Contract Number: DE-EE0005020
Development of a Practical Hydrogen Storage System Based on Liquid Organic Hydrogen Carriers and a Homogeneous Catalyst

FINAL REPORT

Craig Jensen and Daniel Brayton
Hawaii Hydrogen Carriers, LLC
531 Cooke Street
Honolulu, HI 96813
Phone: (808) 445-7248
Email: hhcllc@hotmail.com

Scott W. Jorgensen and Peter Hou
Chemical and Material Systems Lab
General Motors, LLC
General Motors Research and Development Center
Warren, MI 48090

Executive Summary

Two major challenges in the practical utilization of hydrogen as a fuel for vehicles are the development of a means achieving both high gravimetric and volumetric onboard hydrogen storage densities and putting hydrogen fueling infrastructure in place. Liquid organic hydrogen carriers (LOCs) are similar type to our current distribution medium, gasoline. The tanks, piping and refinery systems used to make and deliver gasoline are appropriate for LOCs. The ability to use well-established material reduces costs, risks, and shortens the time to market. Additionally, cheap, abundant LOCs can potentially reversibly release 7-8 wt% hydrogen and can be economically manufactured in the massive quantities required to meet the anticipated demand. The development of LOC based hydrogen storage systems requires: 1) the identification of LOCs with suitable thermodynamics for the reversible uptake and release of hydrogen as well as an acceptable combination of physical properties (*i.e.* low freezing point, low vapor pressure, and low molecular weight); and 2) development of highly active catalysts for the reversible dehydrogenation of the LOCs. In regard to the later requirement, we recently discovered highly active, "pincer" catalysts. The promising preliminary results obtained with these homogenous dehydrogenation catalysts prompted Hawaii Hydrogen Carriers (HHC) and General Motors (GM) to proposed the work reported here. This effort entailed the optimization a hydrogen storage media based on LOC/homogeneous pincer catalyst (carried out at Hawaii Hydrogen Carriers, LLC) and 2) design of a space, mass and energy efficient tank and reactor system to house and release hydrogen from the media (carried out at General Motor Research Center). The LOC optimization efforts entailed a preliminary screening of a variety of candidate LOCs including: ethyl perhydro-carbazole (EHC), methyl perhydro-methylindole (MHI), aminomethyl cyclohexane (AMC), and perhydro-butylpyrrolidine (BHP). Detailed, variable temperature studies were then carried out to determine the kinetic parameters of the catalytic dehydrogenation of the most promising candidates, EHC, MHI, and BHP. Our studies found that the iridium pincer complex, $IrH_2\{C_6H_3\text{-}2,6\text{-}(OPBu^t_2)_2\}$ effectively catalyzes the rapid dehydrogenation of saturated 5-membered, nitrogen-containing rings of the pyrrolidine-based LOCs at rates that are relevant to demands of an onboard PEM fuel cell. Notably, we found that high rates of LOC dehydrogenation, approaching those required for practical viability for use with proton exchange membrane (PEM), can be achieved at 200ºC in the presence of only 100 ppm of the pincer catalyst. This translates to an acceptable catalyst cost of ~$5/L. Thus, effective loadings of the precious metal containing catalyst would not be cost

prohibitive for an onboard, LOC-based hydrogen storage system. at 140ºC. BHP undergoes quantitative dehydrogenation at 140ºC in 18 h which is significantly lower than the 160 and 180ºC temperatures required to achieve the same rates for MHI and EHC, respectively. Thus the best LOC/catalyst combination that identified in our studies is BHP/$IrH_2\{C_6H_3\text{-}2,6\text{-}(OPBu^t{}_2)_2$. The dehydrogenation onset temperatures correlate with collision frequency factors rather than the activation energies. Thus the steric constraints of the approach of the LOC rather than the barrier to C-H bond activation at the iridium center apparently limit the rate of reaction. Additionally, studies of the dehydrogenation of MHI and EHC in the presence of the hydrogen acceptor, t-butylethylene revealed that the favorable thermodynamics of the transfer dehydrogenation reactions did not result in higher conversions to fully dehydrogenated products. Clearly, the resistance to the dehydrogenation of the 6-membered rings is due to a high kinetic barrier rather than an unfavorable dehydrogenation equilibrium. We conclude that the steric accessibility of the LOC to the catalyst metal center is a more important consideration then C-H bond strength in the predicting the dehydrogenation performance of a LOC in our catalytic system. Thus the key to the development of higher performance variations on the LOC/pincer catalyst systems is the development of PCP pincer catalysts with reduced steric constraints on the approach of the LOCs to the metal center. We found that higher initial rates of LOC dehydrogenation are obtained with the AsCAs pincer complex, $IrH_2\{C_6H_3\text{-}2,6\text{-}(OAsBu^t{}_2)_2\}$ than those achieved with its PCP analog. However, the AsCAS complex has a low thermal stability and undergoes significant decomposition within a few hours at reaction temperatures. Scale-up cycling studies of both MHI and BHP solutions containing the pincer catalyst and Pd/C found that virtually complete dehydrogenation and re-hydrogenation occurred on each half cycle without any detectable degradation of the LOC or catalyst over the course of 50 cycles, representing 2 million catalytic turnovers of the pincer catalyst. These results indicate that a PCP pincer catalyst could be utilized in a practical LOC-based hydrogen storage system.

Although we set out to design an entire LOC based hydrogen storage system, only the reactor design was studied in moderate detail. However, advances were made in over-all the engineering design. Traditional hydrogen storage media are endothermic in hydrogen release and therefore pose two problems: high levels of often low grade heat are rapidly released upon refilling the system with hydrogen, and parasitic use of stored hydrogen to generate the heat required to release the hydrogen. LOC systems are also endothermic in hydrogen release but can avoid the first problem if the centralized facility that regenerates the LOC is integrated enough to use the heat generated during re-hydrogenation. Since the hydrogen absorption will not be done onboard, the cooling challenge and the hardware to handle it are eliminated. One of the goals of this project was to minimize the parasitic losses by using an innovative design to take advantage of the unique properties of LOCs. The novel LOC reactor design generated for this project uses the waste heat from the fuel cell and at the same time, reduces the size of the radiator currently used to vent fuel cell heat. The liquid nature of the LOC that allows the use the fuel cell heat which is unusable in a solid hydride bed. Operation of 100kw fuel cell nominally requires 2g/s hydrogen or approximately 30g/s LOC if conversion is under 95% complete. If the LOC is at a relatively warm, 30 ˚C and has a nominal heat capacity of 1.75kJ/kgK, it could be heated in this design to 80 ˚C with approximately 2.7kW which is clearly available in the coolant stream. This would save ~1.3g/min of parasitic hydrogen consumption at full power. Given that both the homogenous catalyst and the carrier compound can be temperature sensitive, we favored a heat-transfer-fluid based system. Furthermore, our design sends the combusted gas to the compressor/expander, thus heat is not lost leaving the burner, so the down side to this design is minimized. The hydrogen initially generated by the homogenous catalyst will go toward saturating the carrier rather than immediately starting bubble formation as in a heterogeneous concept. Accordingly, the mass and volume of the reactor can be significantly reduced since micro-channel heat exchangers can be used. In order to minimize the amount of insulation required (and reduce volume and cost), we chose single unit heat exchangers with one directly feeding the next. Several designs were considered for the internal structure of the reactor, all with the same liquid heat transfer system. The internal volume of the reactors was minimized since in addition to taking up less volume, smaller components are lighter and less expensive. Additional issues that are minimized by making the reactor as small as possible include: heat loss due to unnecessary surface area, and the undesirable heating of adjacent parts. Control and hydrogen flow dynamics are also improved by using the smallest possible reactor. The design of the smallest reactor capable of providing 2g/s hydrogen was based on predicted percent LOC conversions that were obtained using COMSOL Multiphysics, version 4.3b. The most efficient design from a volume and mass perspective was the nested helix design. However, the single helix design was only slightly less efficient and would be much simpler and more reliable from an assembly viewpoint. We conclude that the single helical reactor is the most appropriate advanced design to compare with the baseline.

Table of Contents

Figures

Schemes

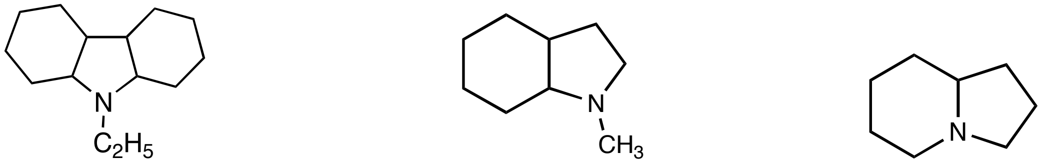
Tables

I. Introduction

For decades, hydrogen has been targeted as the utopian fuel of the future on account of its abundance and environmental friendliness. However, there are major difficulties in the utilization of hydrogen as an onboard fuel. The most significant problems are: 1) simultaneously achieving the requested high gravimetric and volumetric hydrogen storage densities and 2) implementing the appropriate infrastructure. A high density, high stability method for storing hydrogen is essential to the implementation of fuel cells in all but a few niche applications. Liquid organic hydrogen carriers (LOCs) can reversibly release 7-8 wt% hydrogen and be economically manufactured in the massive quantities required to meet the anticipated demand. For the automotive applications, LOCs could utilize existing infrastructure as they are similar to the current distribution medium, gasoline. The tanks, piping and refinery systems used to make and deliver gasoline are appropriate for LOCs. The ability to use well-established material reduces costs, risks, and shortens the time to market. Despite these advantages, the automotive application has the most demanding requirements because of the premium on mass, volume and cost in that highly regulated and competitive marketplace. However, if it cannot be used for practical automotive applications, LOC technology has the advantage of being appropriate for power delivery markets that are less demanding. For example, batteries seek to attain roughly 1/10 the energy density of hydrogen storage systems for vehicles, so accordingly a system useable in vehicles would be more than mass and volume efficient enough for electronics. LOCs could be readily packaged for many other applications such as forklifts, portable power or even small electronics by use of cartridges or hand carried tanks of appropriate size. In each case the same cartridge can be used to return the dehydrogenated fuel so that it may be regenerated. Thus the utilization of LOCs as hydrogen carriers has remained a tantalizing but impractical possibility for over the last 60 years.

Early efforts to develop LOCs were primarily focused on cycloalkanes.[1-6] However, the large enthalpy of dehydrogenation of cycloalkanes (~60 kJ/mol H_2) renders the elimination of hydrogen thermodynamically unfavorable below 300 ˚C which is a major drawback to their utilization in practical systems. The **Δ**H of dehydrogenation is significantly lowered upon introduction of a hetero-atom into the ring system as it significantly reduces the aromaticity of the dehydrogenated molecule. This effect was quantified for a wide variety of heterocyclic compounds through calculation the enthalpy of formation of hydrogenation of aromatic heterocycles and their saturated analogs by Pez et al.[7] In view of their relatively low enthalpies of dehydrogenation pyrrolidines (5-membered heterocycles containing nitrogen): ethyl perhydrocarbazole (EHC), methyl perhydro-methylindole (MHI) and perhydro-indolizidine (HIZ), have been explored as potential

Figure 1. Structures of saturated pyrrolidines.



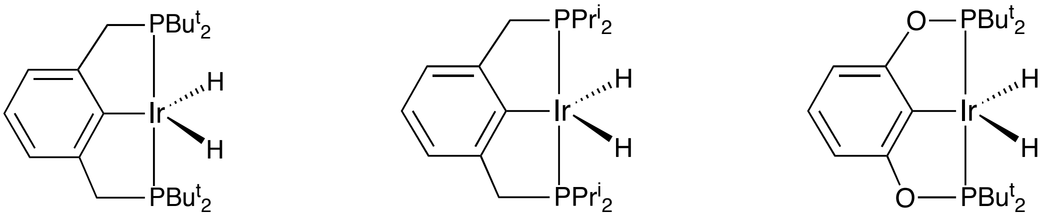
N-ethylperhydroethylcarbazole (EHC) perhydro-methylindole (MHI) perhydro-indolizidine (HIZ)

LOCs.[8-12] While this work generated significant initial excitement, in the end three aspects frustrated the desire to commercialize it; (1) rates at moderate temperatures were too low; (2) even when higher temperature reaction was accepted the catalytic sites would become saturated with hydrogen gas, restricting reactant access and thus hydrogen production; and (3) side reactions created byproducts that required extensive and expensive treatment to return to a useable state [10].

In order to overcome the barrier to practicality that is imposed by the heterogeneous catalysts, we have been developing alternative homogeneous catalysts. It is well known that the high dispersion achieved by homogenous catalysts increases the rate for a given mass of catalytic metal. Also, a homogenous catalyst will generally create dissolved hydrogen and will not become occluded with bubbles. In 1997, we discovered that the "pincer" complex, $IrH_2\{2,6\text{-}C_6H_3\text{-}CH_2PBu^t{}_2\}_2$ (**1**), catalyzes the dehydrogenation of cycloalkanes to arenes.[13-14] This was first report of a homogenous catalyst for this reaction. The unique reactivity of this especially robust and active catalyst can be ascribed to the tridentate "PCP pincer" ligands which contain two coordinating, neutral phosphorus centers as well as an anionic, coordinating carbon site. It has been found that the electronic environment of the catalytic metal center of the pincer complex is highly sensitive to minor changes in the PCP pincer ligand. Following our report that **1** catalyzes the dehydrogenation of aliphatic groups, the related PCP pincer complexes, $IrH_2\{2,6\text{-}C_6H_3\text{-}$

$CH_2PPr^i_2\}_2$ (**2**) and $IrH_2\{C_6H_3\text{-}2,6\text{-}(OPBu^t_2)_2\}$ **(3)** were found to have incrementally improved catalytic activity.

Figure 2. PCP pincer complexes, homogeneous dehydrogenation catalysts.

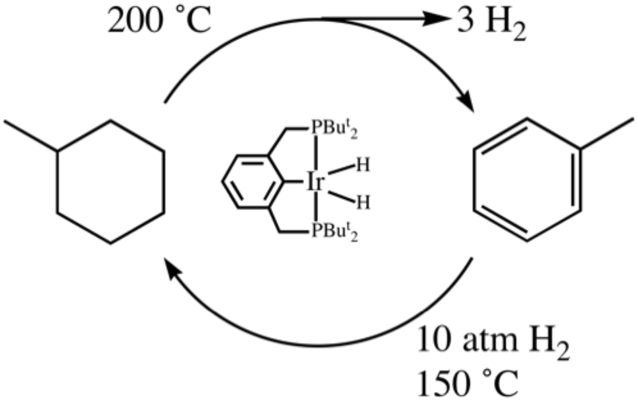


$IrH_2\{2,6\text{-}C_6H_3\text{-}CH_2PBu^t_2\}_2$ (**1**) $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PPr^i_2)_2$ (2) $IrH_2\{C_6H_3\text{-}2,6\text{-}(OPBu^t_2)_2$ (3)

[15-16] It is now well established that dihydro PCP pincer iridium complexes can selectively dehydrogenate aliphatic groups under much milder conditions than those required for the corresponding heterogeneous catalysts, such as platinum on alumina without harm to other functional groups of an organic molecule.

We also found that **1** catalyzes the reverse reaction, the hydrogenation of arenes at 150 ˚C under 10 atm of hydrogen.[5] Thus it is possible to carry out the cyclic dehydrogenation/ hydrogenation of methylcyclohexane to toluene in a single reactor as shown schematically in Scheme 1.[5]

Scheme 1. Reversible dehydrogenation of methylcyclohexane catalyzed by PCP pincer complex.



However, the dehydrogenation of methylcyclohexane is inhibited by the above mentioned stringent thermodynamic constraints, and only low <1 atm equilibrium hydrogen pressures can be achieved below 200 ˚C. In order to avoid the establishment of an unfavorable equilibrium, we conducted studies using a reactor equipped with a Pd/Ag filter tube that was selectively permeable to hydrogen.[5] We were only partially successful at producing the envisioned hydrogen storage system as inadequate performance by the requisite Pd/Ag membrane resulted in less than 10 % conversion of methylcyclohexane to toluene during the dehydrogenation half-cycles. We have also suggested that a practical hydrogen storage system could be based on solutions of saturated cyclic organic liquids and pincer catalyst that are circulated through a heated "hot-tube" for dehydrogenation thus avoid the energy demand of heating the entire hydrogen storage material reservoir.[17] We have found that hydrogen can be evolved from the solutions of cycloalkanes and pincer catalyst at temperatures as low as 100 ˚C. Unfortunately, the rate of hydrogen evolution from the cycloalkane based systems did not even approach those required for practical applications.

More recently, we found complexes **1-3** are highly active homogeneous catalyst for the dehydrogenation of amines [18,19] heterocyclic LOCs such as N-ethylcarbazole (EC) [8,9,12]. Our studies have shown complex **3** to be the most active catalyst for the dehydrogenation of LOCs at temperatures as low as 150˚C. The pincer complex catalyzed system showed significantly faster kinetics even at 2 orders of magnitude lower catalysts loadings than those employed in the heterogeneous system. Thus seemed possible that the homogeneous pincer catalysts could possibly enable the utilization of LOCs as practical hydrogen carriers. Furthermore, preliminary studies of the novel AsCAs pincer complex, $IrH_2\{C_6H_3\text{-}2,6\text{-}(OAsBu^t_2)_2\}$ (**4**), showed it to be an even more active catalyst for the dehydrogenation catalyst for LOCs than **3**.

Figure 3. Structure of N-ethylcarbazole (EC).

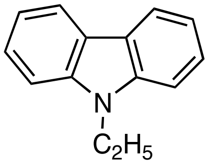
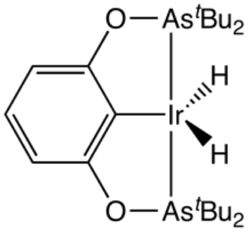


Figure 4. Structure of As-C-As Pincer $IrH_2\{C_6H_3\text{-}2,6\text{-}(OAsBu^t{}_2)_2\}$ (**4**)



These promising preliminary results prompted Hawaii Hydrogen Carriers (HHC) and General Motors (GM) to proposed the work reported here. This effort entailed the development of an optimized catalyst/carrier combination with the best combination of high cycling capacity, rapid dehydrogenation kinetics, high carrier/catalyst cycling stability; and the design of a space, mass and energy efficient tank and reactor system to house the carrier and release the hydrogen.

II. Objectives

The objectives of this project were: 1) optimize a hydrogen storage media based on LOC/homogeneous pincer catalyst (carried out at Hawaii Hydrogen Carriers, LLC) and 2) develop space, mass and energy efficient tank and reactor system to house and release hydrogen from the media (carried out at General Motor Research Center).

III. Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan: (A) System Weight and Volume; (B) System Cost; (C) Effiiency; (E) Charging/Discharging Rates; (H) Balance-of-Plant (BOP) Components; (J) Thermal management; and (Q) Regeneration Processes.

IV. Technical Targets

1. Identification of a low-cost LOC that, in the presence of low loading of a homogeneous pincer catalyst, will release >7 wt% H_2 at sufficiently high rates and low temperatures in a practical, onboard dehydrogenation reactor to meet the demands of an onboard fuel cell.

2. Identification of a LOC/pincer catalyst combination of sufficiently high hydrogen cycling capacity that rapidly dehydrogenates without also undergoing LOC degradation upon cycling.

3. Utilization of the advantages of the liquid hydrogen storage medium to eliminate thermal management problems associated with solid-state hydrogen absorbing materials.

4. Design of a space-, mass- and energy-efficient tank and reactor system to house the LOC and facilitate hydrogen release that can be easily interfaced with a fuel cell. Cost-aware designs with characterization of the hydrogen generation, transient performance, and selectivity through simulations at several critical conditions. Estimations of system hydrogen density and specific mass, flow rates, potential operation ranges. Identification of gains that could be made with improvements in catalyst or carrier, and areas where improved engineering could markedly affect mass, volume or cost.

V. Approach

The originally envisioned project was divided into the following tasks and subtasks using the approaches detailed below.

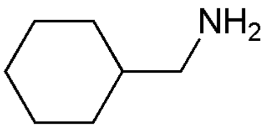
Task 1. Optimization of Catalyst/LOHC Hydrogen Cycling Performance.

Subtask 1.1. Isothermal Kinetics Studies. Our previous studies established the chemo-selectivity, turnover numbers, and relative rates of the catalytic dehydrogenation of amino-LOCs. These studies were in line with the large number of studies of dehydrogenation reactions catalyzed by iridium pincer catalyst that have focused on the determination of turnover numbers, turnover frequencies, and intermediates in the catalytic reaction pathway. However, we did not determine the kinetic properties of activation energy and frequency factor associated with the reactions that are required for the engineering design of an onboard reactor based LOCs.[8,9,12] This task will entail determination of the kinetic properties governing the catalytic dehydrogenation of pyrrolidines LOCs by **1** which is, to our knowledge, the first study of this kind for the dehydrogenation reaction catalyzed by a homogeneous iridium pincer complex. Studies will be carried on the candidate LOCs, ethyl perhydrocarbazole (EHC), methyl perhydro-methylindole (MHI) and perhydro-indolizidine (HIZ), and aminomethyl-cyclohexane (ACH). Product identification and quantification will be accomplished using NMR and GC-MS analysis. We will initially employ catalyst loadings of 1.0 x 10^{-3} M. However, in cases where the rates of dehydrogenation are found to be insufficient for practical applications, we will conduct systematic studies over a range of higher catalysts concentration in order to determine the level of catalyst loading that is required to achieve acceptable rates.

Subtask 1.2. Differentiation of Thermodynamic vs. Kinetic Limitation In cases where incomplete dehydrogention is observed, it imperative to determine if the reaction has been limited by the equilibrium positioning of the hydrogenated and dehydrogenated form of the LOC or slow reactions kinetics. Over the course of our previous studies, we have developed a simple test to make this distinction. Our method involves carrying out the dehydrogenation in a closed system in the presence of a hydrogen acceptor compound such as t-butyl ethylene. In this "transfer dehydrogenation" situation, the extent of the reaction is governed by the thermodynamics of the exchange of hydrogen between the organic molecules rather than those of the liberation of free hydrogen gas from the saturated version of the LOC. Finding that the dehydrogenation of a LOC goes to completion in the presence of the hydrogen acceptor clearly signals that an incomplete "acceptorless" reaction is limited by thermodynamic constraints of the equilibrium between addition/elimination of H_2 whereas the finding of equal levels of dehydrogenation in both the transfer and acceptorless dehydrogenation experiments points to slow kinetics of the dehydrogenation reaction. We plan to carry out such studies whenever incomplete dehydrogenation is encountered.

Substask 1.3. Additive Intervention of Side Reactions. Amino-methylcyclohexane (AMC) is an attractive candidate LOC. In addition to 3 equivalents of hydrogen that can be released from the 6-membered carbon ring, the amine functionality can liberate 2 equivalents of hydrogen upon dehydrogenation to the corresponding nitrile. Thus in addition to lowering H_{dehyd}, the presence of the amine group increases the potential reversible hydrogen wt% of AMC to 8.83. The pincer complex **3** was found to efficiently catalyze the dehydrogenation of AMC. However, the analysis

Figure 5. Structure of Amino-methylcyclohexane (AMC).



revealed the product mixture contained only ~10% of the desired product cyclohexanecarbonitrile together with ~20% cyclohexylmethylcyclohexyl-imine and ~70% biscyclohexylmethylamine Additionally, analysis of a sample obtained from a 1 atm of argon purge of the reaction mixtures shows that the H_2 evolved from the reaction was highly contaminated with ammonia. Although 6.24 wt% hydrogen was released from the reaction mixture, the starting material cannot be regenerated from the observed products thus their formation is incompatible with hydrogen storage applications. The undesired products are probably the result of the intrinsic reactivity of the imine intermediate with nucleophilic amine starting material. The formation of dialkylamines and imines is a common side reaction observed in the metal catalyzed hydrogenation of nitriles to amines. Thus the initial imine product resulting from the dehydrogenation product likely undergoes a nucleophilic addition with starting amine then undergoes sequential ammonia elimination to produce cyclohexylmethyl-cyclohexylimine which can undergo transfer hydrogenation to give biscyclohexylmethylamine. Studies of the hydrogenation of nitriles to amines have shown that the formation of dialkylamines and imines can be minimized by the addition of a base such as alkali metal hydroxides, hydrides, butoxides, and ethoxides to the reaction mixture. Preliminary studies showed that the pincer complex catalyzed dehydrogenation of AMC have shown that the selectivity for nitrile formation over the side reactions is remarkably improved in when the dehydrogenation is carried out in the presence of the hindered base, $NaOBu^t$ and the formation of undesired products is virtually eliminated at the high concentrations of the base. In order to maximize the hydrogen production from this reaction while preventing the formation of the unwanted side products, we will explore the dehydrogenation of AMC over a range temperatures and with varied concentrations of pincer catalyst and $NaOBu^t$.

