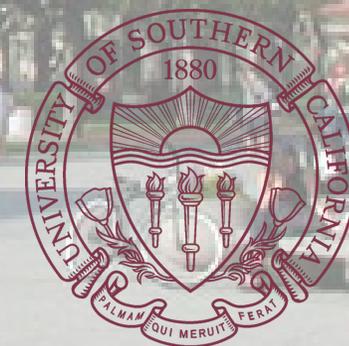


HyMARC Seedling: Hydrogen Release from Concentrated Media with Reusable Catalysts

Travis J. Williams, PI, USC
Robert P. Currier, co-PI, LANL
6-8 June 2022
Project ID ST216
DE-EE-0008825

University of Southern California
Los Alamos National Laboratory



This presentation does not contain any proprietary, confidential, or otherwise restricted information

Project Goal

- **Project Goal: We will demonstrate on-demand H₂ evolution from formic acid and formic acid fuel blends** using a demonstration-scale continuous operation reactor. We will engage molecular mechanistic studies to optimize catalyst and fuel blend.
- **Hydrogen Evolution**
 - We will show that our homogeneous catalyst technology can be scaled to meet the DOE target flow rate of 300 kg H₂ /hr in a continuous flow reactor.

Our catalyst system offer a unique ability to evolve H₂ quickly, scalably, and on-demand from liquid carriers.

- **Demonstration Reactor**
 - We will build and demonstrate a continuous flow reactor as a prototype for stationary H₂ filling based on liquid carriers.

With a physical prototype, we can know mass and energy efficiency and longevity of the process.

- **Mechanistic Studies**
 - By understanding the molecular mechanism of our catalysis, we can transition from formic acid to more hydrogen-dense fuels.

We have shown that mechanistic studies enabled us to utilize methanol blended fuels with greater H₂ density.

Overview

- **Timeline**

- Project start date: 1 October 2019
- Project end date: 31 May 2023

- **Budget**

- Total project budget: \$1,250,000
 - Total recipient share: \$250,000
 - Total federal share: \$1,000,000
 - FY22 DOE funds received: \$173k USC + \$106k LANL
 - FY23 DOE funds planned: \$217k USC + \$120k LANL
 - FY22 cost share funds received: \$83k USC
 - FY23 cost share funds planned: \$86k USC

- **Barriers**

- Generate H₂ from formic acid
 - Increase reaction scale
 - Target: Continuous flow
 - Demonstrate H₂ throughput
 - Should show scalability to 300 kg/hr in principle
 - Remove CO₂ from output stream
 - ANSI target: 2 ppm
- Apply technology to blended fuels
- Understand molecular mechanism

- **Partners**

- University of Southern California (lead)
- Los Alamos National Laboratory

Relevance

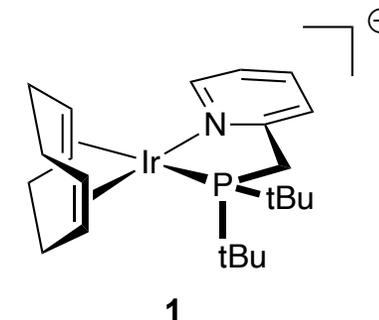
- **Project Objectives:** (1) Demonstrate H₂ evolution from formic acid or a formic acid fuel blend, (2) using a demonstration-scale flow reactor, and (3) use mechanistic studies to optimize catalyst and fuel blend. *Producing hydrogen on demand is a key hurdle in our national transition to clean energy infrastructure.* Making hydrogen efficiently from liquid carriers is important to our ability to make H₂ fuel available in distributed locations, particularly for transportation applications.
- **Hydrogen Evolution Status and Metrics**
 - Increase reaction scale
Outset: 5 mL batch Current: Continuous operation Target: Continuous operation
Achieved 20x scaleup in BP1. Achieved continuous continuous operation in BP2.
 - Demonstrate H₂ throughput
Outset: 1.3 L/hr Current: 160 L/hr peak in flow Target: Scalable to 300 kg/hr
Demonstrated peak H₂ production at 160 L/hr (ambient) in continuous, 2250 psig conditions.
 - Remove CO₂ from output stream (beginning in BP2)
Current: < 5 ppm at ambient BP2 target: 400 ppm BP3 target: 2 ppm
Demonstrated quantitative (< ca. 5 ppm) CO and CO₂ scrubbing at ambient pressure.
 - Weight H₂ released on Medium Basis (*new metric added in BP2*)
Outset: 4.3 wt% Current: 5.3 wt% BP3 target: > 4 wt%
Blending in more MeOH/H₂O will increase the H₂ release capacity of the medium.

While we can hit DOE targets for tube trailer H₂ filling (scalable to 300 kg H₂/hr) with formic acid alone, mechanistic work has enabled us to push beyond what's possible with formic acid by blending in other H₂ carriers

