Development of Oxy-Esterification for Natural Gas Upgrading at the Wellhead

DE-AC05-00OR22725
Oak Ridge National Laboratory, California Institute of Technology, National Renewable Energy Lab, Princeton University, University of Virginia
10/1/18 – 9/30/21

Zili Wu, Oak Ridge National Laboratory
T. Brent Gunnoe, University of Virginia

U.S. DOE Advanced Manufacturing Office Program Review Meeting
Washington, D.C.
June 12, 2019

Project Overview

Timeline

Project Start Date:	10/1/2018
Budget Period End Date:	9/30/2019
Project End Date:	9/30/2021

Barriers and Challenges:

- Develop alkane partial oxidations using inexpensive and air recyclable catalysts
- Avoid solvent oxidation
- Translation of oxy-esterification process from batch reactors to flow reactors

AMO MYPP Connection:

- Process Intensification … "Advance technologies that significantly improve industrial process productivity and energy efficiency through optimized *molecular level kinetics, thermodynamics*, and heat and mass transfer"
- "Process intensification targets dramatic improvements … rethinking existing process designs & operation schemes into ones that are more *precise and efficient.*" & "… helping to reduce the number of discrete equipment needed … reduce energy consumption, minimize process complexity …"

Project Budget and Costs:

Budget	DOE Share	Cost Share	Total	Cost Share %
Overall Budget	$3,277,000	0	$3,277,000	0%
Approved Budget (BP-1&2)	$3,277,000	0	$3,277,000	0%
Costs as of 3/31/19	$297,225*	0	$297,225*	0%

* Not up-to-date due to university invoicing

Project Team and Roles:

- **Zili Wu (ORNL):** synthesize/characterize heterogeneous catalysts and perform flow reactor evaluations
- **William Goddard III (Caltech):** establish mechanisms using QM-based modeling and will correlate reaction energetics
- **John T. Groves (Princeton):** contribute catalyst screening using low-pressure spectroscopic studies to establish molecular kinetics & product distributions as a function of catalyst
- **T. Brent Gunnoe (U. of Virginia):** provide assessment of catalyst performance, including kinetic studies and product yields, in batch reactors
- **William Schinski (retired Chevron):** serve as an industrial consultant and assist with process flow diagrams and process design.
- **Ling Tao (NREL):** provide techno-economic assessments & life cycle analysis to guide experiment toward processes that are optimized economically and environmentally.

Project Objectives

- MYPP … "The main focus for AMO effort is in chemicals and fuel manufacturing …" and "Develop methane direct activation catalysts that will convert natural gas from remote and stranded sources to liquid fuels or chemicals …"

1. Deliver a low temperature/pressure (< 250 °C, 500 psi) process to convert natural gas into high value chemicals (e.g., ethylene, propylene, acetic acid) w/ at least 35% conversion and 80% selectivity
2. Reduce costs for the conversion of natural gas to liquid fuels and high value chemicals
3. Transition our new technology for gas-to-liquid conversions first targeting remote locations

Current gas-to-liquid processes are capital & energy intensive

$$H_2O + CH_4 \Longrightarrow CO + 3\ H_2 \Longrightarrow \text{methanol } (CH_3OH)$$

- Current technologies for gas-to-liquid are indirect and require the formation of CO/H_2 at high temperature and pressure, which is energy- and capital-intense. Distributed conversion of natural gas is not economical, and the result is unproductive flaring.

Technical Innovation

- **Current state-of-the-art for alkane partial oxidation:** Plagued by low selectivity at modest conversions (80% selectivity at 20% conversion)
- **Innovation:** OxE process achieves > 90% selectivity at > 20% conversion
- **Our Approach:** Initial product is an alkyl ester, and the ester group protects against over oxidation. Simple hydrolysis produces alcohol product.

