On-Demand Reactivity Enhancement to Enable Advanced Low Temperature Natural Gas Internal Combustion Engines

Will Northrop – Principal Investigator
Annual Merit Review and Peer Evaluation Meeting
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Project ID: ft086

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Project Overview

Timeline

Project Start Date: 5/1/2018
Project End Date: 6/30/2021
Percent Complete: 25%

Barriers
Lean/Dilute Natural Gas Combustion:
• Methane is a highly stable fuel - requires high ignition energy in lean/dilute conditions
• Cannot be easily used in any advanced compression ignition modes
• Poor low temperature oxidation of methane in existing exhaust aftertreatment catalysts

Budget

Total Project Funding:
  DOE Share = $1,102,367
  Contractor = $294,358
FY 2018 Funding = $25,334
FY 2019 Funding* = $173,599
  * through 5/1/2019

Partners

[Logos of University of Minnesota and Johnson Matthey]
Relevance/Objectives

• Overall Objectives

Demonstrate ≥10% indicated efficiency improvement compared to state-of-the-art lean-burn Natural Gas (NG) dedicated spark ignition (DSI) engine by using fuel pretreatment by oxidative coupling of methane (OCM)

• Objectives in this Period

Experiments and modeling to demonstrate capability of the short contact time reactor to achieve desired OCM conversion and selectivity
# Milestones

<table>
<thead>
<tr>
<th>Tasks/Milestones</th>
<th>Budget Period 1</th>
<th>Budget Period 2</th>
<th>Budget Period 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FY18 Q1</td>
<td>FY19 Q2</td>
<td>FY20 Q3</td>
</tr>
<tr>
<td>1. Perform Bench-Scale Short-Contact Reactor Studies (UMN)</td>
<td>M1.1</td>
<td>M12.1</td>
<td>M13.1</td>
</tr>
<tr>
<td>2. Develop Highly Effective OCM Catalysts and Wash-Coat Technology (JM)</td>
<td>M2.1</td>
<td>M2.2</td>
<td></td>
</tr>
<tr>
<td>3. Design and Characterize Single Cylinder Engine and Reactor System (All)</td>
<td>M3.1</td>
<td>M3.2</td>
<td>M3.3, D3.1</td>
</tr>
<tr>
<td>4. Use CFD Modeling to Guide Reactor Design and LTCI Engine Combustion (CMU)</td>
<td>M4.1</td>
<td>M4.2</td>
<td>M4.3, M4.4, M4.5</td>
</tr>
<tr>
<td>5. Prove NG Engine Efficiency Gains Through 1-D Modeling</td>
<td>M5.1</td>
<td></td>
<td>M5.2</td>
</tr>
</tbody>
</table>

- **Completed**
- **To be Completed**
- **Current**
Approach

- Oxidative coupling of methane introduction
  - Proposed industrially to produce ethylene from natural gas
  - Low conversion and potential for unselective oxidation
  - Oxygen utilization is a challenge - leads to unselective oxidation
  - Could be used to enhance the reactivity of natural gas for engines

Selective oxidation

$$2CH_4 + \frac{1}{2} O_2 \rightarrow C_2H_6 + H_2O$$

$$C_2H_6 + \frac{1}{2} O_2 \rightarrow C_2H_4 + H_2O$$

Unselective oxidation

$$CH_4 + O_2 \rightarrow CO + H_2O + H_2$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
Approach

• Integrate OCM into a reformed exhaust gas recirculation scheme to enable advanced dilute combustion modes
• Use new short-contact time reactor to avoid oxygen utilization problems found in large-scale reactors
Technical Accomplishments

**Task 1:** Bench scale reactor completed and partial oxidation reforming catalyst tested

- Derived from previous work under NSF project
- Opposed flow reactor avoids oxygen distribution problem in OCM
- Partial oxidation experiments conducted
Technical Accomplishments

Task 1: Flow visualized to determine pressure drop through catalytic mesh

- Mesh did not affect the flow in the center region
- The flow direction was changed at the edge by the mesh
Technical Accomplishments

