QUARTERLY PROGRESS REPORT

05/31/14 to 08/31/14

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 fourth report, another catalyst (a control sample) was synthesized. This catalyst does not contain nickel or magnesium but only contains platinum on the support. The catalyst was characterized as before using temperature-programmed reduction (TPR), N_2 physisorption, and XRD. This catalyst was synthesized to determine the effect of platinum only on the reforming reaction. Reaction experiments were done on all the catalysts and the methane and carbon dioxide 10% and 50% conversion rates were obtained. In addition, temperature-programmed oxidation (TPO) experiments were done immediately following the reaction experiments to determine if coke forms.

Temperature-Programmed Reaction (TP-rxn) Experiments:

TP-rxn experiments were carried out to determine the temperature where 10% and 50% conversion of methane and carbon dioxide 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% CH4 and 10% CO2 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.

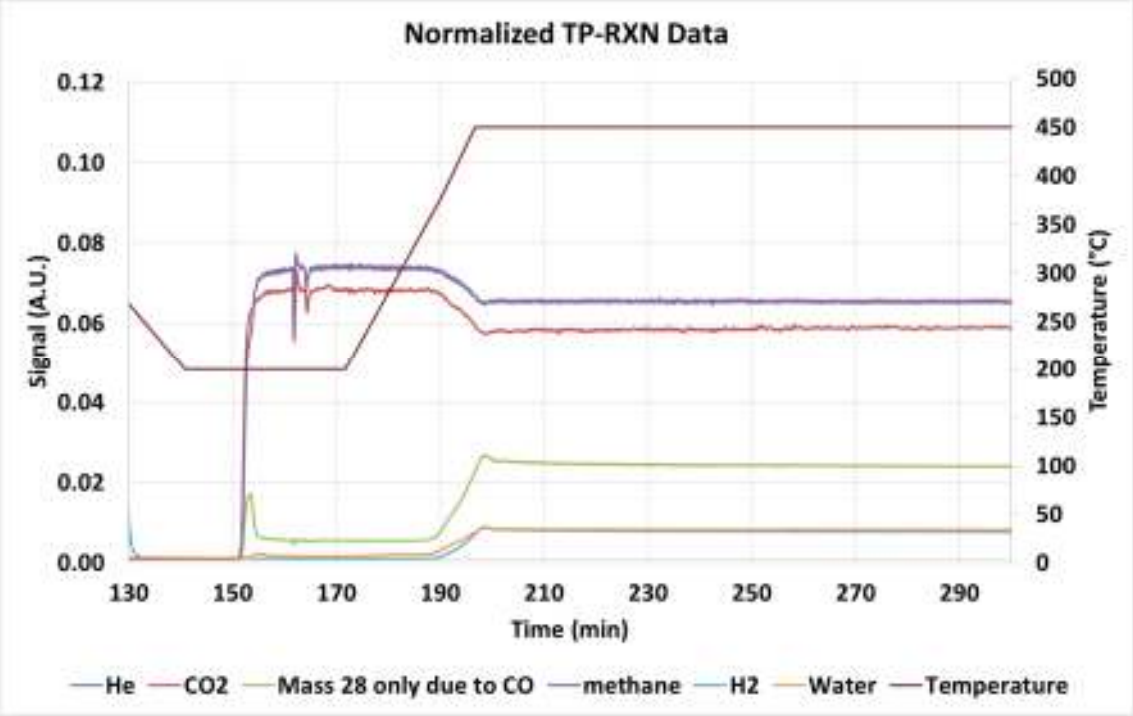


Figure 1: Temperature programmed reaction profiles of 0.5%Pt-8%Ni8%Mg/CeZr catalyst.

An example of an output profile of the temperature programmed reaction experiment can be seen in figure 1. The results from all the reaction experiments are given in table 1. As expected, the support had the highest conversion temperature for methane. Ten percent conversion of methane (X_{10}) was at a temperature of 828°C when no metals were loaded. Whereas 10% conversion of carbon dioxide occurred at 787°C for the support. The newly synthesized catalyst, referred to as sample 2 in table 1; contained no nickel or magnesium helped convert methane at 504°C and carbon dioxide at 759°C. These conversion temperatures were lower than sample 3 which contained nickel and magnesium but no platinum. Sample 3 showed 10% methane conversion at 762°C and 10% carbon dioxide conversion at 742°C. Addition of small amounts of platinum significantly decreased the conversion temperature. The lowest conversion temperatures were achieved at 454°C for methane and 432°C for carbon dioxide.

Table 1: Conversion results

	Sample	X_{10} CH_4 Conversion Temp (°C)	X_{50} CH_4 Conversion Temp (°C)	X_{10} CO_2 Conversion Temp (°C)	X_{50} CO_2 Conversion Temp (°C)
1	**CeZr[a]**	828	n/a	787	n/a

2	**0.5Pt/CeZr**	504	641	759	810
3	**8%Ni8%Mg/CeZr**	762	848	742	813
4	**0.2Pt-8%Ni8%Mg/CeZr**	464	611	450	586
5	**0.5Pt-8%Ni8%Mg/CeZr**	454	603	432	578
6	**1Pt*-8%Ni8%Mg/CeZr**	479	608	467	590
7	**2Pt-8%Ni8%Mg/CeZr**	493	613	479	595

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

[a] CeZr indicates $Ce_{0.6}Zr_{0.4}O_2$ as support in all catalysts

Temperature-programmed oxidation (TPO) studies were done following the reaction experiments. These studies help to quantify the presence of coke on the surface of the catalyst. The studies are done in the same setup as the TP-rxn experiments. After the TP-rxn experiments, the catalyst is rapidly cooled to 60°C under inert helium. Then a 10% oxygen in helium gas mixture is introduced. The temperature is then increased to 900°C at 10°C/min ramp rate and held for one hour. From these tests, no coke formation was detected on any of the catalysts.

Future Tasks:

The future direction will be to do steady state experiments and time on stream experiments. In addition, temperature programmed desorption studies will be done to quantify adsorbed carbon dioxide.

TAG Meetings:

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

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) 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) An accepted abstract to the Southeastern Catalysis Society 2014 annual 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. This NSF program next had a deadline in Nov. 2014.

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

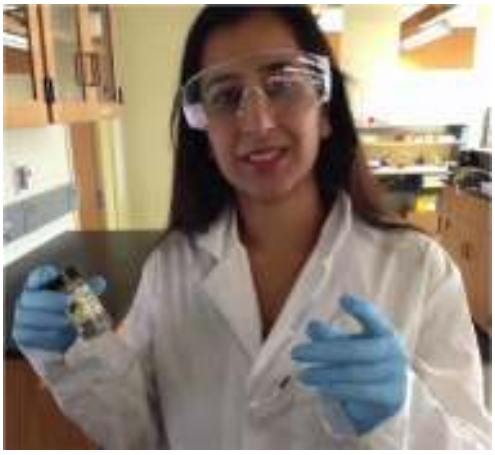
We have none at this time. We expect this to become more prominent as we present our results. We have had one conference call from a lead (from students attending the recent SWANA meeting) and another conference call is scheduled. .

*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