Subtask 1.4 Cycling Studies. LOC/catalyst combinations found to have acceptable dehydrogenation behavior in terms of both reaction rate and capacity will undergo cycling studies. These studies will establish the long term cycling durability of the LOC systems. The re-hydrogenation half cycles will be carried out in an autoclave under 50 bar of hydrogen pressure in the 150-200 ˚C temperature range. The hydrogenation to the fully saturated LOC will be verified by GC-MS analysis. Initially, the re-hydrogenation reaction will be carried out in the absence of any additional catalysts. This will provide a test of the “two-way” effectiveness of the pincer catalyst. If the hydrogenation are found to be incomplete or unacceptably slow, a heterogeneous Ru/C catalyst will be added to insure full re-hydrogenation and/or accelerate the reaction.

Task 2. Design and Modeling of Reactor.

The design and modeling of systems to be conducted at GMRC will provide the experimental work with feedback on the potential system capabilities of discovered catalyst/carrier systems and additionally provide estimates of the progress toward the DOE goals. Synergistically, by working from validated rates and capacities provided in the experimental tasks, the modeling will be able to produce more realistic simulations and thus more accurately converge to near optimal engineering solutions. A benefit of this simultaneous chemistry and engineering approach is that the chemists will be directed toward the most essential improvements needed to achieve DOE’s system based goals, while the engineering team will understand the strengths to exploit and the areas in which the design must accommodate the materials. The result will be a more robust system that advances the capabilities of liquid organic hydrogen carriers.

2.1 Model Development. The sub-task is divided into four parts. The first part is to devise a notional model of the entire system. In part 2, one or more reactor model(s) are developed in detail using COMSOL. As the model or models are completed, they will be validated in part 3 to be certain the fluid mechanics, heat transfer, and reaction proceed as would be expected based on the standard engineering concepts. Part 4 will entail a basic estimate of the cost of the system.

2.2 Function Evaluation. Our experience indicates that the system function and cost is often fixed by the full flow condition. To ensure efficient use of resources, we will evaluate this functionality first. Once the reactor “runs” at the full-flow condition it will be evaluated at idle. Once these extremes have been evaluated, the mid-speed/mid-load condition will be evaluated and finally transient performance will be evaluated.

2.3 System Optimization. This task is centered on improving the storage materials. Based on what we have learned about the system function, we will look for both reactor and balance-of-plant aspects where cost-effective change is possible but the focus will be on what aspects of the LOC enable significant improvements in the overall system.

2.4 Final Simulations. This subtask is analogous to subtask 2.2. Steady state and transient simulations will both be done with multiple reaction paths so that both efficiency and selectivity can be evaluated. At the conclusion of the simulations the data will be evaluated, and documented as part of the final report of the full project.

VI. Results

Subtask 1.1 Isothermal Kinetic Studies

Samples of the candidate LOCs, methylindole (MI), indolizidine (IZ), and_ethylcarbazole (EC) were obtained from commercial sources. They were hydrogenated to the saturated, perhydro-LOCs using standard methods.[9] The PCP pincer catalysts were prepared using standard Schlenk techniques using the methods reported in the literature. Catalysts were then checked for activity under well-established protocols, specifically for the conversion of cyclooctane to cyclooctene with a hydrogen acceptor molecule, tert-butylethylene. The high purity of the perhydro-LOCs and pincer complexes was established by comparison to literature reports by gas chromatograph-mass spectrometry as well as ^{1}H, ^{13}C, and ^{31}P nuclear magnetic resonance (NMR) spectroscopy and found acceptable.

The first step in these studies was to establish benchmarks activities of the homogeneous pincer catalysts for comparisons using our current apparatus and analytical tools rather than to reply on literature values. It should be noted that this system advantageously operates in the neat LOC and does not require a solvent. Dehydrogenation reactions were run with 0.850 mmol of the LOC and 1 mol% of catalyst **3** at the prescribed temperatures (140-200 ºC) and times (0-48 h) within an integrated glass reflux condenser connected to an oil bubbler. Reactions were monitored by GCMS via the disappearance of the LOC and appearance of the dehydrogenated products, the results of which are summarized in Table 1. Preliminary experiments on the LOCs were carried

Table 1. Rate constants (k) for LOCs 2-4 at 160-200ºC.

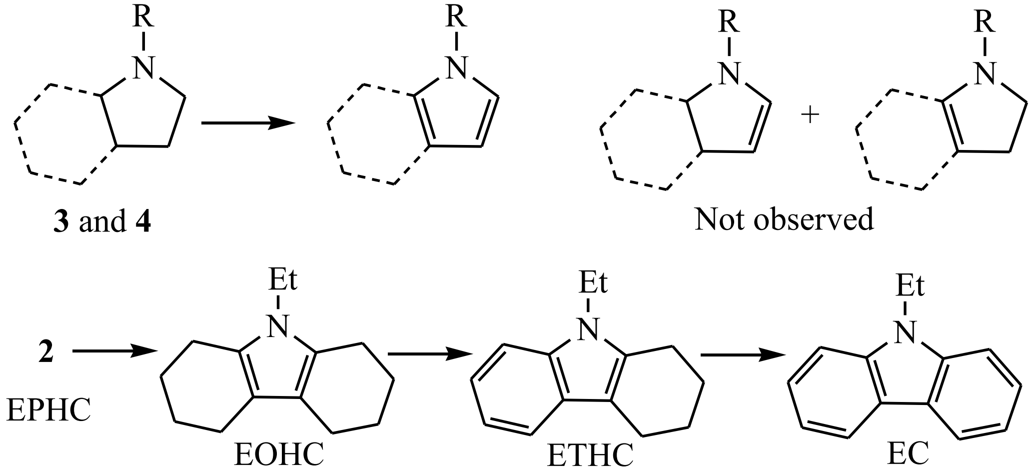
	Rate Constant, k (s^{-1}) (x 10^{-5})		
Temperature	**2**	**3**	**4**
160 °C	N/A	0.07162	0.1371
170 °C	N/A	0.1630	0.7172
180 °C	2.215	0.4401	0.8805
190 °C	3.317	0.8879	4.862
200 °C	7.075	1.840	6.873

out to determine the dehydrogenation onset temperature (DOT), which is defined as the temperature at which at least a 5 % yield of H_2 is obtained within a 24 hour period). The temperature range of the dehydrogenations was constrained by DOT on the low end and catalyst stability on the high end, 200 ºC. In addition to defining the experimental temperature range for our kinetic studies, the DOT is also an important consideration when evaluating a LOC's application potential (as it also reflects the temperature required to start and maintain an onboard reactor). These studies consistent showed that only the 5-membered, nitrogen-containing ring of EHC and MHI undergoes rapid dehydrogenation and the 6-membered ring does not undergo appreciable dehydrogenation at relevant rates.

A linear relationship is observed for the plots of ln[mol] vs time for the LOCs. Thus, the dehydrogenation reactions follow first order or pseudo-first order kinetics. Although elimination of two equivalents of H_2 from the pyrrolidine ring is certainly a multi-step process, as indicated in Scheme 2, intermediates with only one unsaturated carbon-carbon bond were never observed in the dehydrogenation of any of the LOCs . We infer that the lost of second equivalent of hydrogen is much more rapid than the first and that this process involves a single rate-limiting step. In addition to the determination of the rate constants in the practical dehydrogenation temperature window, we also note the hydrogen weight percent that is available within the practically relevant time frame of our studies (36 hours) is also of key importance in evaluating a LOC's application potential.

While EHC has the highest theoretical hydrogen wt% (5.80%) of those tested, it is certainly the most complicated of the LOCs we examined. We found that heating to 180°C (rather than 150°C

Scheme 2. Dehydrogenation pathways of LOCs showing intermediates
(potential and observed) and dehydrogenated products.

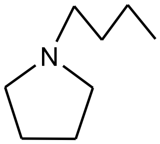


as was previously reported [8]) was required to achieve practical levels of dehydrogenation of EHC within a 24 hour period. The central pyrrolidine portion of the molecule can be selectively dehydrogenated (within a narrow window; 174-178˚C and requiring an increased catalyst loading and time) yielding ethyl octahydrocarbazole (EOHC). At higher temperatures dehydrogenation continues to occur via each successive cyclohexane ring, yielding ethyl tetrahydrocarbazole (ETHC), and eventually ethyl carbazole (EC), Scheme 2. The two main drawbacks of EHC as an LOC are the high DOT and that EC is a solid at ambient temperatures.

MHI is an attractive candidate LOC since: 1) it is a liquid in both the hydrogenated and dehydrogenated forms and 2) its DOT is 20 °C lower (160 °C) than EHC. However, we have found MHI will undergo selective dehydrogenation of only the pyrrolidine regardless of temperature, thus reducing the available hydrogen from 5.81 to 2.88 wt %. Also regardless of temperature, MHI had slower rates of dehydrogenation than EHC. We have also found that at temperatures up to 200°C, only the 5-membered ring of HIZ undergoes rapid dehydrogenation while the 6-membered ring does not undergo dehydrogenation at relevant rates. In view of the much higher cost (>50x) HIZ and similarity of its dehydrogenation behavior to MHI, we eliminated HIZ as a candidate LOC.

Having eliminated HIZ from consideration and finding **3** catalyzes the dehydrogenation of the nitrogen-containing 5-membered ring of MHI and EHC at rates that are inadequate for PEM fuel cell applications in the 150-200ºC temperature range, we extended our screening studies of candidate LOCs. We found that that the 5-member ring of butyl perhydro-pyrolidene (BHP)

Figure 6. Structure of butyl perhydropyrolidine (BHP)



undergoes dehydrogenation at significantly higher rates than MHI. For example, virtually quantitative dehydrogenation was found to occur at 140ºC in 18 h. BHP **4** has the greatest overall potential as a practical LOC among the substrates examined in this study. It is a liquid in both hydrogenated and dehydrogenated forms. Additionally, our studies show it has by far the lowest DOT, 140 °C; the highest rates of dehydrogenation; and an appreciable, 3.14 available hydrogen wt%.

As only the pyrrolidine ring of MHI and **BHP** undergo dehydrogenation and no intermediates were observed, standard first order kinetic analysis was applied to extract the desired kinetic properties. While this works well for **MHI** and **BHP** it is an over simplistic approach for the ethyl carbazole system as above 178 ºC **2**, EOHC, and ETHC are all simultaneously in solution competing for the dehydrogenation catalyst **1**. While flawed, this approach is the only way to directly compare the LOCs, and thus the values reported for EHC herein should take this assumption into consideration. Figure 8 shows a sample of data treatment for **3** in which the natural log of rate constant values (k) at five separate temperatures (160, 170, 180, 190, and 200 ºC) are plotted against inverse temperature (in Kelvin). Activation energy and collision frequency factor numbers were obtained from the linear plot giving the equation, y = -17121(x) + 25.379, Figure 8. The reactions were followed by the disappearance of the completely hydrogenated LOC. The reaction energetic parameters seen in Table 2 were extracted from standard Arrhenius plots of the kinetics, Table 2. Activation energies (E_A) of 115, 142, and 166 (kJ/mol) and frequency factors (A) of 3.56×10^8, 1.05×10^{11}, and 2.17×10^{14} (s^{-1}) were found for EHC, MHI, and BHP

Figure 8. Arrhenius plot (ln k versus 1/T) for MHI.

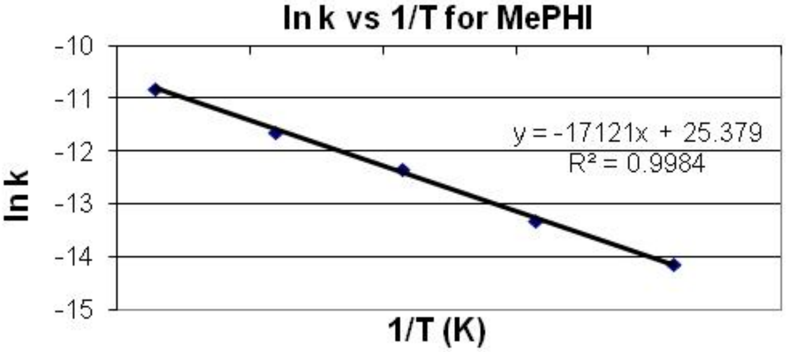
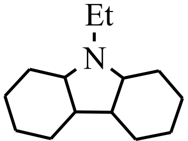
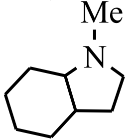
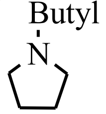


Table 2. Activation energies, frequency factors for LOCs.

LOC	Activation Energy E_a (kJ/mol)	Frequency Factor A (s^{-1})
	115.1	3.562×10^{8}
	142.4	1.052×10^{11}
	166.1	2.170×10^{14}

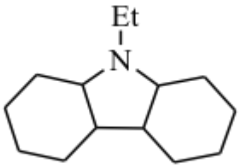
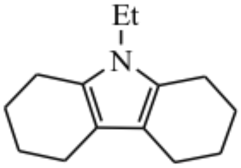
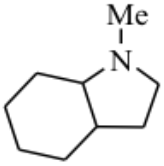
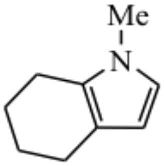
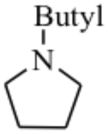
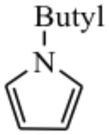
respectively. The variation in these values initially is surprising as the hydrogen storage literature has focused mainly on the enthalpy, for which most pyrrolidine based molecules have similar values.[7,10,11] It should be noted that in the case of EHC, the rate of the catalytic dehydrogenation is prohibitively slow below 180°C and the pincer catalyst undergoes thermal decomposition at significant rates above 200°C. Since data could be obtained only within a narrow temperature range, the reliability of the intercept value obtained from the Arrhenius plots is somewhat questionable.

On first inspection it is surprising that, in general, the fastest rate of reaction is observed for BHP, the substrate with the highest E_a. However, the effective collision frequency factor for BHP was roughly 3 and 6 orders of magnitude greater than EHC and MHI respectively. These values likewise aligned directly with the trend we observed for the DOT. The results point toward a dependence of the frequency factor with the steric constraints of the LOC. MHI has only one cyclohexane ring while BHP has a flexible n-butyl chain thus lower respective DOTs of 160 °C and 140 °C. We envision the two ring systems on each side of the pyrrolidine portion of EHC sterically inhibiting the access to the catalyst. Thus it seems plausible that as steric accessibility of the LOC increases, the effective collisions decreases and more thermal energy is required for dehydrogenation, which is reflected in a higher DOT. The DOTs correlate with collision frequency factors rather than the activation energies. Thus the steric constraints of the approach of the LOC rather than the barrier to C-H bond activation at the iridium center apparently limit the rate of reaction. We conclude that the steric accessibility of the LOC to the catalyst metal center is a more important consideration then C-H bond strength in the predicting the dehydrogenation performance of a LOC in our catalytic system.

As mentioned in the introduction, preliminary studies of the novel AsCAs pincer complex, $IrH_2\{C_6H_3\text{-}2,6\text{-}(OAsBu^t{}_2)_2\}$ (**4**), showed it to have a higher activity as a LOC dehydrogenation catalyst than **3**. This observation was verified in that higher initial rates of LOC dehydrogenation are achieved with the AsCAs pincer complex. However, it was found to have much lower thermal stability than the PCP, undergoing immediate decomposition at 200 ˚C and significant decomposition within a few hours at 150˚. As seen in Table 3, when compared after a 24 hour reaction period, the LOC dehydrogenation activity of the arsenic pincer catalyst is ~50% lower than that of the phosphorus analog. Since decomposition is not seen during catalytic dehydrogenations with **1, 2,** or **3**, this instability is presumably due to the presence of weaker As-O or As-Ir bonds. It should also be noted that the arsenic pincer complex also consistently showed no activity as a hydrogenation catalyst over conditions ranging up to 200 ˚C and a hydrogen pressure of 140 atm. Clearly the arsenic pincer complex is unsuitable for practical applications.

The FY 2012 Annual Merit Review reviewers were concerned that the PCP pincer catalyst is based on a precious metal and therefore might be prohibitively expensive for utilization in a commercially affordable hydrogen storage system. The high cost of iridium is indeed a very

Table 3. Results of dehydrogenation trials of pyrrolidine substrates (1mol%catalyst loading). Yield obtained using the As pincer is followed by yield obtained using the P pincer in parentheses.

Substrate		Temp	Time	Product	yield[a]
EPHC **5**		180 ºC	24 hrs		25 (52)%
MePHI **6**		180 ºC	24 hrs		12 (25)%
BuPy **7**		180 ºC	24 hrs		23 (44)%

a = yield of phosphino iridium pincer catalyst in parentheses

significant consideration. According to our calculations, the cost of the catalyst would be acceptable only if extremely low catalyst loadings were able to effect the dehydrogenation of LOCs at rates that could meet the operational demands of an onboard PEM fuel cell. According to our calculations, an acceptable cost of \$5/liter would allow a catalyst loading of only 100 ppm as opposed to the much higher, 1 mol% catalyst concentrations that were used in our previous studies. We have found that acceptable rates of dehydrogenation can be achieved by the low, 100-ppm catalyst concentrations. These finding suggest the iridium-based catalyst could indeed be economically viable. These considerations led us to examine the dehydrogenation of the solutions of the LOCs containing only 100 ppm of **3**. Surprisingly, we found that the pincer complex exhibits higher catalytic activities at the lower level loadings (rate constants of 1.37×10^{-3} and 2.75×10^{-4} s^{-1} for BHP and MHI respectively). We believe this is an experimental artefact due to the deposition of significant amounts of catalyst on the walls of our reactors when they are loaded with 1 mol% catalyst solutions. Therefore, we feel that the kinetic values obtained at the 100-ppm catalyst loadings are more accurate than those based on the 1 mol% solutions.

Task 1.2 Differentiation of Thermodynamic vs. Kinetic Limitations

As discussed above, **3** efficiently catalyzes the dehydrogenation of the nitrogen-containing 5-membered ring of MHI but exhibits only modest activity with the 6-membered ring. This was also found to be the case for HIZ and EHC. In order to differentiate whether this due to either: 1) the equilibrium position of the liberation of free hydrogen gas from the saturated version of the LOC or 2) slow reaction kinetics resulting from inhibition of the breaking of C-H bonds due to successful competition by the nitrogen atom of the heterocycle for coordination to the metal center of the pincer catalyst, we carried out studies of the dehydrogenation of MHI and EHC in the presence of the hydrogen acceptor, t-butylethylene. In all cases, GCMS analysis of the product mixture contained less than 5% conversion to the fully dehydrogenated products, N-methylindole and N-ethylcarbozole while the partially dehydrogenated products, N-methyl-tetrahydroindolizidine and N-ethyloctahydrocarbazole were obtained in >95% yield. Thus the more favorable thermodynamics of the transfer dehydrogenation reactions did not result in higher conversions to fully dehydrogenated products. We conclude that resistance to the dehydrogenation of the 6-membered rings is due to a high kinetic barrier rather than an unfavorable dehydrogenation equilibrium.

Task1.3 Additive Intervention of Side Reactions

Studies of the catalytic dehydrogenation of AMC by **3** over a range temperatures and varied concentrations of pincer catalyst and $NaOBu^t$ showed that the addition of hindered base (sodium tert-butoxide) is consistently effective in inhibiting the unwanted imine condensation side reaction during the dehydrogenation of AMC. However, only low, <33% conversions to doubly unsaturated cyclohexylnitrile could be achieved. Also in analogy to EHC, MHI, and HIZ, the 6-membered aliphatic ring does not under dehydrogenation.

Task 1.4 Cycling Studies

Two reactors were constructed for our scale-up cycling studies. Initial cycling experiments were run with the homogenous PCP pincer complex serving as both the dehydrogenation and re-hydrogenation catalyst. In our initial study, 100 mL MIH was dehydrogenated and re-hydrogenated 10 times and GCMS and NMR analysis was carried out after each half cycle. No traces of LOC or catalyst decomposition products were detected. However, only 89% re-hydrogenation was achieved in these experiments. In order to achieve 100% re-hydrogenation, a second round of scale-up cycling studies with both MHI and BHP solutions containing 100 ppm of the pincer catalyst and 100 ppm of Pd on carbon black were completed. Fifty cycles of dehydrogenation and re-hydrogen have been carried out. GCMS and NMR)analysis has verified that virtually no degradation of the LOC or catalyst has occurred during the 2 million catalytic turnovers that the pincer catalyst that were performed.

Task 2. Design and Modeling of Reactor.

As the work progressed under a Department of Energy contract, it became clear that the key hurdle was the identification and improvement of the carrier/catalyst combination that would make up a highly functional LOC; accordingly, funds were shifted to favor that work and work on the engineering focused on proper reactor geometry. While the basics of the entire system were set out at the beginning of the work, only the reactor design was studied in moderate detail. Detailed design was outside the scope of the problem. However, advances were made in the engineering design and some attributes of a high performing LOC could be identified based on this level of analysis.

An integrated heat transfer and reactor system

Traditional hydrogen storage media are endothermic in hydrogen release and therefore pose two problems: high levels of often low grade heat are rapidly released upon refilling the system with hydrogen, and parasitic use of stored hydrogen to generate the heat required to release the hydrogen. LOC systems are also endothermic in hydrogen release but by the nature of their fuel cycle design avoid the first problem and can potentially even turn it into an asset. This is possible if the plant regenerating the carrier is integrated enough to use the quality of heat generated during rehydrogenation either in other chemical processes or for use in other heating, for example buildings. On board the vehicle this means that there will not be hydrogen absorption (that was done in the plant), so the cooling challenge and the hardware to handle it may be eliminated.

To illustrate the second problem more fully, consider the case of a bed of solid hydride with an enthalpy requirement of 35kJ/mol hydrogen released, and moderate kinetics. The operating desorption temperature of such a hydride bed will need to be heated to between 150 and 200 C, depending on the kinetics and the peak flow rate that must be attained. Because this is well above the fuel cell operating temperature the copious waste heat from the fuel cell cannot be utilized in releasing hydrogen, and because the difference between the fuel cell and hydrogen release temperature is large, this heat cannot even be accessed economically using a heat pump. Consequently, hydrogen must be burned or electricity from the fuel cell must be used to heat the hydride bed. One of the goals of this project is to reduce to a minimum the parasitic losses by using innovative design to take advantage of the unique properties of LOCs.

As a baseline, we will use an LOC reactor system paired with the advanced burner developed by GM and Sandia in the joint program conducted on a full size $NaAlH_4$-based system [20]. This consists of a catalytic burner for improved heat transfer to a heat transfer oil, integrated with a recuperator [21]. There is extensive data on this system in the literature and we simply incorporate that knowledge rather than redesign the baseline system. This burner drives an LOC heater and the reactor, both of which use a counter current flow configuration. For convenience they will be divided into two conceptual sections, a heating section bringing the fluid to reactor temperature and a reactor where enthalpy of reaction is provided but LOC temperature is largely constant. In practice it may be possible to make this all one heater/reactor. The general heat flow schematic is shown in Figure 8.

Using the established Sandia/GM catalytic burner / recuperator design, the LOC is warmed from tank temperature to reaction temperature by hot heat transfer fluid, and then the reaction is also driven by hot heat transfer fluid. The fluid is heated by combusted hydrogen.

This baseline scheme uses a simple design, a proven and fairly advanced burner, an efficient heating section and a simple and relatively efficient reactor. For further efficiency the combustion gas is sent to the compressor / expander in the fuel-cell balance-of-plant to extract work from the heat in the gas leaving the LOC reactor system. This technique was used in simulations by Ahlawahlia et al. and it has been shown to improve vehicle level energy efficiency [22, 23]. However, in the baseline configuration the heat from the fuel cell coolant is still wasted and the heat in the LOC reaction products is also lost and may even require some cooling.