Approach

- **Research Strategy**

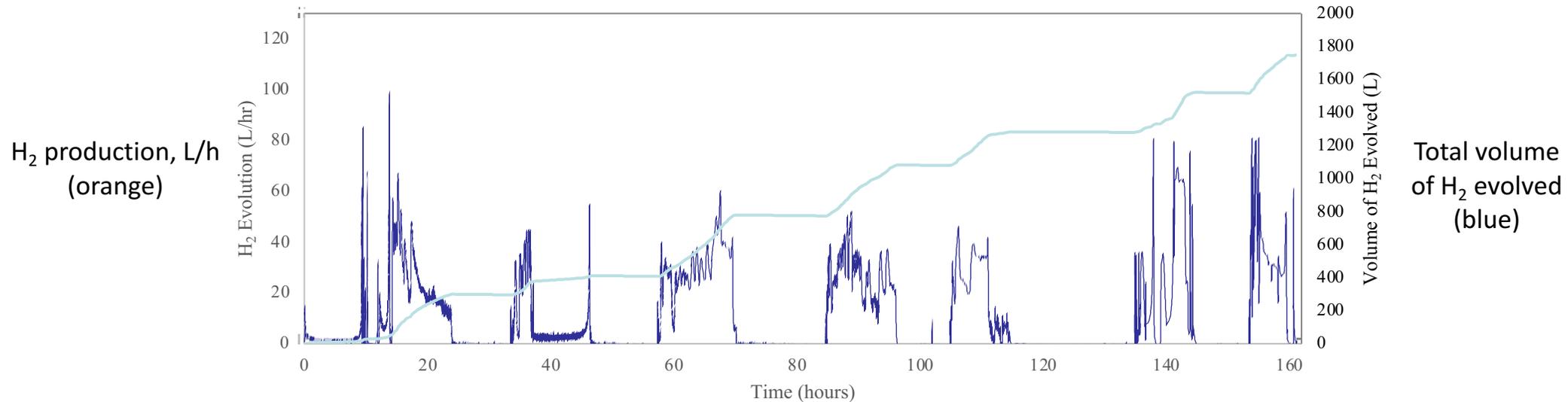
- Scale and analyze the Williams formic acid H₂ release system (**1**)
- Demonstrate the Williams system in a continuous operation reactor; hit H₂ evolution metrics
- Use mechanistic data on system **1** to enable blended fuels
- Screen alternative catalysts to enable blended fuels or mixed catalyst systems



- **Second GNG** (Feb 2022): *Demonstrate catalyst re-use in the demonstration reactor with CO₂ scrubbing: Show gas eluent flow rate with minimally 4 wt% H₂ release based on the liquid fuel medium. Demonstrate that catalyst activity does not drop below 90% over 10 successive cycles of catalyst use with 100 mL FA. Report CO₂ content in gas eluent stream, at or below 400 ppm. Submit minimally one peer-reviewed paper on the mechanism of formic acid dehydrogenation with catalyst **1**.*
 - While this was written contemplating an ambient pressure reaction, H₂ throughput and catalyst stability were established at 2250 psig.
 - CO₂ scrubbing achieved 71.3% H₂ at 2300 psig and 100% at ambient pressure.
- **Mechanistic Studies** enabled a manuscript submission this year. Results in this area have enabled us to move into methanol-blended fuels.
- **End of Project Goal** (May 2023): *Quantify flow rate and reactor size that are needed to meet or exceed 300 kg H₂/hr flow rate. Predict the applicability of our technology to the prototype scale 100 kg H₂/hr flow. Quantify our H₂ output purity and compare against targets for regarding CO₂ (2 ppm, ASTM D7649-10, D7653-10) and CO (ASDTM D7653-10).*

Accomplishment: Reactivity Does Not Diminish through 3.2 L Formic Acid

Total H₂ Production over Conversion



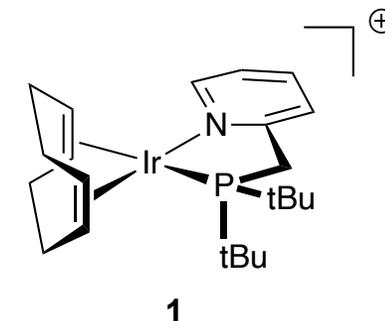
- **Experiment:** Using 25 mg of catalyst **1** and 20.0 g sodium formate, we dehydrogenated **3.248 L of formic acid**, fed continuously into the reactor, evolving 1,750 L of H₂, 2.35 million turnovers. Average turnover frequency was 24,212 hr⁻¹ (1.75 g/hr H₂, optimized for TON, not H₂ velocity) while running. Catalyst deactivation is not apparent. According to our mass flow meter, hydrogen evolved in this experiment accounted for 3.92 wt% of the reaction medium, but we observe that this measurement has low accuracy, near 9% error in some of our observations, but we have no other way to measure hundreds of liters of H₂ in a continuous reaction. In this experiment, we calculate 4.3 wt% H₂ based on unreacted fuel (some remains in the lines, so we assess the actual weight content of H₂ release between **3.9-4.3 wt%**). This is consistent with what we measure by eudiometry on the 100 mL scale, consistently 4.2 wt% H₂ content.
- **We conducted this reaction at 1440 psig, although pressurization was not required for the GNG.**

Accomplishment: CO₂ Scrubbing at Ambient Pressure

- Experiment:** Formic acid (70 mL) was dehydrogenated in a pressure vessel with catalyst **1**, reaching 2300 psig. The product gas was allowed to partition into a pressurized extraction vessel containing water. Once the pressure had equalized between the vessels, a 100 mL volumetric pipet containing 80 mL of 3M KOH was connected to the sampling line of the extraction vessel. The pipet was purged with headspace gas, the pipet headspace was sampled and injected into a gas GC with an 8.8 ppm detection limit for CO. The resulting chromatogram showed near 100% H₂ purity, as no other peaks (CO or CO₂) were detected. This experiment shows that after a water absorption step, 50% H₂ can be purified to > 99% H₂ (nominally < 10 ppm CO, CO₂) using a relatively small amount of CO₂ absorption agent.

Stage	Technique	H ₂	CO ₂	CO
1	High pressure water/gas partition	71.3%	24.7%	4.0%
2	Ambient pressure KOH scrubbing	100%	< 10 ppm	< 10 ppm

We can achieve partial CO₂ removal by water partitioning at 2300 psig and full removal by scrubbing at ambient pressure.



Accomplishment: 5.3 wt% H₂ from a Methanol-Formic Acid Blend

- Experiment:** Methanol-formic acid blend aqueous solution (3.2 mL CH₃OH/1.4 mL H₂O/1.5 mL HCOOH/1.2g NaOOCH) was dehydrogenated in a round bottom flask connected to a water condenser with catalyst **1** and Ru-MACHO. The product gas was allowed to displace into a 0.5M KOH eudiometer to absorb CO₂ and collect only H₂ in the eudiometer. This experiment shows that the achieved amount of H₂ meet an average of 5.33 wt% from this blend (sample calculation below).