**Task 2:** Catalysts evaluated: integral micro-reactor
- Sr/La$_2$O$_3$ catalyst: better low temperature conversion
- Coated meshes provided for opposed flow reactor

**LaSr/CaO**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Methane conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600°C</td>
<td>40.6</td>
</tr>
<tr>
<td>650°C</td>
<td>43.0</td>
</tr>
<tr>
<td>700°C</td>
<td>44.3</td>
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</table>

<table>
<thead>
<tr>
<th>Temperature</th>
<th>C2 selectivity (%)</th>
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</thead>
<tbody>
<tr>
<td>600°C</td>
<td>29.0</td>
</tr>
<tr>
<td>650°C</td>
<td>25.1</td>
</tr>
<tr>
<td>700°C</td>
<td>22.9</td>
</tr>
</tbody>
</table>

**Sr/La$_2$O$_3$**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Methane conversion (%)</th>
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<tr>
<td>600°C</td>
<td>19.8</td>
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<tr>
<td>650°C</td>
<td>14.3</td>
</tr>
<tr>
<td>700°C</td>
<td>15.1</td>
</tr>
</tbody>
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</tr>
<tr>
<td>650°C</td>
<td>36.2</td>
</tr>
<tr>
<td>700°C</td>
<td>35.6</td>
</tr>
</tbody>
</table>

Testing conditions
- Space velocity 50,000 to 100,000 h$^{-1}$
- CH$_4$/O$_2$ ratio from 2:1 to 6:1 molar
- Temperature 600-700°C

Presented here
- Space velocity 50,000 h$^{-1}$
- CH$_4$/O$_2$ ratio 2:1 or 6:1 molar
- Temperature 600-700°C

2:1 CH$_4$/O$_2$ lean
6:1 CH$_4$/O$_2$ rich
Technical Accomplishments

**Task 3:** Two approaches for engine scale reactor considered: opposed flow and traditional monolith reactors

- CFR reactor set up to study autoignition
- Short contact, better $O_2$ utilization
- Residence time may not be sufficient
- Rich reaction with fresh air may be required to mitigate LHV loss

![Graph showing %LHV loss vs. C/O ratio](image)
**Technical Accomplishments**

**Task 4:** Bench-scale short contact time reactor modeled in Fluent and Converge

- Reacting and non-reacting cases modeled
- Reacting cases use literature partial oxidation mechanism

![Non-Reacting CH₄ Comparison](image)

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**Modeling Domain**

- Oxidizer
- Catalytic mesh
- CH₄

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![Diagram of reactor](image)
Technical Accomplishments

**Task 4: Engine-scale CFD model constructed in Converge**

- Gas distribution studied
- Completed non-reacting cases
- Waiting for validation of kinetics for Sr/La$_2$O$_3$ catalyst

![Computational Domain Diagram]

- Gas distribution studied
- Completed non-reacting cases
- Waiting for validation of kinetics for Sr/La$_2$O$_3$ catalyst
This is the first year the project has been presented
Partnerships/Collaborations

Partners

- OCM catalyst research and development
- Catalyst wash-coating for bench and engine-scale reactors
- Computational fluid dynamics of reactors and engines
- Supporting low-dimensional engine modeling efforts

Collaborators

- Provided OCM kinetics for modeling efforts
Remaining Challenges and Barriers

- Achieving acceptable conversion and selectivity over provided OCM catalysts using bench-scale reactor

- OCM reaction is more difficult than reforming:
  - Deactivation at $T > 900^\circ C$
  - Low activity at $T < 600^\circ C$

- Determine appropriate OCM stoichiometry to limit heating value loss – balance with engine efficiency gain

- Short contact time may not achieve sufficient conversion of methane – OCM consists of series of gas + surface phase reactions\(^1\)

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Proposed Future Research

To be completed in FY19/FY20(Q1):

• Characterize OCM in bench scale reactor, achieving >10% conversion and >20% selectivity to C₂ products
• Determine direction for engine-scale reactor design, short contact or monolith
• Configure single-cylinder engine test cell to begin engine reactivity studies

Future*:

• Should project be successful, the project team will seek opportunities to integrate with full scale natural gas engine

*Any proposed future work is subject to change based on funding levels
Thank You

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