2017 NETL CO2 Capture Technology Project Review Meeting

U.S. Department of Energy
Cooperative Agreement Number: DE FE0029570

Low temperature process utilizing nano-engineered catalyst for olefin production from coal derived flue gas

SR
SOUTHERN
RESEARCH

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8/24/2017

Partners:
ARTC
Southern Company

Goals/objectives

- Large volumes of CO_2 emission from fossil fuel based power plants, significant portion of which are often released to the atmosphere.
- CO_2 to chemical possible yet energy intensive (and hence cost prohibitive) due to low energy state of CO_2 molecule.
- Current commercial utilization of CO_2 is very small compared to total emission.
- Research needs to reduce energy demand, low cost materials/process designs, integration with coal-fired power plant.
- The project seeks to develop a technology that can utilize CO_2 from coal-fired power plants to reduce the emissions and create valuable products to offset the cost of Carbon Capture and Storage (CCS).

Goals/objectives (Contd.)

- ☐ This project falls under the purview of area of interest 3 of the FOA : **NOVEL PHYSICAL AND CHEMICAL PROCESSES FOR BENEFICIAL USE OF CARBON.** The objective is to–

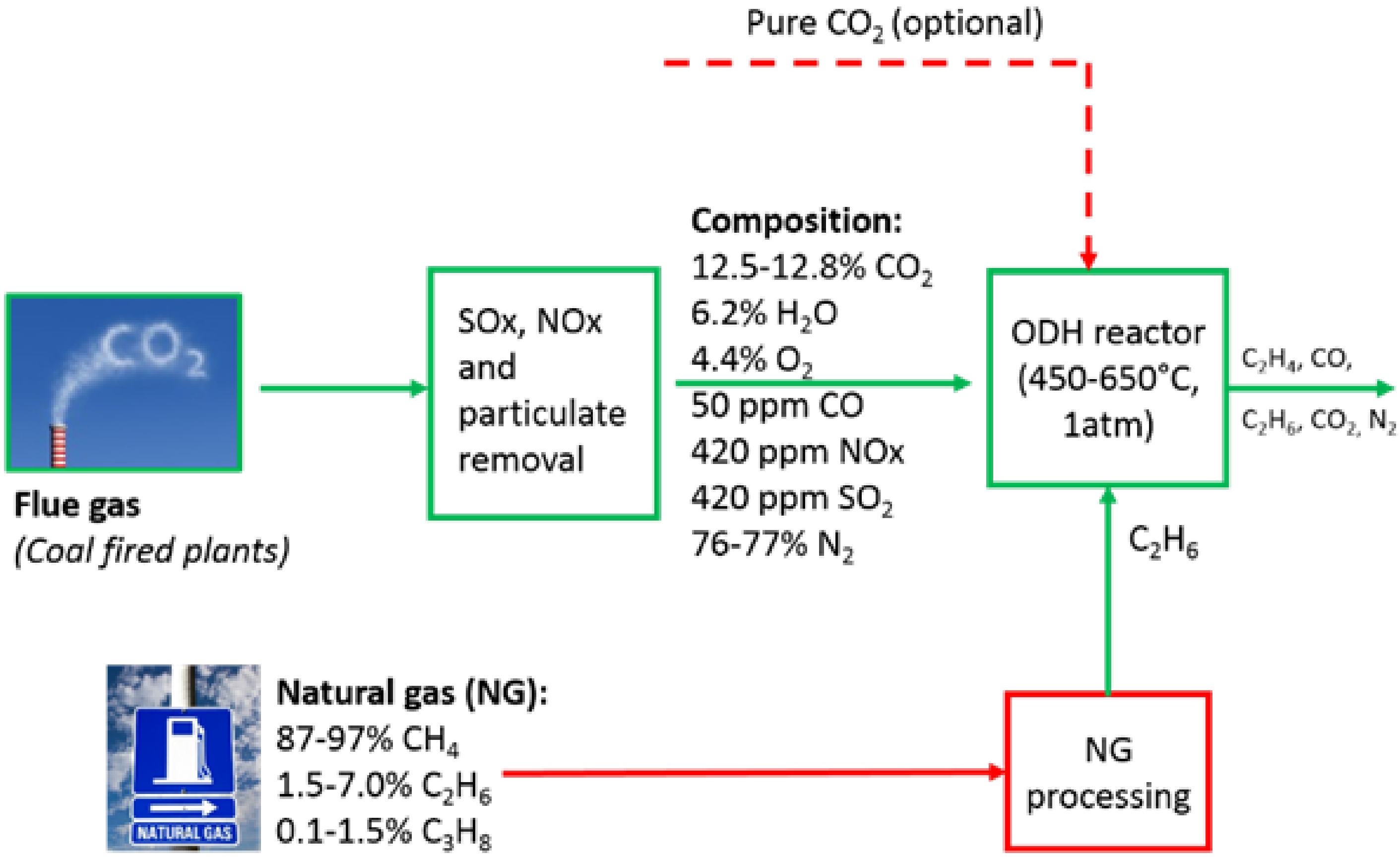
"Demonstrate of innovative concepts for beneficial CO_2 use via novel physical and/or chemical conversion processes, which include high energy systems and nano-engineered catalysts that can transform CO_2 into valuable products and chemicals (i.e., carbon fibers or plastics) while significantly reducing the energy demand/over potential required for the conversion process"

