QUARTERLY PROGRESS REPORT

12/1/14 to 02/28/15

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 sixth report, reaction experiments were done to determine the temperature at which 10% methane (X_{10}) converts. In addition, a time on stream study was done to determine the stability of the optimum catalyst (0.5%Pt/8%Ni8%Mg-$Ce_{0.6}Zr_{0.4}$) which will be referred to as 0.5%Pt from now on. The experiment included a 3-hour time on stream followed by a temperature programmed oxidation experiment (TPO). The oxidation experiment was done to determine if surface coke developed which is an indication of catalyst poisoning.

Reaction testing was done on all catalysts to determine X_{10} conversion temperature of methane. Figure 1 outlines the temperature results of all catalysts. It can be seen that the lowest conversion temperature was obtained from the 0.5%Pt catalyst seen by the blue bar.

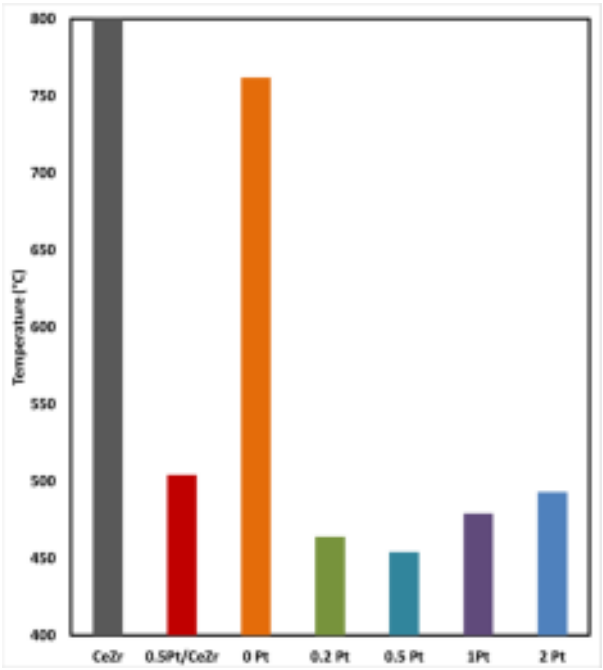

Figure 1: Methane X_{10} conversion temperatures of synthesized catalysts

Single temperature- time on stream study:

Time on stream 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 200°C under He gas only. Upon stabilization of temperature, Methane and carbon dioxide, (both 99.999% pure from airgas), were introduced in a 1:1 ratio with a total composition of 20% reactants in He gas (50 sccm total flow). Finally the temperature is increased to 450°C at a 10°C/min ramp rate and held for 3 hours. Results obtained from the experiment are shown in figure 2.

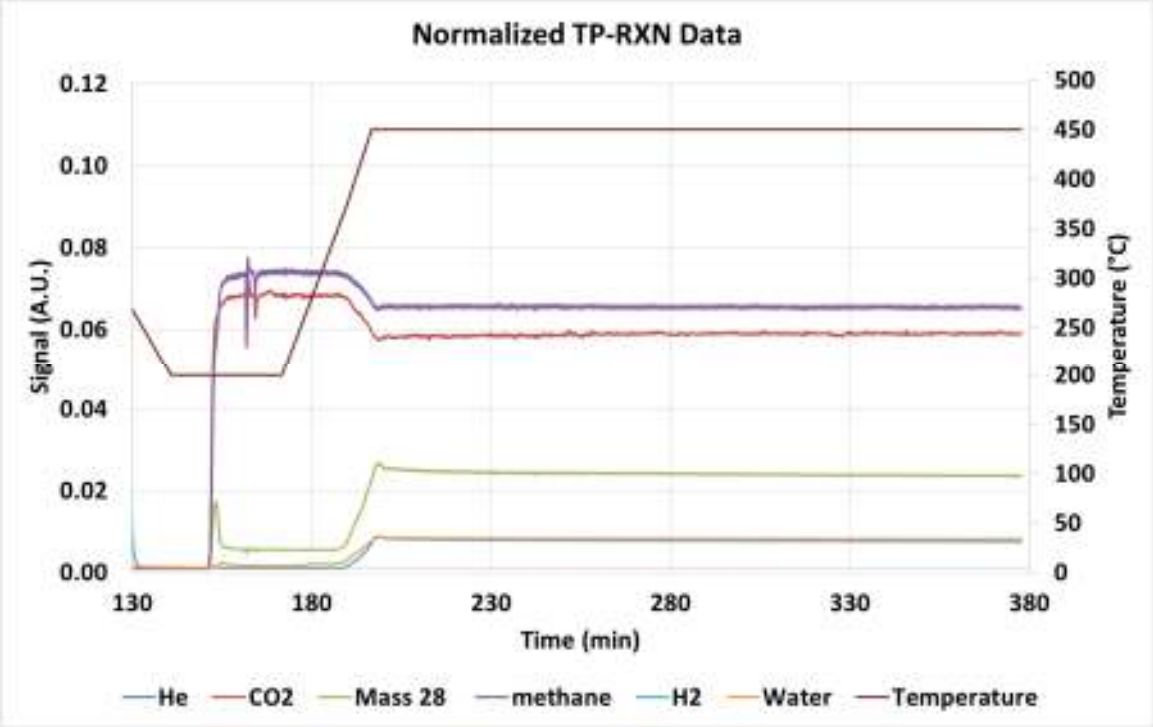

Figure 2: Steady State reaction of 0.5%Pt catalyst at 1atm and 450°C.

It can be seen from figure 2 that there is conversion for both reactants (methane and carbon dioxide). More importantly, 10% conversion of methane (X_{10}) was detected at 447°C which is below our target temperature limit. Additionally, 10% conversion of carbon dioxide was detected at 435°C. As can be seen from the above graph, the catalyst displayed no deactivation when left on stream for three hours.

A temperature programmed oxidation (TPO) study was done immediately following the steady state reaction study. After the steady state experiment, the catalyst was rapidly cooled to 60°C under helium only. A 10% oxygen in He gas mixture was then introduced to the catalyst while maintaining the overall flow rate. The temperature was then increased to 900°C using a 10°C/min ramp rate and held for one hour. No coke formation was detected on the catalyst.

Future Tasks:

The future direction will be to study other precious metal based catalysts. Another precious metal-based catalyst will be synthesized, characterized and compared to the current findings of the platinum catalysts. In addition, steam reforming studies will be performed alongside the current dry reforming studies.

TAG Meetings:

Our first TAG meeting was held on April 2nd, 2014. The date for the next TAG meeting is scheduled for Monday March 9, 2015. It is at USF at 2 pm.

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 peer-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	3rd 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 was accepted 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 several grants which received favorable ratings. It is currently under review at the DOE and NSF is being targeted for the fall CBET submission window.

*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