QUARTERLY PROGRESS REPORT

March 2016 – May 2016

PROJECT TITLE: Development and Evaluation of Contaminant Removal Technologies for Landfill Gas Processing

PRINCIPAL INVESTIGATOR(S):
John N. Kuhn
Department of Chemical & Biomedical Engineering
University of South Florida
Email: jnkuhn@usf.edu
Phone: (813) 974 - 6498

Babu Joseph
Department of Chemical & Biomedical Engineering
University of South Florida
Email: bjoseph@usf.edu
Phone: (813) 974 - 0692

PROJECT WEBSITE: http://www.eng.usf.edu/~jnkuhn/Hinkley2015.html

Work accomplished during this reporting period:

For the period outlined in this third report, the catalyst has been synthesized and several poisoning techniques have been tested to determine the most effective one in terms of the amount of silica loaded onto and into the catalyst.

For the synthesis, the catalyst support (Fig 1a) was synthesized through the co-precipitation method. It consisted of cerium oxide and zirconium oxide in a 0.6:0.4 weight percent respectively. Nickel, magnesium and platinum (Fig 1b/c) were all then deposited onto the support using wetness impregnation method. Nickel was deposited in a 1.34 weight percent while magnesium was deposited in a 1.00 weight percent and finally platinum in 0.16 weight percent.

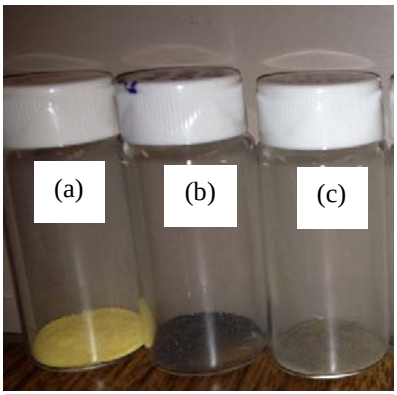


Figure 1: Catalyst support (a), support with Ni and Mg (b), support with Ni-Mg and Pt (c)

The siloxane amounts that were chosen as previously mentioned to poison the catalyst were based on a control of a clean sample (0 days), a lower limit (1week), a middle limit (1 month) and finally a high limit (6 months). These values are based on the same concentration of siloxanes, which was determined as typical representative values from a literature survey.

The challenges faced at this stage in the experimental process is how to dissolve and load the siloxanes onto the catalyst and whether the full effect of the siloxanes will be realized. Using siloxanes as a precursor proved to be an ineffective way for complete deposition onto the catalyst because breaking down the siloxanes into silica is very challenging especially in the case of D4 which is a cyclic

molecule. With that in mind, Ludox® which is a colloidal silica precursor was used. Wetness impregnation was used to load the silica onto the catalyst using Ludox. Looking at the physical appearance of the Ludox poisoned catalyst versus using siloxanes, it is very evident that Ludox was a more effective silica precursor as seen in Figure 2.

With that in mind, all three weight loadings of silica were deposited onto the catalyst using Ludox since it seemed to be the most promising. Once synthesized, the poisoned catalyst must be extensively

Figure 2a: Catalyst poisoned in crucible using siloxanes

Figure 2b: Catalyst poisoned in crucible using Ludox

characterized to determine the extent of silica loading before moving on to reaction studies. X-ray diffraction (XRD) was the first characterization tool used. The results can be seen in Figure3.

