculated from $\pi(d_{\text{in}}^2 - d_{\text{slurry}}^2)/4$. As hydrogen is generated, the slurry density, ρ_{slurry}, decreases to create a foamy mixture of solid, liquid, and gas with a density given in equation Eq. (3).

$$\rho_{\text{slurry}} = \frac{\dot{m}_{\text{slurry}} + \dot{m}_{H_2}}{\frac{\dot{m}_{H_2}}{\rho_{H_2}} + \frac{\dot{m}_{\text{slurry}} f_{\text{inert}}}{\rho_{\text{inert}}} + \frac{\dot{m}_{\text{slurry}} f_{\text{CH}}(1-\alpha_i)}{\rho_{\text{CH}}} + \frac{\dot{m}_{\text{slurry}} f_{\text{CH}}\alpha_i}{\rho_{\text{CHP}}}} \tag{3}$$

The parameters f_{inert} and f_{CH} are the fractions of inert and chemical hydride; and ρ_{H_2}, ρ_{inert}, ρ_{CH}, and ρ_{CHP} are the densities of