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Hydrogen Generation for Future Energy Applications

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Prof. Daniel M Martinez, University of Southern Maine

Dr. Daniel M. Martinez received his B.S. in Chemical Engineering at the University of Rochester in western New York. He continued there to pursue a Ph.D., and after qualifying for entry into the program left for NASA's Goddard Space Flight Center in Maryland to conduct his graduate laboratory research. At Goddard he studied nucleation phenomenon, specifically vapor to particle conversion of metals in a gas evaporation condensation chamber. At the end of his Ph.D. work, Daniel became active in a non-profit energy corporation, AHEAD Energy, whose mission is to increase energy access in the developing world. There he became interested in understanding energy use and impacts from the perspectives of both the developed and the developing worlds and worked as a postdoctoral fellow through AHEAD and the University of Rochester. Since joining USM in 2008, Martinez has worked on both research and teaching at the University of Southern Maine, published an energy textbook, and has been the architect of the Department of Environmental Science and Policy's Applied Energy Curriculum.

Mr. James A Wilson, United States Navy Civil Engineer Corps

ENS James Wilson was born in Portland, Maine and graduated from South Portland High School. He enlisted in the U.S. Navy in September 2005 and attended basic training at Recruit Training Center Great Lakes, IL. For his first assignment, ENS Wilson reported to training squadron VAW-120 in Norfolk, VA as a plane captain for the E2-C Hawkeye and C-2A Greyhound where he advanced to the designation of Aviation Electrician Airman. In 2007 ENS Wilson transferred to Point Mugu, CA and reported to squadron VAW-113. He advanced to Aviation Electricians-Mate Third Class Petty Officer and completed 2 deployments aboard the USS Ronald Reagan in support of Operation Enduring Freedom.

Honorably discharged from the Navy in 2009, he attended the University of Southern Maine (USM) and graduated Magna Cum Laude in May 2013 with a Bachelor's of Science in Electrical Engineering and a minor in Mechanical Engineering. He completed a 10 week internship for NASA at Johnson Space Center where he designed a microstrip patch antenna for the International Space Station for use in RFID technology. After graduating from USM, ENS Wilson reported to Officer Candidate School (OCS) in Newport, RI and was commissioned on September 20th, 2013. Following OCS, he reported to Civil Engineer Corps Officer School (CECOS) in Port Hueneme, CA graduating in CECOS Basic Class 256 in May 2014. In May 2014, ENS Wilson reported to Naval Air Station Corpus Christi as a construction manager where he has currently managed 45 projects worth over $20 million.

ENS Wilson is an Engineer-in-Training (EIT) in the state of Maine and a member of the Institute of Electrical and Electronics Engineers (IEEE). He has completed over 30 hours of flight training including a solo flight and is a member of the Aircraft Owners and Pilots Association (AOPA).

His personal decorations include the Battle "E" (2 awards), Navy Good Conduct Medal, National Service Defense Medal, Global War on Terrorism Medal, Humanitarian Service Medal, and Sea Service Deployment Ribbon. He is aviation (enlisted) warfare specialist qualified. He has received an Admiral's Letter of Commendation, Captain's Letter of Commendation and is a James V. Masi Research Engineering Scholarship and Texas Instruments Electrical Engineering Scholarship award recipient.

Mr. Benjamin Richard Male, United States Navy Civil Engineer Corps

Benjamin Male was born in Schenectady, New York and graduated from Niskayuna High School in 1999. He enlisted in the U.S. Navy in May 2003 and attended basic training at Recruit Training Center Great Lakes, IL. From August 2003 to January 2005, he completed an array of naval technical schools including Naval Nuclear Field ”A” School for Electronics Technicians and Naval Nuclear Power School, both at NNPTC Charleston, SC, as well as Naval Nuclear Prototype at NNPTU Ballston Spa, NY. For his first assignment, he reported aboard the fast attack submarine USS Charlotte (SSN-766) in March 2005 as a Reactor Operator where he progressed to Electronics Technician Petty Officer First Class.

After being honorably discharged from the Navy in 2009, he attended the University of Southern Maine (USM). His senior year, he received the Outstanding Student in Electrical Engineering Award and graduated Summa Cum Laude in May 2013 with a Bachelor's of Science in Electrical Engineering and a minor in Mechanical Engineering. After graduating from USM, Ben reported to Officer Candidate School (OCS) in Newport, RI and was commissioned as an Ensign in the United States Navy on August 23rd, 2013. Following OCS, ENS Male reported to Civil Engineer Corps Officer School (CECOS) in Port Hueneme, CA, graduating in CECOS Basic Class 256 in May 2014. In May 2014, ENS Male reported to Naval Mobile Construction Battalion THREE and is currently serving as a Platoon Commander in Charlie Company in addition to the Chemical, Biological, Radiological and Nuclear Officer in Charge.

ENS Male is an Engineer-in-Training (EIT) in the state of Maine and a member of the Institute of Electrical and Electronics Engineers (IEEE). His personal decorations include the Navy and Marine Corps Achievement Medal, Meritorious Unit Commendation, Battle ”E” Award, Navy Good Conduct Medal (2 awards), National Service Defense Medal, Global War on Terrorism Medal, Sea Service Deployment Ribbon, Arctic Service Ribbon, Sharpshooter Rifle Ribbon, and Sharpshooter Pistol Ribbon. He is submarine (enlisted) warfare and scuba diver warfare qualified.

He enjoys spending time with his two year old son Jack, playing ice hockey, hiking, skiing and scuba diving.

Hydrogen generation for future energy applications: Outcomes of a senior undergraduate engineering design experience and opportunities for undergraduate laboratory instruction

Abstract:
This paper outlines a two-semester senior engineering design project that was carried out to study a moderately well-defined chemical reaction involving sodium borohydride in aqueous conditions to generate hydrogen for fuel cell applications. Sodium borohydride hydrolysis has been studied extensively since the early 1940's as a promising hydrogen storage material, which provides a content-rich study area for engineering design coursework and undergraduate laboratory experiences related to energy, hydrogen, and energy storage potential. Throughout the two-semester project design course, a two-student engineering team carried out literature reviews and bench work that lead them to investigate diverse research and design methods, including: 1) recording hydrogen generation via volumetric measurements; 2) product characterization using light microscopy and FTIR spectroscopy, 3) reaction calorimetry using infrared thermography; and 4) experimentation with reactive polymers to help improve reaction completion and to better control end products. Results of the senior design project are presented within this paper, highlighting individual experiments that could be performed at the undergraduate level to introduce a variety of concepts and methods important to future engineers and applied scientists that will be expected to help solve grand societal challenges related to energy and environmental degradation.

Introduction

The study of energy, sustainability, and "green" technologies within science and engineering curriculum in the United States has increased markedly since the mid 2000s. Course curriculum and undergraduate laboratory experimentation often tie closely with the research motivations of the course instructors and help foster interest at the undergraduate level in solving global energy problems as they relate to fossil energy use, resource depletion, and global pollution concerns. Example experimental activities conducted as undergraduate laboratory experiences often include biodiesel production from vegetable oil, solar photovoltaic cell testing, and fuel cell system design and testing, and/or hydrogen generation, which is the topic of this article.