- ☐ Novel approaches to breaking the bonds between carbon and oxygen to generate carbon monoxide (CO), oxygen (O_2), and/or elemental carbon that can be used as building blocks for the chemical industry.
- ☐ Early technology readiness levels, typically 2-3.

Proposal summary

- ☐ The process uses ethane and CO_2 to produce ethylene via oxidative dehydrogenation (ODH) pathway.
- ☐ Sourcing ethane from abundantly available and low priced natural gas and CO_2 from coal fired flue gas stream with partial removed impurities.
- ☐ Use of nano-engineered mixed oxide catalysts.
- ☐ Catalyst screening using pure ethane and pure CO_2.
- ☐ Catalyst stability and performance evaluation on the screened catalysts in presence of 'partially removed' flue gas impurities (SOx, NOx, H_2O, O_2).
- ☐ Produces ethylene and CO, two highly desirable platform chemicals which are proposed to be co- or separately processed.

Proposal summary (Contd.)



Pure CO_2 (optional)

Flue gas
(Coal fired plants)

SOx, NOx and particulate removal

Composition:
12.5-12.8% CO_2
6.2% H_2O
4.4% O_2
50 ppm CO
420 ppm NOx
420 ppm SO_2
76-77% N_2

ODH reactor (450-650°C, 1atm)

C_2H_4, CO, C_2H_6, CO_2, N_2

C_2H_6

Natural gas (NG):
87-97% CH_4
1.5-7.0% C_2H_6
0.1-1.5% C_3H_8

NG processing

A commercial embodiment for the proposed ODH process

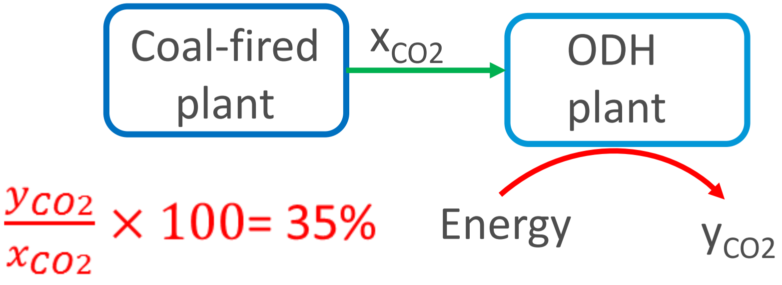
Relevance

- Ethylene is the highest producing petrochemical in the world (334 billion lb/year)[1]. U.S. produces ~20% of the worldwide ethylene[2].
- Ethane is abundantly available here in the U.S. due to the growth of shale gas. Currently a great deal of purified and separated ethane is readily available at an already lower cost (~$68 per metric ton).
- Globally, ethylene production is ranked as the second largest contributor of energy consumption (1% of world's total energy) and GHG emissions (180-200 million tons of CO_2 per year) in the global chemical industry[3,4].
- Coal based electric power sector in U.S. emitted 1241 million tons of CO_2 in 2016 alone[5].

