QUARTERLY PROGRESS REPORT

June 2016 – August 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 fourth report, the poisoned catalysts have been tested using physisorption to determine the effect of silica on the surface area and pore volume of the catalysts. In addition, temperature programmed reduction (TPR) was done to determine the effect of poisoning on the reducibility of the catalysts. The two tested catalyst systems are 1.34wt% Ni 1.00wt%Mg doped with 0.16wt%Pt on a $(Ce_{0.6}Zr_{0.4})O_2$ support and 1.34wt% Ni 1.00wt%Mg on a $(Ce_{0.6}Zr_{0.4})O_2$ support. The high temperature catalyst which does not contain Pt was done twice. The initial time, the catalyst was calcined at 600°C post poisoning. The second time, it was calcined at 800°C to determine if calcination temperature had an effect on the surface area in the high temperature range. BET surface areas are presented in Table 1.

Table 1: BET surface areas and bulk properties

	SSA (m^2/g)	PV (cc/g)	PD (nm)
6 month Pt	59.1	0.120	6.4
1 month Pt	34.4	0.080	7.2
1 week Pt	31.5	0.072	9.5
Fresh Pt*	31	0.07	11.6
NiMg only Calcined at 600°C			

6 month NiMg	73.8	0.13	5.2
1month NiMg	36.3	0.087	11.4
1 week NiMg	27.0	0.06	11.4
Fresh NiMg	40	0.1	11.4
NiMg only Calcined at 800°C			
6 month NiMg	22.9/33.5	0.06/0.08	8.2/8.2
1month NiMg	28.9	0.07	7.2
1 week NiMg	35.0	0.1	11.3
Fresh NiMg	40	0.1	11.4

***From previous study**

It can be seen that the calcination temperature post poisoning has a significant effect on the surface are and bulk properties of the catalyst. For example, the 6 months poisoned catalyst calcined at 600°C had a surface area of 73.8 m^2/g whereas the catalyst calcined at 800°C had an average surface area of 28.2 m^2/g. The same trend was shown for the 1 month poisoned catalysts where the 800°C calcined catalyst had a lower surface area compared to the 600°C calcined catalyst. The only exception was the 1 week poisoned catalyst at 800°C which had a surface area of 35.0 m^2/g whereas the 600°C catalyst had a surface are of 27 m^2/g, however that is within experimental error.