Replication	Total Vol (mL)	Leftover mass (g)	Unreacted		Average			
			liquid (g)	H ₂ wt%	Ave. Vol (mL)	leftover wt (g)	Ave. unreacted liquid (g)	Ave. H ₂ wt%
1	1640	4.34	3.14	5.59	1560	4.38	3.15	5.33
2	1430	4.27	3.03	4.68				
3	1610	4.50	3.26	5.75				

Sample calculation:

- 3.20 mL CH₃OH = 0.791 g/mL x 3.2 mL = 2.53 g
- 1.50 mL HCOOH = 1.22 g/mL x 1.5 mL = 1.83 g
- 1.40 mL H₂O = 1.40 g

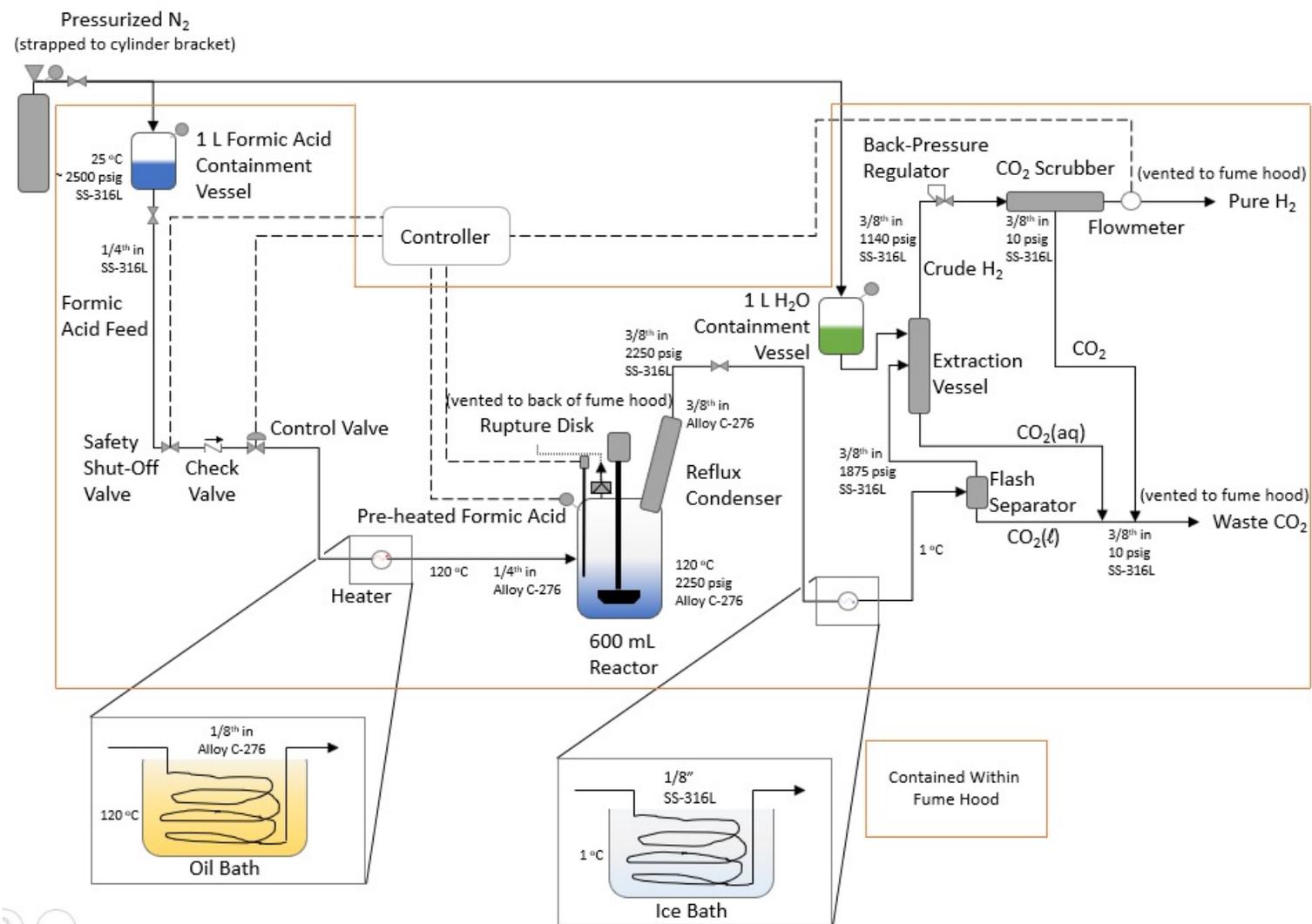
Total initial liquid mass = **5.76 g**

Unreacted solid/liquid = 4.38 g – 1.20 g NaOOCH – 0.0388 g [cat] = **3.14 g** unreacted liquid mass

$$\text{wt\% H}_2 = \frac{1.641 \text{ L of H}_2 \div 22.4 \frac{\text{L}}{\text{mol}} \times 2.0 \text{ g/mol}}{5.7612 \text{ g} - 3.1391 \text{ g}} = \mathbf{5.59 \text{ wt\%}}$$