Hydrogen's Potential

For several decades, hydrogen has been viewed as a potential replacement to fossil fuels as the world's primary energy carrier. Indeed, hydrogen's potential is intriguing for many reasons. Firstly, hydrogen is the most abundant element in the universe, whose utilization is "only" limited by our ability to efficiently free it from the bonds it shares with other elements. Secondly, hydrogen has the highest theoretical specific energy of any of the non-nuclear fuels (140 MJ/kg compared to 50 MJ/kg for diesel). Thirdly, hydrogen is clean burning, whether by direct combustion or by use in the fairly mature, but seemingly novel technology, fuel cells. All of these reasons, especially within the context of its use with fuel cell power plants, make hydrogen a promising candidate to harbor a cleaner energy infrastructure.

Fuel Cells and Hydrogen Sources

Fuel cells were conceptualized in 1801 by Humphry Davy and the first working fuel cell was invented in 1839 by William Grove, which makes the technology rather old. However, it wasn't until 1959 when Cambridge engineering professor Francis Bacon developed a practical five kilowatt fuel cell power plant that demonstrated the technology's potential as an alternative to the internal combustion engine. Since then, fuel cells have been used extensively in manned and unmanned space applications, as stationary distributed power plants, and most recently in vehicles and portable electronics.

The refinement of proton exchange membrane fuel cells (PEMFCs) in the past 15 to 20 years has spurred much activity in transportation and portable power applications, and many universities (and high schools) began purchasing small PEMFC systems in the early to mid-2000s to teach about the technology as part of engineering and science curricula. The addition of fuel cell experimentation in science and engineering curricula also offers opportunities to discuss and experiment with different methods of producing hydrogen in future energy scenarios.

Hydrogen Carriers

As stated above, hydrogen, although extremely abundant, is not naturally available in pure gaseous form. Rather, it must be separated from compounds that contain or "carry" hydrogen. Currently, the most commercially viable carrier of hydrogen is natural gas, whereby hydrogen is extracted from methane molecules via a process known as catalytic steam reforming. The hydrogen gas is then bottled at high pressure and distributed to the consumer. Natural gas can also be reformed on-site to generate the hydrogen needed to power large stationary fuel cell systems. Both methods result in the production of carbon dioxide, a gas suspected of being harmful to the global environment, especially at high concentrations.

Also, hydrogen can be separated from oxygen in water via a process known as electrolysis. (The electrolysis of water to generate gaseous hydrogen and oxygen is a well-known method and commonly is used by instructors in undergraduate chemistry laboratories to demonstrate the phenomenon.) The benefit of using this method to produce hydrogen is that it is pollution-free if the electricity used to facilitate the separation comes from a renewable energy source. It is also a very common method for producing hydrogen to power the small PEMFCs used by schools, since water and electricity are readily available and only small amounts of hydrogen are needed to power the small PEMFCs. The small voltage requirements also allows for integration of a small solar PV cell to generate the electricity, further demonstrating the "clean" nature of the technology.

Finally, there exists a class of solid state chemical hydrogen carriers, which show promise for being used to power fuel cells for transportation or portable power applications. These carriers include: 1) reversible metal hydrides, such as lanthanum nickel hydride, in which hydrogen is stored via chemisorption of hydrogen onto a metal at heightened pressure; and, 2) irreversible chemical hydrides, such as sodium borohydride, which, depending on the material, are formed by either covalent or ionic bonding between the hydrogen and the metal. Metal hydrides offer the advantage of storing and releasing hydrogen at moderate temperatures and pressures when compared to using gaseous hydrogen that requires very high pressure, or liquid hydrogen, which requires extremely low temperatures to be useful. Metal hydrides also offer the possibility for refueling on-board, once hydrogen is released, which is important for applications in transportation. Chemical hydrides operate at room temperature and pressure and only require water to break hydrogen bonds via hydrolysis, which is a major advantage over most other hydrogen storage methods. However, since the process is not easily reversible on board, they end up generating a great deal of unusable reacted byproduct, and total system requirements make their use problematic. But their study does provide an excellent case study for experimentation at the undergraduate level.

Sodium Borohydride Hydrolysis as Laboratory Experiment

Sodium borohydride, $NaBH_4$, is a very interesting choice to demonstrate chemical storage options for hydrogen fuel cell applications. It is a white powdery substance that was developed by Brown and Schlessinger for the U.S. military in the 1940s[1]. It reacts readily and exothermically with water to release gaseous hydrogen. The rate at which hydrogen is released can be controlled with metal catalysts or by affecting the pH of the system (adding acid to accelerate or adding base to retard). $NaBH_4$ also is an effective reducing agent and is used widely in synthetic chemistry. Thus, there exists a very extensive body of literature regarding the reaction for numerous applications.

Additionally, starting around 1999, the Department of Energy (DOE) made investments in funding for aqueous-phase, catalyzed hydrolysis of $NaBH_4$ for transportation applications, due to some promising research carried out by Amendola et al[2,3]. Indeed, the storage capacity of $NaBH_4$ theoretically meets the DOE 2015 specifications for its FreedomCAR program[4], but the chemical reaction does suffer from storage reductions due to hydration of the borate byproducts, as shown in the following reaction below:

$$NaBH_{4(s)} + (2 + x)\ H_2O_{(l)} \rightarrow NaBO_2 \bullet xH_2O_{(s)} + 4H_{2(g)} + \text{heat} \qquad (1)$$

According to Marrero-Alfonso et al[5], eq. 1 demonstrates that, ideally, only two moles of water are needed to release four moles of hydrogen gas. However, in reality, the sodium metaborate product, $NaBO_2$, can exist as a hydrated compound, which reduces the hydrogen capacity of the reaction, since hydrogen generation comes from both $NaBH_4$ and H_2O. This excess water requirement has been the biggest issue related to NaBH4’s viability as a hydrogen storage material, which has caused the DOE to focus on funding for other hydrogen storage alternatives.

Despite the DOE decision to halt funding for sodium borohydride research for transportation applications, the reaction remains a topic of interest for many researchers, especially as an option for portable applications. Moreover, the vast literature that exists as a result of steady government R&D funding in the early to mid-2000s, allows for a robust undergraduate experience for studying a relatively simple reaction system to understand chemical hydrogen storage and generation.

Depending on how a sodium borohydride curriculum is developed, students can gain practical skills in: 1) determining hydrogen gas production via water displacement; 2) chemical reaction and product characterization using light microscopy and FTIR spectroscopy methods; 3) reaction calorimetry, and (4) gel and foam formation via the cross-linking of borate anions to simple polymers like polyvinyl alcohol and acetate which alters hydrogen gas evolution during hydrolysis.

Senior Design Project

The hydrogen generation project described in this paper was conducted primarily by two senior engineering students that had completed only one introductory course in chemistry (common in many mechanical and electrical engineering programs). A key aspect of the project was the introduction of analytical concepts within an engineering research and design problem. This paper describes how the sodium borohydride hydrolysis reaction was integrated into the project to answer specific design questions and how the students developed a series of experimental procedures to achieve basic understanding of the reaction mechanism in order to affect hydrogen production specifically under various operating parameters. From a student perspective, the experimental study of the hydrolysis of sodium borohydride in the presence of acids and polymer mixtures demonstrates key aspects of energy, hydrogen, and energy storage potential of boron-containing chemical compounds.