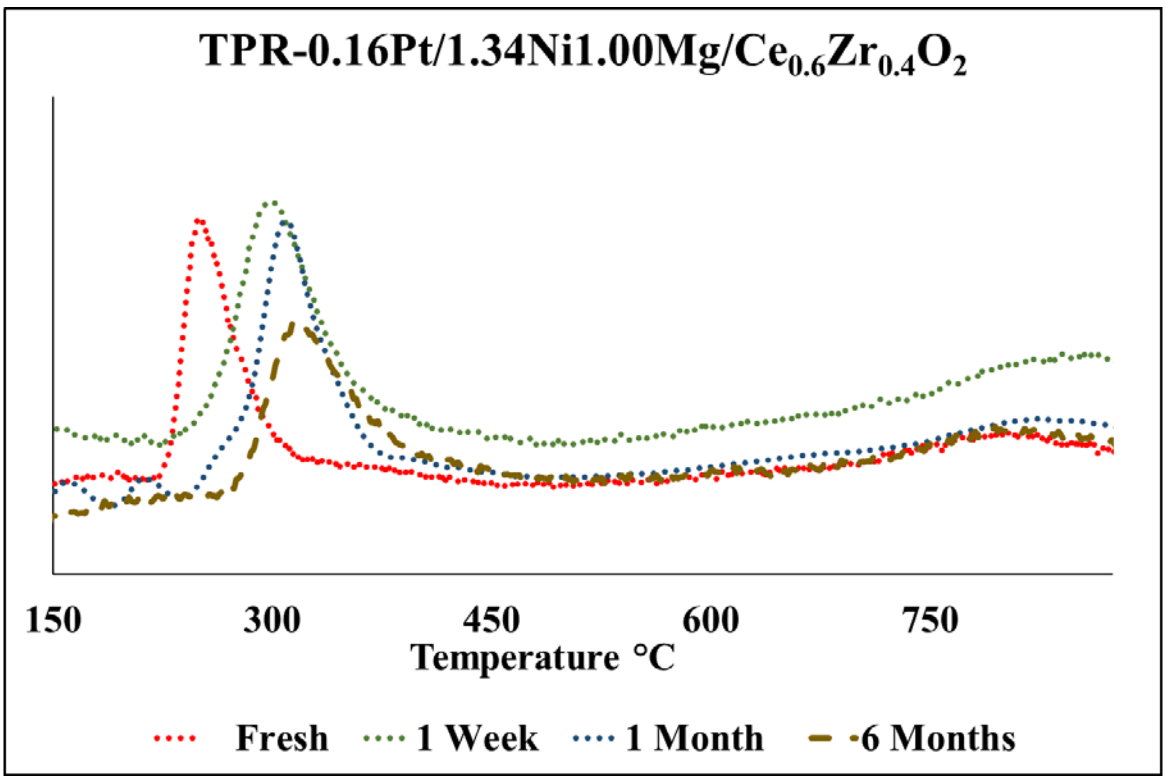

Figure 1: Temperature programmed reduction profile of 0.16Pt catalyst fresh and poisoned

TPR

Temperature programmed reduction (TPR) experiments were done to determine the reducibility of the catalyst and if siloxanes had an adverse effect. In Figure 1, the 0.16Pt catalyst is shown. From the figure, it can be seen that the fresh catalyst had the lowest reduction temperature at 248°C. Whereas addition of just 1 week's worth of silica has shifted the reduction temperature to 304°C. The same trend continues with 1 month having a reduction temperature of 311°C and 315°C for 6 months. This indicates that addition of silica to the catalyst has adversely affected the reduction temperature and will likely affect the reaction temperature as well. The same trend was also true for the NiMg only catalyst as can be seen in Figure 2. The unpoisoned catalyst had a reduction temperature of 382°C, the temperature increased with increased loadings of poison to reach a high of 546°C for the 6 months poisoned catalyst.

Finally, we have updated the costing literature review from the most recent quarterly report. It is shown in Table 2.

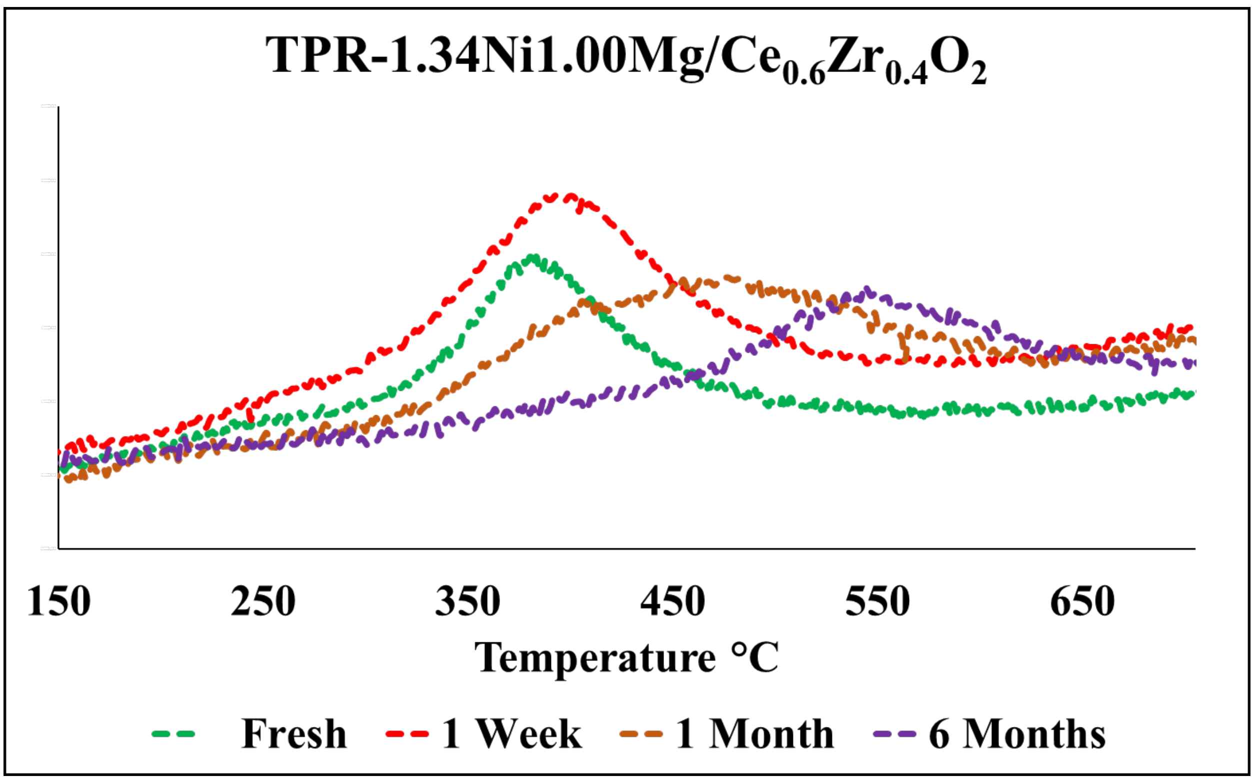

Figure 2: Temperature programmed reduction profile of NiMg catalyst fresh and poisoned

Furthermore, we have begun working on a simulation model using COMSOL® Multiphysics to model a variety of scenarios for flow and removal of siloxanes. This will help with developing a cost analysis and narrowing down the most efficient as well as economical removal technology and conditions.