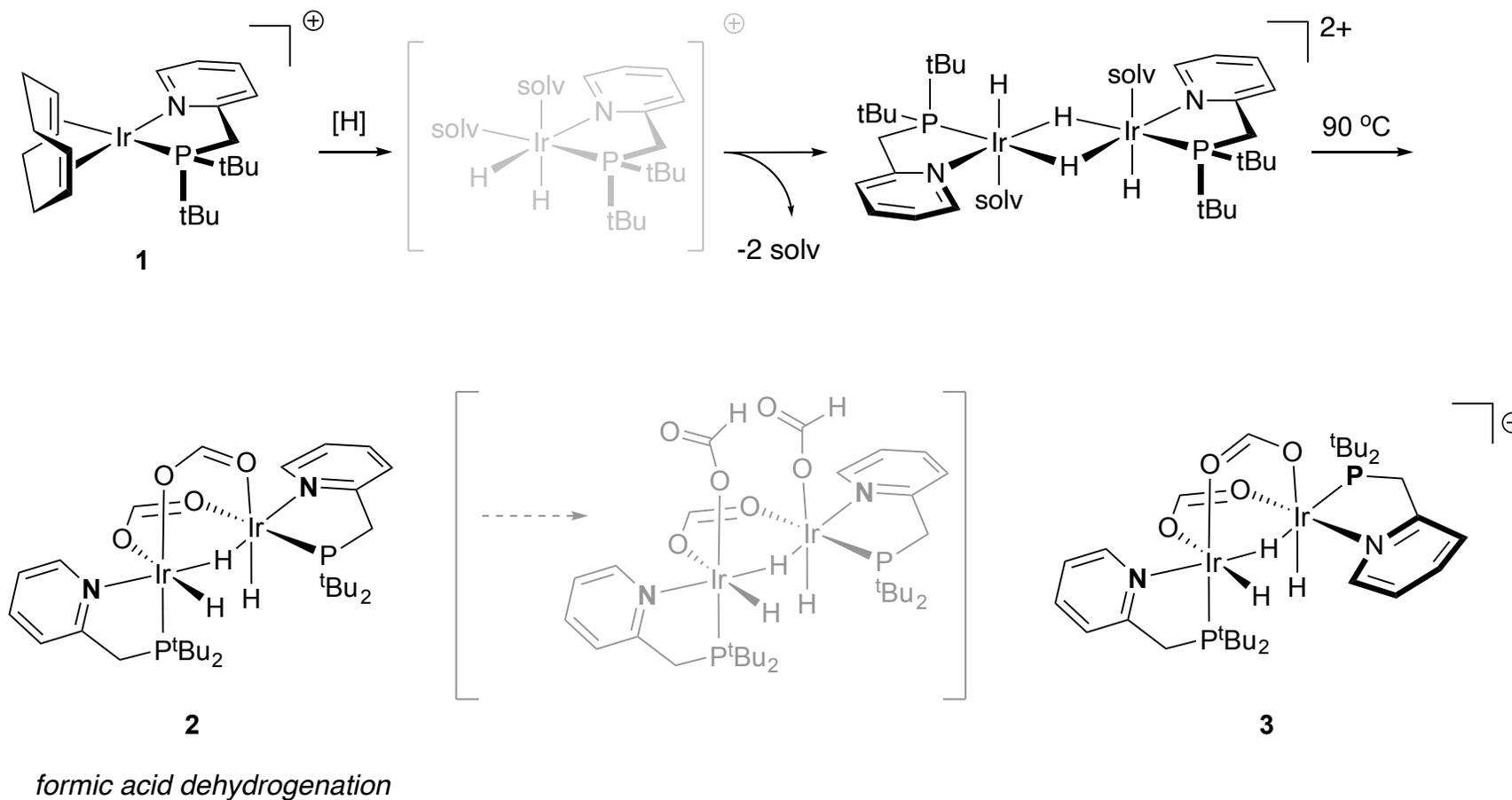
Blending aqueous methanol into formic acid enable > 4.3 wt% H₂ release from the medium.

Progress: Constructed the Proposed Demonstration Continuous Reactor



- **Demonstration Reactor** design was led by the LANL team with construction and implementation at USC. Work has now progressed to building an apparatus for in-line CO₂ separation.

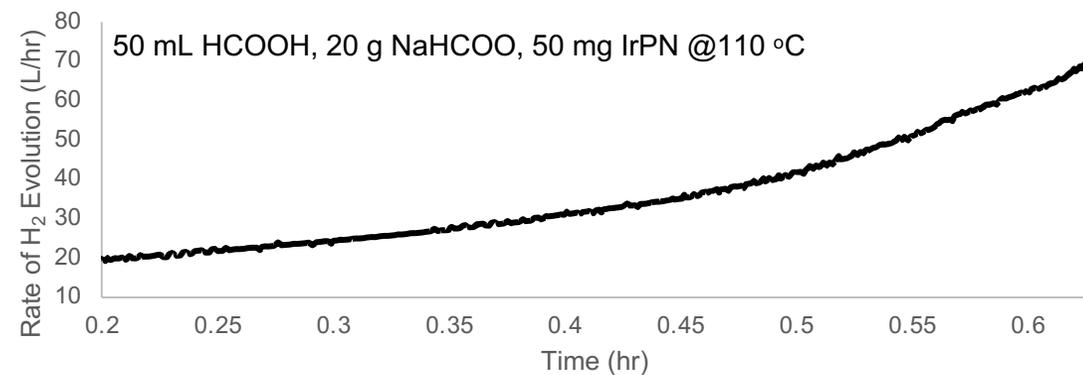
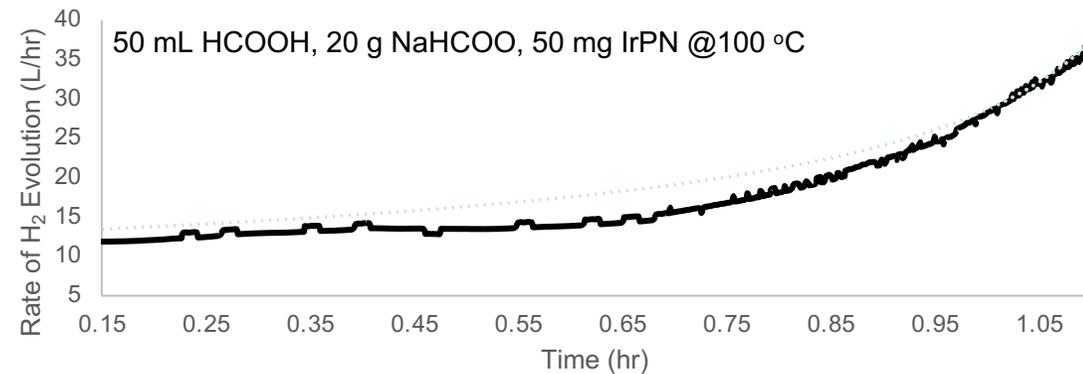
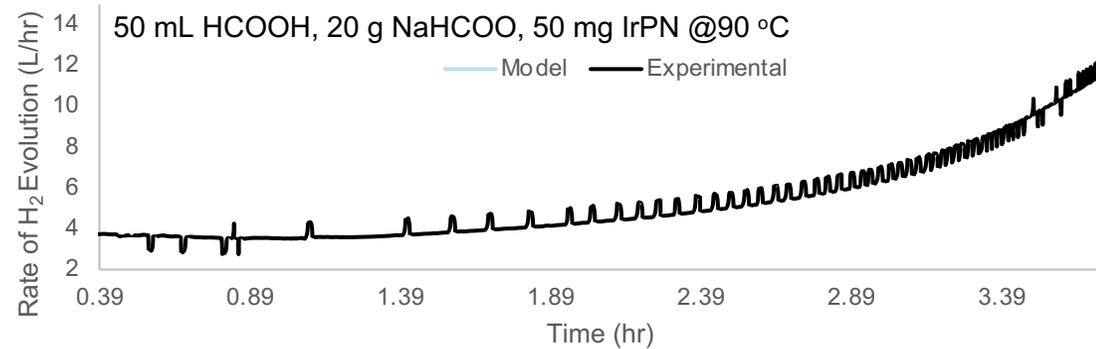
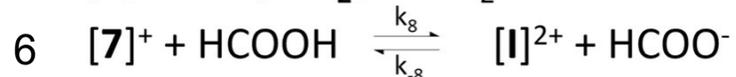
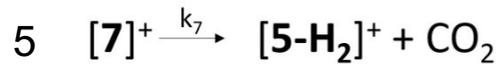
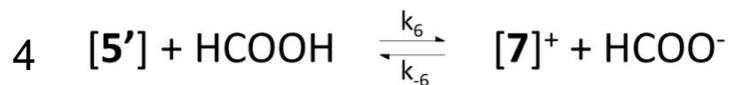
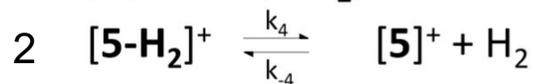
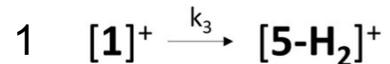
Progress: Mechanistic Starting Point