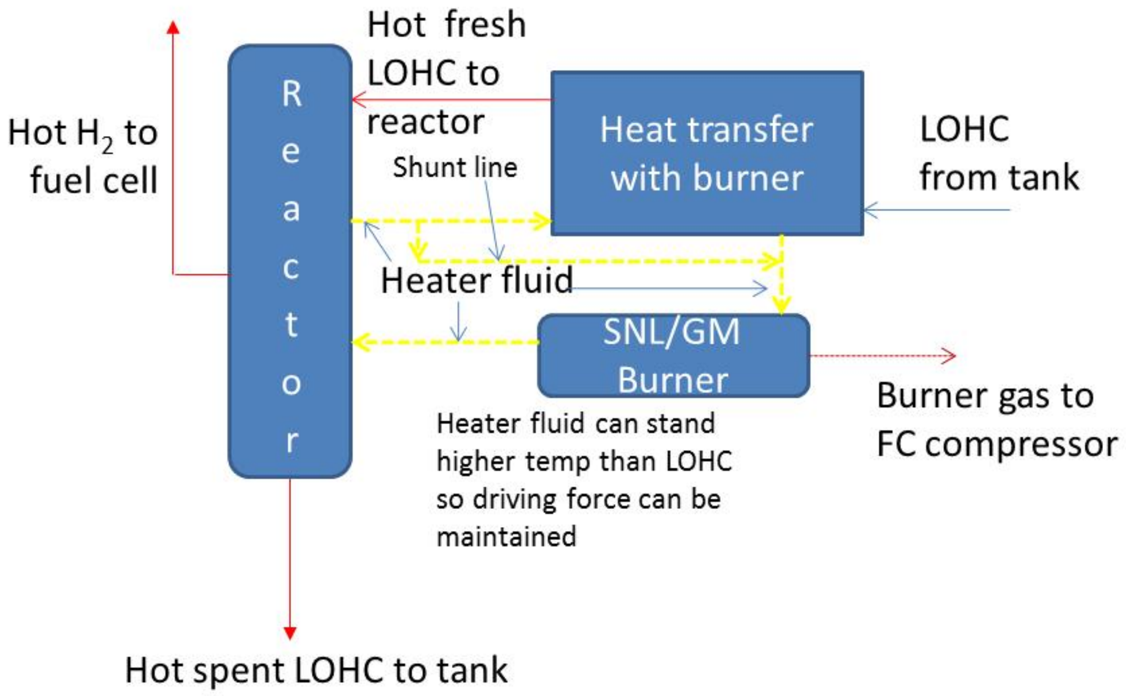


Figure 8. Baseline heat transfer scheme.

In the new LOC reactor design generated for this project we are able use the waste heat from the fuel cell and at the same time reduce the size of the radiator currently used to vent fuel cell heat. We would claim this cost and mass as an offset to the cost and mass of the LOC system. It is the liquid nature of the LOC that allows us to use the fuel cell heat which was unusable in a solid hydride bed. The LOC will come in a steady stream from the fresh fuel side of the tank, and it will generally be at or near ambient temperature. It will certainly be much cooler than the fuel cell coolant which is nominally 80C and may be hotter. Consequently, the temperature gradient between fuel cell coolant and LOC will be approximately fixed and of an appropriate magnitude for heating the LOC part of the way to operation temperature. It is simply a matter of using a heat exchanger to draw heat from the coolant, and the fairly regular temperature of the LOC makes control of the coolant temperature easy. Roughly ¼ of the energy in the hydrogen consumed by a fuel cell is vented via the coolant as heat, and this is sufficient to heat the LOC to the coolant temperature. A well-chosen countercurrent heat exchanger can easily raise the temperature of an incoming liquid stream to the incoming temperature of a heat transfer liquid. Thus for example in a 100kW fuel cell system we can anticipate up to 50kW of heat is available in the coolant at a temperature of at least 80C. Operation at 100kw requires nominally 2g/s hydrogen or approximately 30g/s LOC if conversion is under 95% complete. If the fresh LOC is at a relatively warm 30C and has a nominal heat capacity of 1.75kJ/kg°K, it could be heated in this design to 80C with approximately 2.7kW which is clearly available in the coolant stream. This would save ~1.3g/min of parasitic hydrogen consumption at full power.

Two more heat transfer steps are still needed to bring the LOC from fuel cell temperature to operating temperature for hydrogen release and then to provide the enthalpy of reaction to release the hydrogen. This heat can only be provided by burning hydrogen. Two possibilities present themselves, direct combustion in the reactor or a burner and heat transfer loop. While direct combustion avoids using a heat transfer fluid, there are problems. Even in catalytic systems combustion tends to occur near the entrance. A complex arrangement of burners along the length may alleviate this problem but the system is likely to still be very hot in places and much cooler in others. This concept will be revisited below. A heat transfer fluid can provide a smoother temperature distribution in the components containing LOC. Given that both the homogenous catalyst and the carrier compound can be temperature sensitive, we have favored a heat-transfer-fluid based system. Furthermore, by sending the combusted gas to the compressor/expander we will not waste the heat leaving the burner (that which is not captured by the coolant), so the down side to this design is minimized.

The highest temperature zone in our system is the reactor where the enthalpy of reaction is provided. The heat transfer fluid is heated to a high enough temperature to provide a suitable gradient (this depends on the reactor design) to transfer the heat required to drive the rate of reaction desired. Since the aim is to maintain the temperature of the LOC and provide the heat of reaction a counter flow arrangement may seem less needed. However, if a counter current arrangement is used the heat transfer fluid leaving the reactor can then flow into the last stage of the preheating section, bringing the entering LOC up to operation temperature. This also lowers the temperature of the heat transfer fluid further, which is desirable because the cooler fluid can extract more heat from the burned hydrogen in a counter flow burner design. The gas exiting the burner can also be used in the preheating section to bring the entering LOC closer to the operation temperature. Finally, the reacted LOHC has significant heat still in it and in the worst case that will heat the system in the shared fuel and waste fuel tank. In fact that heat may need to be vented to avoid problems in the storage tank. Accordingly, it is doubly desirable to use the spent LOC to preheat the incoming LOC. In order to send the spent LOC to the tank at a low temperature, this heat exchanger should either take the incoming LOC up from fuel cell coolant temperature or possibly even be the first heat exchanger so that the spent LOC is potentially returned at near ambient temperature. If needed the hot hydrogen could also be used to heat the incoming LOC and this would have the desirable side effect of lowering the hydrogen temperature so that the fuel cell BOP will not have to do so. More importantly, cooling the hydrogen will also reduce the vapor pressure of any LOC in the gas stream and thus reduce the amount of hydrogen clean up required. The general heat flow schematic of the proposed system is shown in Figure 9. Depending on other constraints, some sections might be omitted.

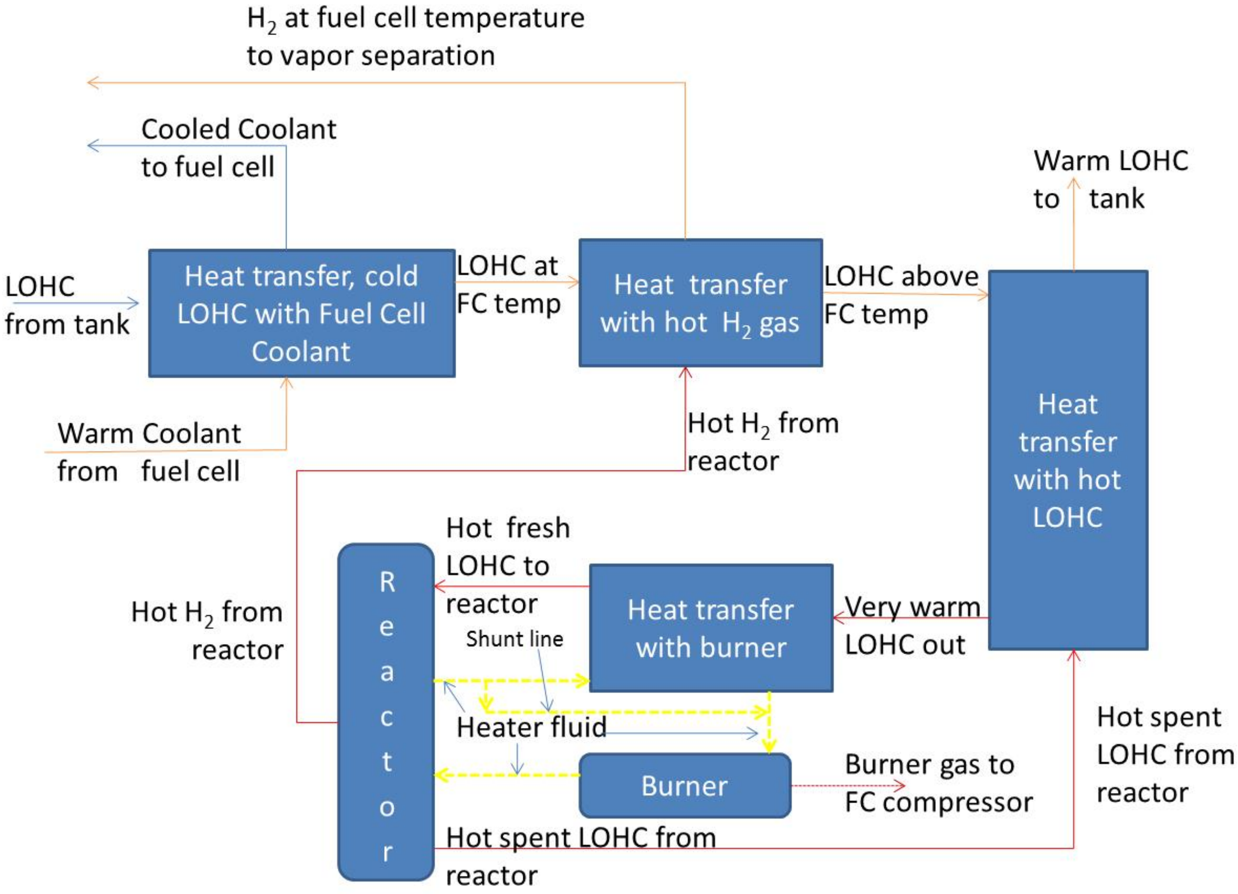


Figure 9. Proposed heat transfer scheme.

The waste heat from the fuel cell and both the hot hydrogen and spent LOC is extracted in a series of heat exchange operations to heat the incoming LOC, reducing the amount of hydrogen that must be burned significantly. The three to five sections of the LOC preheat portion should generate little or no hydrogen gas in the LOC. Furthermore, the hydrogen initially generated by the homogenous catalyst will go toward saturating the carrier rather than immediately starting bubble formation as in a heterogeneous concept. Accordingly, microchannel heating may be feasible. For expediency one could use the data generated in the Hydrogen Storage Engineering Center of Excellence or similar works to approximate the size of the heat exchangers needed [24]. If for any reason this is not desired, normal counter flow heat exchangers would work as well.

In order to minimize the amount of insulation required (and reduce volume and cost), we chose to design these heat exchangers into a single unit with one directly feeding the next. This also lowers the area where heat can leave the system because the walls between the various stages are not exposed to the environment and thus cannot lose heat to the environment. This also has the desirable effect of eliminating tubing between sections. The reactor and preheater can be further integrated with the burner, to finally optimize the system in this regard. This is illustrated schematically in the Figure 10. Additionally, the compact nature will help with packaging the system. The exact location of units in the design can be changed to some extent to accommodate packaging restrictions, for example instead of being stacked linearly as shown in Figure 10, the heating sections could be arranged in other configurations around the reactor. By appending a series of microchannel reactors to each other the LOC is heated through a series of temperature stages with minimal loss of heat to the exterior of the system. Since losses ultimately are made up by burning more hydrogen, this efficiency reduces hydrogen consumption.

Overall then the integrated preheater-burner-reactor has four inputs, air and hydrogen to the burner, fuel cell coolant to the preheat entry section and of course LOC. The corresponding four exit streams are cooled hydrogen, spent and cooled LOC, cooled (but still quite warm) combustion gas, and cooled fuel cell coolant. There may be still further opportunity to make use of the energy from the burned hydrogen to offset existing needs. So long as a compressor expander is used to condition the air and hydrogen in the fuel cell, the burner gas could be used in that unit. The ultimate goal of course is to lose none of the energy generated by burning hydrogen so that effectively the only consumption is that to drive the pumps and the enthalpy of reaction. While this perfect situation cannot be obtained, we have attempted to come close. Calculation of the exact savings requires a complete system including the carrier and catalyst, which is not feasible currently as will be

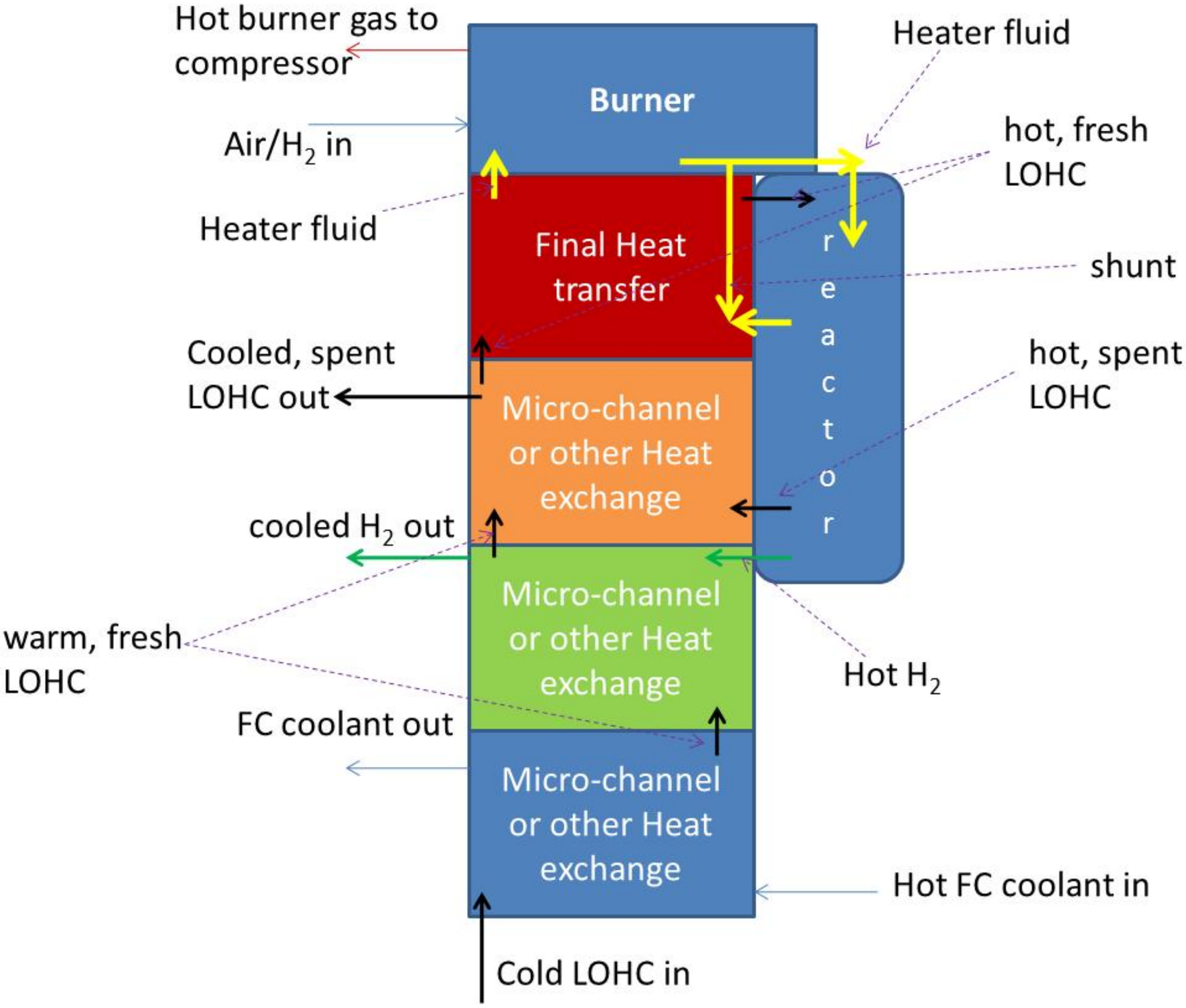


Figure 10. Schematic of integrated heater reactor.

discussed below. As a measure of the efficiency gain possible, the highly efficient burner in the Sandia program reached maximum efficiency of 90% in optimal conditions but was as little as 80% efficient in many other conditions. Losses were primarily due to heat in the exhaust and losses through the walls. Losses in piping were not measured but would certainly exist. We expect this design to capture or use most of that heat, so ~10% improvement is possible.

For insulation we have selected a bead-supported, crude-vacuum, insulation. This is less expensive that multi-layer vacuum insulation (MLVI) and can be flexible in shape. While bead supported insulation is not as good as the MLVI, it is still highly effective and will not degrade as noticeably over time due to permeation or outgassing; it will be still an insulator even if vacuum is lost entirely. If slightly more heat loss is acceptable, or a slightly higher volume is acceptable, then the vacuum can be eliminated entirely, further lowering cost and ensuring the insulation quality will not change.

The specific design of the system is of course highly dependent on the LOC reaction properties. As the right combination was not yet discovered we chose the operating properties of a representative one, with an inlet temperature of 443K for LOC and 483 K for inlet heating oil. The enthalpy of dehydrogenation reaction is assumed to be 60kJ/mol H_2. We assume the integrated preheater - reactor will be operating at an inlet of 8 bar on the LOC side to provide sufficient pressure drop to accommodate transport, clean up and conditioning of the hydrogen.

As a high risk concept for later work one might consider attempting to remove the burner altogether, see Figure 11. While it would take careful balancing, the concept outlined above without the burner might directly catalytically burn hydrogen outside the reactor, and if needed also in a final LOC heat-up stage prior to the reactor as well. This heating must be done in a very controlled manner avoiding overheating the LOC. One would still use the exiting gas and LOC streams in micro channel heaters as described above to extract as much heat as possible. The advantages would be 1) the reduced weight - both the burner and the heat transfer fluid are removed, and 2) faster control – there is no thermal inertia due to heat transfer fluid and its heat capacity, and 3) lower cost – due to reduced parts. Balancing heats and temperatures across the reactor is the challenge in this scheme. Somehow the distribution of hydrogen combustion must be either uniform or tailored over the reactor to provide sufficient heat to drive the reaction at all locations, and yet not raise wall temperatures so high as to harm the homogenous catalyst. This has proven very difficult in other work and was not attempted in this project (SNL).

Reactor simulation

The reactor itself is the most unique part of the design. It is important that to the extent possible it is energy efficient, dependable, responsive to changes in hydrogen demand, and cost effective. While this is true of all the components in some sense, the demands and difficulty of achieving them are probably highest in the reactor. Accordingly, we considered several designs for the internal structure of the reactor, all with the liquid heat transfer system chosen above.

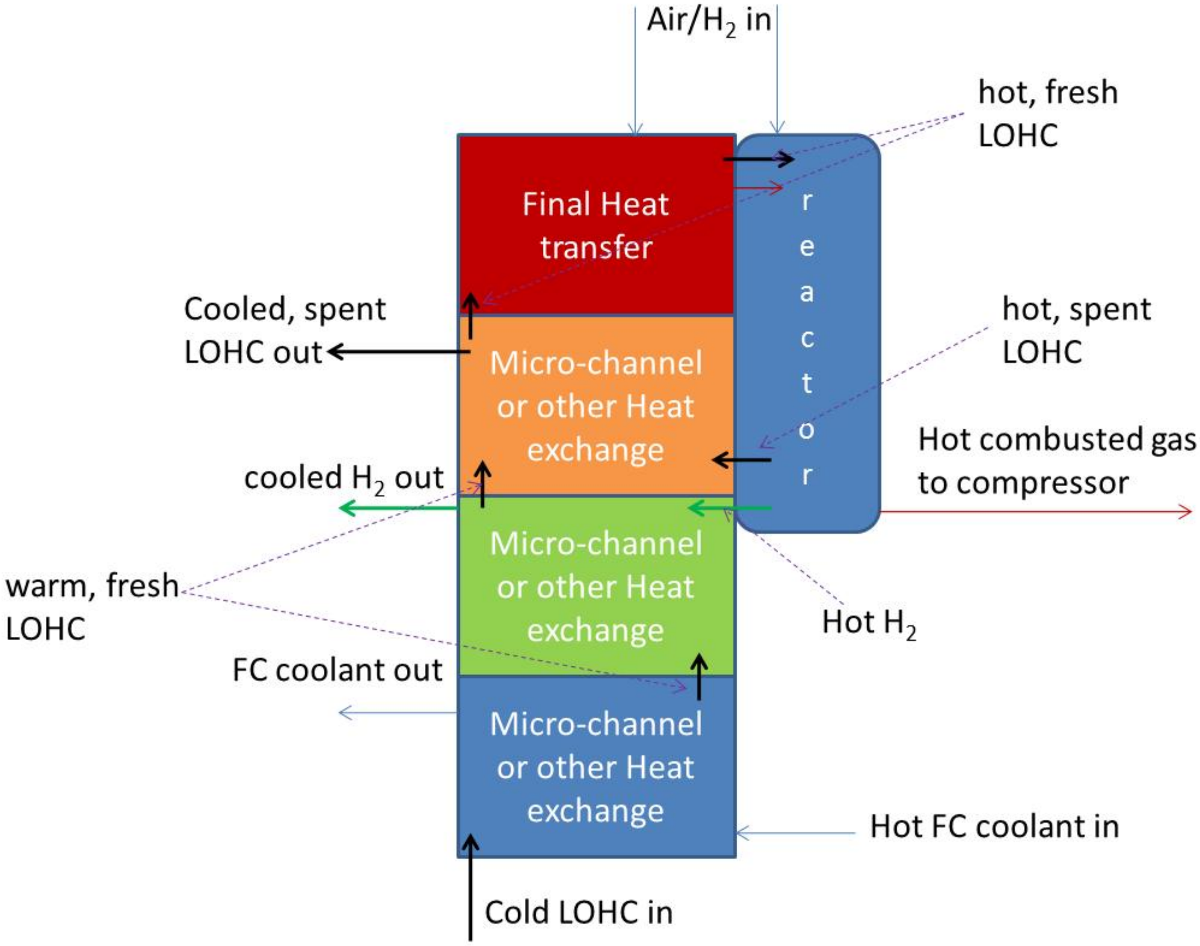


Figure 11. Advanced concept integrated heater reactor. In this concept careful routing of hydrogen to catalytic coatings on the exterior wall of the reactor drive reaction, no burner unit is required.

There are several ways to measure the quality of a design, we will use reactor length to achieve 2g/s H_2 flow at a chosen reactor temperature. By using standard reactor tubing diameter and material of construction, the cost and mass will be proportional to the length, so this metric also indicates the impact on those important variables. Finally, while some of the alternate designs will have different aspect ratios, they all have a proportional relationship between length and volume as well, so decreased length means decreased volume of the system. As will be explained more completely below, reactor volume has a strong impact on transient behavior so decreased length also improves responsiveness. Optimally the reactor would be very short – the smaller the better.

Practically a reactor less than 1.5 meters would fit transversely in the vehicle which would improve packaging options. Several such reactors might be packaged as a bundle and would have the advantage of allowing individual reactors to be valved on or off when desired to achieve faster turn-up and turn-down of hydrogen flow. A good target for this stage of development would be 7 such reactors in a hexagonal array with a total length of 10.5 meters.

The baseline system is a recognized efficient reactor design, a counter current flow reactor with LOC inside and heat transfer fluid outside. All required heat is provided by a burner with a recuperator. This system uses several established techniques to increase reactor efficiency and thus reduce the required length and the required parasitic hydrogen consumption.