Investigating the Reaction’s Hydrogen Generation Rate

The reaction that the students were given by the faculty design mentors was that of simple hydrolysis of sodium borohydride with water:

$$NaBH_{4(s)} + 2H_2O_{(l)} \rightarrow NaBO_{2(s)} + 4H_{2(g)} + \text{heat} \qquad (2)$$

(Eq. 2 is simply eq. 1 with $x = 0$.) The student team was then expected to perform a literature review of sodium borohydride hydrolysis with an emphasis on hydrogen generation, accelerated by acetic acid addition. Acetic acid was chosen because of its low cost, easy accessibility and relative “greenness.” Some suggested articles were provided to initiate the review, with general instructions to devise an experiment that could measure the hydrogen generation rate, characterize reactants and products, and devise a strategy for estimating and measuring heats of reaction and how to possibly control it with polymer addition.

First Experiment: Hydrogen Production

From literature review, the students were able to determine a general procedure for measuring hydrogen gas evolution via acetic acid acceleration (e.g. Murugesan et. al.[6], Akdim et. al.[7]). Their first hydrogen production experiment was very primitive. Two 30 mL vials were connected so that a reaction could take place in one and a displacement of water could take place in another to obtain a volume of hydrogen gas. It was quickly discovered that the setup was insufficient. A larger flask was implemented and a 100 mL graduated cylinder was used to measure displacement. The 100 mL flask was still insufficient so a 250 mL graduated cylinder was then used. The reaction chamber also was upgraded to a 500 mL 3-pronged reaction glass flask.

The final setup included a thermocouple that logs data over time, a gas flow rate meter, a 10 mL dropping funnel, water trap, silica gel trap, 500mL graduated cylinder, and the 500mL 3-pronged reaction glass flask, which was thermally insulated, and a flask stand. The idea came from Ferreira, 2011[8]. The combination of the water trap and silica gel trap ensured that no moisture is reaching the flow-meter. This allows for a pure gas flow reading and true displacement. The design included Teflon taping all fittings to improve airtight integrity as well as insulating the reaction chamber to ensure more accurate temperature readings. The final setup is shown in figures 1 and 2.

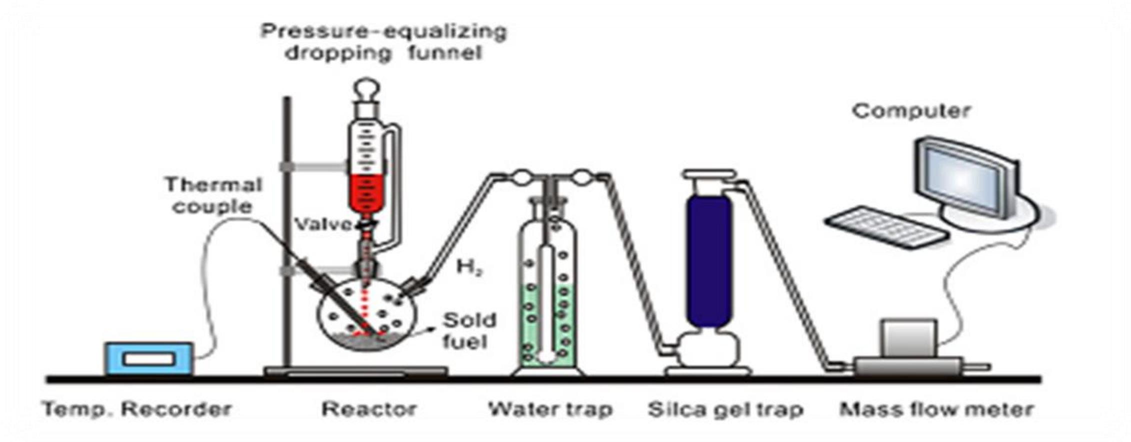

Figure 1: Hydrogen Production Experimental Setup Schematic[8] (Ferreira, M. J. F. “Batch sodium borohydride hydrolysis systems: Effect of sudden valve opening on hydrogen generation rate”. *International Journal of Hydrogen, Energy* XXX (2011): 1-7.)

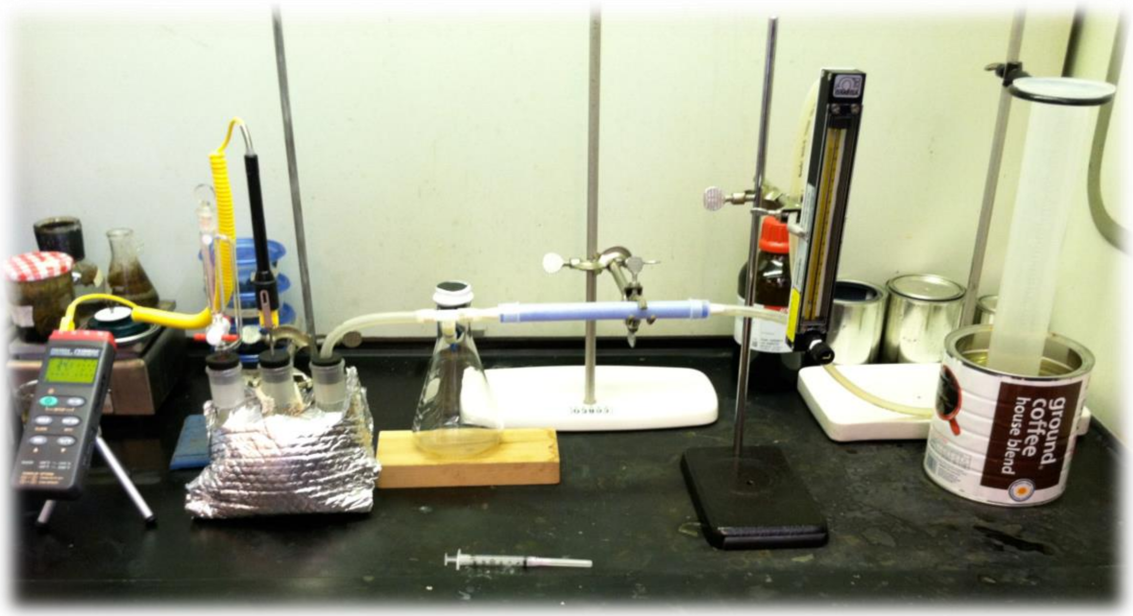

Figure 2: Enhanced Hydrogen Production Experimental Setup

As the students refined the experiment, they discovered that excess length of tubing affected final measured hydrogen displacement, which prompted them to remove the water trap and reduce tubing lengths. They reliably found a four-to-one water to $NaBH_4$ ratio for reaction completion, which is consistent with literature results that suggest the production of hydrates borate products. A sampling of their displacement results is tabulated in Table 1.

Table 1: Hydrogen Displacement Experimental Results

Run	$NaBH_4$ (g)	5% CH_3COOH (ml)	H_2O Displaced (ml)
1	.100	2	275±5
2	.101	2	275±5
3	.102	2	280±5
4	.051	1	90±5
5	.052	1	115±5
6	.051	1	90±5

Second Experiment: Reactant and Product Identification

Another objective in this project was to determine the byproducts of the reactions and to characterize the physical properties of the end products. Samples were prepared by injecting aqueous solutions of acetic acid into glass vials through a septum, as seen in figure 3. A small, 10mL syringe was used to inject the aqueous acetic acid into the vial so it was able to react with the sodium borohydride to what appeared to be completion. The students allowed 24 hours to elapse before taking the products out and then examining them under a microscope. Also, the samples were safe housed to be used for further analysis.