Traditional Oxychlorination

$$CH_4 \xrightarrow[\text{Temp} > 300\ ^\circ C]{\text{catalyst, HCl, } O_2} CH_3Cl$$

Our First Generation Process

$$CH_4 \xrightarrow[150\ ^\circ C]{\text{iodate, KCl, HX}} CH_3X$$

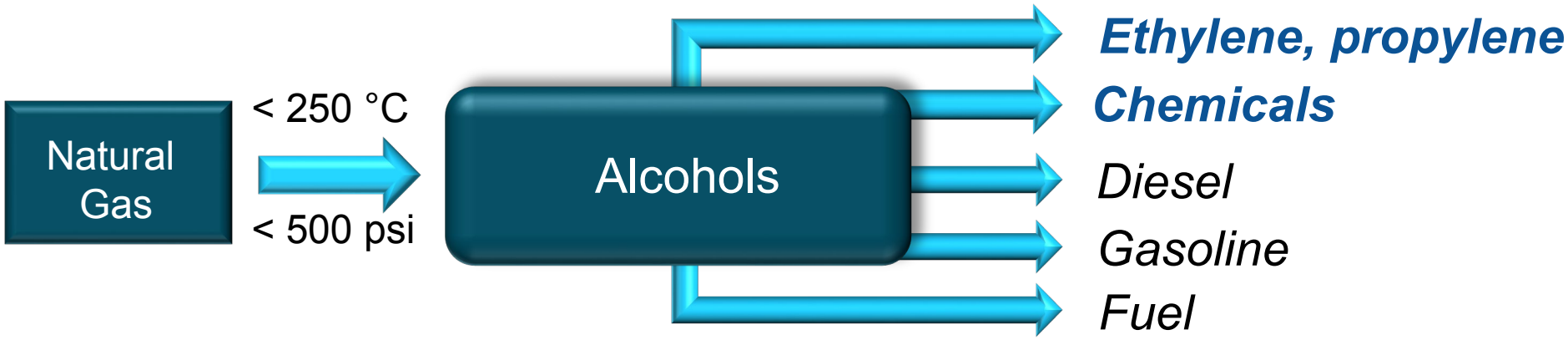
X = ester group

Project Develoment

$$RH \xrightarrow[< 250\ ^\circ C,\ 500\ psi]{\text{catalyst, HX, air}} RX \xrightarrow[- HX]{H_2O} \text{methanol \& ethanol}$$

R = methyl or ethyl

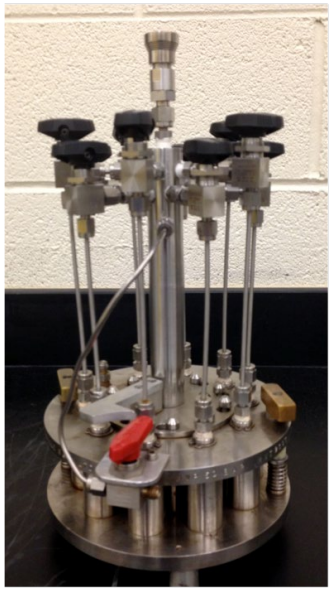
New process will provide at least 35% conversion and > 80% selectivity with an air-recyclable catalyst



Technical Innovation

OxE Methanol

- Less rigorous natural gas cleanup (not S sensitive)
- Operating pressures ~100 psi and temperature < 250 °C ... lower CAPEX & OPEX
- Uses air not pure oxygen (no air separation unit)
- Fewer/smaller unit-ops allow smaller footprint that will enable on-platform application
- Liquid intermediate (methyl acetate) gives shippable methane derivative after first step
- Lower CO_2 emission than conventional methanol & steam cracking
- Above factors enable on-site or on-platform gas conversion