The integrated system described above will lower the parasitic power (heat required to release hydrogen) in several ways. First the heat required to reach ~80C is provided by the fuel cell, then the incoming and outgoing flows exchange heat so the heating to reaction temperature requires at most minimal heat input, and finally the reactor is either surrounded or at least bordered by other hot sections of the system further reducing losses. However, there may be ways to better transfer heat in the reactor itself and thus reduce the system contact area and mass required to release hydrogen. This is important not only in terms of cost but also low mass helps in transient operation (though not so much so in steady state). A lower mass will require less start up heat and a smaller volume of LOC in the reactor will be able to stop generating hydrogen faster. This would be true even if there is no way to quench the system other than to allow the LOC to stop flowing and lose all its hydrogen.

In order to try to improve upon the baseline design, the reactor must be shorter yet efficiently transfer heat and allow for hydrogen evolution without compromising the conversion. In addition, the temperature must not get so high that the catalyst is deactivated. The ability of a reactor design to perform these requirements can be appraised by simulating the flows, temperatures and hydrogen production in steady state. Dynamic situations are much harder to simulate but we know smaller and less massive systems will have better dynamic control. Our preference will be for the reactor that is compact, light and not especially complicated to build. A lower number of possible failure modes would also be desirable.

Another factor in this section of the design appraisal is the fact that the transient time can be stretched by use of hybridization. Fuel cell vehicles will at least initially be fuel cell – battery hybrids. Since the battery pack already exists on the vehicle it makes sense to use it to slow the required response rate of both the fuel cell and the reactor. This lowers the impact of the transient response on the reactor selection.

Initially more than 16 designs were contemplated. Many are variants of other designs in the set, for example the heat transfer fluid can be placed inside the inner tubes or can go in the shell volume with potential for better performance one way than the other. As simulations progressed it was clear that 3D work including the impact of gravity was required. These simulations take much longer than simpler 2D with no gravity. Using simpler simulations as a screen a reduced set of designs was studied in the more complex simulations.

Aluminum was chosen as the material for the structure of the reactors based on mainly two considerations. First, the reactors should be kept as light as possible to avoid deterioration of the vehicle's fuel economy. Aluminum is light and sufficiently strong for this application. The second consideration is the heat exchange efficiency of the reactor. Aluminum has relatively high heat conductivity for structural metals, which will improve the efficiency of heat transfer in the reactor system. For simplicity in the simulations we assume the insulation is adiabatic on the outer surface of the reactor by setting an insulating boundary conditions in the model.

The actual LOC is not known so the physical and chemical qualities of the LOC, and the heat transfer fluid were assumed to be those common to organic liquids. The density ρ (kg/m^3) changes with temperature T (K) and is assumed to follow the relationship as formula (1) where T is temperature in Kelvin (K).

$$\rho = 1061.6 - 0.6231*T \tag{1}$$

In order to allow an initial design evaluation, the chemical properties of the LOC were assumed to be similar to those of a more successful carrier/catalyst pair, as mentioned above. It is assumed the LOC has been fairly rapidly heated to operating temperature and enters the reactor starting to yield hydrogen. For the heat transfer fluid, the inlet temperature and pressure are 483K and 1 atm respectively. The required output quantity of hydrogen is set at 2 g/s. To be cost effective, the conversion of LOC in the dehydrogenation reactor should be as high as possible. Obviously, heat transfer in the reactor should be as efficient as possible as well.

For ease of comparison between designs, the volume flow rates of the heat transfer fluid are set the same. The radius and the default length of the tube through which LOC flows are set to be 0.02m and 1m respectively. The thickness of the inner tube is 0.006m. Heat conduction in the wall of the inner tube was considered. However, the surfaces of the inner tube wall were considered to be highly conductive so that the transfer of heat across the interfaces can be simplified.

The design of the baseline tubular reactor with counter flow is shown in Figure 12. The reactor is placed horizontally with flow along the z direction and gravity along the x - axis, which in this configuration points down. For this reactor design, two operational possibilities are studied. In the first one the LOHC moves through the inner tube while the heat transfer fluid flows through the annular space in the counter direction. The first alternative design is simply the reverse case with LOHC flowing in the annulus and heat transfer fluid inside the tube, of course their flow directions remain counter to each other.

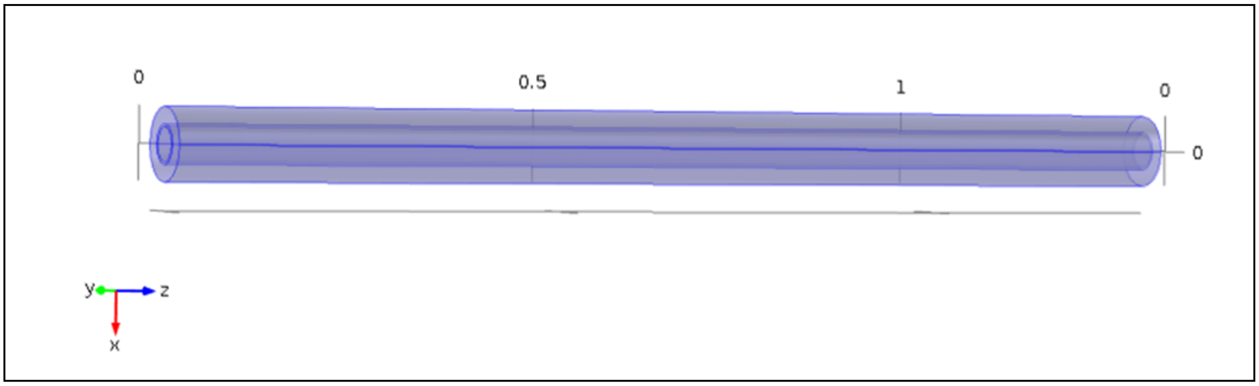


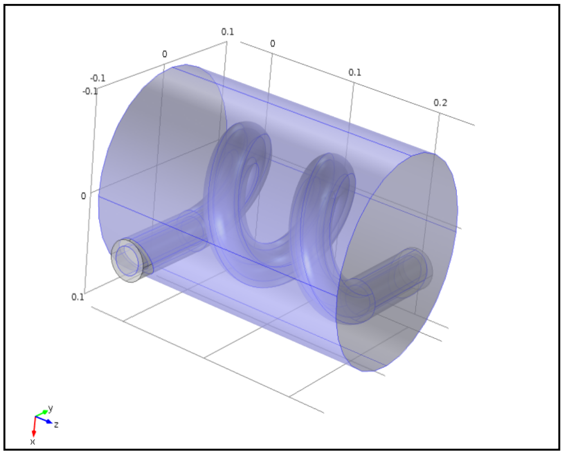
Figure 12. Tubular reactor in a counter flow design; gravity is along the direction of the x-axi**s.**

The next alternative is a more advanced design, a helical reactor with counter flow; the design is shown in Figure 13. Similar to the baseline reactor, it is placed horizontally with gravity along the x-axis. In this design, LOC goes through the inner tube while the heat transfer fluid goes through the shell space in a direction counter to the net z component of the LOC flow. This design induces shear and has the extra advantage of shortening the reactor. Since increasing the reaction rate is one of the key challenges in this project, we attempted to use engineering to reduce the impact of low rate. Low rate requires a long reactor potentially longer than the vehicle. Using a helical design not only increases rate by mixing the fluid but it also allows for a longer reactor (if the LOC is inside the tube) in a shorter but wider system envelope.

Figure 14. shows the design of a nested helical reactor with net counter flow. The reactor is placed horizontally, with gravity along the x-axis. LOC flows through the inner tubes while the heat transfer fluid moves through the shell in the opposite direction to the net z-component of the LOC flow. The number of the turns and the major radius of the inner helix are adjusted to keep the length of the two helical tubes the same. Alternative designs for Figures 13 and 14 can be created having the LOC flow in the shell and placing the heat transfer fluid in the tube(s). This intuitively seems less likely to succeed as ‘dead spots’ in the flow and heat transfer are likely to form in the shell, but it is possible the obstruction of the helical tube may induce sufficient shear and or turbulence to overcome this potential defect in design.

Figure 15 shows the design of nested a helical reactor with cross flow. The reactor is placed horizontally, with gravity again along the x-axis. LOHC flows through the helical tubes while heat transfer fluid enters the shell from the bottom of the reactor and comes out from the top of the reactor. The number of the cycles and the major radius of the inner helix are adjusted to keep the length of the two helical tubes the same.

Figure 16 shows the design of a vertical tubular reactor. The reactor is placed vertically, with gravity being along the direction of z-axis. There are five tubes for LOC to flow through. Heat transfer fluid enters the shell from one side below and comes out of the upper tube on the other side of the shell. An advantage of this design is that bubbles forming in the LOC will tend to further mix the liquid as they rise. This comes at a cost however as there is not much vertical space in a vehicle. For other potential applications this design might be more profitable. A number of other designs were developed but due to the redeployment of funding they could not be explored in simulations. They are shown and described briefly in the appendix.



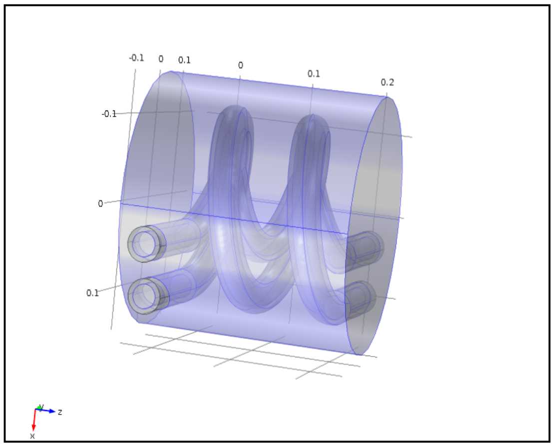
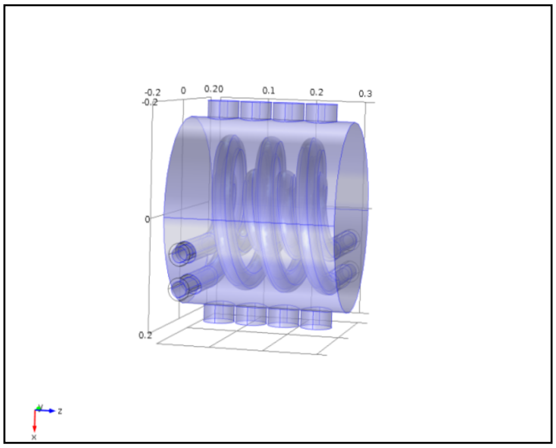


Figure 13. Helical reactor with net counter design; gravity is along x-axis direction.

Figure 14. Nested helical reactor, counter flow flow design; gravity is along x-axis direction.



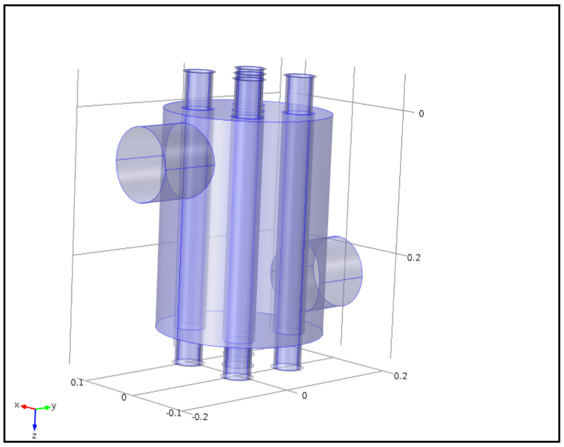


Figure 15. Nested helical reactor in a cross flow design; gravity is along the along the z-axis direction

Figure 16. Vertical tubular reactor; gravity is gravity is along the x-axis.

The flows of both the LOC and heat transfer fluid are non-isothermal. Recall that dehydrogenation is an endothermic reaction for the known LOCs. Temperature distributions within both the LOC and the heat transfer fluid will reflect these two facts, as will the local heat exchange rate between the fluids. The density of each fluid is a function of temperature and the formation of bubbles will greatly disturb the density distribution in the fluids. Gravity can therefore affect the flow pattern and break the laminar flow to induce greater mixing, thereby positively affecting the efficiency of heat exchange. In this work, the fluids are considered to be Newtonian and to a first approximation incompressible. While the formation of bubbles generates a great deal of compressibility, the constant pressure means the impact can – again to first approximation - be captured simply by allowing the fluid density to drop. A significant assumption in this work is that the bubbles remain distributed and the fluid density remains locally uniform resulting in a drop in density, and expansion of the fluid and an acceleration of flow as hydrogen is released (see Figure 17).

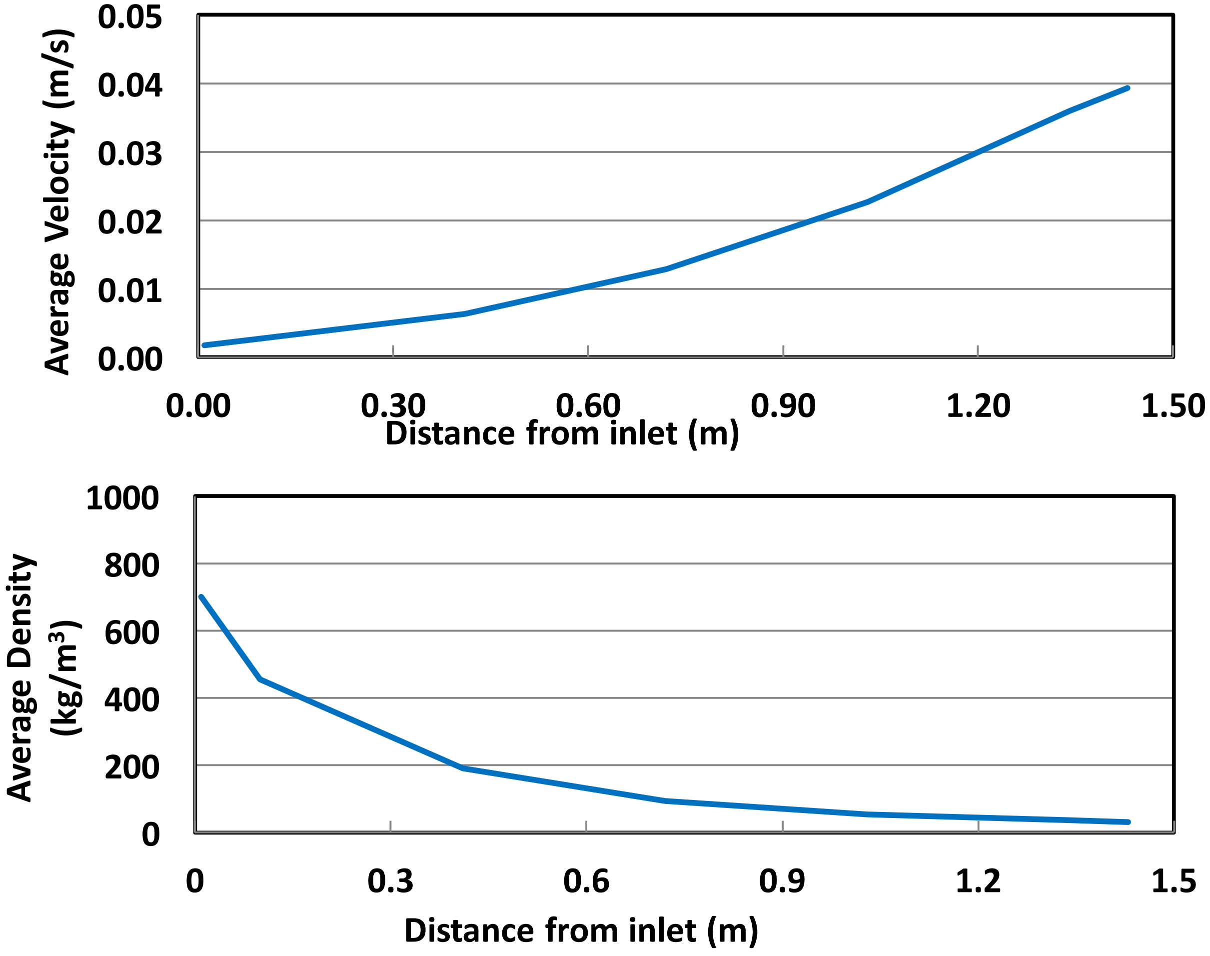
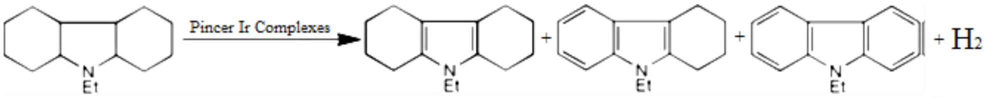


Figure 17. Impact of hydrogen generation on velocity and density.

This assumption is essential as explicit tracking of individual bubbles proved beyond the capabilities of our software and computers. It is possible that at the slow flows required at this level of kinetics even the small bubbles formed by dissolved hydrogen coming out of solution will not stay distributed. The volume expansion would still occur in this case but the liquid flow would not accelerate as much as the gas flow. This would result in more complete reaction but less than 2g/s hydrogen production.

As hydrogen is produced the average density of a fluid parcel falls and accordingly the velocity increases. Due to gravity, even for a tubular reactor there is no radial or axial symmetry. Examining the mass, momentum, and heat transfer processes with 3-D model is the most appropriate method though reduced models can help sort options initially. The software used in this work is COMSOL Multiphysics, version 4.3b, which is capable of modeling physics and coupling related processes.

The dehydrogenation of N-ethyl perhydrocarbazole catalyzed by PCP pincer iridium complexes was the chemical system modeled as it had produced the best results at the time we needed to lock down the model. The reaction releasing hydrogen can be expressed as:



(1)

For simplicity, the reaction used as a prototype for LOHC reaction simulation follows formula (2),

$$A \rightarrow B + 3H_2 \quad (2)$$

The kinetics of the reaction provided by the research group of Jensen et al. can be described using a pseudo first order formula (3).

$$k = 9.45\times10^{10} \times \exp(\frac{-133000}{RT}) \qquad (1/s) \quad (3)$$

The rate of hydrogen production R_{H2} can then be expressed as:

$$R_{H2} = 3\times k \times C_A \quad (4)$$

Where, C_A is the concentration of hydrogen loaded LOC.

The catalyst concentration in the inlet reactant is around 0.5%wt. The inlet concentration of LOC is 4348 mol/m^3.

Reactor internal-volume

The reactor's internal volume should be minimized for multiple reasons. In general smaller components in addition to taking up less volume will be lighter and less expensive if no added cost arises due to actual miniaturization. For a reactor there are the addition issues of minimizing heat loss by eliminating unnecessary surface area, and the fact that a reactor is a hot part and therefore the undesirable heating of adjacent parts is minimized by making the reactor as small as possible.

Since the reactor's function is to provide a flow of high quality hydrogen and then return the spent LOC in good condition to the fuel tank, the reactor size will be set by safety considerations, the quality of hydrogen and spent LOC, reactor dynamics, and providing sufficient maximum hydrogen flow. There are no safety concerns that argue for a larger reactor, and so long as the temperature is well controlled the degree of both reaction completion and selectivity will not require a larger reactor. Control and hydrogen flow dynamics are improved by using the smallest possible reactor. Thus the correct size is the smallest reactor capable of meeting the maximum hydrogen flow requirement.

There are many different hydrogen demand patterns possible in driving a vehicle, but sustained full power will be the most demanding on the reactor. The reactor will derive hydrogen from all the LOC within it, but the rate of hydrogen production in any given small portion of the reactor will vary with the degree of reaction that has already occurred. The net hydrogen derived from the full length of the reactor must meet the flow requirement. In a highly demanding transients, even if the reactor could not meet the change in H_2 flow required, power could briefly be taken from or delivered to the battery until the required production of H_2 was established (see below); but under sustained full power demand, all power must come from converting hydrogen. For this reason the maximum hydrogen flow requirement sizes the reactor.

Following this logic, the reactor will be the smallest one capable of providing 2g/s hydrogen at the percent LOC conversion desired. DOE specifies the mandatory minimum efficiency, but a higher conversion is desirable. If conversion is not as high as possible then there will be LOC that was paid for, carried by the vehicle, heated to reaction temperature but did not yield hydrogen. The result is that cost, net specific mass, and density of the system are all hurt by lower efficiency. Balancing the desire for perfect hydrogen extraction from LOC is the practical fact that very high conversion extends the required reaction time and since in a flow system more time equates to more reactor volume then the cost and mass of the system will increase to extract the last of the stored hydrogen. A compromise must be reached, and cost and mass are the metrics by which optimization will be judged. Figure 18 shows results for various percent conversion. The reactor

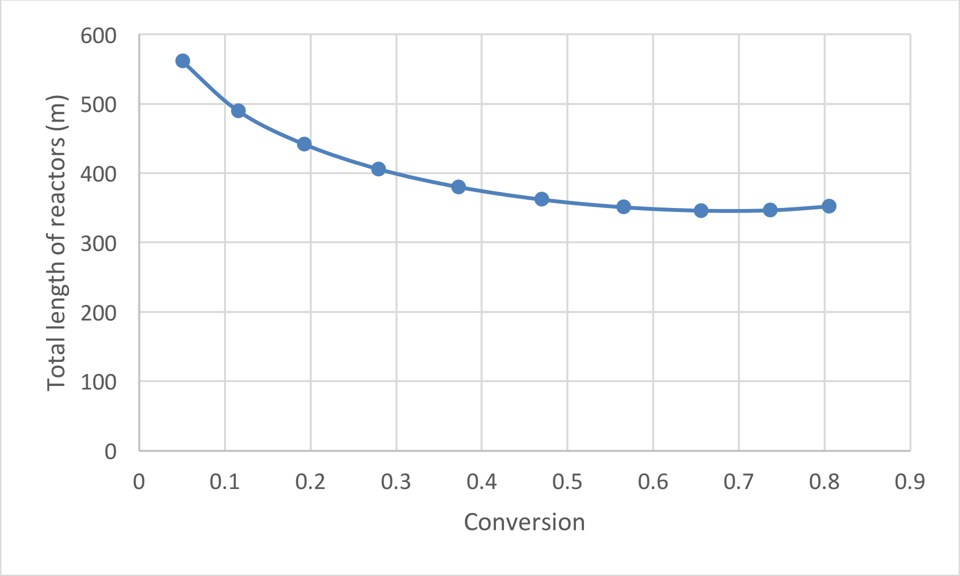


Figure 18. How conversion affects reactor size – Assuming fixed kinetics and a 2g/s hydrogen flow requirement and several equal-length baseline design reactors. The summed total length of all the reactors required to produce 2g/s H_2 varies with % conversion, as shown here.

size required is quite high because the kinetics achieved to date are still fairly slow relative to the flow rate required by an automobile. Leaving the absolute value in Figure 18 aside,

it is clear that initially the improved conversion using longer individual reactors shortens the total amount of reactor tubing needed to meet the hydrogen flow requirement. In the Figure 18 calculation, the lowest conversion of 5% is achieved in half meter long reactors while at the other end of the curve a 5 meter reactor (which would need to be curved back on itself in a 'U' shape if it were to fit even lengthwise in a vehicle) achieves 80% conversion. In all cases several reactors working in parallel are required to meet the 2g/s requirement, though at higher conversion even though the reactors are longer, fewer are needed because each one produces more hydrogen. As noted above it is expected that at some point a longer reactor will pay diminishing returns since the unreacted mass is ever decreasing. We see in Figure 11 that for the baseline design that occurs at roughly ~70% conversion which happens to occur in a 4.2 meter reactor. Using groups of individual reactors greater than this length requires an increased amount of total tubing to meet the 2g/s hydrogen flow requirement. An alternate view is that to simultaneously achieve greater conversion and a 2g/s hydrogen flow in reactors over 4.2m in length, the reactors get longer faster than the required number of reactors decreases.

Clearly, until the reaction kinetics are increased to the point where the reactor becomes fairly short, the optimal cost for the owner might be at only partial conversion. Fortunately - from an efficiency perspective, the totaled summed length of the reactors past the optimum increases only slowly relative to the increase in conversion, so most likely the maximum conversion will be sought out to reap optimal value from the fuel.

We evaluated the reactor designs above and the most efficient from a volume and mass perspective was the nested helix design. Data on the initial evaluations is provided in the appendix. However, the single helix design was only slightly less efficient and would be much simpler and more reliable from an assembly viewpoint. We take the single helical reactor as the most appropriate advanced design to compare with the baseline.