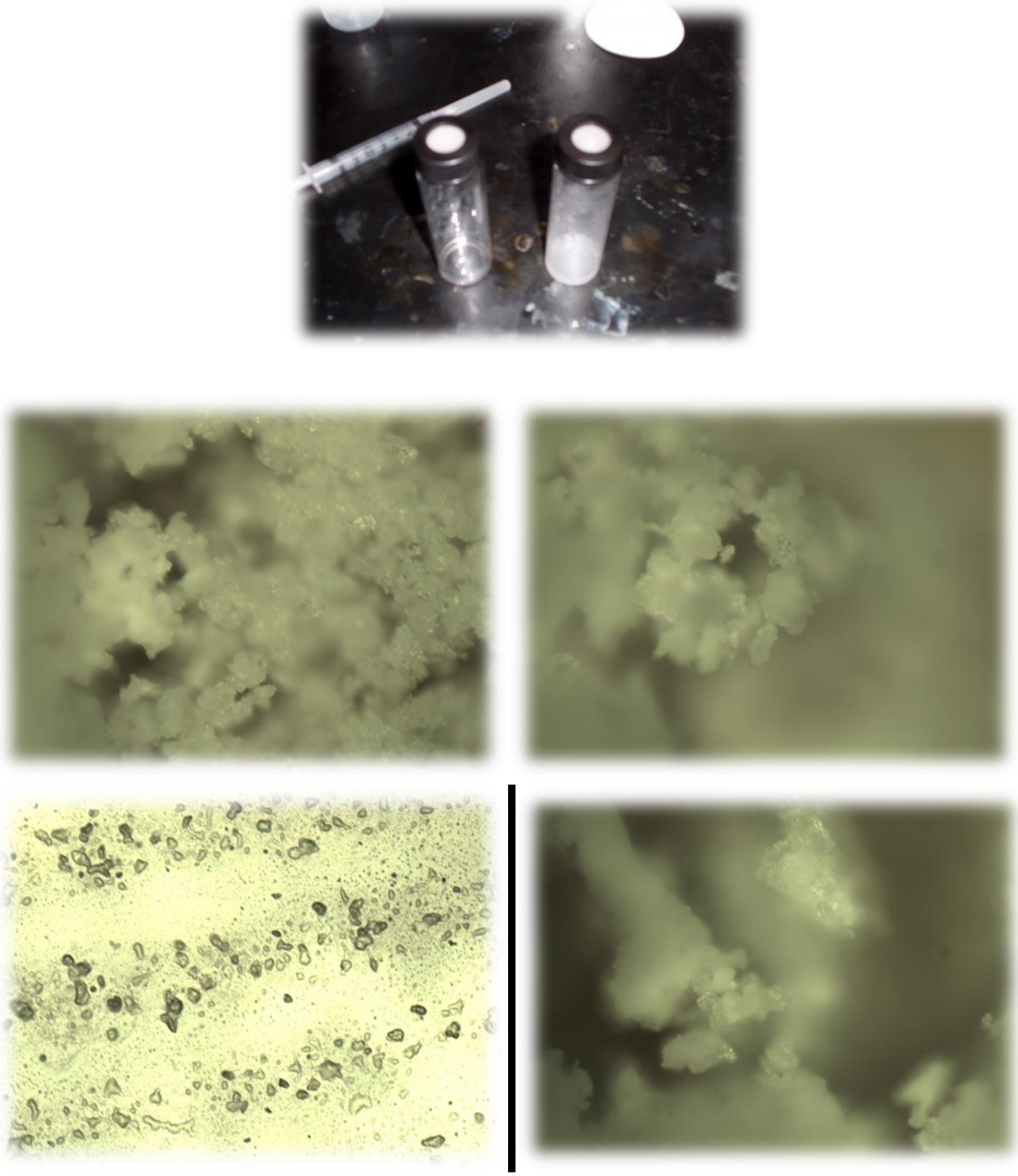

Figure 3: Septum Vials and Micrographs of Acetic Acid and Sodium Borohydride Reaction Byproducts

While qualitative in nature, microscopy offers students insight into the morphology of the reaction products and its application is especially helpful for students with limited chemistry preparation. The light microscope images obtained by the students indicate glassy and crystalline byproducts, with sections of unreacted or partially reacted borohydride crystals. It is interesting to note that the microscope images in Figure 3 are indicative of many of the images obtained by the students, and demonstrate novice experience with a microscope. With practice, the microscope images became markedly improved.

Additionally, Fourier transform infrared spectroscopy (FTIR) was used by the students to help ascertain reactant and product com-positions. In FTIR, IR radiation is passed through the sample of interest, where some of the radiation is absorbed and the rest transmitted. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range, and the resulting spectrum creates a molecular "footprint" of the sample. FTIR is another technique which is helpful for undergraduate student learning because of its relative simplicity to use and because of the large databases that exist for product characterization.

