QUARTERLY PROGRESS REPORT

09/1/14 to 11/30/14

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 fifth report, temperature programmed desorption (TPD) studies were done to determine catalyst basicity. Desorption studies were done for both carbon dioxide (CO_2) and methane (CH_4). The data was then analyzed to determine the amount of CO_2 and CH_4 adsorbed onto each catalyst if any.

Temperature-Programmed Desorption (TPD) Experiments:

Desorption studies were done using a Cirrus MKS mass spectrometer. The catalyst is placed inside a u-tube reactor cushioned by inert glass wool on either side. The reactor is placed in-line with the feed stream and placed inside a u-tube furnace. The catalyst is initially reduced under a 5% H_2 in He gas mixture at 300°C for one hour. The catalyst is then cooled to 50°C under He gas only. Upon stabilization of temperature, a 10% CO_2 in He mixture is introduced for 30 mins. The catalyst is then purged with He alone for another 30 mins. Finally the temperature is increased to 800°C at a 10°C/min ramp rate and held for 10 minutes. The same procedure was done using CH_4 instead of the CO_2.

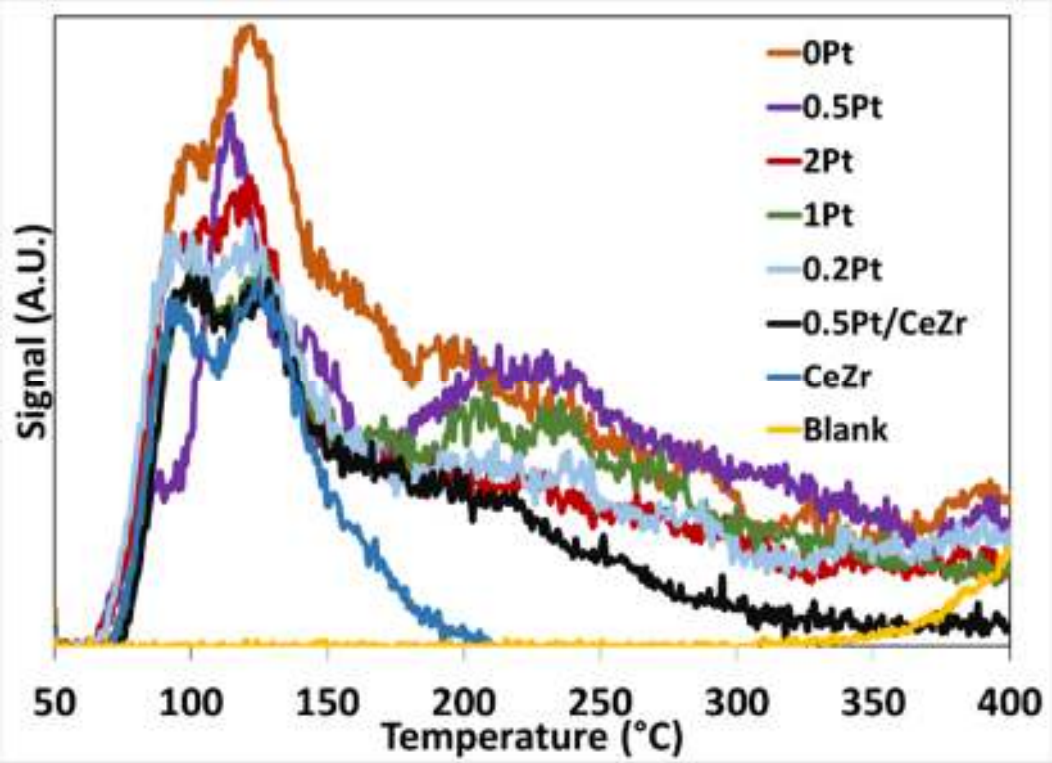

Figure 1: CO_2- Temperature programmed desorption profiles.

An example of an output profile of the temperature programmed desorption experiment can be seen in figure 1. The results from all the desorption experiments are given in table 1. As expected, the addition of platinum reduced the amount of basic sites in the catalyst. The catalyst with the most platinum (2%), had a significantly smaller amount of CO_2 desorbed compared to the catalyst with no platinum but only nickel and magnesium. The highest amount of CO_2 desorbed was 1.40µmole/g.cat which was on the nickel magnesium catalyst without platinum. The support alone only desorbed 0.38µmole/g.cat which is not surprising since there were no metals loaded.

Table 1: Conversion results

Sample	**Notation**	**Amount CO_2-desorbed (µmole/g.cat) (Temp 50-400°C)**
$Ce_{0.6}\ Zr_{0.4}\ O_2$	CeZr	0.38
0.5%Pt- $Ce_{0.6}\ Zr_{0.4}\ O_2$	0.5Pt/ CeZr	0.71

$Ce_{0.6}$ $Zr_{0.4}$ O_2 - 8Ni8Mg	0Pt	1.40
0.2%Pt- $Ce_{0.6}$ $Zr_{0.4}$ O_2 -8Ni8Mg	0.2Pt	1.29
0.5%Pt- $Ce_{0.6}$ $Zr_{0.4}$ O_2 -8Ni8Mg	0.5Pt	1.30
1%Pt- $Ce_{0.6}$ $Zr_{0.4}$ O_2 - 8Ni8Mg	1Pt	1.07
2%Pt- $Ce_{0.6}$ $Zr_{0.4}$ O_2 - 8Ni8Mg	2Pt	0.98

Methane desorption studies were also done using the same system described for the CO_2 desorption studies. However, under the experimental conditions used, no quantifiable amount of methane was desorbed.

Future Tasks:

The future direction will be to do steady state experiments and time on stream experiments. In addition, other precious metal based catalysts will be synthesized, characterized and compared to the current findings of the platinum catalysts.

TAG Meetings:

Our first TAG meeting was held on April 2nd, 2014. The date for the next TAG meeting will be determined in the very near future.

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

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 written and is currently under editorial review. 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, Nada	2nd year PhD student	Chemical Engineering	USF	Kuhn/Joseph

*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.*

We have none at this time. A first manuscript entitled "Low temperature dry reforming of methane over Pt-Ni-Mg/ceria-zirconia catalysts" has been submitted for publication and is currently under peer-review.

*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 submitted to the 2015 North American Catalysis Society 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 in Feb. 2014. 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 was submitted in Nov. 2014 and is currently under review.

*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