Engineering technologies for fluid chemical hydrogen storage system

Bart A. van Hassel *, Randolph C. McGee, Allen Murray, Shiling Zhang

United Technologies Research Center, 411 Silver Lane, East Hartford, CT, USA

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ABSTRACT

An efficient gas/liquid separator (GLS) was developed for separating hydrogen gas from spent liquid organic and inorganic hydrogen carriers onboard light-duty vehicles. The results show that the capacity of the GLS is sufficient for an 80 kWe PEM fuel cell, as used in light-duty vehicle applications. A discrepancy was observed between the calculated droplet size distribution at the outlet of the GLS and the experimental results. This was explained by film formation and breakup inside the vortex finder when the GLS was operated at flow rates that exceeded its critical gas velocity.

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1. Introduction

Automobile users have been accustomed to using liquid fuels ever since Bertha Benz filled the tank on the maiden trip of the world's first automobile at the world's first filling station (a City Pharmacy in Wiesloch, Germany), back in 1888 [1]. This event was only 18 years after the establishment of the US Weather Bureau [2], which started recording data in several Midwestern cities such as Chicago. Since then a trend has been discovered between greenhouse gas emissions by human activities (to which transportation is contributing about 29% in the US [3]) and global warming [4]. It is an enormous challenge to society to change to more sustainable forms of transportation.

The convenience of dispensing a liquid fuel with a high volumetric energy density rapidly into a compact affordable low-pressure conformal tank remains highly desirable during this transition. Liquid Organic Hydrogen Carriers (LOHC) and liquid inorganic hydrogen carriers (LIHC) have been developed for this purpose and some examples are shown in Table 1. A common characteristic of the listed hydrogen carriers is that hydrogen gas can be released in a reactor onboard a vehicle in order to power a fuel cell or internal combustion engine.

This paper discusses the development of a gas/liquid separator system downstream of such a reactor in order to separate the hydrogen gas from the liquid spent fuel, which is important for meeting the SAE J2719 hydrogen quality guidelines [14]. This work has been performed as part of UTRC's contribution to the DOE-funded Hydrogen Storage Engineering Center of Excellence

(HSECoE [15]). This center focuses on the design and engineering of materials-based hydrogen storage systems for light-duty vehicles that shall meet all 18 hydrogen storage targets [16] simultaneously.

The H_2 release by these liquid H_2 carriers tends to be endothermic and a significant fraction of the stored H_2 gas needs to be burned in for instance a micro-channel combustor [17]. This reduces the onboard efficiency. Ammonia Borane (AB) is a noticeable exception and releases H_2 gas in an exothermic reaction. The spent fuel shall be collected at the refueling station and sent to a central processing plant for off-board regeneration of the hydrogen carrier [6,7,12]. Finding an energy-efficient regeneration process has been proven to be a difficult challenge, especially for the liquid inorganic hydrogen carriers [13].

2. Experimental

A schematic diagram of the gas/liquid separator (GLS) that was developed in close collaboration with the Eaton corporation and tested at UTRC is shown in Fig. 1. The GLS comprises a demister pad, a static vane pack, a vortex containment plate and a vortex finder. It operates in a horizontal orientation in order to have a low profile onboard of a fuel cell vehicle. The two-phase mixture of hydrogen gas and spent fuel enters the GLS from the left and first passes through the demister pad on which small droplets (e.g. mist) coalesce into larger droplets that are easier to separate by the vortex that is induced by the static vane pack with a proprietary vane angle. Dry hydrogen gas is extracted from the center of the vortex by the vortex finder. Droplets spin out of the vortex against the inside surface of the GLS and form an oil film that drains under gravity into a collection tank from which it can be discharged into a spent fuel tank. The GLS was designed to have a high dynamic range due to the simultaneous use of three separation mechanisms: gravity settling, inertial impaction, and centrifugal separation. Relentless efforts on weight and volume reduction resulted in a total weight of 5.8 kg and 2.7 L. This improved the system gravimetric capacity from 31 gH_2/kg system to 41 gH_2/kg system and the system volumetric capacity from 36 gH_2/L system to 40 gH_2/L system (=2017 system target) [18–20].

* Corresponding author.
  E-mail address: vanhasba@utrc.utc.com (B.A. van Hassel).

The HSECoE selected slurries of AB or aluminum hydride (AlH$_3$) in silicone oil AR-20 as prototypical fluid forms of an exothermic and endothermic chemical hydrogen storage material that would enable a hydrogen storage system capable of meeting all of the 18 DOE targets for light-duty vehicles simultaneously [18]. It was decided to evaluate the performance of the GLS as close as possible to the required operating conditions for this slurry-based chemical hydrogen storage system. However the AB and Alane slurries were only available in very limited quantities, which would have been insufficient for testing the GLS. Therefore the GLS was characterized with a two-phase silicone oil AR-20/N$_2$ gas mixture but at the flow rates required for an actual GLS (liquid: 0.2–0.7 L/min, gas: 300–900 slpm).