- **Starting Point:** The original report of the Williams Ir_2H_3 system included a mechanistic proposal that accounted for experimental data available at the time.

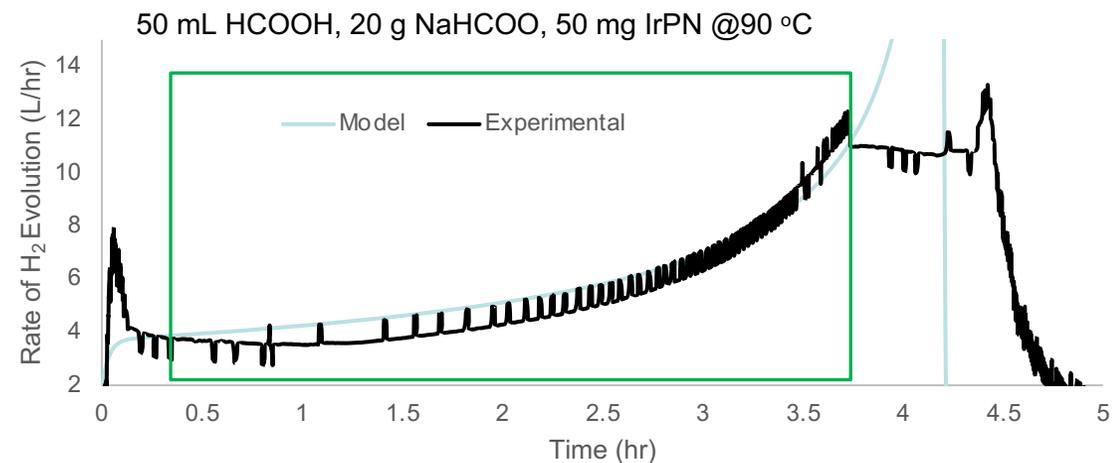
Progress: Empirical Kinetic Modeling

- Experiment:** A system of differential equations was written in the form of the mechanism predicted by synthetic studies on catalytic intermediates and theoretical calculations on reaction mechanism. Rate data from the continuous reactor were used to ground this model and calculate rate constants for fundamental steps.
- Problems encountered:** Initial rate data are unreliable because of time required for the reactor's temperature to equilibrate. Data at the end of the reaction are unreliable because NaO_2CH precipitates from solution. Thus, data in the central region of the conversion curve were used to ground the model (right). Further, we have not been able to secure structural characterization on inhibited species "I".

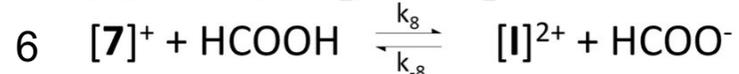
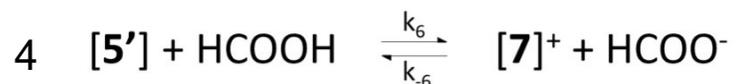
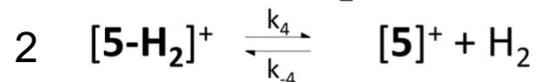
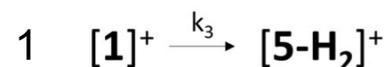


Progress: Empirical Kinetic Modeling

- **Data Selection:** Data are modeled in a window (green) between temperature stabilization and formate precipitation.
- **Calculated Rate Data:** The table below shows measured rate constants for each of the elementary steps. Practitioners can use these measurements, along with initial conditions of catalyst and reagent loading to predict observed reaction kinetics for deployment of the system.
- **Temperature Response:** We measure an activation barrier (5H₂ to 7) of $\Delta H^\ddagger = 22.1$ kcal/mol, $\Delta S^\ddagger = \text{ca. } 13$ eu, $\Delta G^\ddagger = 25.9$ kcal/mol (Eyring), which is near with a theoretical $\Delta G^\ddagger = 23.8$ kcal/mol. With these parameters, practitioners can calculate temperature response of rate.