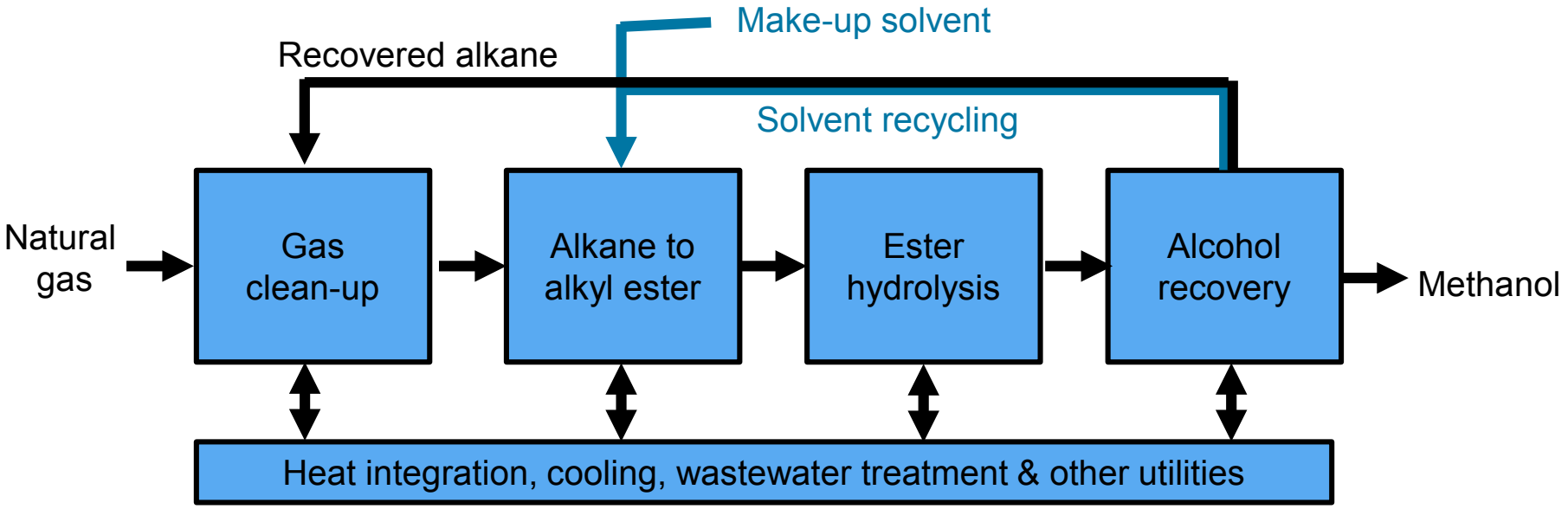
Conventional Syngas Methanol

- Sulfur impurities must be removed from feed due to catalyst sensitivity
- Operating pressures 1000+ in reformer & MeOH synthesis add compression cost
- Requires air separation unit for pure O_2
- Very large reformers, compressors & MeOH units
- Syngas intermediate is not shippable
- Production of CO_2 increasingly problematic?
- Reduced scale operation not reasonable

Shell Pearl gas-to-liquids facility

OxE can provide lower cost than methanol via syngas, potentially low enough to give ethylene below steam cracker cost

Technical Approach



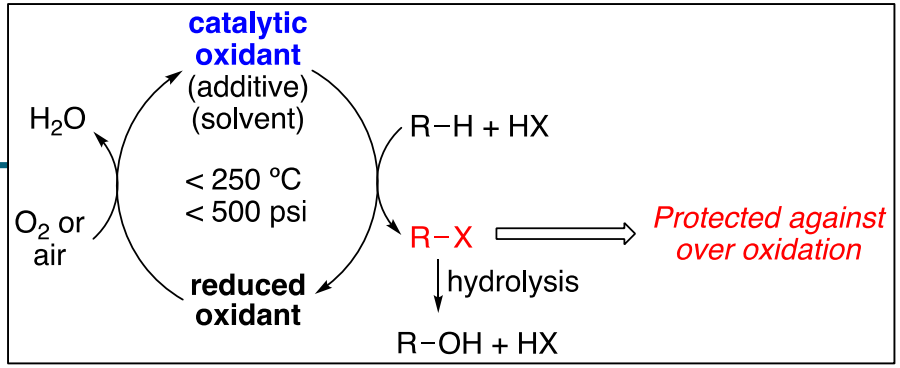
Objective 1: Use of inexpensive, heterogeneous metal oxide catalysts in batch reactors that achieve 35% conversion with 80% selectivity for mono-functionalized products from methane and ethane (< 250 °C, 100 psi). Data suggest higher conversions and selectivity are possible.