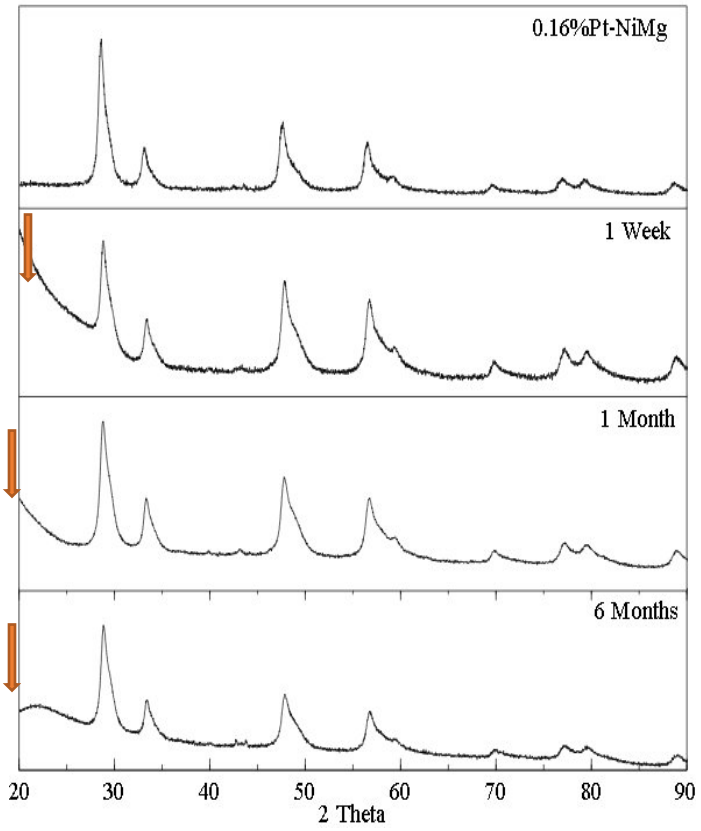


Figure 3: X-ray diffraction patterns of catalyst poisoned using Ludox as a silica precursor

From Figure 3, it is evident that silica has been deposited onto the catalyst even at the smallest amount used. This can be seen by the change in the diffraction pattern at the lower 2theta (20-25°). The first diffraction pattern at the very top shows a fresh, un-poisoned catalyst. It can be seen that only peaks associated with Ceria are shown. On the other hand, the other three diffraction patterns shown the presence of silica as indicated by the arrows.

In addition, we have initiated process simulations for the removal of siloxanes. A student team has also been grouped to design a reactive adsorbent bed for the removal of siloxanes via decomposition. The student team of 4 senior students designed a reactor system for the deposition of siloxanes over a bed of abundant oxide materials.

Finally, we have conducted some costing analysis for LFG purification and compared the results to the literature. A comparison of the results are shown below. The results are compared both on the cost per volume of LFG processed and cost per contaminant removed. Literature uses both and we tried to make a complete comparison given the flowrates and contaminant concentration both vary. Our results are consistent with costs for multiple adsorption beds (see de Arespacochaga *CEJ* 2014) and higher than less extensive cleaning (single beds, Gadde *SEE* 2006). Given that adsorption scales rather linearly with size due to high fraction of purification costs associated to adsorbent replacement, the results from different scales match rather well. Further investigation is needed to examine the downside to scaling down cheaper large scale purification systems (e.g., Sulferox) to the scale of LFG which typically is suggested to use adsorption beds as the most financially attractive option. Also, further literature review on the possibility of adsorbent regeneration will be completed.

LFG flowrate (Nm^3/min) [a]	**Contaminant (Concentration)**	**Technology**	**Cost per volume ($/Nm^3$) [b]**	**Cost per mass contaminant removed ($/kg) [b]**	**Reference**
70.8 [c]	H_2S (700 ppm) Siloxane (15 mg/m^3)	Iron sponge, AC bed	0.04	33.0 (~88% H_2S)	USF
1.36	H_2S (2000 ppm) Siloxane (n/a)	biological sulfur removal and condensation	0.0066	2.17 (100% H_2S)	Gadde SEE 2006
"	"	Previous + 2 carbon beds	0.0194	6.39 (100% H_2S)	"
3.17	H_2S (3000 ppm) Siloxane (14 mg/m^3)	Optimized BTF + drying, Iron sorbent, + AC	0.04	8.50 (~97% H_2S)	de Arespacochaga *CEJ* 2014
"	"	BTF + drying, Iron sorbent, + AC	0.06	12.8 (~97% H_2S)	"
"	"	Drying , Iron Sorbent, + AC bed	0.13	27.6 (~97% H_2S)	"
Comparisons				Not adj	
	H_2S only	AC bed	0.02 – 0.03		Mescia *IJHE* 2011
	H_2S only	Sulferox		0.24-0.30	Mota *Biofuel* 2011

	H_2S only	H_2SPLUS (225 kg/d max)		2.20 (OP-EX only)	"
0.125	H_2S (1000 ppm)	Sulfatreat	0.025	17.7	Abatzoglou *Biofuels, Bioprod. Bioref* 2009
0.94	H_2S (1000 ppm)	Fe adsorbent	0.031	6.6 [d]	"
"	H_2S (1000 ppm)	Na_2CO_3 AC	0.034	22.5 [d]	"

[a] 1 Nm^3 = 35.3 SCF

[b] All monetary values adjusted to 2016 USD, which could involve both a Euro to USF conversion and a time value of money correction

[c] As reference points of 700 ppm H_2S at 70.8 Nm^3/min (2500 SCFM), 108 kg S/day removed and daily flow is 1E5 Nm^3/day.