Kinetic Model



Measured rate constants at 100 °C

$$k_3 = 1.49 \times 10^{-2} \text{ s}^{-1}$$

$$k_4 = 5.30 \times 10^2 \text{ s}^{-1} \text{ (Rate limiting at high [formate])}$$

$$k_{-4} = 0.0 \times 10^0 \text{ s}^{-1} \text{ (Irreversible)}$$

$$k_5 = 5.59 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_{-5} = 0.0 \times 10^0 \text{ s}^{-1} \text{ (Irreversible)}$$

$$k_6 = 5.65 \times 10^1 \text{ M}^{-1} \text{ s}^{-1} \text{ (Rate limiting at low [formate])}$$

$$k_{-6} = 0.0 \text{ M}^{-1} \text{ s}^{-1} \text{ (Irreversible)}$$

$$k_7 = 1.46 \times 10^2 \text{ s}^{-1}$$

$$k_8 = 5.40 \times 10^0 \text{ M}^{-1} \text{ s}^{-1}$$

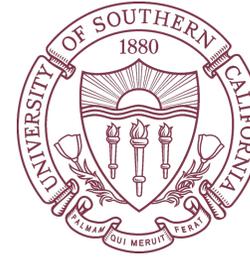
$$k_{-8} = 7.64 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$$

Responses to Previous Year Reviewers' Comments

- The project reviewed very well at 2021 AMR. Reviewers requested additional data on rate, temperature, and pressure modeling. Specifically, two project weaknesses were highlighted:
- Co-generation of CO₂ and hydrogen requires separation, which may be expensive.
 - Consistent with the reviewer's position, we found in BP2 that an inexpensive separation (water partitioning) afforded partial purification of hydrogen, where a more expensive scrubbing approach was very effective.
 - In BP3 we will further develop our CO₂ separation method according to the diagram in slide 9. This will enable us to understand cost and efficiency of product purification at pressure and enable a comparison of purification costs against saved gas compression costs.
- The apparent lack of data on hydrogen release versus T and P is a weakness; regeneration efficiency is unclear and plans to measure efficiency are not communicated.
 - Slides 12 and 13 present our empirical rate data for hydrogen release, which is new this year.
 - Thermochemistry reported in slide 13 enables practitioners to calculate rate response to temperature change, although these data are preliminary and we will continue to revise them as we collect more kinetics data to support Eyring analysis.
 - We find that the reaction is insensitive to pressure within the safety limits of our apparatus (2250 psig).
 - While we were not tasked with studying CO₂ rehydrogenation in our original SOPO, we have encountered a triiridium oxide cluster that has emerged from our blended fuel work. This cluster is capable of reversible hydrogenation of CO₂ to a mix of formic acid, methanol, and methyl formate. In response to the reviewer's criticism, we plan to develop this discovery in the coming year.

Collaboration and Coordination

- **Core Project Team** meetings occur bi-weekly among all USC and Los Alamos investigators. The videoconference modality has enabled this to continue through the COVID lockdown.



- **HyMARC Collaboration** meetings occur monthly by videoconference between the USC group (Williams) and our HyMARC contact at PNNL (Autry, Johnson). This enables the seed project team to remain connected to directions in HyMARC and plan for technology validation and transfer.



Remaining Challenges and Barriers

- **Transition Pressurized Conditions**

- Our strategic decision to move from ambient to elevated pressure introduced considerable cost and technical challenges, but this decision is supported by the urgency of providing H₂ on demand with reduced compression cost. Addressing H₂/CO₂ separation at pressure remains a significant challenge that we will address in the coming year.

- **Leverage Reaction Mechanism Work to be Enabling Toward Project Goals**

- While we anticipated that quantum chemical calculations would be the route that enabled our entry into methanol-blended fuels, we found that synthetic and screening efforts were more effective.
- Realizing useful kinetics in methanol conversion continues to be a challenge: methanol is slow; formic acid is fast. Addressing this gap will most likely be accomplished by further synthetic work in catalyst development.
- A preliminary empirical rate model, based on batch reactor kinetics, was challenging to generate. Fitting calculation with large data sets are time-intensive and we continue to refine both our model and our strategy to fit data.

Proposed Future Work

- **Demonstrate Formic Acid Dehydrogenation in Automation**
 - Our demonstration reactor is capable of continuous operation through the capacity of its fuel tank, but we have not yet fully automated its feedback loop systems necessary for autonomous operation. This will be addressed in BP3.
- **Link Empirical Kinetic Modeling with De Novo Mechanistic Work**
 - Kinetic data from continuous reactions have enabled us to ground a kinetic model for our overall process. We are using these data to measure thermochemical benchmarks in our proposed mechanism and benchmark calculation against experiment. We are still working to establish error bars in our measured values and ensure that we are comparing correctly.
- **Address CO₂ Scrubbing at Pressure**
 - Our decision to work at pressure significantly increased the challenge of H₂/CO₂ separation. We build our proposed separation apparatus in BP3 and proceed to optimize purity polishing up to the ASDTM standards in our end of project goal.

Any proposed future work is subject to change based on funding levels

Summary

- **Hydrogen Evolution Demonstrated to Date Exceeds BP2 GNG Target**
 - We have demonstrated continuous operation of formic acid dehydrogenation in our reactor and so doing observed little if any decline in catalyst productivity.
 - All hydrogen evolution rate and catalyst longevity data were collected at elevated pressure (ca 2250 psig), despite our initial plan to achieve all deliverables at ambient pressure.
- **Mechanistic Studies Opened a Route to Methanol-Blended Fuels**
 - We exceeded the H₂ weight content in our medium by realizing simultaneous dehydrogenation of formic acid and aqueous methanol: while formic acid is limited to 4.3 wt% H₂, we have now realized 5.0 wt%.
 - We have developed a kinetic model for actual H₂ evolution rates that correlates well with the structural catalytic intermediates that we have observed and calculated.
- **Reactor Construction** was delayed by COVID-19 but has now progressed to product separation.
- **Scrubbing CO₂ from our Product Stream** was accomplished at the level of our end of project goal, but we will now turn attention to accomplishing the same under pressurized conditions.