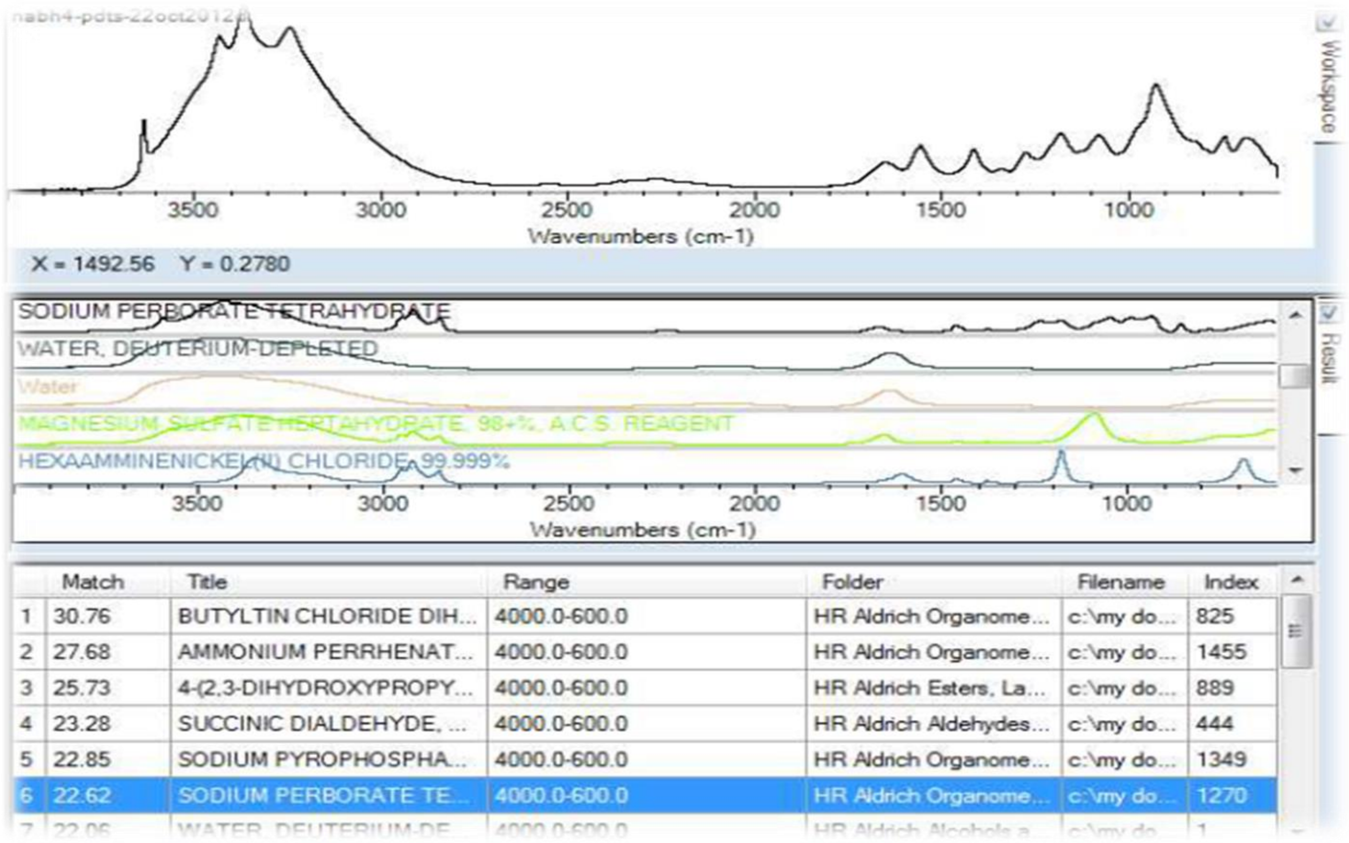

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Figure 4: FTIR Spectra of Reacted Sodium Borohydride

Third Experiment: Heats of Reaction

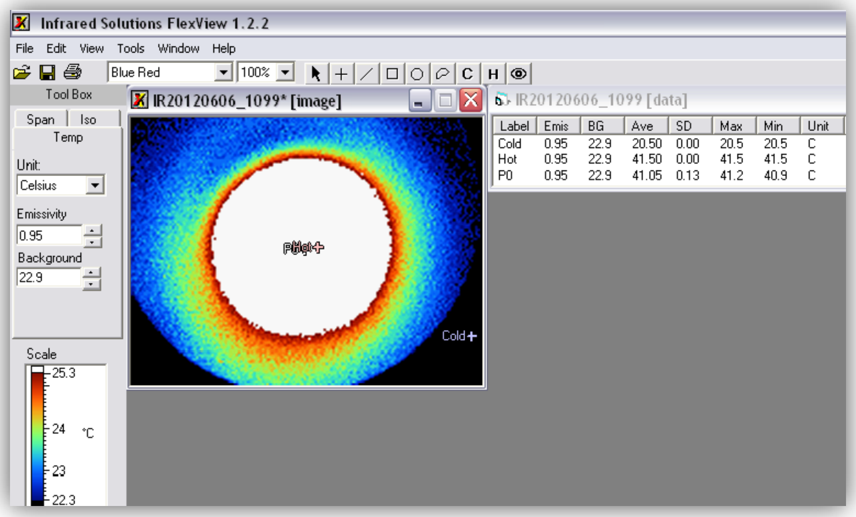
A design problem regarding the use of $NaBH_4$ as a hydrogen storage system is that in order to produce hydrogen at a rate fast enough to be useful in a fuel cell, the hydrolysis reaction must be enhanced using catalysts or acid accelerators, like the acetic acid used in this project. As a result, these systems produce rapid heat evolution. In general, heating can vary depending on amounts of reagents, types of catalysts, and amount and types of acid used to accelerate the exothermic reaction.

Thus, the measurement of the heat evolved during the uncatalyzed and catalyzed $NaBH_4$ hydrolysis reaction is important from practical and fundamental viewpoints. This is especially important for assessing thermal risks related to reactor performance at an industrial scale, where the capability of a system to enter into a runaway reaction must be well understood[9]. Additionally, the need for thermodynamic data is of great interest for determining the reaction mechanism in order to potentially fine tune the reaction.

Thus, temperature became an additional variable to measure and understand for the students. While temperature was measured with a thermocouple within the reaction flask depicted in figure 2, the students focused much of their time experimenting with a thermal imaging camera to view the reaction as it was happening.

The thermal imaging tests were conducted using a Fluke i45 thermal imaging camera aimed at the reaction inside of a small container to obtain temperature profiles for the reaction. Approximately 0.2 g of sodium borohydride was reacted with 1 mL of aqueous acetic acid (5% by weight). The experiment was conducted using a 20 mm lens. The highest observed temperature was approximately 58 C, while ambient was 19 C. Using the accompanying software, the students were able to locate the hot and cold spots for each associated image as well as the entire temperature profile. (See figure 5.)

The students noted some limitations with the thermal imager. The particular device was unable to capture video data. This results in having to take multiple screen shots, which took about five seconds to capture and return to normal to capture each successive image. In addition, when rescaling the temperature range as the reaction progresses, the color scheme sometimes changes and looks much different to the previous images, which may cause issues when publishing. The thermal imager has a time stamp when the pictures are taken, but it appears that only the minute can be determined when it is taken, when extracted the images from the storage card, which makes determining the rate of temperature change less precise.



Unit: Celsius

Emissivity: 0.95

Background: 22.9

Label	Emis	BG	Ave	SD	Max	Min	Unit
Cold	0.95	22.9	20.50	0.00	20.5	20.5	C
Hot	0.95	22.9	41.50	0.00	41.5	41.5	C
P0	0.95	22.9	41.05	0.13	41.2	40.9	C

Figure 5: Thermal Image for Acetic Acid and Sodium Borohydride/Water Reaction

The students confirmed that the reaction proceeds exothermically, but it was evident that their inexperience with chemical principles and methods prohibited a robust analysis of the characteristic reaction. Regardless, the student team was encouraged to tabulate heats of formation (ΔH_f) and specific free energy of formation (ΔG_f) for their proposed reaction in an effort to compare to measured temperature values. (See Table 2.)

Table 2: Heats of Reaction and Formation for the Reaction[10]

Compound	**Molecular Weight (g/mol)**	**ΔHf (kcal/mol)**	**ΔGf (kcal/mol)**
Water	18.0153	-68.315	-56.687
Acetic Acid	60.053	-115.8	-93.2
$NaBH_4$	37.8328	-45.08	-29.62
H_2	2.0159	0	0
$NaBO_3*4H_2O$	153.8606	-505.3	–
C_2H_2	26.04	54.194	50.0
C_2H_4	28.0542	12.49	16.28
C_2H_6	30.0701	-20.24	-7.86

Observing the reactants and products listed in Table 2 demonstrated the need for the students to properly balance chemical equations and to be more steadfast in literature review. Specifically, the students proposed that acetylene was a product of the reaction between sodium borohydride, water and acetic acid. However, sodium borohydride is not known to reduce acetic acid and the acid's presence is there only to reduce the pH of the system and facilitate faster hydrogen release. It became clear that more time spent on chemical principles would improve this aspect of the design experience. However, the use of infrared thermography to observe reaction progression in real time is an interesting application that could gain traction as an analytical and/or diagnostic method.

