QUARTERLY PROGRESS REPORT

03/1/15 to 05/30/15

PROJECT TITLE: Single Step Conversion of Landfill Gas to Liquid Hydrocarbon Fuels

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Research Description:

This research project involves intensifying conversion of landfill gas to liquid hydrocarbon fuels to improve overall economics. The goal of the project is to develop and optimize a catalyst that can generate syngas from landfill gas via a dry and tri reforming process. The generated syngas can then be turned in a single step conversion process of methane into useable hydrocarbons using Fischer-Tropsch synthesis (FTS). To do so, the entire operation has to be done under low temperatures (T < 500°C) with at least 10% conversion of the reactants. A main challenge with this is to maintain the desired H_2: CO ratio of 2:1 for use in FTS while tuning the reforming processes to operate at similar conditions as the fuel synthesis.

Work Completed To-Date:

For the period outlined in this report, the same support comprised of $Ce_{0.6}Zr_{0.4}$ was loaded with palladium and/or nickel and magnesium. The synthesis was done using the same techniques used for the platinum samples. The support was synthesized using co-precipitation and the metals were loaded using wetness impregnation.

Characterization experiments were also done to determine the properties of the palladium loaded catalysts. Temperature-programmed reduction (TPR) experiments were done to determine the reduction temperatures of the three catalysts synthesized: 0.5%Pd/$Ce_{0.6}Zr_{0.4}$-8wt%Ni8wt%Mg, 2%Pd/$Ce_{0.6}Zr_{0.4}$-8wt%Ni8wt%Mg and 0.5%Pd/$Ce_{0.6}Zr_{0.4}$ (control sample). Results from the TPR studies are shown in Figure 1. From the figure, it can be seen that addition of palladium has improved the reduction temperature of the catalysts. However it is important to note that all three samples had two distinct reductio peaks and generally similar reduction profiles.

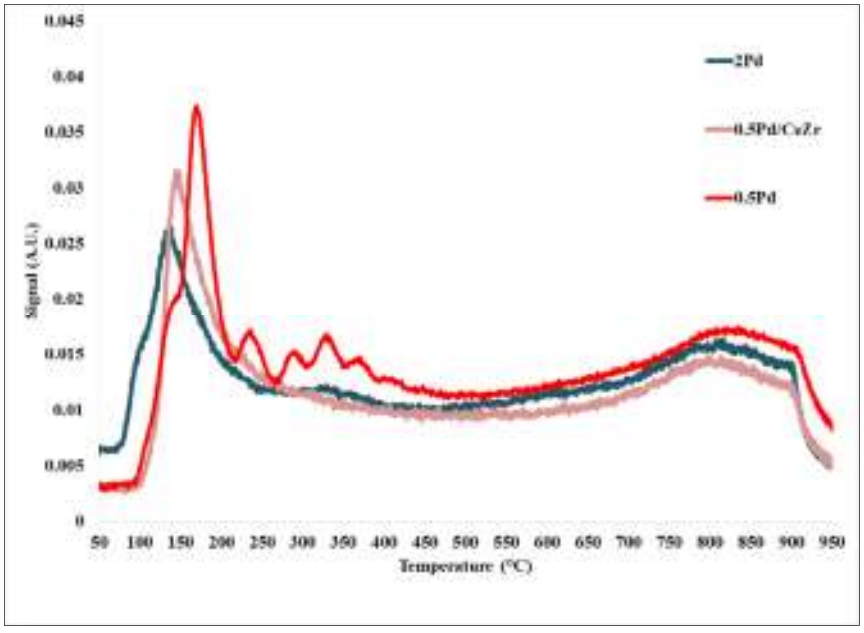

Figure 1: TPR of palladium loaded

Temperature-programmed desorption of carbon dioxide (TPD-CO_2) were also done on the catalysts to determine the basicity of the catalysts. The results are shown in Figure 2. From the figure, it is evident that the basicity of the catalyst increased with increasing palladium loading.

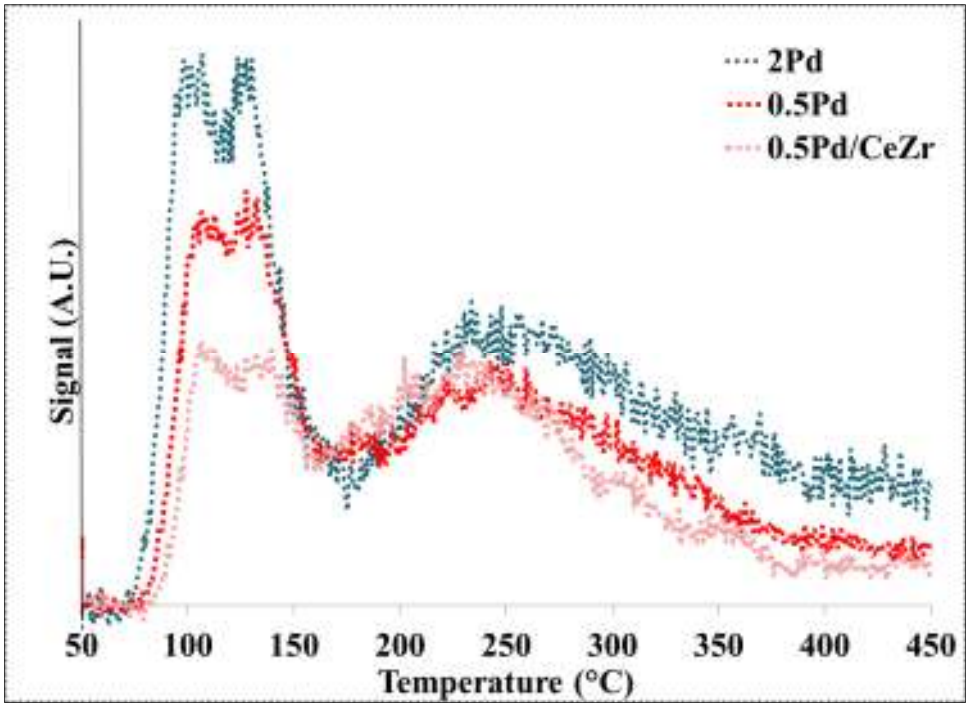

Figure 2: TPD-CO_2 of palladium loaded catalysts

Surface areas and pore volumes were obtained using BET and are summarized in the following table.