Objective 2: Translate chemistry from *Objective 1* into flow reactors.

Project risks & unknowns

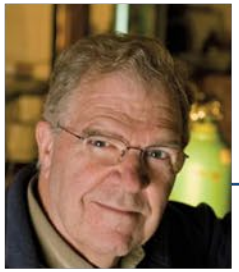
1. Can oxidation of carboxylic acid be mitigated?
2. Can economics of oxidant regeneration be made commercially viable?
3. Can protecting effect be translated into gas phase process?

Technical Approach

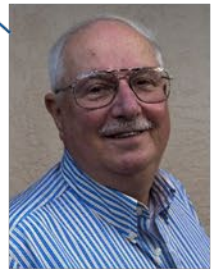


Gunnoe Group
University of Virginia
Expertise: alkane oxidation, high pressure reactions, catalyst evaluation

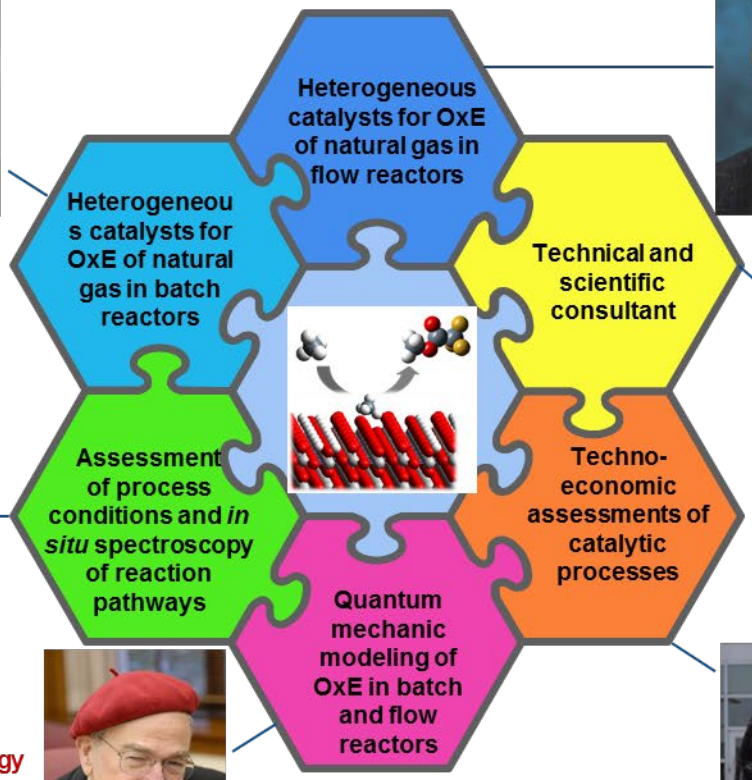
Wu Group
Oak Ridge National Laboratory
Expertise: oxide catalysis, reaction mechanism and kinetics, *in situ/operando* spectroscopy of gas phase reactions



Groves Group
Princeton University
Expertise: catalytic oxidation, *in situ* spectroscopy for solution phase reactions, reaction mechanisms



Bill Schinski
Retired, Chevron
Expertise: steam reforming catalysts; hybrid metal/zeolite Fischer-Tropsch catalysts for enhanced product distributions; low-temperature methanol catalysis; and direct methane-to-methanol routes.