Fourth Experiment: Polymer Addition a la Elmer's Glue

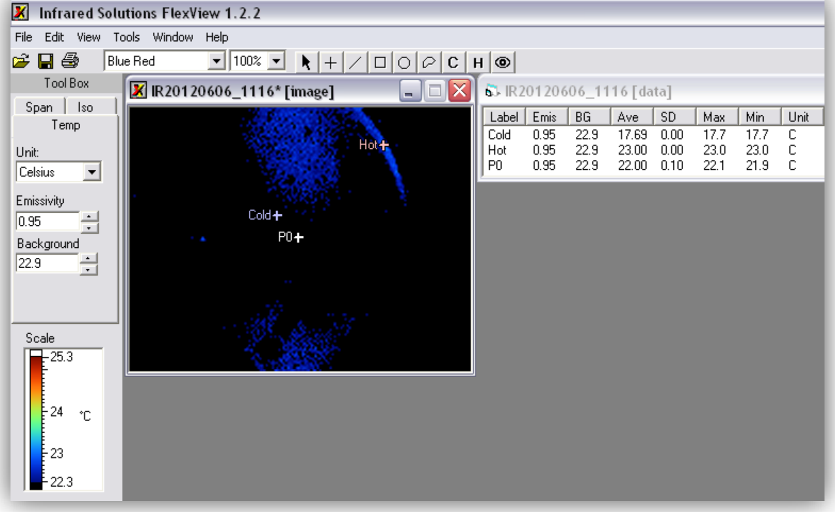
Despite the incomplete information obtained in the heats of reaction study, the issue of controlling hydrogen release as well as mitigating rapid heating during hydrolysis remain as relevant design constraints. From previous experience with using other boron-containing materials, such as borax (sodium tetraborate) and boric acid, the instructors suggested that the students explore the potential of using benign polymers such as polyvinyl alcohol and polyvinyl acetate to initiate a cross-linking event.

The reaction of hydroxyl borates with diols is a well-documented process, and a common demonstration of this class of reaction uses borax to cross-link diol groups in polyvinyl alcohol (PVA) in aqueous solution to make an elastomeric gel, often referred to as "slime." When mixed with polyvinyl acetate (PVAc)[11] the gel formed is less slimy and stickier in nature, and that product is often referred to as "gluep" or "gack." The slime or gluep reactions are very popular laboratory demonstration activities in polymer education [12].

What is intriguing about boron crosslinking reactions, is that as crosslinks form and grow, they must draw external energy. That is, crosslinking should be an endothermic process. Combining it with the hydrolysis reaction could thus help regulate some of the thermal effects. Thus, the student group set out to experiment with the new material system and focused on methods that they were most comfortable using for identification: thermal imaging, light microscopy, and FTIR. Since this part of the project occurred near the end of the two-semester experience, the students opted to use Elmer's clear school glue for their analysis.

Thermal Imaging

For the PVAc reaction, 0.2 g of $NaBH_4$ was reacted with an excess of aqueous PVAc (Elmer's clear school glue). The amount of glue used was liberal. Multiple thermal images of the reaction were taken. A representative image is shown in figure 6.



Unit: Celsius

Emissivity: 0.95

Background: 22.9

IR20120606_1116 [data]

Label	Emis	BG	Ave	SD	Max	Min	Unit
Cold	0.95	22.9	17.69	0.00	17.7	17.7	C
Hot	0.95	22.9	23.00	0.00	23.0	23.0	C
P0	0.95	22.9	22.00	0.10	22.1	21.9	C

Figure 6: Thermal Image for Elmer's Glue and Sodium Borohydride

The overall result of the reaction was endothermic and it appeared that the temperature reduced by as much as 5 C from ambient, which is a significant finding and confirmed the hypothesis of the crosslinking mechanism. The students were curious to see what happened when they added acetic acid to the mixture. They found that when acetic acid was applied, the reaction became exothermic briefly until transitioning back to endothermic. So, it appears that crosslinking is the dominant feature. The cross-linked polymers formed by this reaction could potentially provide temperature control.

Light Microscopy

When done in excess water, the borohydride hydrolysis reaction looks very much like a carbonated beverage, however, with hydrogen gas efervescing through the aqueous medium. Similarly, when aqueous PVA or PVAc is added to sodium borohydride, what forms is a bubbling, crosslinked polymer that takes the form of a foam instead of the sol-gel slime that forms when those polymers react with borax. In PVAc in particular, the hydrogen gas is initially trapped by the sticky polymer and a very interesting cell structure forms. (See figure 7, right) This could potentially be useful as an intermediate storage medium for hydrogen gas, especially if diffusion through the bubble could be controlled. Micrographs of the foams are also provided in figure 8.

Figure 7: Bubble formation in Water/NaBH4 system and Glue/NaBH4 system

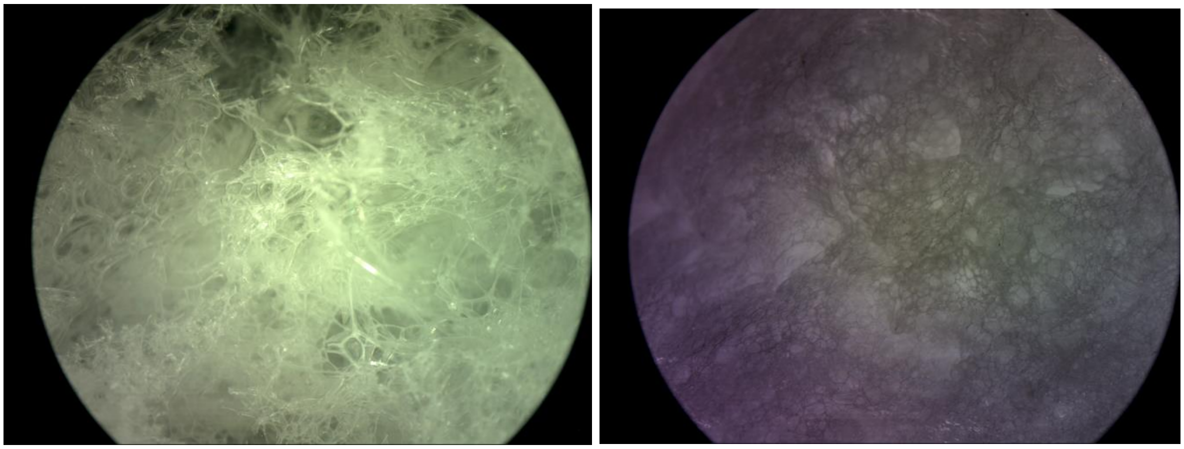
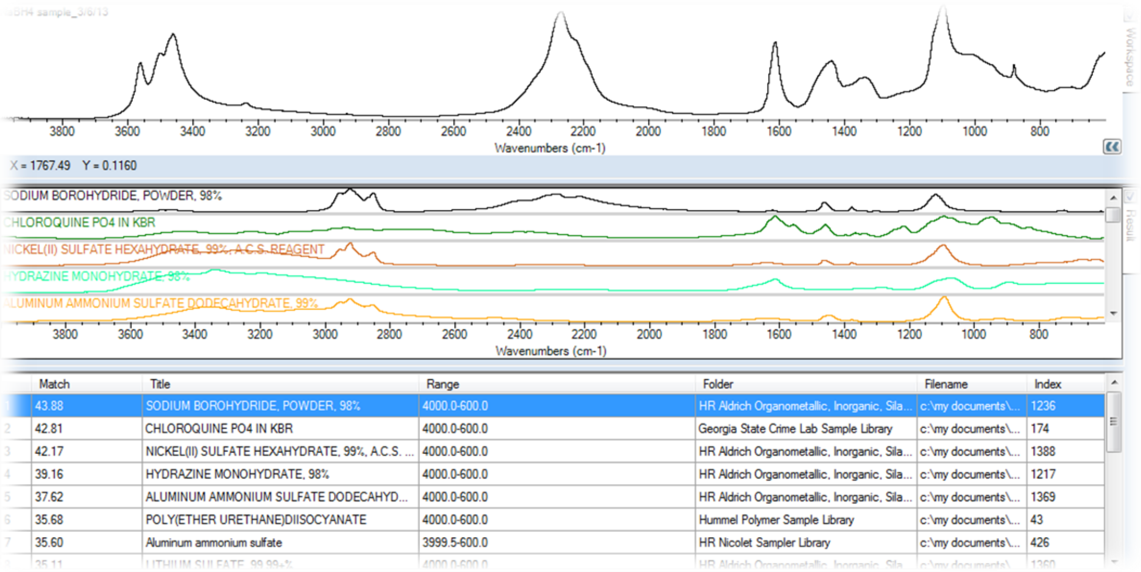