To put the baseline and proposed reactors on a similar footing, the length of the helix, not the reactor shell, was used as the reactor length in Figure 19. The actual helical reactor system is roughly 4 times shorter, but also has about 4 times greater cross section. Even on an even footing the helical reactor returns nearly double the conversion relative to the baseline for any specified length of reactor, presumably due to better mixing and heat transfer.

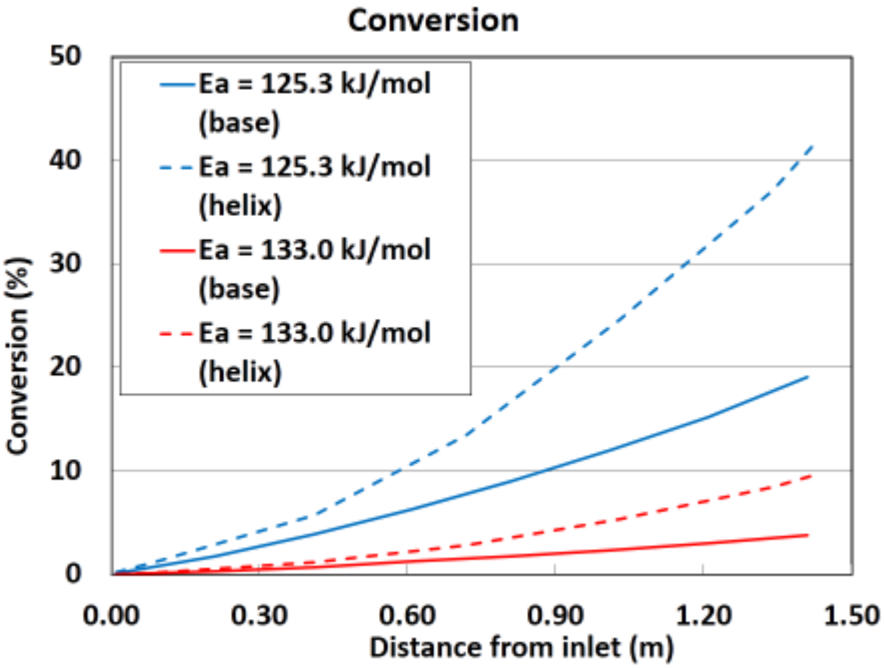


Figure 19. Improvement in conversion for helical reactor – Conversion as a function of reactor length is evaluated at two levels of kinetics. The helical reactor outperforms the baseline design significantly regardless of kinetics and at all positions along the reactor.

Further study of a longer helical reactor led to the final simulation at 125.3kJ/mole activation energy with 4.2m of reactor coiled in an approximately 75cm long shell. The conversion at the skin or by integration over the diameter exceeds 95% as shown in Figure 20. Of course to achieve such conversion with the kinetics available today a very low linear flow rate of 2mm/s is required, so the time to transit this reactor is on the order of thousands of seconds. The dynamic behavior and the start / stop control would be very poor. Still, this shows that even at presently accessible kinetics a reactor that might be packaged on a large vehicle can achieve good conversion. It might even be suitable for stationary or mobile applications, but faster reaction is needed for automotive use.

Quantifying the improvement needed, about 60 of these 75cm long reactors is required in this best case comprising about 250 meters of total helical reactor tubing. This is about 25 times the target

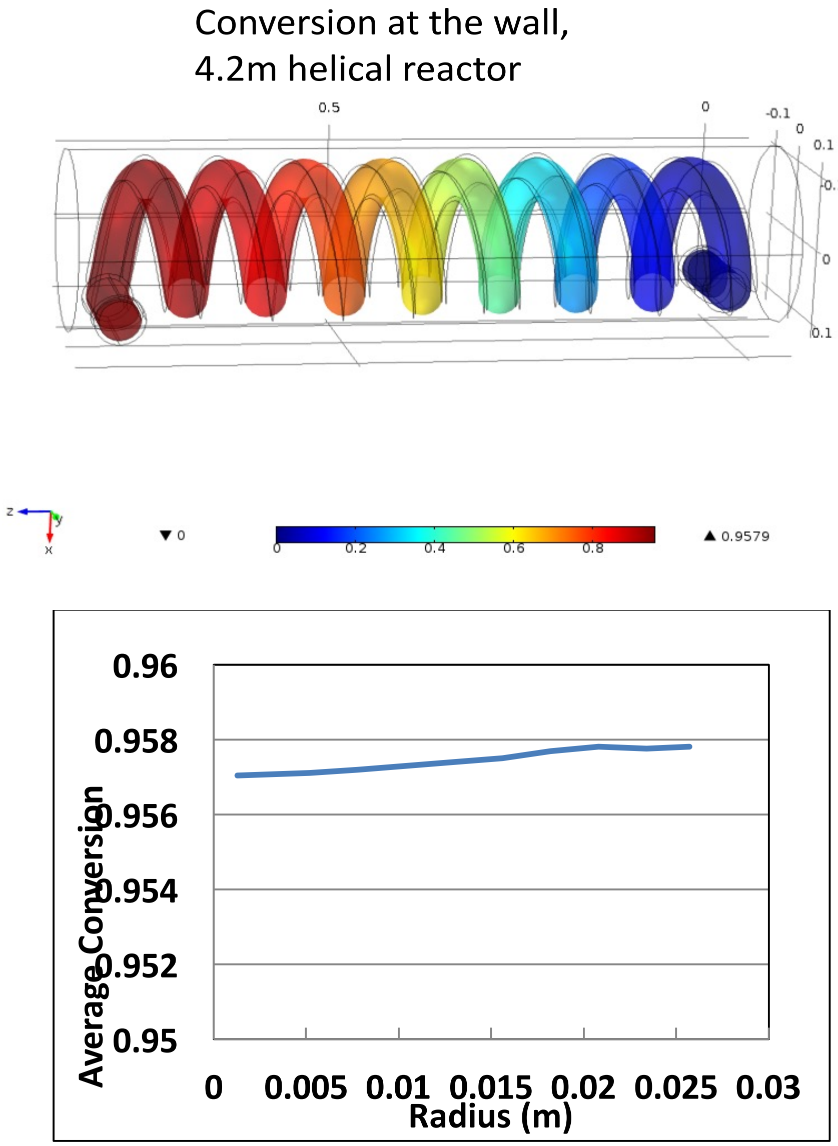


Figure 20. Conversion >95% in a helical reactor – Conversion as a function of progress along the reactor is evaluated at 125.3kJ/mol in the upper image. Net conversion is not far from the skin level conversion, the averaged exit conversion is 95% as shown in the lower image.

level mentioned in the beginning of this report. The cost and packaging would not come near the values for a compressed tank, though there is a significant improvement of more than 50% length reduction relative to the baseline. A more reasonable situation would be 10 or fewer reactors each using less than 0.5m of helical tube. In an advanced design, flow might be individually regulated to each of the 10 reactors using only as many as needed at full flow and the rest at minimal flow, essentially only enough to maintain reaction temperature. Flow would be about 0.1m/s. A reaction rate increase of about 50 is required to achieve 2g/s H_2 in this design. This is not outside the realm of conception.

Balance of plant

Without knowledge of the actual chemical system to be used it is difficult to make meaningful progress past the initial rough considerations laid out at the beginning of the project. These considerations are reported here as a guide.

Use of a battery pack in the hydrogen delivery system design

The reactor itself is meant to heat fluid not cool it. Addition of cooling coils or a thermoelectric other cooling system would permit faster turn down of H_2 generation, but would add significant cost, mass and complexity. A simpler design is to just stop the flow at key off or in very low demand periods. When the LOC flow is stopped the fluid in the reactor will continue to react and hydrogen will flow to the power plant. Assuming a hybridized fuel cell or ICE power plant, this hydrogen can easily be converted to electricity but there would be no use for that electricity. The excess current produced at shut down or in idle conditions could be routed to the battery for use later. If the fuel cell is specified to produce full rated vehicle power or nearly full power, then the battery control strategy could be adjusted to leave the battery in a safe, lower, state of charge, such that a full breaking event could be absorbed followed by the power delivered from the hydrogen evolved in complete reaction of the LOC in the reactor. This would then leave the battery nearly fully charged (or as near as preservation of calendar life allows) for the next start or for vehicle launch and drive away from a long idle. This allows the hydrogen generation to ramp up to driving load slowly.

This design element is critical in that it decouples the time constant of reaction from that of the fuel cell. Allowing the hydrogen flow to drop from 2g/s to no flow over several minutes allows a very simple reactor design and control system. If the hydrogen flow needed to stop in a fraction of a second a secondary storage unit with fast kinetics (compressed gas or a very facile hydride) its attendant mass, volume, cost, and complexity would be required.

If the battery may not be used to buffer transients in H_2 demand, then a metal hydride tank would be preferred. For some time it has been possible to tune the release temperature and pressure of laves phase hydrides. The TiCrMn system is well studied and quite attractive except for cost and mass [14]. Generally 2% of the mass of the system is retrievable hydrogen and reaction goes to full release at modest temperatures, easily available from the fuel cell or the exit flows from the reactor system. If the reactor is sized to contain an amount of LOC that would supply no more than 10 seconds of hydrogen then 1kg of hydride will suffice. Such a bed would be compact and affordable and yet change the time constant for changing hydrogen flow from fractions of a second to tens of seconds.

This further illustrates why achieving fast kinetics is fundamental to reducing size, mass, complexity and cost of an LOC system and improving function and versatility. The time constant of the reactor is dependent on its volume and the reactor is set to deliver full flow based on the kinetics and temperature of operation. Minimization of the cost and the complexity of storing electricity or gaseous hydrogen is yet another reason why fast kinetics are crucial from a system standpoint and why the funding in this program was appropriately reapportioned by DOE to pursue that key element of a functional system.

Pressure regulation, pumps, and system clean up

While a pressure regulator would serve to ensure the pressure does not exceed the fuel cell inlet limit, it may not be needed. The ultimate source of the pressure is the flow of LOC into the reactor which is established by the fuel pump along with the relative consumption and generation rates of hydrogen. Hydrogen flows out to only two units, the fuel cell and the burner. LOC returns to the fuel tank which is optimally ambient pressure.

Accordingly, a simple feedback loop from the fuel cell indicating high, low or acceptable pressure should suffice to maintain proper pressure without the expense and added failure modes of a regulator. If more pressure is desirable the reaction rate is increased by increasing the temperature of the heat transfer fluid or increasing the flow of LOC. The pressure can be decreased through lowering the flow resistance for the exiting LOC or lowering the temperature in the reactor. LOC flow can be regulated by simple trim valves at the entrance and exit that can progressively close or open to increase or decrease the pressure needed to allow gas and or liquid to exit. Balancing these inputs allows flow and pressure to be controlled. The trim valve would either need to seal effectively at 8 bar, or be backed by an open/shut valve that can dependably serve the function of maintaining pressure for long periods of inactivity.

Because the LOC has a vapor pressure any remaining hydrocarbon in the hydrogen must be removed so it does not impact the fuel cell. In an SOFC this would not be a problem and for non-automotive where an SOFC can be used there may not be a need to clean up the small amount of lost hydrocarbon. However, the relatively complex LOC molecules are likely to have some impact on the catalyst in a PEM fuel cell. A simple way to do this is to cool the hydrogen as near ambient as can be arranged and then polish the hydrogen with a traditional automotive ORVR canister. This device is made in the millions each year and is well understood. It uses activated charcoal to remove hydrocarbons larger than ethane from a gas stream. The canister as used on an ICE powered vehicle cleans itself by periodically reversing the flow and sending the vapor to the engine. In a fuel cell this could not work but if the removed vapor could be sent to the spent fuel section of the tank that would be desirable. In the worst case the canister must be used like an oil filter which requires periodic maintenance to prevent engine damage.

Unlike an oil filter, which is disposed of, the canister would be removed and the adsorbed carrier removed by either heat, vacuum, or chemical extraction and could most probably be returned to service. It may prove more economical to open the canister and treat large volumes of near saturated carbon and reuse the cleaned material in new canister shells. This level of economic analysis of the supporting infrastructure is outside the scope of the present work.

In a further effort to minimize costs, a series of automotive qualified fuel pumps were considered. At first approximation, a 16:1 carrier to hydrogen mass-ratio and a 2 g/s flow rating would lead to a 32 g/s requirement for the pump which is easily met with existing pumps. However, the requirement is higher due to parasitic hydrogen consumption and pressure requirements.

So long as the hydrogen release temperature exceeds the fuel cell temperature some hydrogen must be burned to release the hydrogen. The amount will be equal to at a minimum the enthalpy of the reaction and the differential between fuel cell temperature and operating temperature for the content of the reactor. Once at operating temperature the heat of the exiting fluid can heat the incoming fluid with minimal addition of further heat (relative to the high value of the reaction enthalpy). Making a best case estimate of ΔH=40kJ/mol H_2 (the LOC used in this project had a higher enthalpy and the parasitic loss scales linearly) , or 40kW due to enthalpy for a 2 g/s flow rate of hydrogen, an additional 0.33g of hydrogen is needed for enthalpy. This 'extra' hydrogen also requires heat to release and a regression clearly develops. Furthermore, the system is unlikely to be more than 95% efficient despite the extensive recuperation and use of waste heat. Since the presumed enthalpy is about 1/6 the lower heating value, the total amount of hydrogen required is determined by assuming (1/6) of the released hydrogen is burned at 1/0.95 efficiency to achieve the release of the full amount. Then 2=X*5/(5+1/0.95) or 2.42g of hydrogen must be produced for every 2g delivered to the power plant, excluding the sensible heat needed at start up to bring the reactor to operation temperature. Again using the 16:1 mass ratio, 38.7g/s of carrier must be pumped to achieve maximum hydrogen flow. To account for initially heating the reactor, higher LOC viscosity at low temperature, degradation of the pump over time and other requirements, a 50cc/s at room temperature pump requirement is set.

The pump is the primary source of pressure in the design. We made this design choice to avoid an expensive, inefficient and noisy compressor. Using the fuel pump to generate and hold system pressure adds the need to deliver LOC at 8 bar to satisfy DOE requirements. Future power plants (fuel cell or ICE) may not need so much extra head pressure, which will only make pump sourcing easier and less expensive. Currently there are tier 1 suppliers with pumps that will deliver 32 gal/hr at 100 psig (8 bar absolute), or roughly 35 cc/s, two of these pumps would handle the flow easily and at all but wide open throttle one could be shut down to save on power with the other pump running a high efficiency.

The heat transfer fluid will be very hot and a high temperature pump is required to handle it. The pressure in the heat transfer loop will be modest, only enough to generate flow and overcome friction. Accordingly, a more expensive and reliable high temperature pump is specified. It is unclear if the price could be significantly reduced at automotive volumes.

Valves, piping, and ancillaries

The piping can be of normal mild steel until the reactor is reached at which point a metal not susceptible to embrittlement is indicated, as it will be exposed to pure hydrogen at elevated temperature and 8 bar. This also applies to the valves, those contacting only the carrier can be of a mild steel or other inexpensive metal that can tolerate 8 bar pressure and the full range of automotive ambient temperature. Typical fuel lines should suffice. The hydrogen will flow in high alloy steel, 316L or better.

A gas - liquid separation is required to remove the hydrogen from the spent LOC. A number of designs are possible. However, for fast start it is important that the gas pressure be maintained in the separator so it does not flood during start up. Accordingly, a pressure tight valve is needed at the exits of the separator.

Optimally the fuel tank will be operated at ambient, so there is a need for an orificto let down the pressure from the system pressure of 8 bar absolute to ambient of nominally 1 bar absolute and a pressure tight on off valve which activates at shut down.

Fuel tank and filler

The fuel tank is designed to operate at ambient pressure so the materials of construction can be light and inexpensive. Conventional fuel tanks will work along with the straps and fixtures normally used in vehicles. These increase the ease of integration because no unusual parts are required. The tank itself will need to be of the bladder variety to minimize volume.

Unlike conventional vehicles, the LOC will return to the fuel tank. The volume of new and spent fuel together is essentially constant so a single tank with a dividing bladder is an optimal design for volume minimization. This can either be a single dividing bladder which uses fewer raw materials but has increased complexity, assembly cost, and more failure modes. It is also possible to use a two bag design which uses more material but is easier to implement. It also offers at least potentially a unique way to measure the amount of fuel left. Bladder tanks cannot easily use the float mechanism used in conventional tanks. However, a conductive element placed between the bladders could still slide along a restive element (as in the current sender card) and record the approximate volume of fuel in the lower bag, and by difference the volume in the upper bag. Assuming the new fuel is in the lower bag and the spent fuel in the upper bag this is a simple way to measure the volume of fuel remaining.

The filler will be more complex than is typical of today's gasoline vehicle, because fuel must be removed as well as delivered. A dual pipe filler is required, one pipe for spent and one for new fuel. It will be important that the two fuel streams never be errantly switched. Two designs are obvious, a concentric nozzle with, for example new LOC in the inside tube and spent LOC returned in the annular outside tube, or a side by side arrangement with tubes of different size or shape so that the nozzle can fit only one way.

A second difference is the need to remove a liquid from the tank as well as to deliver it. When delivering a liquid, a pump at the station and a passive receiver in the vehicle are highly effective, but this will not work as well for a two fluid system. Options include sealing connections for both fluid streams well (dry-break type connectors) so that as fresh LOC is pushed in by the pump at the forecourt, the spent LOC is forced out of its portion of the tank. This would require the tank to withstand the delivery pressure but that probably would be only a few millibar and is easily done. An alternative would require only one pressure seal (on the spent fuel side of the filler) and vacuum remove the spent LOC. In this case the fresh LOC would be pumped in just as with gasoline today, but at the same time the used LOC would be removed by vacuum through the dry-break connection. This would require only a single dry break so long as the flows were matched. However, this also puts added burden on the forecourt in the form of a vacuum pump and a method to scrub hydrocarbons out of the effluent from that pump. It is unclear which system would be superior overall, but we will assume that a double dry-break connection with only a fuel pump in the forecourt is the preferred system because it would be easier to achieve implementation of the infrastructure.

Implications for superior LOC properties

The impact of LOC properties on the overall system performance can be obvious or obscure. Some obvious desirable characteristics are high usable specific mass of hydrogen, high usable hydrogen density, low cost because they directly lower mass, volume and cost, but also because they reduce the mass, volume and cost of the tank and system too, by reducing the size and robustness of the tank. Likewise, it is fairly apparent that in order to be pumped the LOC must be a flowing liquid at the lower ambient requirement so the melting point must be somewhat lower than the specified -40ºC so that the viscosity will be acceptable. To minimize the amount of vaporized LOC that must be scrubbed out of the gas stream, the boiling point should be well above the operating temperature and certainly well above the upper ambient requirement of 60ºC with solar load (about 80 ºC).

The enthalpy is an important parameter of the LOC because it impacts both effective hydrogen capacity and hydrogen release efficiency. The 90% onboard efficiency requirement limits the LOC to materials with no more than 24 kJ/mole reaction enthalpy. Even if this were not the case one would like to minimize this value because it limits capacity; the hydrogen consumed in releasing hydrogen does not count in capacity. Another crucial parameter of an LOC that interacts with enthalpy is release temperature; if it is less than 100C then there is hope that eventually this energy can be obtained from the fuel cell for free. For materials with normal liquid entropy, thermodynamics implies that the limit for the enthalpy of hydrogen release will be about 30 kJ/mol. If meeting the 60% cycle efficiency is more important than the 90% onboard efficiency then this would be the logical enthalpy target. Thus one feature of the optimized LOC is the enthalpy will range from 24 to 30 kJ/mol.

As discussed above, kinetics are the key to a reactor of modest size, complexity and cost. Obviously, kinetics relate to how fast a reaction may proceed, and it would be expected that kinetics will set the transient response. Yet we have shown that this need not be the case if the battery is used judiciously or a small, rapid response hydride bed is added. But as we have shown, kinetics has a significant impact on reactor size. Independent of kinetics we know that about 39 cc/s of LOC must be processed 95% of the way to completion if the 2 g/s maximum flow rate will be met. If kinetics are extremely fast the reactor volume can be small. Consider an LOC with a reaction rate constant that allows complete conversion in 1 second. The reactor would need to only be about 40cc in volume. However, if a parcel of LOC takes a minute for complete conversion then the reactor will be roughly 2 liters in volume; 39ccs will flow in and out each second, but a larger volume of partly reacted LOHC is required to generate the 2 g/s of hydrogen at this lower reaction rate. This is undesirable for two reasons; first, the larger reactor weighs more, takes up more room, and will cost more due to its greater material cost, but also the reactor will not be able to easily slow its hydrogen production rapidly. Using a 2 liter reactor and LOC that takes 1 minute to react to completion, when the vehicle is switched off the reactor will still generate nearly 26 grams of hydrogen after key off. If the battery were not near top of charge most conveniently this hydrogen would be converted in the fuel cell, and at 50% conversion efficiency this would require storage of 435 Wh of electricity. This is a significant amount of energy for a simple HEV.

However, if the kinetics are an order of magnitude slower the problem becomes intractable. If ten minutes are required to achieve 95% LOC conversion, and accounting for the increased hydrogen production required to supply the enthalpy of reaction in addition to the 2 g/s maximum delivery, the reactor will hold 13.7 kg of LOC, fill just over 17 liters of space, and will release about 260g of H_2 after shut down. This would convert to roughly 4 1/3 kWh, an amount of energy storage that is only possible in a plug-in hybrid or EV.

Complete or near complete conversion in 1 minute requires a first order or pseudo first order rate constant of the order of $0.1s^{-1}$ at the operating temperature in the reactor; the rate constant will be $0.0077s^{-1}$ for an LOC that takes 10 minutes to reach 95% conversion. So a second trait of a superior LOC is a rate constant of greater than $0.01\ s^{-1}$ with a rate constant better than $0.1\ s^{-1}$ being desirable.

The cost of the LOC is also a less than straightforward matter. Clearly a low cost is desirable. But because the carrier and catalyst are reused the cost of hydrogen will be the cost of whatever input materials and energy are required for regeneration (hydrogen may or may not be needed in gas form to regenerate the LOC) plus the replacement cost of that fraction of the LOC lost each time through the cycle. Let's assume $20/kg for the raw cost for new, fully hydrogenated LOC. At 7% specific mass hydrogen, the cost per kg of hydrogen carried is ~$286 so a 5kg tank would be valued at ~$1429; fortunately, that cost is almost all recaptured when the spent fuel is returned. Still, if 1% of the LOC is lost to spillage, irreversible reaction to incorrect molecules, destruction of catalyst, and miscellaneous losses, then $14.3 or nearly 30 cents per kg of delivered hydrogen comes simply from carrier volume make up. That 30 cents are entirely outside the cost of hydrogen or energy, and it is roughly 10% of the total cost allowed for hydrogen generation and delivery. A dry break connection should limit spillage to under a cc per fill up. However, it is clear that the reactor operation temperature must we well below the catalyst degradation temperature. Also a very high specificity in the regeneration reaction is a requirement, 99% or better is an excellent target. So two more attributes of superior LOC are high specificity in regeneration and at least 20C difference between operation temperature and the onset of catalyst thermal degradation.

Another aspect of fuel cost is the fact that a precious metal is used as catalyst. At between 100 and 1000 dollars per troy ounce over the last decade, iridium (Ir) is of high value, and is currently trading at the high end of the range. It is key that the Ir content be low enough to make the LOC affordable. 500ppm Ir in the LOC translates to 0.5g Ir per kg LOC or 1/65 of a troy ounce, so at the maximum price of $1000/per troy ounce, iridium will contribute ~$15/kg of LOC. Obviously this is a high fraction of the previously mentioned $20/kg, but there are a large number of bulk hydrocarbons that sell for much less than $5/kg, e.g. gasoline at less than $1/kg before taxes. Assuming a net hydrogen storage of 7%, a tank holding 5kg useable hydrogen will hold 71.5kg of LOC containing about $1100 of Ir. The impact of Ir price on system cost can be seen in Figure 21.