Technical Backup and Additional Information

Please include this “divider” slide before your technical backup slides [maximum of 20].

These technical backup slides will be available for your oral presentation (but only as needed for Q&A) and will be included in the web PDF files released to the public.

Note that there are two **REQUIRED** slides in this section and several suggested slides.

Technology Transfer Activities

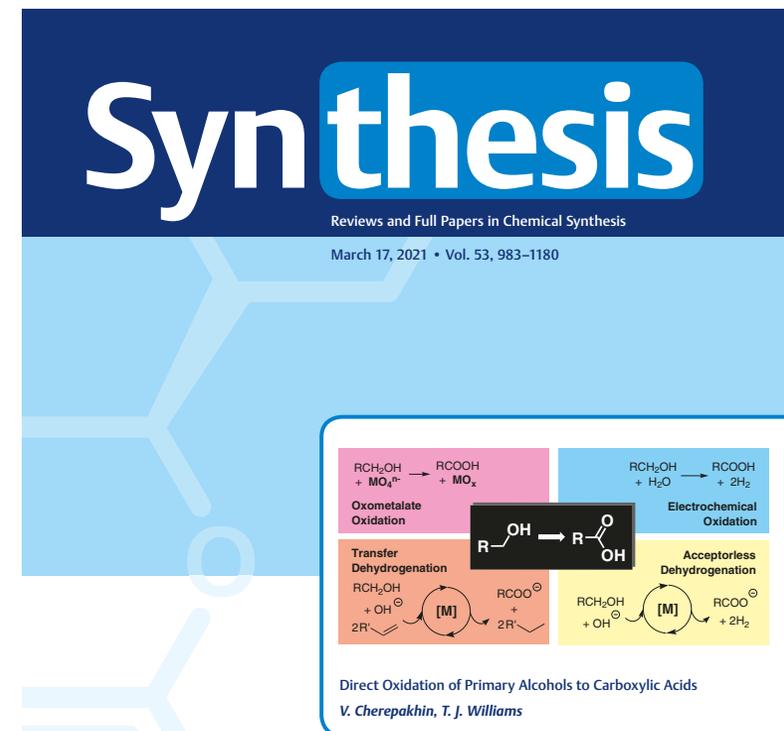
- **Licensing Strategies** are developing. The PI is discussing technology transfer options with two California startup companies, OCOchem and Catapower.



- The technology and project remain very early phase, so it is not timely to move these relationships toward investment at this point.
- A **US Patent Pending**, Alfonso, N. Williams, T. J.; Currier, R. P.; Chavez, A. J.; Do, V. K. "Reactor for On-Demand High Pressure Hydrogen" US prv 63/173,459, was filed on April 11, 2021 to cover the design and function of our demonstration reactor. This was converted to national phase on April 11, 2022.

Publications and Presentations

- Cherepakhin, V.; Williams, T. J. "Direct Oxidation of Primary Alcohols to Carboxylic Acids" *Synthesis* **2021**, 53, 1023-1034. DOI: 10.1055/s-0040-1706102.
 - This is a cover story in *Synthesis* that is a review of methods that oxidize R-OH groups. It incorporates mention of catalysts involved in this project, so DOE support is cited.
- Alfonso, N.; Do, V. K.; Chavez, A. J.; Chen, Y.; Williams, T. J. "Catalyst Carbonylation: A Hidden, but Essential, Step in Reaction Initiation" *Catal. Sci. Tech.* **2021**, in press. DOI: 10.1039/D1CY00322D.
 - This is a review of catalytic processes that involve catalyst carbonylation both as deleterious or beneficial functions of the catalytic cycle. We did this research as part of our investigation regarding discovery of our carbonylated catalytic cycle and reported the eye-opening results in this feature article. The narrative cites DOE sponsorship.
- Do, V. K.; Alfonso Vargas, N.; Chavez, A. J.; Zhang, L.; Cherepakhin, V.; Lu, Z.; Currier, R. P.; Dub, P. A.; Gordon, John C. Williams, T. J. "Pressurized Formic Acid Dehydrogenation: An Entropic Spring Replaces Hydrogen Compression Costs" *Catal. Sci. Tech.* **2022**, in revision.
 - This research paper shows how any why pressurization of formic acid dehydrogenation reactions deliver superior performance under pressurized conditions.
- Williams, T. J. "Hydrogen Release from Concentrated Media with Reusable Catalysts" Oral (virtual/recorded) presentation. HyMARC Seedling Webinar, 13 January 2021.



6

Reviewer-Only Slides

(Note: please include this “divider” slide between those to be presented and the “Reviewer-Only” slides. These slides will be removed from the published web PDF file.)

Approach: Identifying Promising H₂ Carriers

Hydrogen Carrier Metric

Is the gravimetric/volumetric density greater than 350 bar H₂ (23 g/L)?

What 'use case' are you targeting?

What is the enthalpy release on regen?

What temperature is required to reach 1 bar H₂?

What is ΔG (100 °C, 1 bar) for H₂ release?

What is ΔG (40 °C, 200 bar) for H₂ uptake?

Are catalysts currently available to yield 1 kg H₂/minute?

What is the selectivity for H₂ release?

What are the viscosity, melting point, and vapor pressure at the release temperature?

