QUARTERLY PROGRESS REPORT

02/28/14 to 05/31/14

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

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COMPLETION DATE: 05/28/2014

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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 third report, the previously synthesized catalysts were characterized using temperature programmed reduction (TPR). This technique helps to characterize the catalyst's reducibility. Hydrogen gas is adsorbed on the metal oxide surface and then the reduction occurs from which oxygen from the sample combines with hydrogen to form water. This in turn generates a curve that is proportional to the extent of reduction as a function of temperature. This determines the best reduction temperature to achieve the active metal phase, which assists in demonstrating low temperature conversion. In addition, it helps to show how different species within the catalyst interact and affect each other. [1, 2]

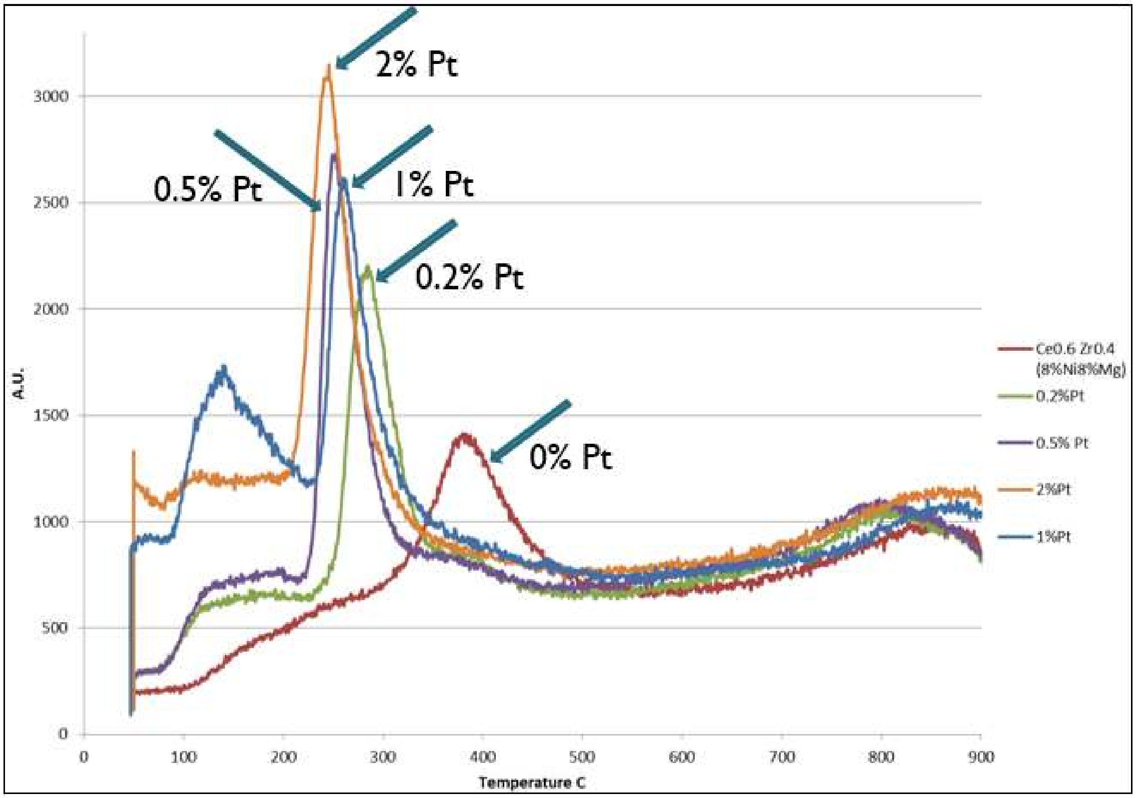

Figure 1: Temperature programmed reduction profiles of synthesized catalysts.

The results of the temperature programmed reduction experiments can be seen in figure 1. The catalyst without any platinum content reduced at a much higher temperature than catalysts with platinum. As the platinum content increased, the reduction temperature was successfully decreased as evident in figure 1 above. The following table summarizes the findings of the reduction profile.

Table 1: TPR of synthesized catalysts

Sample	Reduction Temperature (°C)
Support : $Ce_{0.6}Zr_{0.4}O_2$ (8%Ni 8%Mg)	382
Support + 0.2%Pt	283
Support + 0.5%Pt	248
Support + 1%Pt	*247
Support + 2%Pt	242

*Two different synthesized samples were tested and the average of the two is reported.

Preliminary reaction experiments were also carried out to determine the temperature where 10% conversion of methane occurs. The experiments were performed in a lab-scale microreactor at atmospheric pressure, with the products being analyzed by a Cirrus MKS Mass spectrometer. The feed composition was 10% CH_4 and 10% CO_2 with a He balance, and the total flow rate was 50 SCCM. The catalyst amount used was 75.4-75.7 mg. The temperature was controlled via heating from 50°C to 900°C at a ramp rate of 10°C/min.

As expected, the conversion temperature was highest with the nickel/magnesium only catalyst. Adding platinum helped lower the conversion temperature. This is consistent with the results from the TPR.

Sample	10% CH_4 Conversion Temperature (°C)
Support : Ce 0.6 Zr 0.4 (8%Ni 8%Mg)	762
Support + 0.2%Pt	464
Support + 0.5%Pt	454
Support + 1%Pt	500*
Support + 2%Pt	511

*Two different synthesized samples were tested and the average of the two is reported.

Future Tasks:

The future direction will be to choose the optimum catalyst that effectively reforms methane at a low temperature. Then a reaction temperature will be chosen. The catalyst will then be tested at the reaction temperature for time-on-stream studies.

TAG Meetings:

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

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 have already been done and three abstracts were accepted for upcoming summer conferences. 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.

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

The work was presented at:

a) 2014 USF Graduate and Postdoc Research Symposium.
b) 2014 UG Research and Arts Colloquium
c) Two accepted abstracts for the 38th International Phosphate Fertilizer & Sulfuric Acid Technology Conference
d) An abstract accepted for the SWANA 2014 summer conference

*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 expect to hear back in August 2014.

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

We have none at this time. We expect this to become more prominent as we present our results.

*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

References:

[1] D.M. Walker, S.L. Pettit, J.T. Wolan, J.N. Kuhn, Applied Catalysis A: General 445 (2012) 61-68.

[2] F. Giordano, A. Trovarelli, C. de Leitenburg, M. Giona, Journal of Catalysis 193 (2000) 273-282.