Sample	S_{BET} (m^2/g)	Pore Volume (cc/g)	Pore Diameter (nm)	Amount CO_2-desorbed (µmole/g.cat) (Temp 70-550°C)
0.5%Pd- $Ce_{0.6}$ $Zr_{0.4}$ O_2 - 8Ni8Mg	28	0.06	9.55	1.23
0.5%Pd- $Ce_{0.6}$ $Zr_{0.4}$ O_2	43	0.08	4.33	0.93
2%Pd- $Ce_{0.6}$ $Zr_{0.4}$ O_2 - 8Ni8Mg	24	0.11	9.56	2.91

Overall, as the metals were loaded onto the support, the surface area of the catalyst decreased. This is an expected outcome due to the blockage of some pores by the metals.

Future Tasks:

The future direction will be to test and compare the palladium catalysts to the findings of the platinum catalysts. In addition, steam reforming studies will be performed alongside the current dry reforming studies on both catalyst systems. Also, a project culmination report will be prepared and submitted.

TAG Meetings:

Our second TAG meeting was held on Monday March 9, 2015 and the project website has been updated.

TAG Members:

Canan "Janan" Balaban	Asst. Director	Florida Energy Systems Consortium
Roger Lescrynski	Solid Waste Project Manager	Public Works - Solid Waste Division
Tino Prado	Engineer, Owner	Prado Tech.
Tim Roberge	Engineer	Oxy
John Schert	Executive Director	Hinkley Center
Devin Walker	Process Engineer	BASF
Matt Yung	Researcher	Nat. Renewable Energy Lab
Sam Levin	President	S2Li
Kelsi Oswald	Director	Pinellas County Dept. of Solid Waste

Project Website Address (URL): (http://www.eng.usf.edu/~jnkuhn/Hinkley.html)

Informational Dissemination:

Several poster presentations and a talk have already been done. A manuscript has been accepted and another is about to be submitted. The list is below under metric 4.

Metrics:

1. List graduate or postdoctoral researchers funded by THIS Hinkley Center project.

Name	Rank	Dept.	Institution	Professor
Elsayed,	3rd year PhD	Chemical	USF	Kuhn/Joseph

Nada	student	Engineering		

*2. List undergraduate researchers working on **THIS** Hinkley Center project.*

First Name	Last Name	Institution	Professor
Nathan	Roberts	USF	Kuhn/Joseph
Tyler	Hickerson	USF	Kuhn/Joseph
Roxann	West	USF	Kuhn/Joseph
Gabriel	Guevara	USF	Kuhn/Joseph
Jing	Lin	USF	Kuhn/Joseph

*3. List research publications resulting from **THIS** Hinkley Center projects.*

A first manuscript entitled "Low temperature dry reforming of methane over Pt-Ni-Mg/ceria-zirconia catalysts" has been published in Applied Catalysis B: Environmental. (doi:10.1016/j.apcatb.2015.05.021)

> Elsayed, N.H., Roberts, N., Joseph, B., and Kuhn, J.N., "Low temperature dry reforming of methane over Pt-Ni-Mg/ceria-zirconia catalysts" accepted in *Applied Catalysis B: Environmental*.

An invited manuscript to a special issue (in *Topics in Catalysis*) on renewable fuels will be submitted in early June.

*4. List research presentations resulting from **THIS** Hinkley Center project.*

The work was presented at:

a) A talk was presented at the 2014 FAME conference
b) 2014 USF Graduate and Postdoc Research Symposium.
c) 2014 UG Research and Arts Colloquium
d) Two posters at the 38th International Phosphate Fertilizer & Sulfuric Acid Technology Conference
e) A poster presented at the SWANA 2014 summer conference
f) A poster presented at the Southeastern Catalysis Society 2014 annual meeting
g) A poster presented at the College of Engineering Research Day 2014
h) An abstract accepted to the 2015 North American Catalysis Society Meeting
i) An abstract has been submitted to 2015 AICHE meeting

*5. How have the research results from **THIS** Hinkley Center project been leveraged to secure additional research funding?*

The initial results from this project were used as preliminary data for a proposal submitted to NSF. We heard back in July. Although two of the reviewers rated the proposal as "excellent" (which is the highest rating) and two reviewers rated the proposal as "very

good" (which is the second highest rating), it was not selected for funding. A revised proposal will be submitted in Nov. 2015.

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

We have none at this time.

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

They have not been used at this time.

Student Researchers:

The primary student researcher on this project is Nada Elsayed. With this project, Nada was able to join the group as a PhD student. Nada is seen below in the lab while loading a reactor with one of the catalysts she synthesized. An undergraduate student, Nathan Roberts, is also working on this project. His efforts are aimed at catalyst synthesis at this time. Additionally, a senior design group is contributing by conducting a techno-economic analysis of the intensified catalyst system.

Seen in the picture is Nada Elsayed