Goddard Group
California Institute of Technology
Expertise: computational modeling, catalytic mechanisms, alkane oxidations, atomistic and kinetic modeling

Tao Group
National Renewable Energy Lab
Expertise: economic, strategic and engineering analysis, process design, techno-economic analysis, separation technologies, process intensification, and R&D process research.

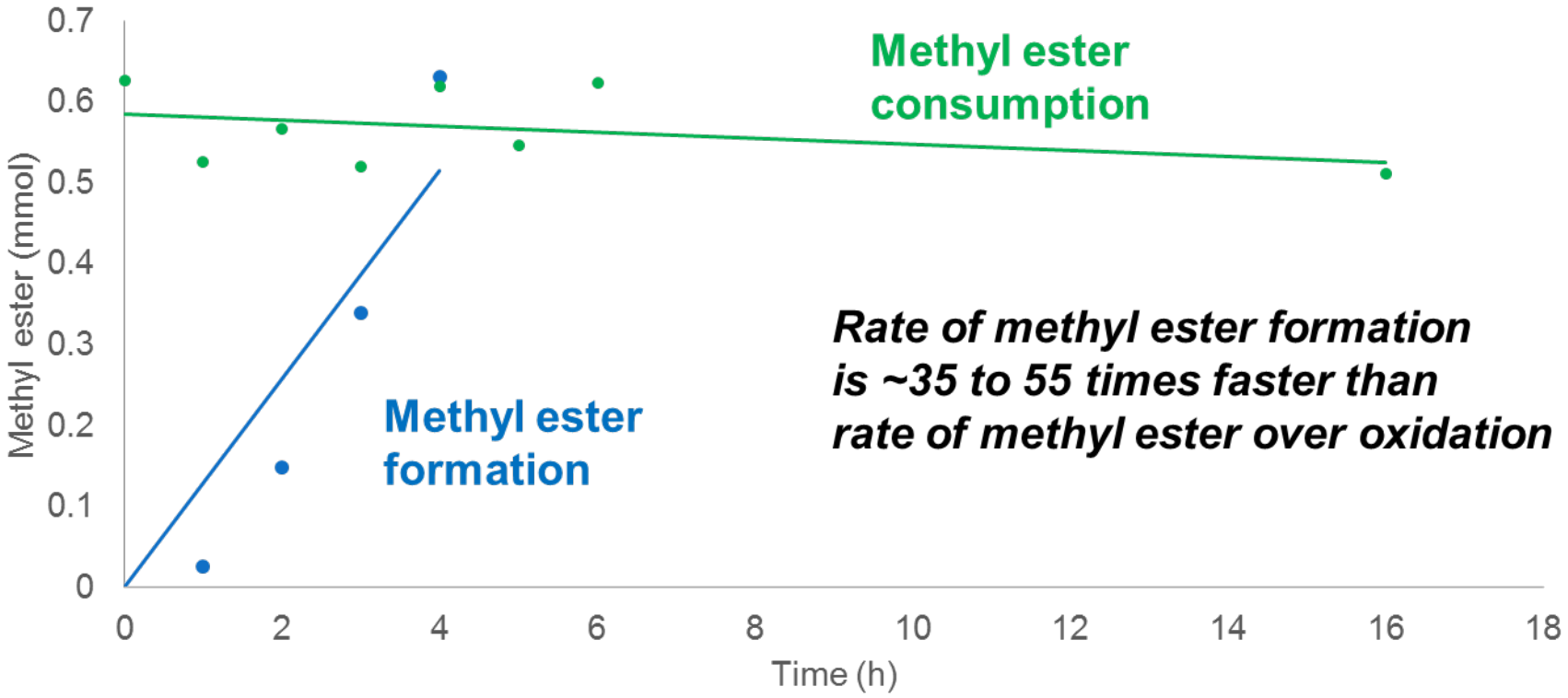
Results and Accomplishments

→ We demonstrated inexpensive metal oxide that converts methane to methyl ester with yields up to 65% based on stoichiometric oxidant. Chloride is not required for these new reactions, which reduces complexity. Combined experimental and computational studies are elucidating details of reaction.