The experimental setup for testing the GLS performance was documented in Ref. 21. It incorporated a gas-cooler (Exergy, tube-in-tube heat exchanger, at 20 °C) downstream of the GLS. The liquid carry-over amount (CO) is defined as the weight of the silicone oil that was collected in a coalescence filter (Parker Hannifin Corporation) downstream of this gas-cooler and this is the sum of any droplets that passed through the vortex finder and any vapor that would have condensed on the heat exchanger surface and drained by gravity. The Separation Efficiency (SE) of the GLS is defined as:

$$SE\,(in\%) = 100 * \left(1 - \frac{CO}{F}\right)$$

where CO = liquid carry-over amount collected at gas outlet (g) and F = silicone oil amount fed into GLS (g). The SE is hence defined as the carry-over amount relative to the silicone oil amount that was supplied to the GLS. A Malvern Mastersizer was used to measure the droplet size distribution at the outlet of the GLS in order to diagnose the performance of the GLS and to validate the Computational Fluid Dynamics (CFD) model.

The chemical hydrogen storage system with AB in silicone oil AR-20 as the H$_2$ storage material relied on the hot recirculation of spent fuel in order to improve the onboard energy efficiency [18]. Experiments at elevated temperature (170 °C) showed a significant carry-over of silicone oil vapor, which was undesired. This was due to the high vapor pressure of silicone oil AR-20, to be discussed in Section 4.3. The operating temperature of the GLS was reduced to a maximum temperature of 70 °C in order to reduce silicone oil vapor carry-over. Silicone oils with a significant lower vapor pressure were identified but not tested experimentally.

3. Model development

A Simulink framework was developed for comparing different H$_2$ storage systems on a common basis, as reported in Refs. [22,23]. UTRC used the gas and liquid flow rates from those simulations in order to determine that the flow regime at the inlet of the GLS would be in the annular-dispersed or stratified wavy flow regime according to the Taitel and Dukler generalized flow regime map for horizontal two-phase flow [24]. It was not feasible to measure the silicone oil droplet size distribution due to the relative high silicone oil concentration at the inlet of the GLS. Therefore the Harwell procedure was followed in order to estimate the inlet droplet size distribution [25]. In this procedure, the 'Sauter mean' of the drop diameter can be estimated from the following correlation [26]:

$$\langle x \rangle_{Sa} = 1.91 D_t \frac{Re^{0.1}}{We^{0.6}} \left(\frac{\rho_g}{\rho_l}\right)^{0.6} + D_t \frac{m_l}{\rho_l \mu_l}$$

where Re and We are the Reynolds and Weber number, respectively. They are defined as,

$$Re = \frac{\rho_g v_t D_t}{\mu_g}$$

Table 2
GLS operating conditions for CFD modeling (70 °C, 12 bar).

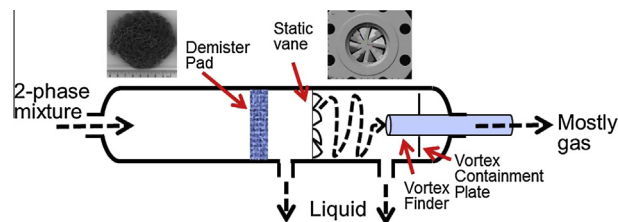| CFD run	Silicone oil AR 20 flow rate (lpm)	N2 gas flow rate (slpm)
301	0.72	900
302	0.72	700
303	0.72	600
304	0.72	300
311	0.20	900
313	0.20	600
314	0.20	300

Fig. 1. Schematic diagram of a GLS for separating H$_2$ gas from the spent H$_2$ carrier in a liquid form.

$$We = \frac{\rho_g v_t^2 D_t}{\sigma}$$

and where $\langle x \rangle_{Sa}$ is the Sauter mean drop diameter, D_t is the internal diameter of the pipe, ρ_g and ρ_l are the gas and liquid densities, μ_g is the gas viscosity, v_t is the mean gas velocity within the pipe and σ is the interfacial surface tension, m_l is the silicone oil mass flux through the inlet tube cross sectional area (kg/m^2/s); μ_l is the silicone oil viscosity (Pa s).

The Sauter mean droplet diameter was converted to a volume-average drop diameter through the following approximation:

$$d_{50} = \exp(\sigma^2/2) * \langle x \rangle_{Sa}$$

which is based on a log-normal drop size distribution [27]. The probability density function of the lognormal distribution is defined as,

$$dv = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{\ln d_p - \ln d_{v50}}{\sigma}\right)^2\right] \frac{dd_p}{d_p}$$

and where dv is the fraction of the liquid volume contained in drops with diameters between dp and $dp + ddp$ and σ is the standard deviation. A characteristic width $\sigma = 0.81$ was used in this study, which was reported by Al-Sarkhi and Hanratty [27]. Silicone oil with a surface tension of 9.65×10^{-3} N/m and a dynamic viscosity of 20 mPa s was used as the agent for turning AB into a slurry. Examples of the estimated droplet size distributions at the inlet of the GLS are shown in Fig. 2a.

Ansys Fluent was employed to simulate the gas and liquid separation process in the GLS. The geometric features of the GLS

Table 1
Liquid organic and inorganic hydrogen carriers.

		Material gravimetric capacity (gH$_2$/kg material)	Material volumetric capacity (gH$_2$/L material)	Regeneration efficiency	Refs.
LOHC	N-ethylcarbazole	0.0583	61.8	>60%	[5–7]
	Methylperhydroindole	0.0290	26.1	unknown	[8]
	Pentane thiol	0.0580	48.7	unknown	[9,10]
	CBN heterocycle	0.0470	42	unknown	[11]
LIHC	NH$_3$BH$_3$ in silicone oil (50 wt.%), 2.35 equivalent	0.0767	67.5	8–28%	[12,13]
	AlH$_3$ in silicone oil (50 wt.%)	0.0504	60.4	24%	[13]