Table 2: Cost analyses of biogas purification

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)	Kent thesis
1.36	H_2S (2000 ppm) Siloxane (n/a)	biological sulfur removal and condensation	0.01	2.17 (100% H_2S)	Gadde
"	"	Previous + 2 carbon beds	0.02	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)	"
1.8	H_2S (400 ppm) Others not quantified	Iron sponge, condenser, AC bed. & HT polisher	0.06	82 (~2% Si, ~0.4% Cl, 97% H_2S)	Papadias
2.2	H_2S (62 ppm) Others not quantified	"	0.04	271 (~1% Si, ~30% Cl, 69% H_2S)	"
0.94	H_2S (1000 ppm)	Fe adsorbent	0.03	6.6 [d]	Abatzoglou review)
"	H_2S (1000 ppm)	Na_2CO_3 /AC	0.04	22.5 [d]	Abatzoglou review)
133	H_2S (600 ppm) Siloxanes (0.5-1 ppm) Halogen (~5 ppm)	Varies (catalytic scrubbing, bio and biochemical scrubbing, and carbon and resin adsorption)	<0.01		Arnold review

“	“	Condensation and adsorption	0.025		“
Comparisons					
	H_2S only	AC bed	0.02 – 0.03		Mescia
	H_2S only	SulFerox		0.24-0.30	Mota
	H_2S only	H_2SPLUS (225 kg/d max)		2.20 (OP-EX only)	“
	H_2S (1000 ppm)	Sulfatreat	0.03	17.7	Abatzoglou review
	H_2S only	LoCat		0.45-1.2 (OP-EX only)	Arnold review
	H_2S only	Biological desulfurization		0.11 to 0.28	Sun review
	H_2S only	Iron chloride		0.96	“
	H_2S only	Impregnated activated carbon		4.34	“

[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. Rounded to 2 decimal places.
[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. From the sulferox fact sheet this makes it the most reasonable, which is in agreement with this review [38].
At 600 SCFM or 17 Nm^3/day, the daily flow is 2.5E4 Nm^3/day. At 700 ppm H_2S, the amount of Sulfur removed per day is 26 kg. From the fact sheet, this is in the disposable adsorption area.
This report specifies 35 ppm as US LFG average. [18] Using this average, the amount of sulfur removed decreases to 1.3 kg/day (at 600 SCFM) and 5.4 kg/day (at 2500 SCFM).
[d] A value seems incorrect in the reference, as the amount of adsorbent is 5 x greater amount , but 40 % less capacity.

Future Tasks: The future direction would be to continue to characterize the materials. We will be taking a closer look at the surface and structure of the catalyst using SEM. Then reaction studies will be done to determine the effect of the poisoning on the catalyst if any. The modeling will continue and various adsorbents and conditions will be studied before a detailed economic analysis can be done.

TAG Meetings:
A TAG meeting was not held during this reporting period.

Metrics:

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

   None. Two publications are in preparation.

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
   - An abstract have also been accepted for the AICHE annual meeting.

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. Submitted January 2016. $300,000 requested.

   PI: Kuhn, co-PIs: Ergas, Joseph and Zhang. "Flexible Process for Thermochemical Conversion of Biogas to Fuels and Chemicals" Concept paper invited for full submission to DOE EERE. Submitted February 2016. $2,000,000 requested.

   PI: Kuhn, co-PIs: Ergas, Joseph and Zhang. "Flexible Process for Thermochemical Conversion of Biogas to Fuels and Chemicals" Full proposal submitted to DOE EERE. $1,812,319 (total project cost with costshare = $2,026,429) requested.

   Subcontract PIs: Joseph and Kuhn. Very large team grant for Department of Energy, "Modular Chemical Process Intensification Institute for Clean Energy Manufacturing". Pending.

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 (4th year PhD student). Anthony Elwell is an undergraduate (senior) researcher also assisting with this research. The below pictures are of the team.