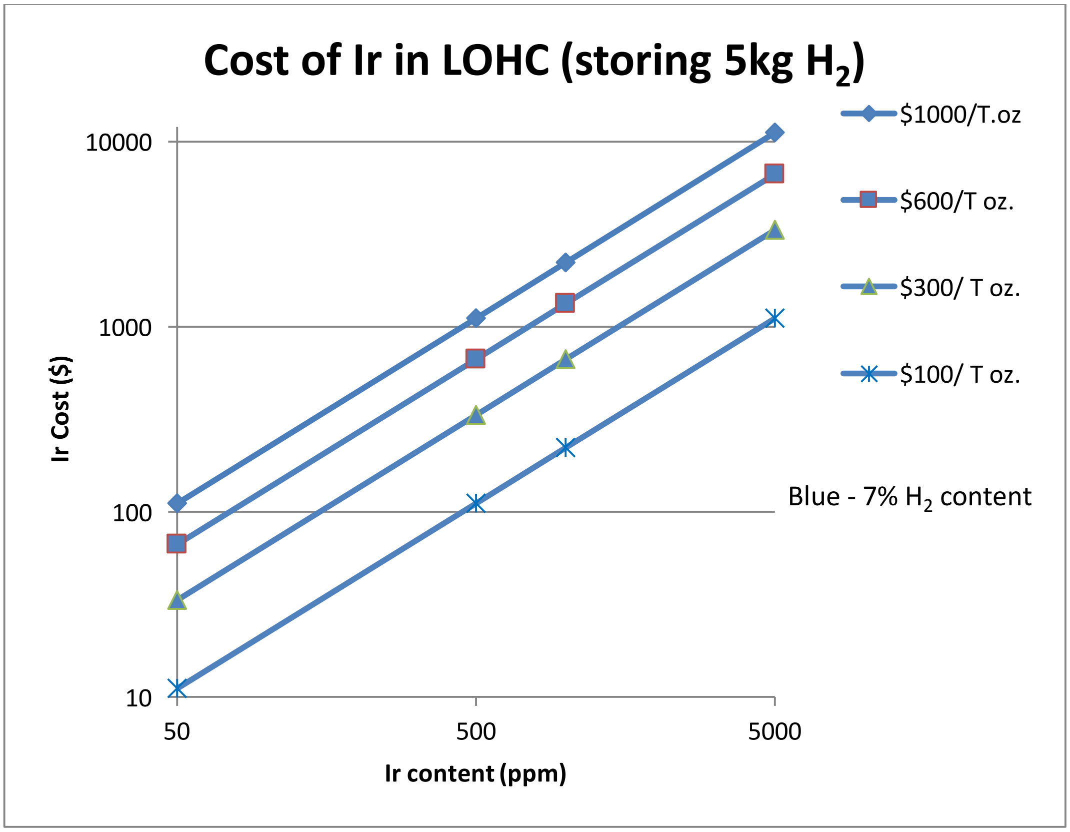


Figure 21. Iridium cost for 5kg H_2 storage. The cost of Ir is shown for various Ir prices at a constant 7 weight percent hydrogen in the LOC.

Exchanging a tank of fuel might cost on the order of 30 dollars because by returning spent LOC at the same time the customer only pays for the hydrogen, transportation of the LOC to the station, the small amount of make-up volume lost in the regeneration cycle, overhead, capital and profit. But the actual LOC in a tank of fuel would be worth at least 100 times that amount; while this cost will be distributed over many hundreds of tanks of fuel through regeneration, it may be an incentive for fuel theft. Ir is never found at 500ppm in natural ores, so LOC would present both an attractive "mine" for Ir extraction, and a ready market for its sale.

On a larger scale, the price of LOC and the volume that would be in use means an energy supplier would have capital costs to consider. Energy companies have alternative uses for capital and frequently use a hurdle rate for capital in the area of 20%. While not a machine or property, none the less LOC would likely be treated financially in a way similar to capital goods because any particular supplying company will have a large amount of money tied up in the total quantity of LOC they have on hand at any time, and so roughly 20% return would be expected. Assuming customers completely fill their tank 25 times a year on average then every $100 of LOC will need to find its 20% return over 25 sales events or 80 cents per fill up per $100 of LOC. Again based on 6% net specific mass hydrogen (7% total hydrogen) 1kg of hydrogen will require 16.7kg of LOC. Assuming again $20/kg replacement cost for LOC that would be $354 worth of LOC. Accordingly, each kg of hydrogen will need to bear $2.8 of 'capital return' cost. This is in addition to the volume-make-up cost of $3.54/1% lost in transportation, delivery and regeneration. Clearly this could be a problem because the lower bound of the current DOE range of hydrogen cost is $2/kg, less than the capital return cost on $20/kg LOC. The upper end of the range is currently $6/kg, so there is room for the LOC method to be viable, but clearly fuel-cycle volume losses, Ir content, and regeneration costs must be minimized and Ir cost must be contained.

Delivery cost for hydrogen may be significantly reduced by use of LOC. The hydrogen density would be on the order of 1kg hydrogen in 18 to 20 liters of LOC. Because the LOC is not pressurized or reactive, typical tanker trucks could be used though not at full efficiency since room must be left for returning the fuel. Still one could easily imagine a 1/10 of the tanker being left empty as it leaves the regeneration plant in order to accept spent fuel while regenerated fuel is dropped off. During fuel exchange, each newly empty section would be subsequently filled with spent fuel. A bladder in the tanker would allow near full utilization. Still assuming only 90%

utilization, LOC allows for transport of hydrogen at 50g/L, and in a less expensive delivery truck relative to a high pressure 6-pack truck. A tank truck of 25,000L is not exceptional in today's market, and under the assumptions above it would transport 1250kg of usable hydrogen. This should significantly lower the cost of delivery, but it is reasonable to think it will still amount to more than 50 cents per kg of useable hydrogen. All things considered, \$20/kg LOC, and 500pm Ir, would seem to be the upper limits for a viable system unless the useable hydrogen capacity can be improved or the cost of the catalyst reduced.

The foregoing suggests several areas where research could improve the viability of the LOC system: 1) a catalytic metal that offers a cost to reaction rate ratio that is several times lower than Ir; 2) a catalyst with a reaction rate constant of $0.01 s^{-1}$ or higher; and 3) a carrier that significantly exceeds 7% specific mass with an enthalpy of ≤ 30 kJ/mol. Each of these would have multiple beneficial effects and would be worthy of pursuit.

VIII. CONCLUSIONS

A variety of candidate LOCs including: ethyl perhydro-carbazole (EHC), methyl perhydro-methylindole (MHI), aminomethyl cyclohexane (AMC), and perhydro-butylpyrrolidine (BHP) were screen for their suitability for practical applications. Detailed, variable temperature studies were carried out to determine the kinetic parameters of the catalytic dehydrogenation of the most promising candidates, EHC, MHI, and BHP in the presence of the iridium pincer complex, $IrH_2\{C_6H_3\text{-}2,6\text{-}(OPBu^t_2)_2\}$. Our studies have found that the PCP pincer complexes effectively catalyze the rapid dehydrogenation of saturated 5-membered, nitrogen-containing rings at rates that are relevant to demands of an onboard PEM fuel cell. Dehydrogenation onset temperatures of 180, 160, and 140 °C, activation energies (E_A) of 115.1, 142.4, and 166.1 (kJ/mol); and frequency factors (A) of 3.562×10^8, 1.052×10^{11}, and 2.170×10^{14} (s^{-1}) were found for EHC, MHI, and BHP respectively. We have found that high rates of LOC dehydrogenation, approaching those required for practical viability for use with proton exchange membrane (PEM), can be achieved at 200ºC in the presence of only 100 ppm of the pincer catalyst. This translates to an acceptable catalyst cost of ~\$5/L. Thus, effective loadings of the precious metal containing catalyst would not be cost prohibitive for an onboard, LOC-based hydrogen storage system. BHP undergoes quantitative dehydrogenation at 140ºC in 18 h which is significantly lower than the 160 and 180ºC temperatures required to achieve the same rates for MHI and EHC, respectively. Thus the best LOC/catalyst combination that identified in our studies is BHP/$IrH_2\{C_6H_3\text{-}2,6\text{-}(OPBu^t_2)_2$. The dehydrogenation onset temperatures correlate with collision frequency factors rather than the activation energies. Thus the steric constraints of the approach of the LOC rather than the barrier to C-H bond activation at the iridium center apparently limit the rate of reaction. Additionally, studies of the dehydrogenation of MHI and EHC in the presence of the hydrogen acceptor, t-butylethylene also consistently showed that only low levels of dehydrogenation of the outer, non-hetero atom containing ring. Thus the more favorable thermodynamics of the transfer dehydrogenation reactions did not result in higher conversions to fully dehydrogenated products. Clearly, the resistance to the dehydrogenation of the 6-membered rings is due to a high kinetic barrier rather than an unfavorable dehydrogenation equilibrium. We conclude that the steric accessibility of the LOC to the catalyst metal center is a more important consideration then C-H bond strength in the predicting the dehydrogenation performance of a LOC in our catalytic system. Thus the key to the development of higher performance variaitons on the LOC/pincer catalyst systems is the development of PCP pincer catalysts with reduced steric constraints on the approach of the LOCs to the metal center. We found that higher initial rates of LOC dehydrogenation are obtained with the AsCAs pincer complex, $IrH_2\{C_6H_3\text{-}2,6\text{-}(OAsBu^t_2)_2\}$ than with those achieved with its PCP analog. However, the AsCAs pincer complex has much lower thermal stability than the PCP and undergoes significant decomposition within a few hours at the temperatures required for the dehydrogenation reaction. Scale-up cycling studies with both MHI and BHP solutions containing low, 100 ppm loadings of the pincer catalyst and Pd/C. GCMS and NMR analysis verified that virtually complete dehydrogenation and re-hydrogenation occurred on each half cycle with no detectable degradation of the LOC or catalyst over the course of 50 cycles, representing 2 million catalytic turnovers of the pincer catalyst. These results indicate that a PCP pincer catalyst could be utilized in a practical LOC-based hydrogen storage system.

Although we set out to design an entire LOC based hydrogen storage system, only the reactor design was studied in moderate detail. However, advances were made in over-all the engineering design. The novel LOC reactor design generated for this project uses the waste heat from the fuel cell and at the same time, reduces the size of the radiator currently used to vent fuel cell heat. The liquid nature of the LOC that allows the use the fuel cell heat which is unusable in a solid hydride bed. Operation of 100kw fuel cell nominally requires 2g/s hydrogen or approximately 30g/s LOC if conversion is under 95% complete. If the LOC is at a relatively warm, 30 ˚C and has a nominal heat capacity of 1.75kJ/kgK, it could be heated in this design to 80 ˚C with approximately 2.7kW which is clearly available in the coolant stream. This would save ~1.3g/min of parasitic hydrogen consumption at full power. Given that both the homogenous catalyst and the carrier compound can be temperature sensitive, we favored a heat-transfer-fluid based system. Furthermore, our design sends the combusted gas to the compressor/expander, thus heat is not lost leaving the burner, so the down side to this design is minimized. The hydrogen initially generated by the homogenous catalyst will go toward saturating the carrier rather than immediately starting bubble formation as in a heterogeneous concept. Accordingly, the mass and volume of the reactor can be significantly reduced since micro-channel heat exchangers can be used. In order to minimize the amount of insulation required (and reduce volume and cost), we chose single unit heat exchangers with one directly feeding the next. Several designs were considered for the internal structure of the reactor, all with the same liquid heat transfer system. The internal volume of the reactors was minimized since in addition to taking up less volume, smaller components are lighter and less expensive. Additional issues that are minimized by making the reactor as small as possible include: heat loss due to unnecessary surface area, and the undesirable heating of adjacent parts. Control and hydrogen flow dynamics are also improved by using the smallest possible reactor. The design of the smallest reactor capable of providing 2g/s hydrogen was based on predicted percent LOC conversions that were obtained using COMSOL Multiphysics, version 4.3b. The most efficient design from a volume and mass perspective was the nested helix design. However, the single helix design was only slightly less efficient and would be much simpler and more reliable from an assembly viewpoint. We conclude that the single helical reactor is the most appropriate advanced design to compare with the baseline.

References

[1] R.P. Linstead, S.LS. Thomas, J. Chem. Soc. (1940) 1127.
[2] M. Taube, D. Rippin, W. Knecht, D. Hakimifard, B. Milisavljevic, and N. Gruenenfelder. Int. J. Hyd. Energy, 10 (1985) 595.
[3] J.K. Ali, E. J. Newson, D.W.T. Rippen, Chem. Eng. Sci. 48 (1994) 2120.
[4] N. Meng, S. Shinoda, Y. Saito Int. J. Hydrogen Energy 22 (1997) 361.
[5] C.M. Jensen, Proceedings of the U.S. DOE Hydrogen Program Review, Herndon, VA. (1997)
[6] S. Hodoshima, S. Takaiwa, A. Shono, K. Satoh, Y. Saito Appl. Catal. A 282 (2005) 235.
[7] G.P. Pez, A.S. Scott, A. Cooper, H. Cheng, United States Patent 7101530 (2006).
[8] Z. Wang, I. Tonks, J. Belli, C. Jensen. J Organomet. Chem. 694 (2009) 2854.
[9] Z. Wang, J. Belli, J.; C.M. Jensen Faraday Discuss 151 (2011) 297.
[10] A.C. Cooper Final report, DOE Award No. DE-FC36-04GO14006, April 2012.
[11] A. Moores, M.Poyatos, Y. Luo, R.H. Crabtree, New J Chem 30, (2006) 1675.
[12] D. Brayton, D., C.M. Jensen, Chem Commun 50, (2014) 5987.
[13] M. Gupta, C. Hagen, W.C. Kaska, R.E. Cramer, C.M. Jensen, J. Am. Chem. Soc.119 (1997) 840.
[14] C.M. Jensen. Chem. Commun., 1999, 2443.
[15] F. Liu, A.S. Goldman, Chem. Commun. (1999) 655.
[16] D. Morales-Morales, R. Redón, C. Yung, C.M. Jensen; Inorg. Chim. Acta 357 (2004) 2953.
[17] C.M. Jensen, United States Patent 6074447, (2002).
[18] X.Q. Gu, W. Chen, D. Morales-Morales, C.M. Jensen, J. Mol. Catal. A 119 (2002) 189.
[19] X. Zhang, A. Fried, S. Knapp, A.S. Goldman, Chem Commun. (2003) 2060.
[20] T. Johnson, S. Jorgensen, D. Dedrick. Faraday Discussion 151(1), 2011. pp 327-52.
[21] T. Johnson, M. Kanouff. Int J Hyd Energy, 37, 2012. Pp 2304-19.
[22] R. Ahluwalia, T. Hua, and J Peng. http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/liquid_carrier_h2_storage.pdf
[23] R.K. Ahluwalia, T.Q. Hua, J.K. Peng. Int J Hyd. Energy, 37, 2012. pp 2891-910.
[24] D. Haley, V. Narayanan. IMECE2011-64176, Proceedings of the ASME 2011 International Mechanical Engineering Congress & Exposition, November, 2011.
[25] T.Voskuilen, Y. Zheng, T. Pourpoint. Papers- American Institute of Aeronautics and Astronautics; 11; 2009, 6954-6963.

Publications

1. Synthesis, Characterization, and Dehydrogenation Activity of an Iridium Arsenic Based Pincer Catalyst, Daniel Brayton, Paul Beaumont, Erin Fukushima, and Hope Sartain, David Morales-Morales, Craig M. Jensen, *Organometallics* 2014. *33*, 5198.

2. Solvent-free Selective Dehydrogenation of Indolic and Carbazolic Molecules with an Iridium Pincer Catalyst; Daniel Brayton and Craig Jensen *Chemical Communications* 2014, *50,* 5987.

3. Dehydrogenation of Pyrrolidine Based Liquid Organic Hydrogen Carriers by an Iridium Pincer Catalyst, an Isothermal Kinetic Study, Daniel F. Brayton and Craig M. Jensen *International Journal of Hydrogen Energy* 2015, 40, 16266.

Presentations

1. "Development of Liquid Organic Hydrogen Carriers." Daniel Brayton, Craig Jensen. Materials Challenges in Alternative & Renewable Energy 2012, Clearwater, FL, USA. 02/28/12

2. "Development of Liquid, High Capacity Hydrogen Carriers." C.M. Jensen, D. Brayton, S. Jorgensen, G. Severa, E. Rönnebro, M. Chong, T. Autrey, A. Karkamkar, S. Orimo. Materials for Hydrogen Storage – Future Perspectives, Kirkenes, Norway. 06/20/12.

3. "Development of Liquid, High Capacity Hydrogen Carriers." C.M. Jensen, D. Brayton, S. Jorgensen, G. Severa, E. Rönnebro, M. Chong, T. Autrey, A. Karkamkar, S. Orimo. International Symposium on Metal-Hydrogen Systems; Kyoto, Japan. 10/06/12.

4. "Development of Liquid, High Capacity Hydrogen Carriers." C.M. Jensen, D. Brayton, S. Jorgensen, M. Chong, J. Wang, S. Orimo. 7th EMPA Hydrogen and Energy Symposium, Stoos, Switzerland. 01/22/13.

5. "Development of High Capacity Liquid Hydrogen Carriers." Craig M. Jensen. International Institute of Nano and Molecular Medicine, University of Missouri, Columbia, MO, USA. 04/05/13.

6. "Development of High Capacity Liquid Hydrogen Carriers." Craig M. Jensen. Hydrogen Production, Storage, and Utilization Symposium, 245th National Meeting of the American Chemical Society, New Orleans, LA, USA. 04/08/13.

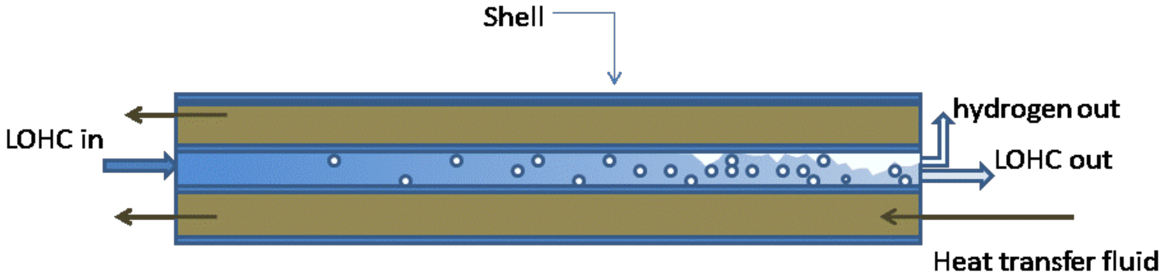
7. "Development of a Hydrogen Storage System Based on Liquid Organic Carriers and Homogenous Pincer Catalysts." Craig M. Jensen. Simposio Latinoamericano de Quimica de Coordinacion y Organometalica 2013. Huatulco, Mexico. 10/14/13.

8. "Update on Hydrogen Storage Research and Development Activities in Hawaii." Derek Birkmire, Marina Chong, Elham Sadeghmoghaddam, Daniel Brayton, Adrian Narvaez, Craig M. Jensen. The Materials Challenges in Alternative & Renewable Energy 2014, Clearwater, FL, USA. 02/17/14.

Appendix

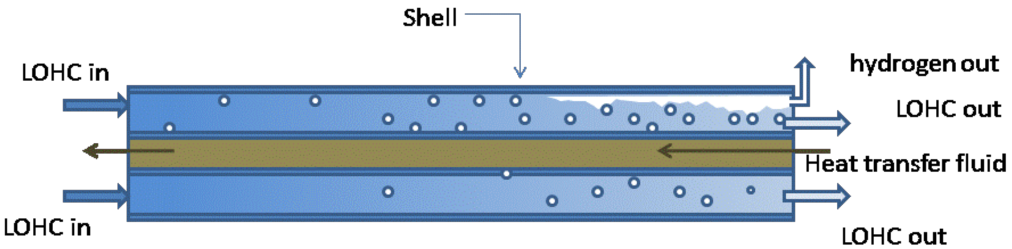
Reactor designs

As the reactor is probably the most critical part of the system, significant effort was put into developing designs that would offer one sort of advantage or another. In all 18 designs were developed. We include them here along with a short description of their individual features.



Counterflow, reactor
Option #1

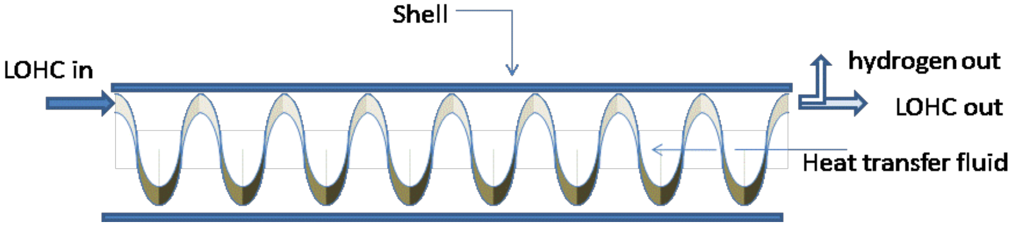
1) Baseline: As described in the main report, a simple countercurrent heat exchanger with LOHC in the tube and heat exchange fluid in the shell was the baseline. It has the advantages of being well understood, very efficient in heat transfer, simple to construct and readily available.



Counterflow, reactor
Option #2

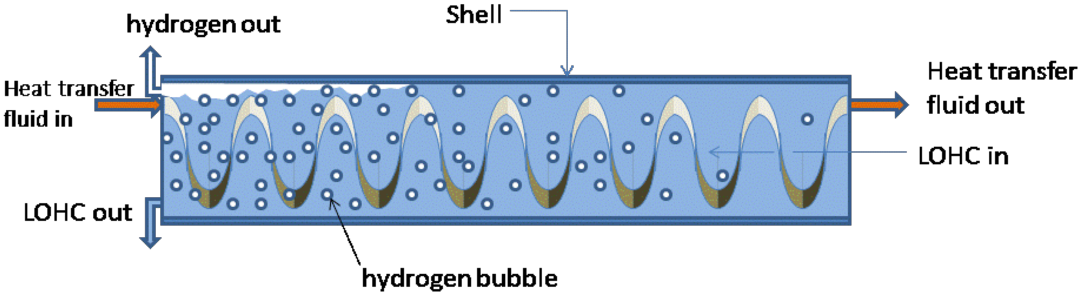
2) In option 2 the only change is that the LOHC flows in the shell and the Heat transfer fluid in the tube. It has the advantages of the baseline reactor but is unlikely to be superior because the heating is likely to be less effective.

Counterflow, helical reactor
Option #3



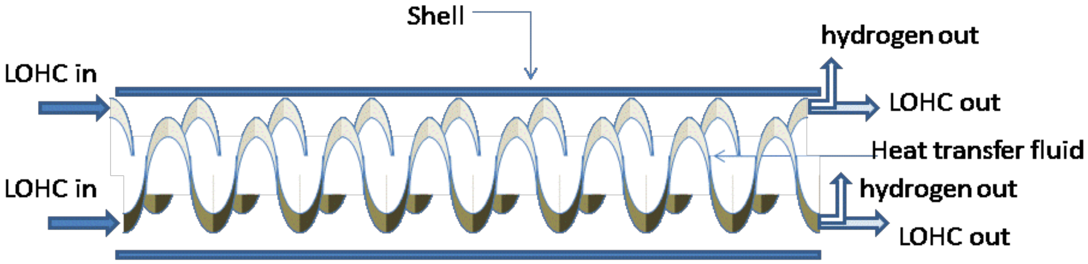
3) Option 3 is a helical version of the baseline. The helical flow induces better heat transfer and should be more efficient. Assembly is only slightly more difficult.