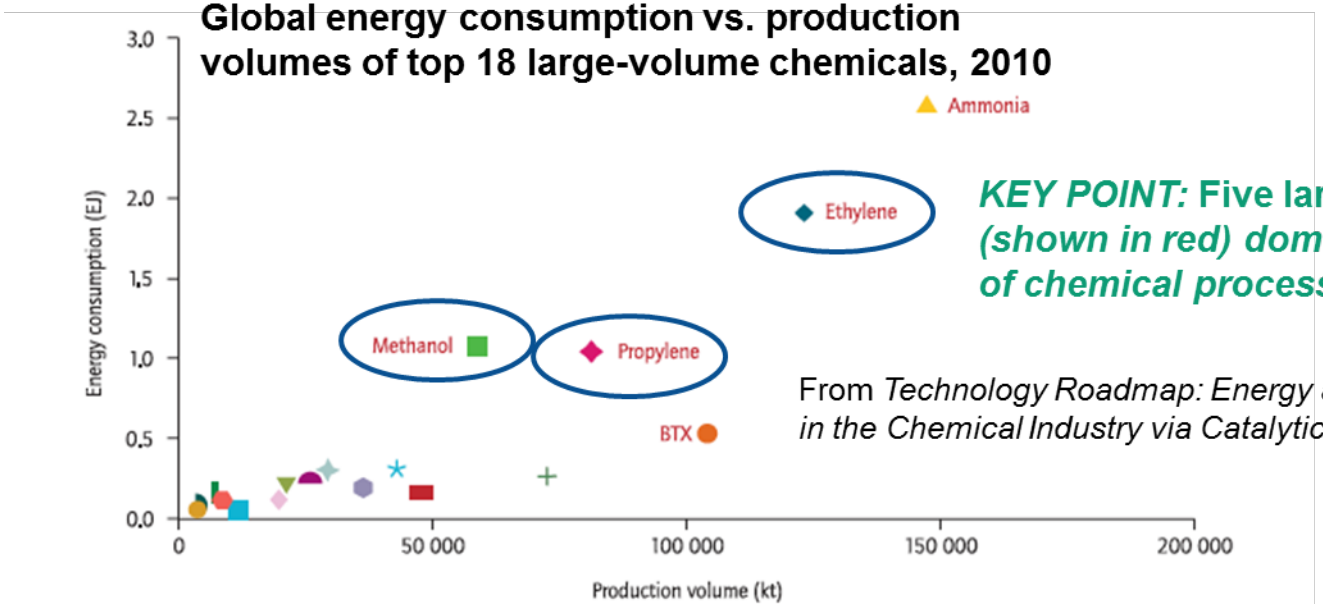
→ For new oxidant, demonstrated that the rate of methane functionalization is more rapid than methyl ester oxidation, confirming the protecting role of the ester.

→ A heterogeneous flow reactor has been designed and construction begun.

→ Designed a flow diagram with major unit operations to represent a conceptual process concept & identified 3-5 key process related targets & process metrics that are required for future economic assessment.



Transition (beyond DOE assistance)



KEY POINT:* Five large-volume chemicals *(shown in red) dominate energy consumption of chemical processes

From *Technology Roadmap: Energy and GHG Reductions in the Chemical Industry via Catalytic Processes*

→ Current processes for methanol, ethylene & propylene are energy intense

→ Global gas-to-liquid is expected to continue … opportunity for new processes (esp. stranded natural gas)

→ First patent awarded (*Compositions & Methods for Hydrocarbon Functionalization* Gunnoe, Groves et al.; US 9,604,890 B2)

→ Project success will reduce commercialization risk, ultimately will partner with catalyst development company

→ Partnership with Bill Schinski provides key industrial consultant