Figure 8: Micrographs of the Glue/$NaBH_4$ system

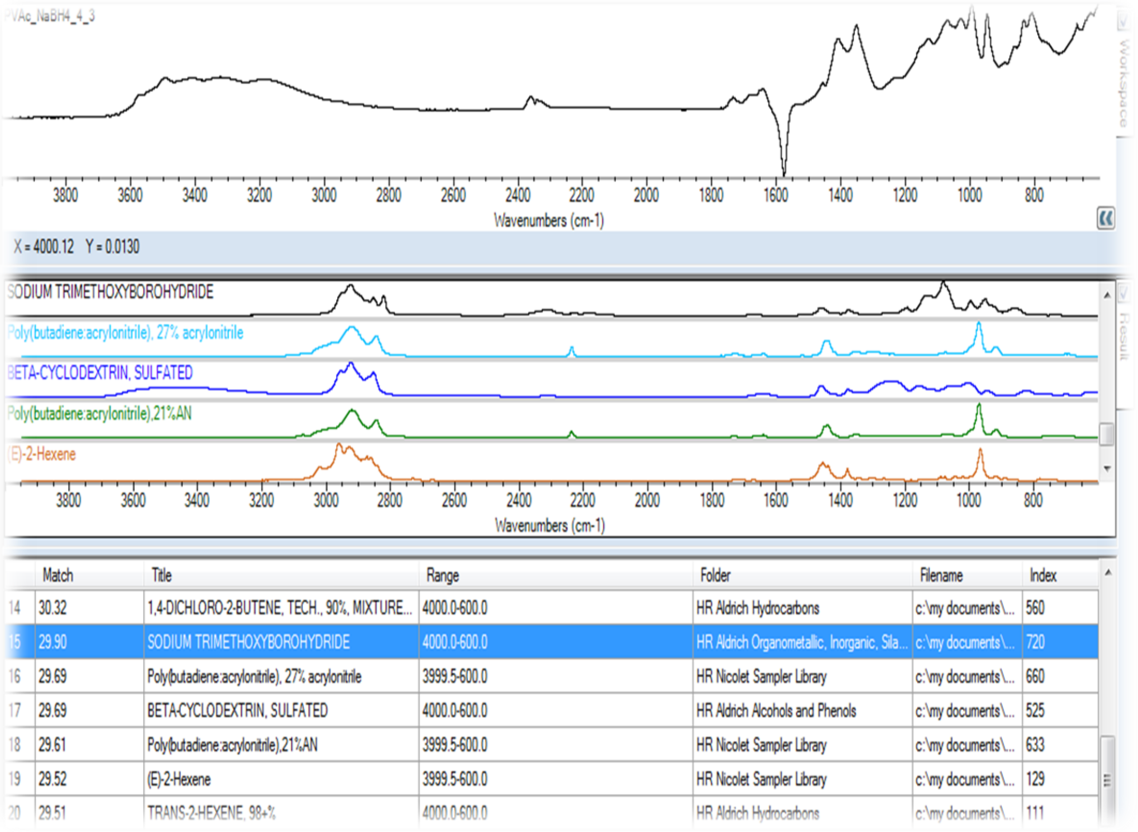
FTIR

Finally, samples of the glue/$NaBH_4$ reaction end products were analzed under FTIR and both Boron-Oygen stretches and deformations at 1340 cm^{-1} and 850 cm^{-1} indicate changes in the IR spectra that supports the theory of boron adsorption on the polymer backbone. This finding is consistent with spectral changes for PVA-borax and PVA-boric acid systems[13], which is an ecouraging finding. (See figures 9 and 10)



	Match	Title	Range	Folder	Filename	Index
1	43.88	SODIUM BOROHYDRIDE, POWDER, 98%	4000.0-600.0	HR Aldrich Organometallic, Inorganic, Sila...	c:\my documents\...	1236
2	42.81	CHLOROQUINE PO4 IN KBR	4000.0-600.0	Georgia State Crime Lab Sample Library	c:\my documents\...	174
3	42.17	NICKEL(II) SULFATE HEXAHYDRATE, 99%, A.C.S. ...	4000.0-600.0	HR Aldrich Organometallic, Inorganic, Sila...	c:\my documents\...	1388
4	39.16	HYDRAZINE MONOHYDRATE, 98%	4000.0-600.0	HR Aldrich Organometallic, Inorganic, Sila...	c:\my documents\...	1217
5	37.62	ALUMINUM AMMONIUM SULFATE DODECAHYD...	4000.0-600.0	HR Aldrich Organometallic, Inorganic, Sila...	c:\my documents\...	1369
6	35.68	POLY(ETHER URETHANE)DIISOCYANATE	4000.0-600.0	Hummel Polymer Sample Library	c:\my documents\...	43
7	35.60	Aluminum ammonium sulfate	3999.5-600.0	HR Nicolet Sampler Library	c:\my documents\...	426
8	35.11	LITHIUM SULFATE, 99.99+%	4000.0-600.0	HR Aldrich Organometallic, Inorganic, Sila...	c:\my documents\...	1360

Figure 9: Sodium Borohydride



	Match	Title	Range	Folder	Filename	Index
14	30.32	1,4-DICHLORO-2-BUTENE, TECH., 90%, MIXTURE...	4000.0-600.0	HR Aldrich Hydrocarbons	c:\my documents\...	560
15	29.90	SODIUM TRIMETHOXYBOROHYDRIDE	4000.0-600.0	HR Aldrich Organometallic, Inorganic, Sila...	c:\my documents\...	720
16	29.69	Poly(butadiene:acrylonitrile), 27% acrylonitrile	3999.5-600.0	HR Nicolet Sampler Library	c:\my documents\...	660
17	29.69	BETA-CYCLODEXTRIN, SULFATED	4000.0-600.0	HR Aldrich Alcohols and Phenols	c:\my documents\...	525
18	29.61	Poly(butadiene:acrylonitrile),21%AN	3999.5-600.0	HR Nicolet Sampler Library	c:\my documents\...	633
19	29.52	(E)-2-Hexene	3999.5-600.0	HR Nicolet Sampler Library	c:\my documents\...	129
20	29.51	TRANS-2-HEXENE, 98+%	4000.0-600.0	HR Aldrich Hydrocarbons	c:\my documents\...	111

Figure 10: PVAc and Sodium Borohydride

Conclusions

The two-semester engineering design project presented in this paper demonstrates the benefits of employing open-ended projects in upper level undergraduate curriculum. The students, despite having limited background on chemical principles, were able to learn new methods and techniques that they are likely to be exposed to in industry and thy can better appreciate the need for working with new technologies and the likely need to interact with other science professionals that can assist in the research and development process.