Future Tasks: The future direction would be to continue to characterize the materials. The catalyst will be characterized using several different techniques such as temperature programmed reduction (TPR), identifying the surface area using BET, and taking a closer look at the surface and structure of the catalyst using SEM. Those characterization techniques will help to show the reducibility of the catalyst, the surface area of the catalyst. Then reaction studies will be done to determine the effect of the poisoning on the catalyst if any.

TAG Meetings:

A TAG meeting was held on April 13, 2016. Both the video and audio are at the link provided below.

Link: http://www.eng.usf.edu/~jnkuhn/Hinkley2015.html

This table identified the TAG member attendees at the meeting.

Name	Position	Affiliation	Email
Tim Vinson	Research Coordinator	Hinkley Center	tvinson@ufl.edu
Kelsi Oswald	Director	Pinellas County Department of Solid Waste	koswald@co.pinellas.fl.us
Canan "Janan" Balaban	Asst. Director	Florida Energy Systems Consortium	cbalaban@ufl.edu
Devin Walker	Process Engineer	BASF	dmwalker@mail.usf.edu
Matt Yung	Researcher	Nat. Renewable Energy Lab	Matthew.Yung@nrel.gov

John Schert, Ralph Hirshberg, Berrin Tansel, and Tim Roberge were not able to attend.

Metrics:

1. List research publications resulting from **THIS** Hinkley Center project.

   None

2. List research presentations resulting from (or about) **THIS** Hinkley Center project.

   - A poster at the USF COE Research Day (see bottom picture).
   - A poster at the Graduate Research Colloquium.
   - A poster at the USF Undergraduate Research and Arts Colloquium

3. List who has referenced or cited your publications from this project.

   None

4. How have the research results from **THIS** Hinkley Center project been leveraged to secure additional research funding? What additional sources of funding are you seeking or have you sought?

   PI: Ergas, co-PIs: Kuhn, Joseph and Zhang. "Sustainable Bioenergy Production from the Organic Fraction of Municipal Solid Waste" Preproposal submitted to EREF.

   PI: Kuhn, co-PIs: Ergas, Joseph and Zhang. "Flexible Process for Thermochemical Conversion of Biogas to Fuels and Chemicals" Concept paper submitted to DOE EERE.

5. What new collaborations were initiated based on **THIS** Hinkley Center project?

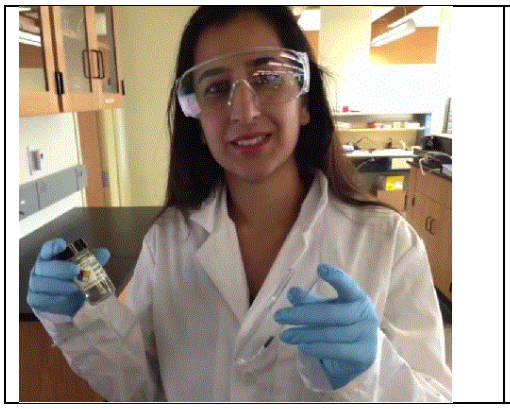
   No change.

6. How have the results from **THIS** Hinkley Center funded project been used (not will be used) by the FDEP or other stakeholders?

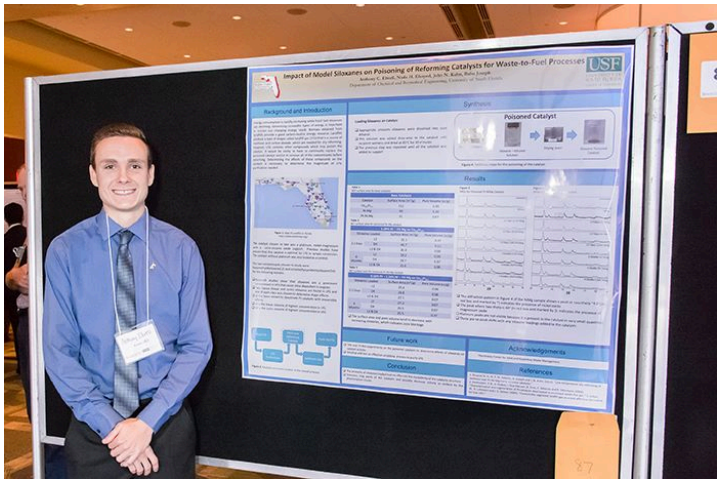
   None

Pictures:

The primary student researcher on this project is Nada Elsayed. Anthony Elwell is an undergraduate researcher also assisting with this research.



Nada Elsayed is seen in the pictures above. On the right, she is with the USF COE Dean (Robert Bishop) during the award of a plaque for her USF GSS fellowship.



Tony is a junior Chemical Engineering student working on this project. He recently presented a poster on this project.