Formic Acid (neat)

53.6 g H₂/L

On-demand power (150 kW)

31.4 kJ/mol H₂

25 °C ($\Delta H/\Delta S = -128$ °C)

-49.1 kJ/mol H₂

36.2 kJ/mol H₂ (estimate)

2 kg cat @ 1 kg H₂/min

50% w CO₂, < 10 ppm CO

0.5492 cP
8.4 °C
> 760 mmHg (BP is 101 °C)

2:1:1 Formic Acid: MeOH: Water

75.2 g H₂/L

On-demand power (150 kW)

39.0 kJ/mol H₂

25 °C ($\Delta H/\Delta S = -42$ °C)

-23.8 kJ/mol H₂

13.7 kJ/mol H₂ (estimate)

(experimental)

(experimental)

ca. 0.5 cP
ca. -20 °C
> 760 mmHg (BP is ~77 °C)

Progress Toward Milestones: BP1

Milestone Schedule

Milestone #	Project Milestones	Type	Task Completion Date (Project Quarter)				Progress Notes
			Original Planned	Revised Planned	Actual	Percent Complete	
2.1	Prepare a supply of (cod)Ir(2-di-tert-butylphosphinomethylpyridine) triflate, the precursor to catalyst 1.	Milestone	5/31/2020	(closed)	(closed)	100%	Complete
2.2	Demonstrate reusability of known catalyst 1 on a scale of 100 mL or more.	Milestone	8/31/2020	(closed)	(closed)	100%	Complete and replicated at PNNL.
1.1	Complete technical diagrams for the demonstration reactor apparatus that uses formic acid as the hydrogen carrier and catalyst 1 as the catalyst.	Milestone	11/30/2020	(closed)	(closed)	100%	Diagrams are included and parts are ordered. Revisions might be necessary if recommended.
1.2	Complete construction of the demonstration reactor apparatus.	Milestone	2/28/2021	(closed)	(closed)	85%	Some parts are on back ordered. Fabrication is in progress. This is a major ongoing effort of Q5.
1.3	Show high efficiency H ₂ release from formic acid in the demonstration reactor.	Milestone	2/28/2021	(closed)	(closed)	75%	We made a big step by showing that we could evolve H ₂ pressure in batch. We have now run our first reaction in the demonstration reactor.
3.1	Prepare DFT models of the experimental intermediates and transition states in the Williams mechanism of formic acid dehydrogenation with catalyst 1.	Milestone	2/28/2021	(closed)	(closed)	90%	Underway. Calculations are now fully refined in one mechanism and progress is rapid in the other. I'm not going to mark this off until we have the refined numbers on the 4/5/6 cycle.
Go/No-Go 1	<p>i. Demonstrate generation of 600 mL H₂/hr with commensurate rate of 925 mL/hr or formic acid consumption and minimally 3.5 wt% H₂ release from the formic acid using < 250 ppm catalyst loading.</p> <p>ii. Show a calculation of how this prototype-scale reactor can scale to the DOE target of 300 kg H₂/hr.</p>	Go/No-Go #1	2/28/2021	(closed)	(closed)	100%	Realized in batch as USC, both at ambient and elevated pressure. Exported for duplication at PNNL. This was a major accomplishment of Q4. GNG was qualified as complete.

Progress Toward Milestones: BP2

Milestone Schedule

Milestone #	Project Milestones	Type	Task Completion Date (Project Quarter)				Progress Notes
			Original Planned	Revised Planned	Actual	Percent Complete	
2.3	Screen LANL and Prakash catalysts for their reactivity (separately) towards formic acid and MeOH dehydrogenation.	Milestone	5/31/2021	(closed)	(closed)	100%	
1.4	Show catalyst longevity in the demonstration reactor. Quantify catalyst decomposition.	Milestone	8/31/2021	(closed)	(closed)		Data included herein
2.4	Screen the most promising LANL and Prakash catalysts in blended fuels. Candidate systems are those that exceed metrics of milestone 2.4.	Milestone	11/30/2021	(closed)	(closed)	100%	This resulted in qualifying methanol as a competent fuel component for multiple catalysts.
1.5	Integrate CO ₂ scrubbing and polishing using the USC sorbent technology.	Milestone	2/28/2022	(closed)	(closed)	100%	Data included herein
2.5	Show preliminary data for a methanol- formic acid blended fuel system that will enable a decision to include or exclude methanol from the final fuel blend.	Milestone	2/28/2022	(closed)	(closed)	100%	Data included herein
3.2	Complete modeling of formic acid dehydrogenation with catalyst system 1.	Milestone	2/28/2022	Summer 2022		90%	Manuscript in preparation
Go/No-Go 2	<p>i. Demonstrate catalyst re-use in the demonstration reactor with CO₂ scrubbing: Show gas eluent flow rate with minimally 4 wt% H₂ release based on the liquid fuel medium.</p> <p>ii. Demonstrate that catalyst activity does not drop below 90% over 10 successive cycles of catalyst use with 100 mL FA.</p> <p>iii. Report CO₂ content in gas eluent stream, at or below 400 ppm.</p> <p>iv. Submit minimally one peer-reviewed paper on the</p>	Go/No-Go #2	2/28/2022	(closed)	(closed)	100%	GNG was cleared on 2/24/2022

Progress Toward Milestones: BP3

Milestone Schedule

Milestone #	Project Milestones	Type	Task Completion Date (Project Quarter)				Progress Notes
			Original Planned	Revised Planned	Actual	Percent Complete	
3.3	Report an empirical kinetic model and grounding data for formic acid dehydrogenation with catalyst 1.	Milestone	2/28/2022	5/31/2022		90%	Models are developed and are being grounded to data, but refinement to reduce modeling error is underway.
2.6	Deliver a blended fuel and catalyst system that is superior to neat formic acid.	Milestone	5/31/2022	(open)	(open)	50%	5.3 wt% H ₂ release has been realized.
3.4	Calculate performance of systematically-substituted catalyst analogs to improve catalyst performance in blended fuel	Milestone	8/31/2022	(open)	(open)	0%	
1.6	Quantify H ₂ release and CO, CO ₂ contamination in the H ₂ eluent stream from blended fuels.	Milestone	11/30/2022	(open)	(open)	10%	Models are developed and are being grounded to data.
EoP Goal	Quantify flow rate and reactor size that are needed to meet or exceed 300 kg H ₂ /hr flow rate. Predict the applicability of our technology to the prototype scale 100 kg H ₂ /hr flow. Quantify our H ₂ output purity and compare against targets for regarding CO ₂ (2 ppm, ASTM D7649-10, D7653-10) and CO (ASDTM D7653-10).	Go/No-Go #1	3/31/2023	(open)	(open)	25%	We have shown that purity goals are attainable.