QUARTERLY PROGRESS REPORT

12/1/13 to 02/28/14

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 ($T < 500°C$). A main challenge with 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 second report, several catalysts were synthesized and extensively characterized. The challenge faced at this stage included synthesizing the catalyst with the optimal formulation to achieve our low temperature reforming goal and characterizing it.

Figure 1: Shows the synthesized catalysts. (1)Ceria Zirconia support, (2) Support with nickel and magnesium loadings, (3-6) Support with 1:1 nickel:magnesium and various platinum loadings.

The approach used to solve these obstacles included synthesizing a support made of a single composition of 60% ceria and 40% zirconia $(Ce_{0.6}Zr_{0.4})O_2$ via a co-precipitation method. This ratio was used because of a previous work by Walker et al.[1] that showed this ratio to have the best performance.

The support was then doped with a 1:1 ratio of nickel to magnesium that was equal to 8% of each by weight of the catalyst. This is done because as a catalyst, Ni promotes methane and water, which ultimately enhances hydrogen production. The magnesium is added because it also enhances the carbon dioxide adsorption but it also acts as a stabilizer to prevent the aggregation of the nickel.

In addition, the different platinum loadings were added to this metal supported catalyst that ranged from 0.2% to 2% by weight of platinum as can be seen in figure 1 above. Platinum is added in order to enhance the reduction for the reforming process as it activates the methane at lower temperatures. In addition, platinum helps to minimize coke formation. Several different loadings of platinum were added to the catalyst support in order to test and determine the optimum catalyst that will lower the conversion temperature.

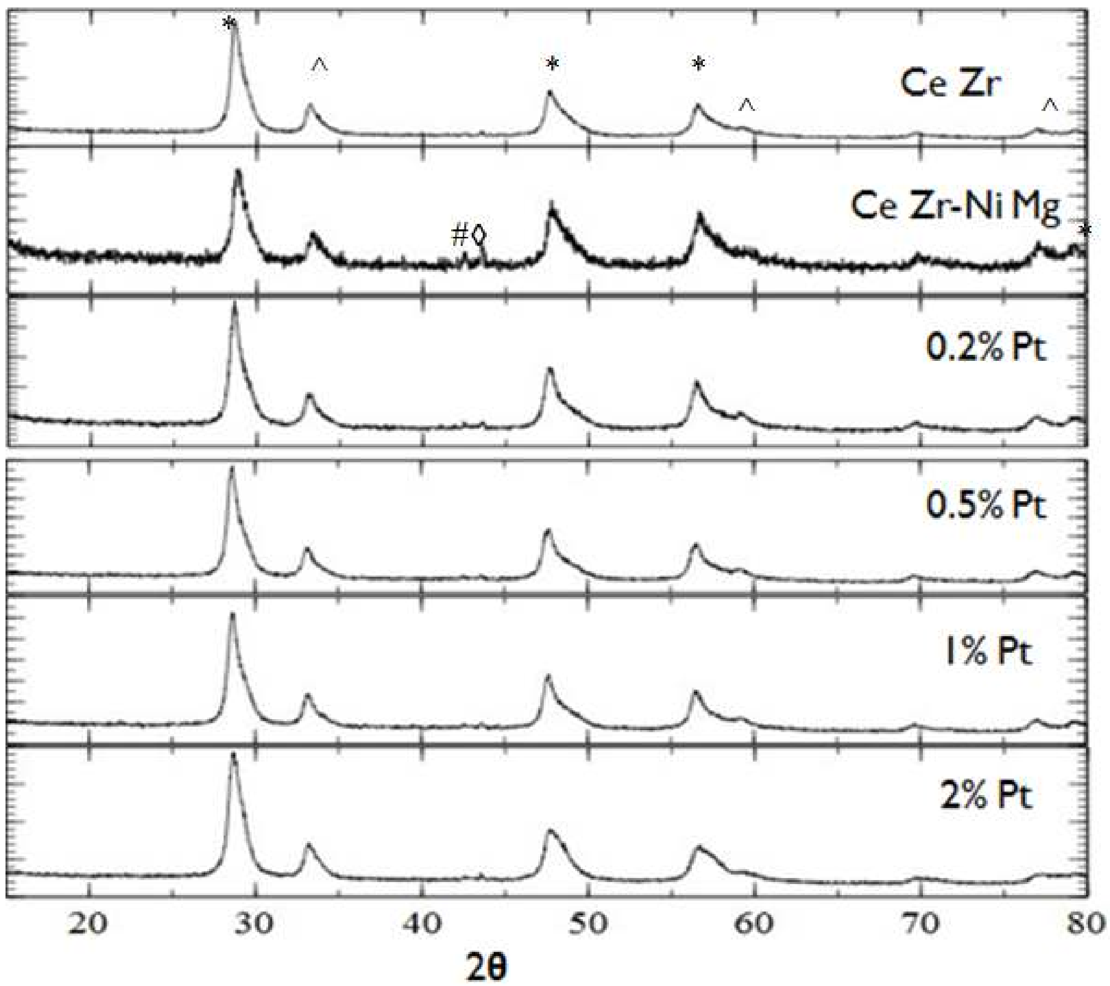

Figure 2: XRD of synthesized catalysts. (*) CeO_2, (^) ZrO_2, (#) NiO, (◊) MgO.

The synthesized catalysts were characterized using x-ray diffraction (XRD) and the surface areas were obtained using BET. The XRD results are shown below in figure 2. The first XRD graph shown at the top was of the $Ce_{0.6}Zr_{0.4}$ support. Only CeO_2 and ZrO_2 were seen as expected. Once the nickel and magnesium were loaded onto the support, the XRD of that catalyst shows NiO and MgO diffraction lines as denoted by the (#) and (◊) symbols respectively. The remaining XRD graphs are for the catalysts with different platinum loadings. It is important to point out that as expected no significant diffraction line shifts were observed in those samples because platinum is present in small amounts.

A quantachrome Autosorb IQ was used to get the BET surface areas of the synthesized catalysts. Table 1 below shows the surface areas in m^2/gram of catalyst.

Table 1: BET surface areas of synthesized catalysts

Sample	Surface Area (m^2/g)
Ce 0.6 Zr 0.4 (8%Ni 8%Mg)	40.1
0.2%Pt	29. 4
0.5%Pt	33.2
1%Pt	36.2
2%Pt	21.9

The catalyst that had the largest surface area was the one without any platinum loaded on it. This is expected as the addition of platinum can reduce the surface area because it may block some pores or fill them in completely.

Future Tasks:

The future direction would be to ensure that the catalyst synthesized will be effective by completing the characterization in order to begin the reforming experiments. At this point, we have begun to characterize the catalyst using x-ray diffraction (XRD), and identifying the surface area using BET. Those characterization techniques will help to show the crystal structure and the surface area of the catalyst. The next characterization technique will be temperature programmed reduction (TPR) to determine the reducibility of the catalyst. After the characterization is complete and the optimum catalyst is chosen, reaction and reforming experiments will be done to test the catalyst's performance.

TAG Meetings:

Our first TAG meeting is planned for April 2014. We will be sending out the details 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:

We have submitted two abstracts for this work.

Metrics:

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

Name	Rank	Dept.	Institution	Professor
Elsayed, Nada	2^{nd} 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.*

We have none at this time. We have two abstracts submitted.

*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. Yolanda Daza is a senior group member in the PI's group and offering assistance to Nada with some aspects of the project. We are recruiting an undergraduate research to also assist with this research. 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 Yolanda Daza(left) and Nada Elsayed (right).

References:

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