Counterflow, helical heater
Option #4

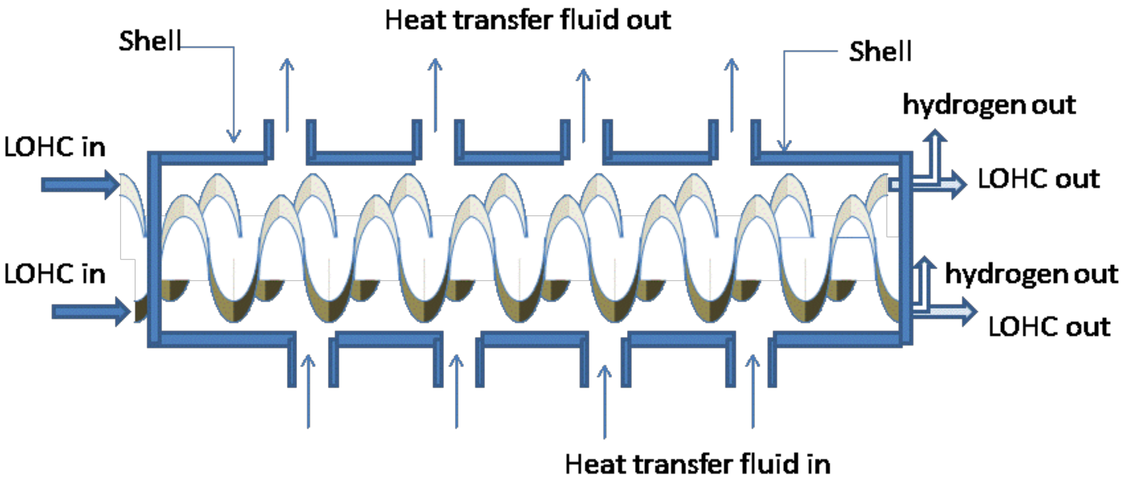


4) Option 4 is the same as 3 but again with LOHC in the shell. The possibility of dead spots exists but the flow should also be very complex which could have advantages.

Nested helical reactor, counterflow
Option #5

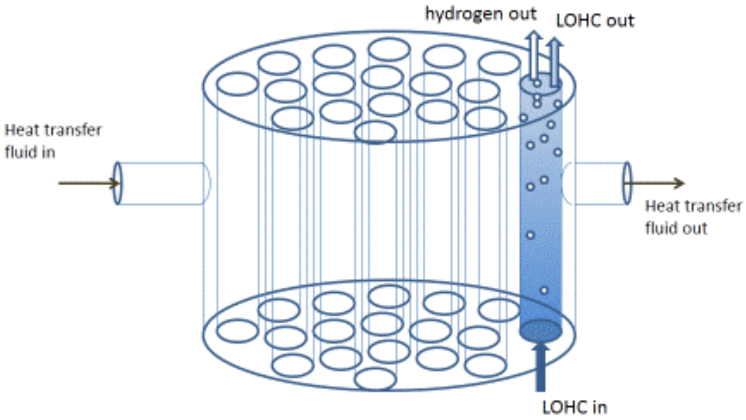


5) Option 5 features a double nested helix, this will have more complex heat transfer flow and may improve heat transfer, it also allows for a shorter reactor to process more LOHC. However assembly will be complicated and more costly and a more complex manifold is required. Conceivably the flows in the two tubes may not balance easily unless the length and pitch are identical, but that is not clear.
An option 5a would have the flow of LOHC in the shell. This might be needlessly more expensive though heat transfer would improve over design 4.



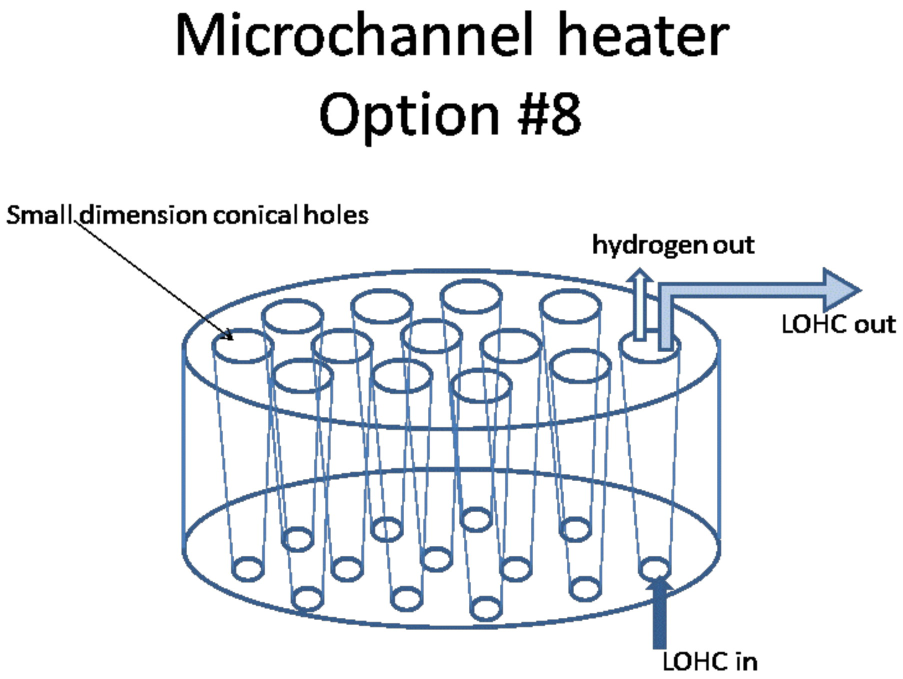
Nested helical reactor, cross flow
Option #6

6) Option 6 is again the same reactor with LOHC in the tubes as in option 5, but with cross flow of heat transfer fluid. This would give very uniform heating temperature as there is little chance for it to cool, but the cost and complexity are much higher. A significant manifold is required and as the reactor gets longer more and more coolant supply tubes are needed. Dead spots can be expected.



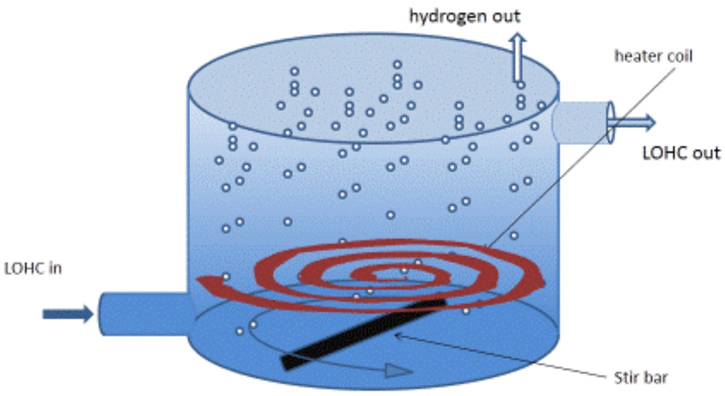
Vertical tube reactor
Option #7

7) Option 7 is the first vertical option considered. This is a cross flow design and it is not clear that all tubes would see the same temperature, however the temperature along a tube should be fairly constant. This would also require an LOHC manifold but one option would be to feed the output of one tube into the inlet of its neighbor with the LOHC flow alternating up and down in the figure and moving from the coolest to hottest part of the reactor. The tubes cannot be more than about a foot long in order to find a place to package the reactor and required headers in a vehicle.



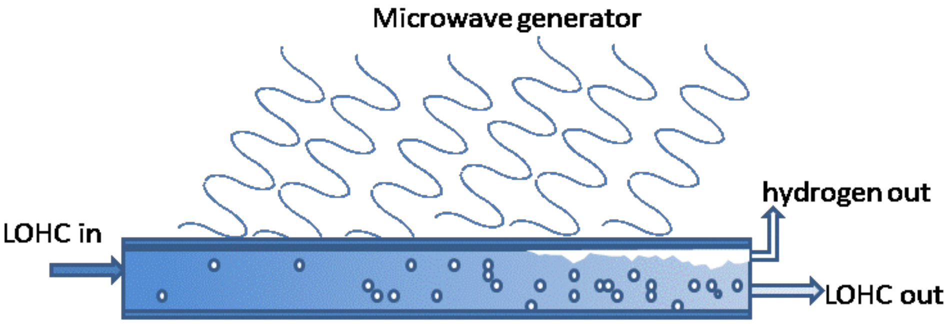
8) Microchannel reactor. Here the very high heat transfer of microchannel reactors is the attraction but we expect a conical tube will be needed to allow hydrogen to exit. Design would be very delicate with this reactor to ensure good conversion on the one hand and prevent hydrogen from filling the tubes on the other hand. This reactor was outside our ability to model with confidence, but may be of interest to subject matter experts in microchannel reactor design.

CSTR with coil heater
Option #9

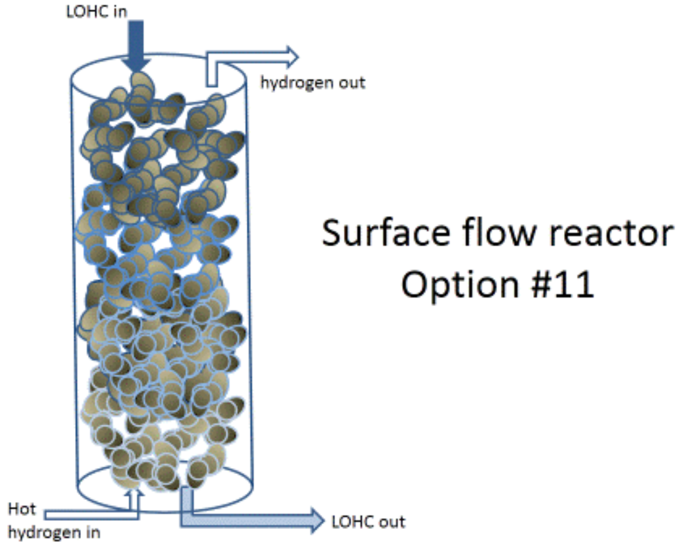


9) CSTR and coil is a totally different reactor concept based on an industrial standard design. Heat transfer fluid flow in the coil and the stirrer causes the LOHC to mix and heat. Equations for establishing exit concentration are well known. However, for high conversion a very large tank, on the order of the fuel tank size, are needed with near current kinetics. If very fast kinetics are developed this may be worth revisiting.

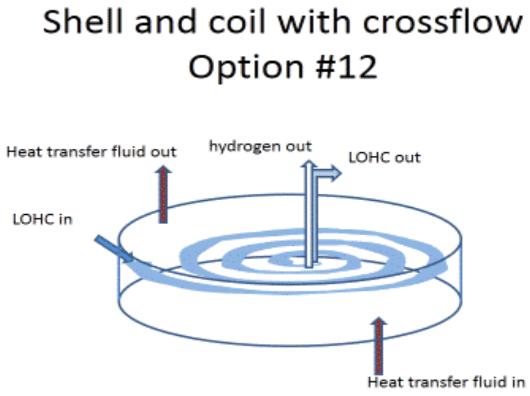
Microwave heater
Option #10



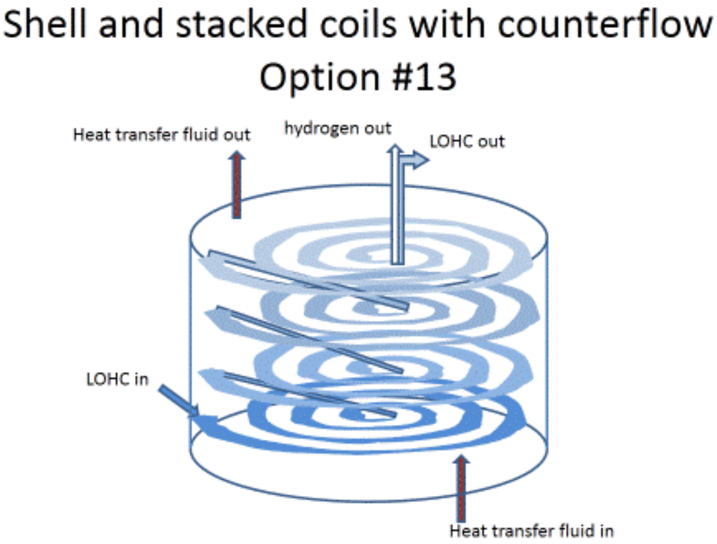
10) Microwave heating is the unique part of option 10. An obvious downside is the fact that .electricity from a fuel cell contains only half the energy of the hydrogen used so this will not be efficient unless a very special catalyst is developed that is both inexpensive and also uses the energy in microwaves effectively with no loss. This may be a lower mass system as no burner or coolant and tubing are required.



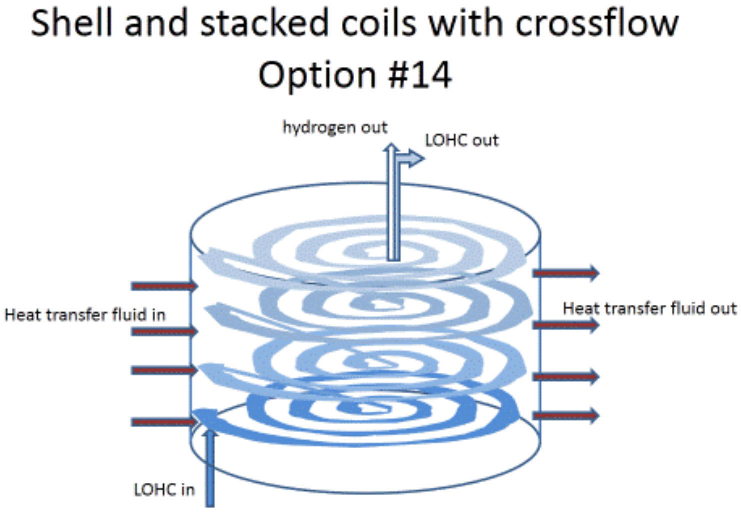
11) Essentially a packed column reactor this would most likely need to be vertical and so it would need to be short. A unique feature is the heat is provided by hot hydrogen running counter flow to the LOHC. The system is not likely to do well in volume because reaction is basically in a film rather than a bulk volume. For non-automotive application this could be attractive.



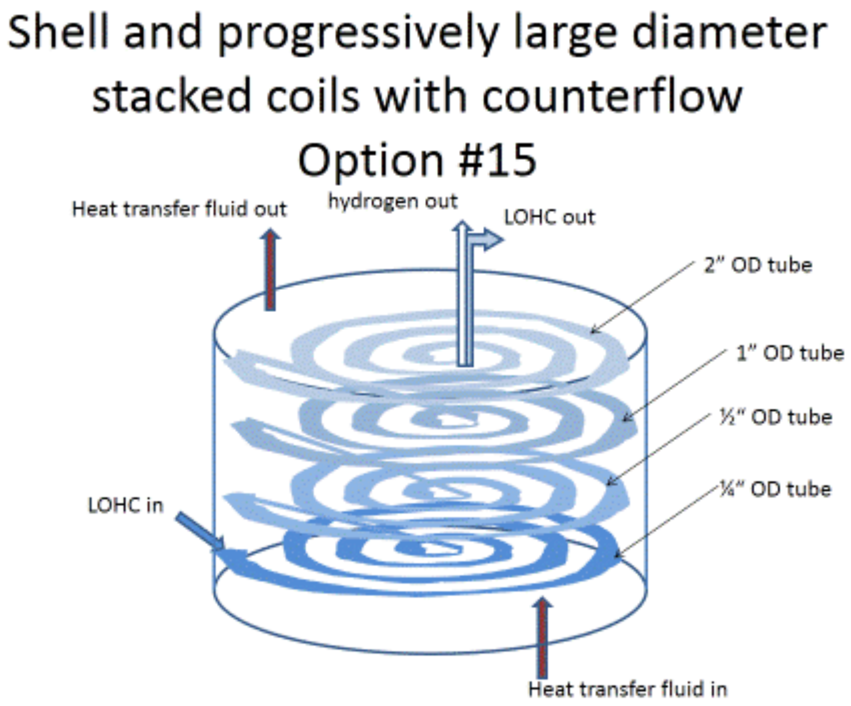
12) Crossflow shell and coil, with LOHC in the coil. This would be a very flat reactor and should use volume well if the coil fills much of the shell. The temperature and heat flow in the LOHC should be very even. Assembly will be somewhat more complicated but not as bad as other crossflow designs. This is probably the design most worthy of study in future work.



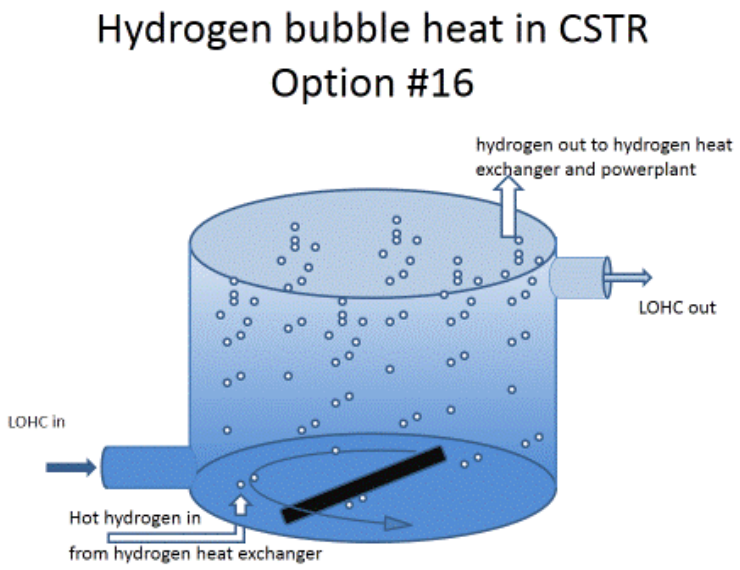
13) Stacked coils and cross flow is very similar but the outlet of one coil feeds the one above it (or optionally below it. Again the temperature should be relatively steady because only a few stacked coils will be possible to package in a vehicle. Assembly will be slightly more complex and presumably in real implementation a skeletal carrier structure will hold the coils apart.



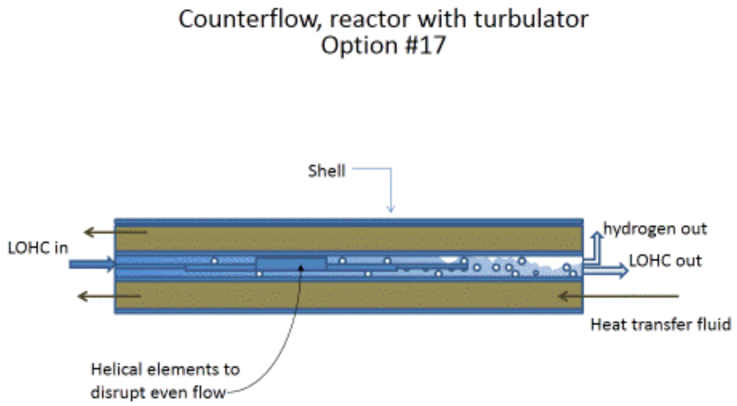
14) This is similar to option 13 but with crossflow. The advantage is a shorter stack but it comes at the expense of a more complex assembly and several inlet and outlet pipes which most likely will need a header.



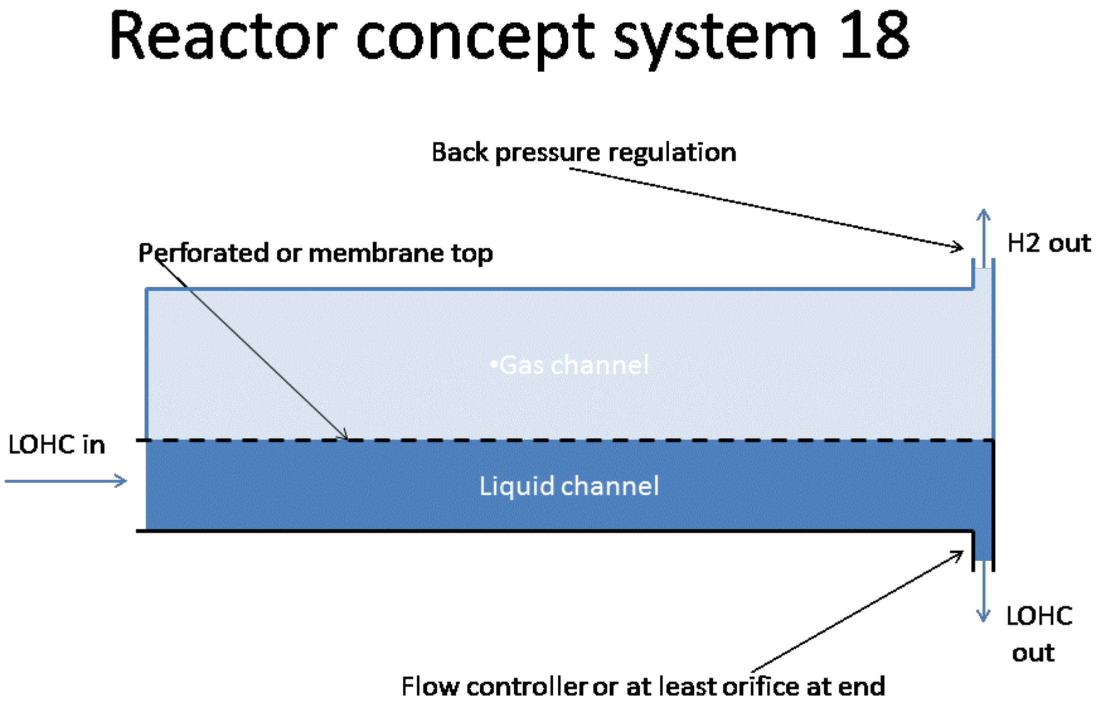
15) Stacked coils with progressively large diameter. This is the same as Option 13 but each set of coils is larger in ID so that as the hydrogen is generated it has some room to flow without forcing out partly reacted LOHC. While doubtlessly more expensive to build than option 13, in large quantity the difference may not be great since no extra assembly actions are required, only a proper flair on the end of the coil to braze easily to the next coil in the stack. Again a skeletal structure is likely to be required to hold the coils in place.



16) A bubble heated CSTR is a simpler variant of option 5 where hot hydrogen is used to heat the bath rather than a heating coil. It will still be large unless kinetics are very fast.



17) Turbulator added to option 1. Here a roughly helical shape inside the linear tube induces shear without the need for twisted tubing. However the turbulator must be added and assembled.



18) Perforated divider design. This design is least likely to eject unreacted LOHC as the hydrogen can escape the liquid stream and flow in a channel specifically for H_2. The challenges would be volume and primarily pressure balancing in all conditions and transients so that liquid did not flood the top section. Heat transfer would be very uneven as well.

Only some of the designs could be modeled in the time and funding eventually allocated to engineering. Based on engineering insight, modeling difficulty, and probable cost we chose a subset to model in COMSOL and evaluate.

Initial design evaluation data.

The baseline, and options 3, 5, 6, and 7 were considered for simulation. Since there is a meaningful investment of time setting up the simulation, and the calculations take some time to converge, we selected those models that were most likely to improve meaningfully on the baseline. This left out options 2 and 4. Option 8 was less likely to yield meaningful results with our tools and options 9-18 seemed likely to need very large tanks, long calculation times, or in the case of option 11 information we did not have and could not approximate. The following work led to the runs cited in the report body.

We wanted to make the simulations as simple as possible but also have some fidelity. With the fluid heating and then changing density due to small bubble formation it seemed worth checking if gravity would matter. Leaving gravity out would simplify things significantly. Figure A1 shows that gravity has an important impact on heat transfer. This is not too surprising as the flow is laminar and anything, such as buoyancy, that disrupts the flow will increase heat transfer overall.

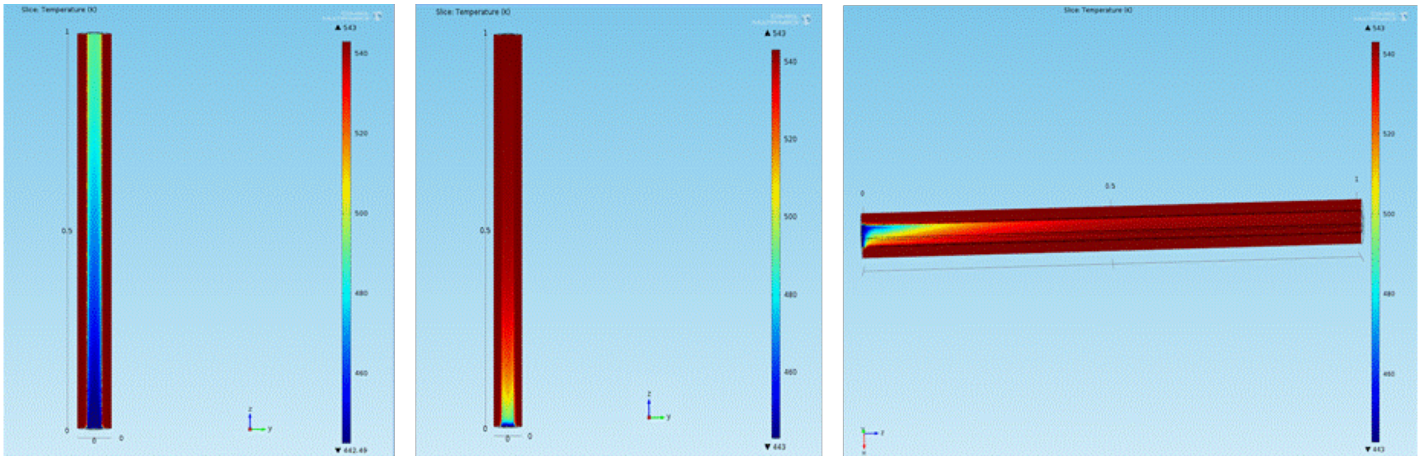


Figure A1: Impact of gravity on LOHC. In the left pane and middle images we see heat transfer with identical flow conditions with the exception that gravity is not considered in the left image. The right image shows that indeed the buoyancy of causes LOHC to rise and mix, this is the source of the improved heating. No hydrogen production is considered at this stage.