The students came away from the project with an intimate appreciation for the intricacies of generating hydrogen from chemical hydrides and were able to contribute to generating new knowledge with respect to polymer interaction with the borohydride system. What most surprised them was the need for constant iteration in the testing and design process, especially for measuring water displacement during the hydrogen generation experiment. This is consistent with the non-intuitive nature of gases and pressure, particularly hydrogen. It is the lightest, least dense gas, requiring massive amounts to be useful.

The students also felt that use of the thermal imaging camera "was a great tool that provided useful data in ascertaining the type of reaction taking place." More than being able to feel a warm container or a change in a thermocouple reading, the students could visualize the reaction behavior, which helped grasp the process more concretely. They noted that for the acetic acid and sodium borohydride reaction, it was clearly exothermic given the images, however, the PVAc reaction appeared to take much longer to complete. They said, "using a video thermal imaging camera and quantifying the reactants will prove useful in determining just how much acetic acid should be used depending on how much heat a system can withstand."

It was also interesting to see the students observe that the concentration of acid was also important. They noted that, "by using 5% acetic acid instead of glacial, the hydrogen yield is significantly higher. This phenomenon is due to the large number of water molecules present in the 5% acetic acid." They observed a rate limiting reaction step within the context of a goal of generating hydrogen, which help, again, make a practical conceptualization of a well-understood reaction process.

Finally, we note that while this learning experience was placed within the context of a design project, there are many components of the project that can be separated out as individualized laboratory experiences for both chemical and engineering curricula.

REFERENCES

1. Schlesinger, H.C.; Brown, H.R.; Hoekstra, L.R. "Reactions of Diborane with Alkali Metal Hydrides and Their Addition Compounds. New Syntheses of Borohydrides. Sodium and Potassium Borohydrides" *J. Am. Chem. Soc.* **1953**, *75*, 199–204. doi:10.1021/ja01097a053

2. Amendola, S. C., Sharp-Go1dman, S. L., Janjua, M. S., Kelly, M. T., Petillo, P. J. and Binder, M., 2000a, "An ultrasafe hydrogen generator: aqueous, alkaline borohydride solutions and Ru catalyst", *Journal of Power Sources*, 85, pp. 186-189.

3. Amendola, S. C., Sharp-Go1dman, S. L., Janjua, M. S., Kelly, M. T., Petillo, P. J. and Binder, M.,2000b, "A safe hydrogen generator using aqueous borohydride solutions and Ru catalyst", *Int. J. Hydrogen Energy*, 25, pp. 969-975.

4. FreedomCAR & Fuel Partnership, 2015 http://hydrogendoedev.nrel.gov/pdfs/progress06/iv_a_4_klebanoff.pdf

5. Eyma Y. Marrero-Alfonso, Amy M. Beaird, Thomas A. Davis, Michael A. Matthews, Industrial & Engineering Chemistry Research - Ind Eng Chem Res , vol. 48, no. 8, pp. 3703-3712, 2009.

6. Murugesan, A., Umarana, C., Chinnusamy, Krishnan M., and Subraimanian R. et al.,(2009).Production and analysis of biodiesel from non edible oils. A Review. Renew. Sustain Energy Rev., 13: 825-834.

7. Akdim, O. "Acetic acid, a relatively green single-use catalyst for hydrogen generation from sodium borohydride". *International Journal of Hydrogen Energy* 34 (2009): 7231-7238.

8. Ferreira, M. J. F. "Batch sodium borohydride hydrolysis systems: Effect of sudden valve opening on hydrogen generation rate". *International Journal of Hydrogen Energy* XXX (2011): 1-7.

9. Bennici, S., Garron, A., & Auroux, A. (2010). Maximizing the hydrogen yield in the catalyzed hydrolysis of pure borohydride powders. *International Journal of Hydrogen Energy*, 35(16), 8621-8625.

10. Weast, Robert C. *Handbook of Chemistry and Physics 64th Edition.* New York: CRC Press, 1984. Zhang, Jinsong. "Heat of reaction measurements of sodium borohydride alcoholysis and hydrolysis". *International Journal of Hydrogen Energy* 31 (2006): 2292-2298

11. Airgas. *Material Safety Data Sheet - Vinyl Acetate.* 28 Apr. 2010. Web. 9 Sep. 2012. <http://www.airgas.com/documents/pdf/001095.pdf>.

12. The history of Silly Putty is quite amusing. In 1943 James Wright, an engineer, was attempting to create a synthetic rubber. He was unable to achieve the properties he was looking for and put his creation (later to be called Silly Putty) on the shelf as a failure. A few years later, a salesman for the Dow Corning Corporation was using the putty to entertain some customers. One of his customers became intrigued with the putty and saw that it had potential as a new toy. In 1957, after being endorsed on the "Howdy Doody Show", Silly Putty became a toy fad

13. Harada, A.; Takagi, T., Kataoka, S.; Yamamoto, T.; & Endo, A. (2011). Boron adsorption mechanism on polyvinyl alcohol. *Adsorption*, 17(1), 171-178.

Additional interesting and helpful references for further reading

a. Froudakis, George E. "Hydrogen storage in nanotubes and nanostructures".*Materials Today* 14 (2011): 324-328.

b. Gislon, P. "Hydrogen production from solid sodium borohydride". *International Journal of Hydrogen Energy* 34 (2009): 929-937.

c. Yu, Lin. "Hydrolysis of sodium borohydride in concentrated aqueous solution". *International Journal of Hydrogen Energy* 36 (2011): 7416-7422.

d. Muir, Sean S. "Progress in sodium borohydride as a hydrogen storage material: Development of hydrolysis catalysts and reaction systems". *International Journal of Hydrogen Energy* 36 (2011): 5983-5997.

e. Gribble, Gordon W. “Sodium borohydride in carboxylic acid media: a phenomenal reduction system”. *Chemical Society Reviews* 27 (1998): 395- 404.
f. Retnamma, Rajasree. “Kinetics of hydrolysis of sodium borohydride for hydrogen production in fuel cell applications: A review”. *International Journal of Hydrogen Energy* 36 (2011): 9772-9790.
g. American Chemical Society. *Chemistry: A Project of the American Chemical Society*. New York: W.H. Freeman and Company, 2005.

Appendix A

Materials and Instrumentation

The laboratory experiment can be modified to the materials, supplies, and instrumentation available.

Chemicals List
Sodium Borohydride
Borax
Distilled Water
Acetic acid (table vinegar adequate for the experiment)
Polyvinyl alcohol, 87% hydrolyzed (Clear Elmer’s Glue is adequate for the experiment)

Water Displacement Experiment
Graduated Cylinders
Large Reservoir Containers
Tygon Tubing
Stop watch

Require stoichiometric calculation to determine water requirement, as well as water/acid ratios for affecting hydrolysis rate

Chemical Reaction Characterization Methods
FTIR Spectroscopy
Infrared Thermometer or Infrared Thermal Imaging Camera
Light Microscopy
Chemical sensors and probes
DSC/TGA (micro calorimetry is a good alternative)