We then sought a context for the impact of kinetics on conversion. Using the baseline reactor we see that even in a simple model with no density change, faster kinetics has an

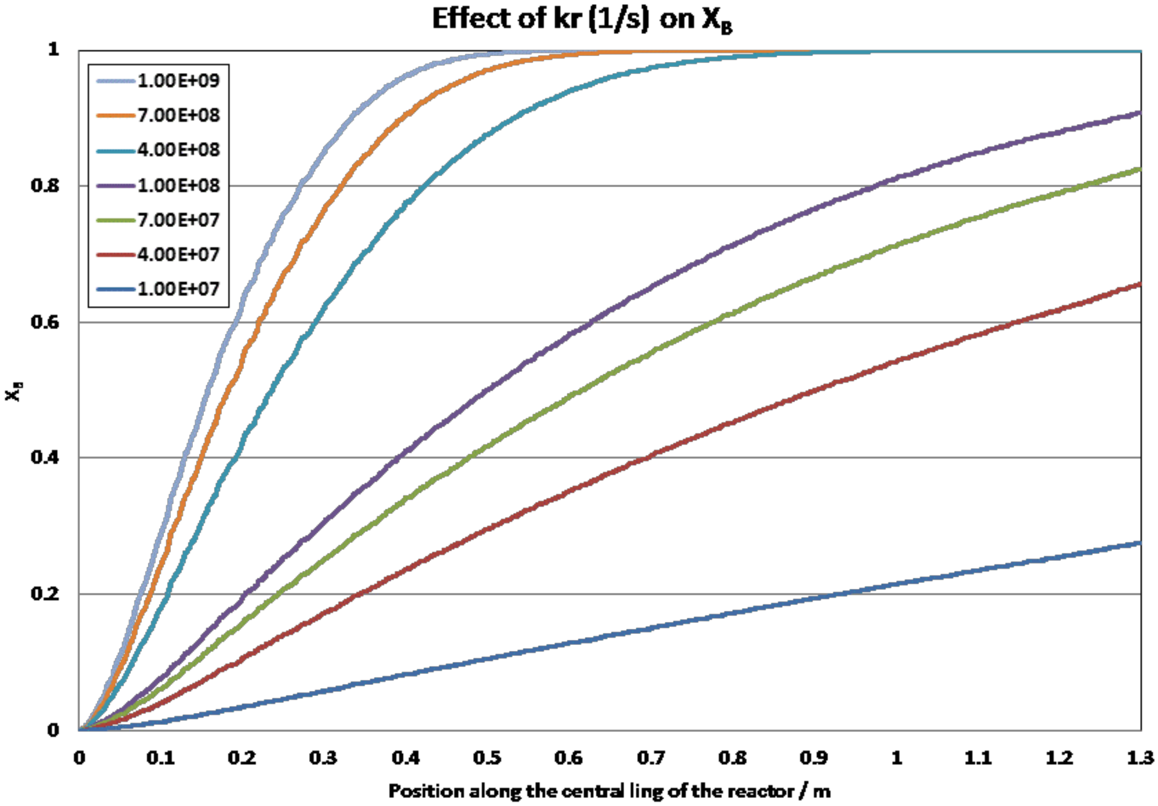


Figure A2. Conversion as a function of kinetics and position in the reactor. A simple model where reaction does not impact density is used. Actual results will differ but the general relationship is expected to be represented correctly.

enormous impact on the length of reactor required. In A2 we see that an order of magnitude change in k_r (reaction rate constant) more than triples the length of reactor needed and often reduces conversion at constant position by more than a factor of 3.

Option 3 was then considered and the impact of kinetics is not much changed (Figure A3). However the absolute level of reaction is significantly greater. This points to better heat transfer and or mass transfer rather than a chemical rational for the improved performance.

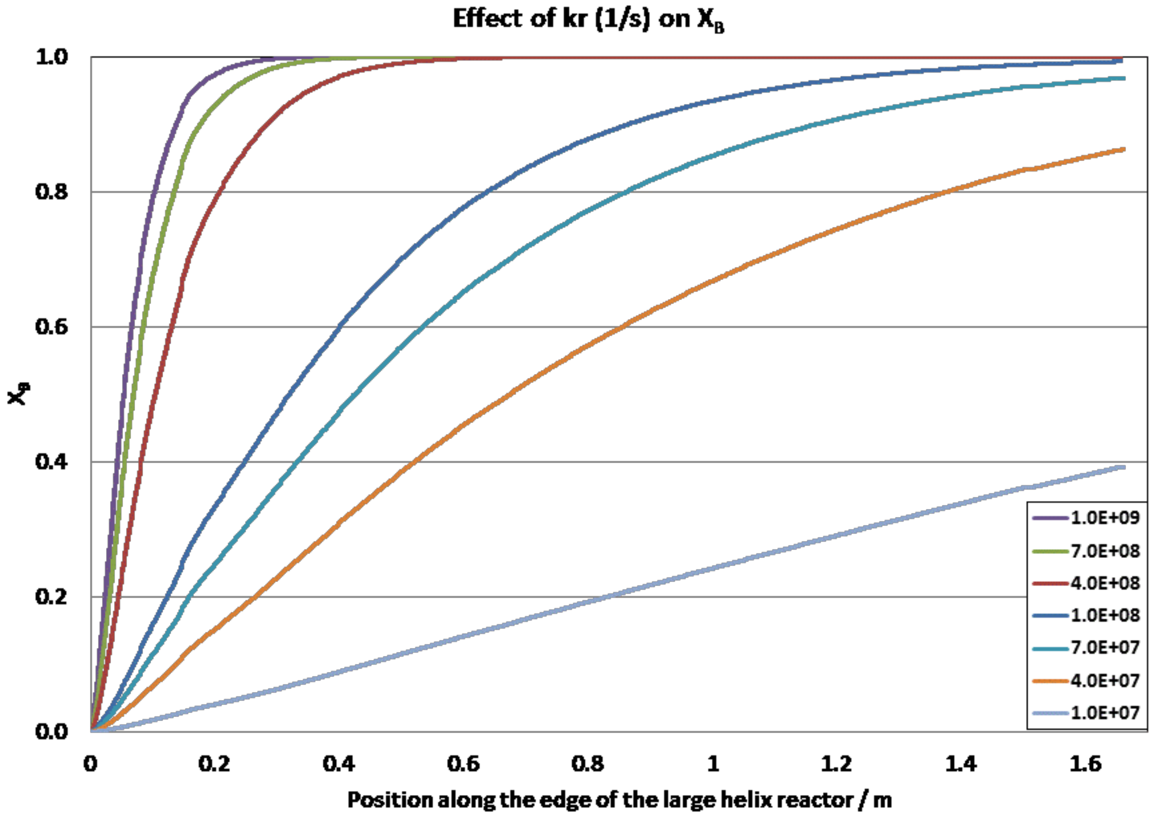


Figure A3. Kinetics impact for option 3. Impact of kinetics is greater but the overriding effect is greater conversion than in the baseline configuration.

The excellent heat transfer comes in part form flow in the tubes but also from the complex mixing on the shell side as illustrated in figure A4.

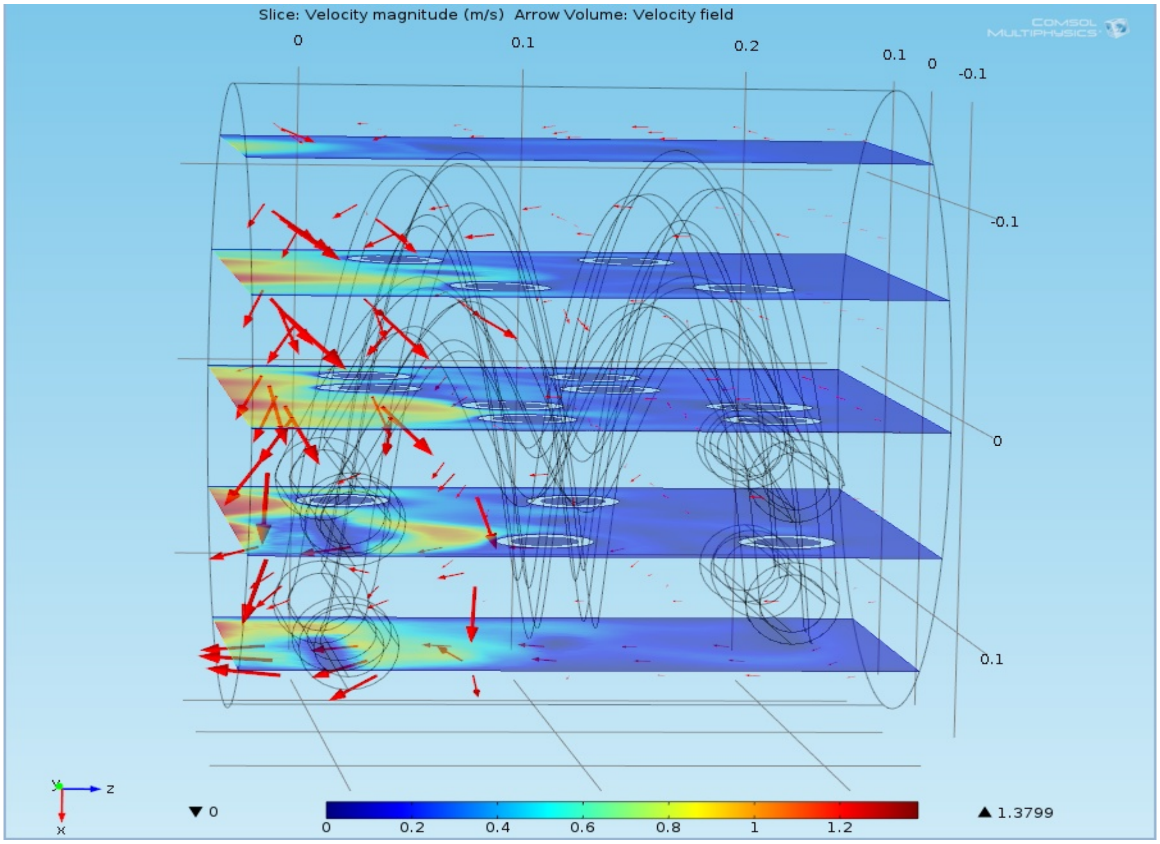


Figure A4 velocity field in the shell of option 3. The helixes disrupt the flow and cause mixing.

In order to know where to focus our effort we then compared the chosen options at this level of fidelity. The results are figures A5 and A6. In each we see the impact of both steady state and response to dynamics. The situation at T=0 is that the reactor is full of 50% reacted LOHC. Flow then begins and unreacted fluid enters. The faster the change to a constant profile the more responsive the reactor will be. The lower the conversion in the steady state the longer and more massive (and costly) the reactor will be. The options 5, 6 and 7 were not meaningfully better and were dropped on the basis of complexity.

Focusing on these two options we looked at the impact of expansion due to hydrogen production. In Figure 6 from the body of the report we saw a near 20-fold increase in velocity along the tube. This also disrupts flow even at this level of modeling where the rise of individual bubbles is not included. This in part accounts for the higher conversion than in the initial models. Figure A7 for example shows the conversion is nearly double once volume expansion is allowed.

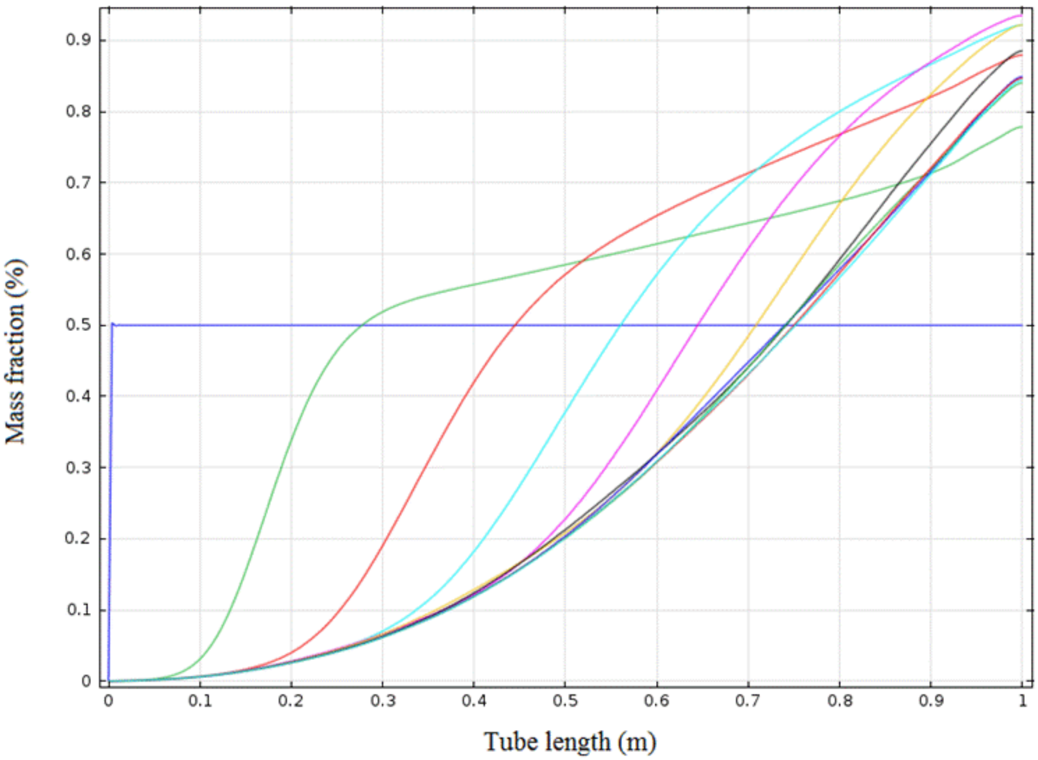


Figure A5. Baseline response to transient. The box profile is time zero and each subsequent line is 100s of response time. Near steady state is achieved at 600s.

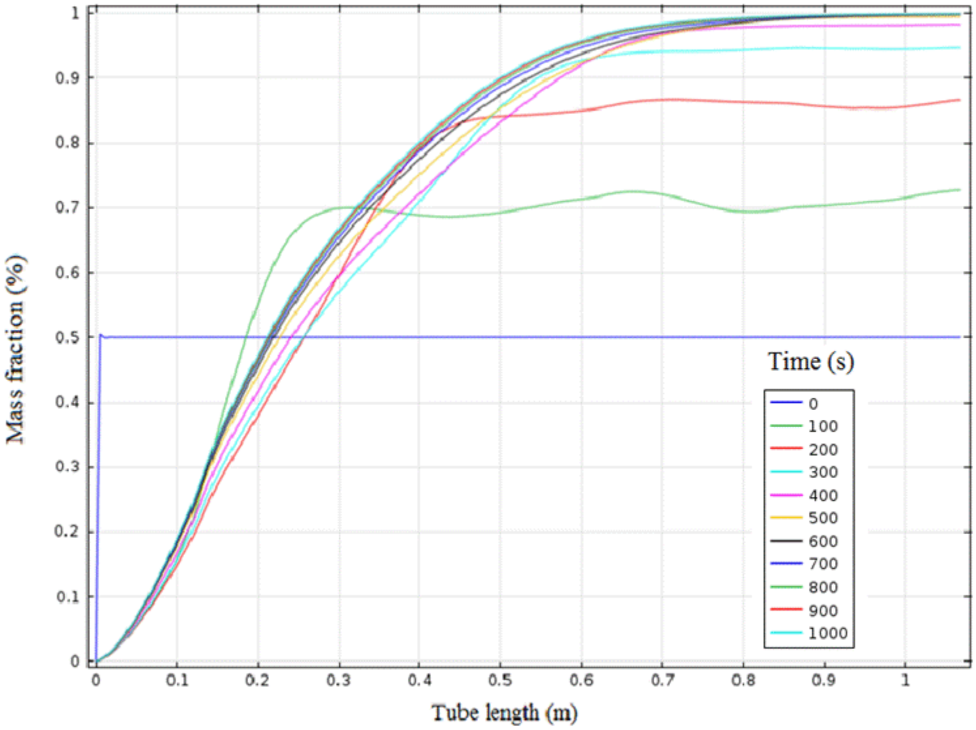


Figure A6. Helical reactor transient response. Near steady state response is reached in 200s and less than half the length of reactor is required for 90% conversion.

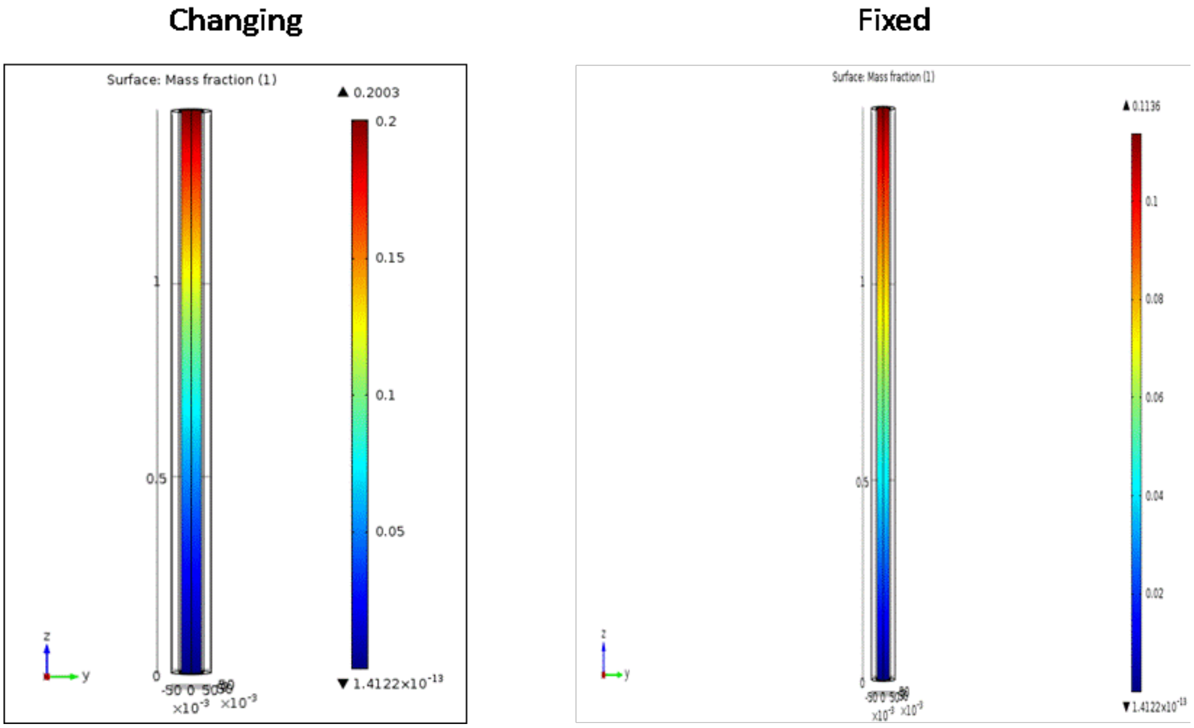


Figure A7 impact of increasing volume with conversion. While the figures look similar the scales are different with full scale in the changing volume case being twice that in the fixed volume case. The conversion reached in the fixed volume case is reached at about 0.8m in the changing volume case, roughly 2/3 of the way to the outlet.

Finally in order to find the right length for the reactor we did a series of ever longer reactors. The results showed little impact of pressure drop through the reactor. This is expected because the reactor is running at 8 bar and pressure drop is low. Still it is reassuring that the model for a 4m reactor has the same conversion at 2.1m as the outlet of a 2.1m reactor (Figures A8 and A9).

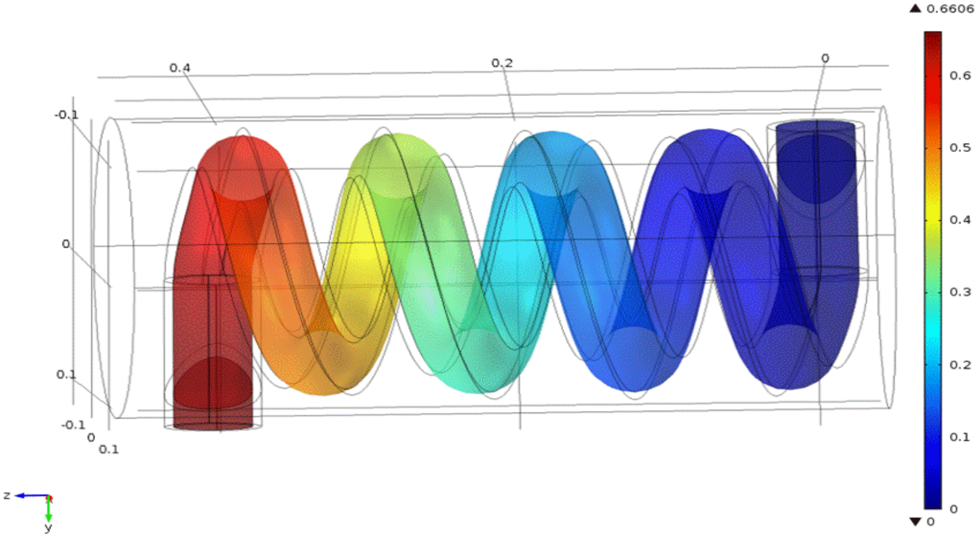


Figure A8. Conversion in a 2.12m helical reactor

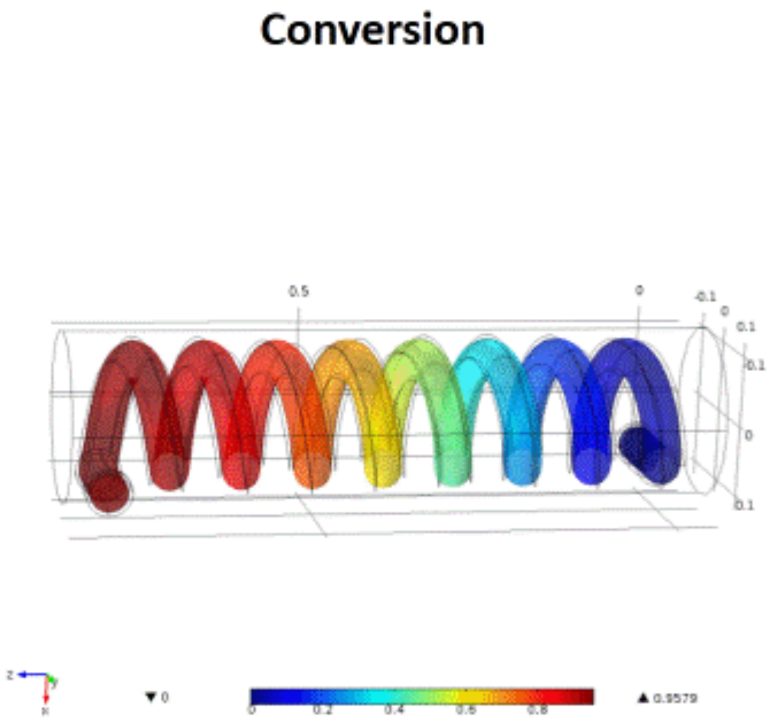


Figure A9. Conversion in a 4.2m helical reactor.