[1] http://energy.globaldata.com/media-center/press-releases/oil-and-gas/us-and-china-driving-global-ethylene-capacity-to-record-208-million-tons-per-year-by-2017-says-globaldata. [2] Maffiaet al (2016). *Topics in Catalysis*: 1-7. [3] Ren et al *Energy* 31.4 (2006): 425-451. [4] Yao, Y. et al (2015). *Industrial & Engineering Chemistry Research*, *55*(12), 3493-3505.
[5] https://www.eia.gov/tools/faqs/faq.php?id=77&t=11

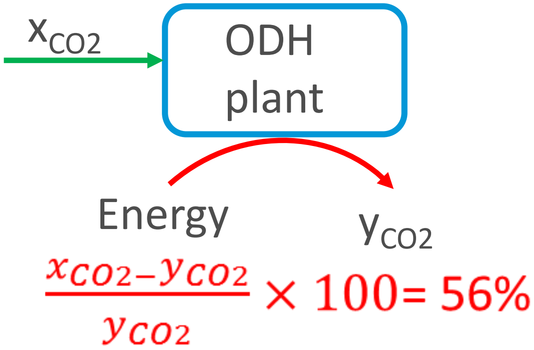
Relevance (Continued)

- ☐ Due to large scale of ethylene production, the scale of CO_2 consumption via proposed ODH would be significant.
- ☐ Initial estimates suggest a 1 million tons/year capacity ethylene plant operated in the proposed process next to a 200MW coal fired plant could potentially consume all CO_2 emitted from the power plant.
- ☐ A combined coal fired power plant and the proposed ODH plant can reduce 35% of the overall CO_2 emission **(Fig 1).**
- ☐ A stand alone ODH plant would consume 56% more CO_2 as a reactant than it would emit because of the energy requirement of the process **(Fig 2).**



$$\frac{y_{CO2}}{x_{CO2}} \times 100 = 35\%$$

Fig. 1



$$\frac{x_{CO2} - y_{CO2}}{y_{CO2}} \times 100 = 56\%$$

Fig. 2

Comparison with state of art

Two competing processes -

(1) Ethane steam cracking (SC) and

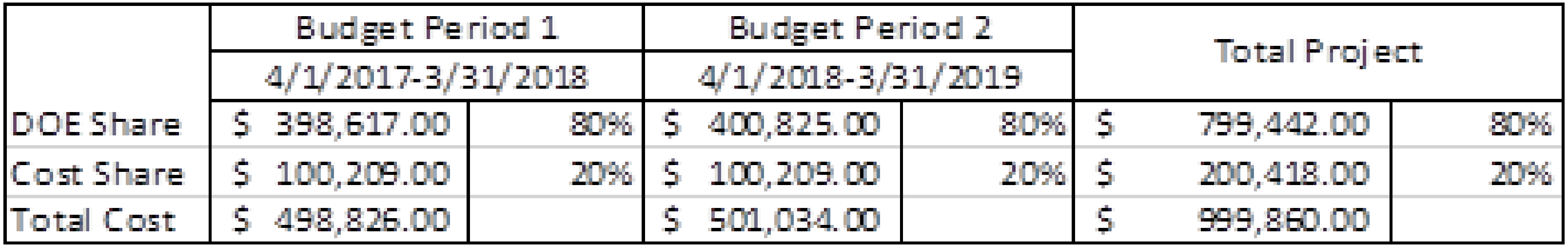
(2) Ethane oxidative dehydrogenation by O_2 (ODH(O_2))

Aspects	**SC**	**ODH (O_2)**	**ODH (CO_2)**
Commercialization status	Commercial	Research	Research
Reactants except hydrocarbons	Steam	Air /O_2	CO_2
ΔH, kJ/mol	137	-105	134
Operating Temperature	750-900°C	<500°C	<700°C
CO_2 emission	+	+	- (consumption)
Major by-product(s)	C_1-C_4 alkanes/olefins	CO_2	CO
Selectivity to Ethylene	80% (yield)	Up to 90%.	>90%
Catalyst	Steam	Expensive mixed oxides	Low cost mixed oxides.
Chemical safety risk	Low	Highest	Lowest

Project budget and participant roles

DOE/NETL Share: $ 799,442 (80%) **Southern Research:** $200,418 (20%)

Project duration: 2 years April 1, 2017-March 31, 2019



	Budget Period 1		Budget Period 2		Total Project	
	4/1/2017-3/31/2018		4/1/2018-3/31/2019			
DOE Share	$ 398,617.00	80%	$ 400,825.00	80%	$ 799,442.00	80%
Cost Share	$ 100,209.00	20%	$ 100,209.00	20%	$ 200,418.00	20%
Total Cost	$ 498,826.00		$ 501,034.00		$ 999,860.00	

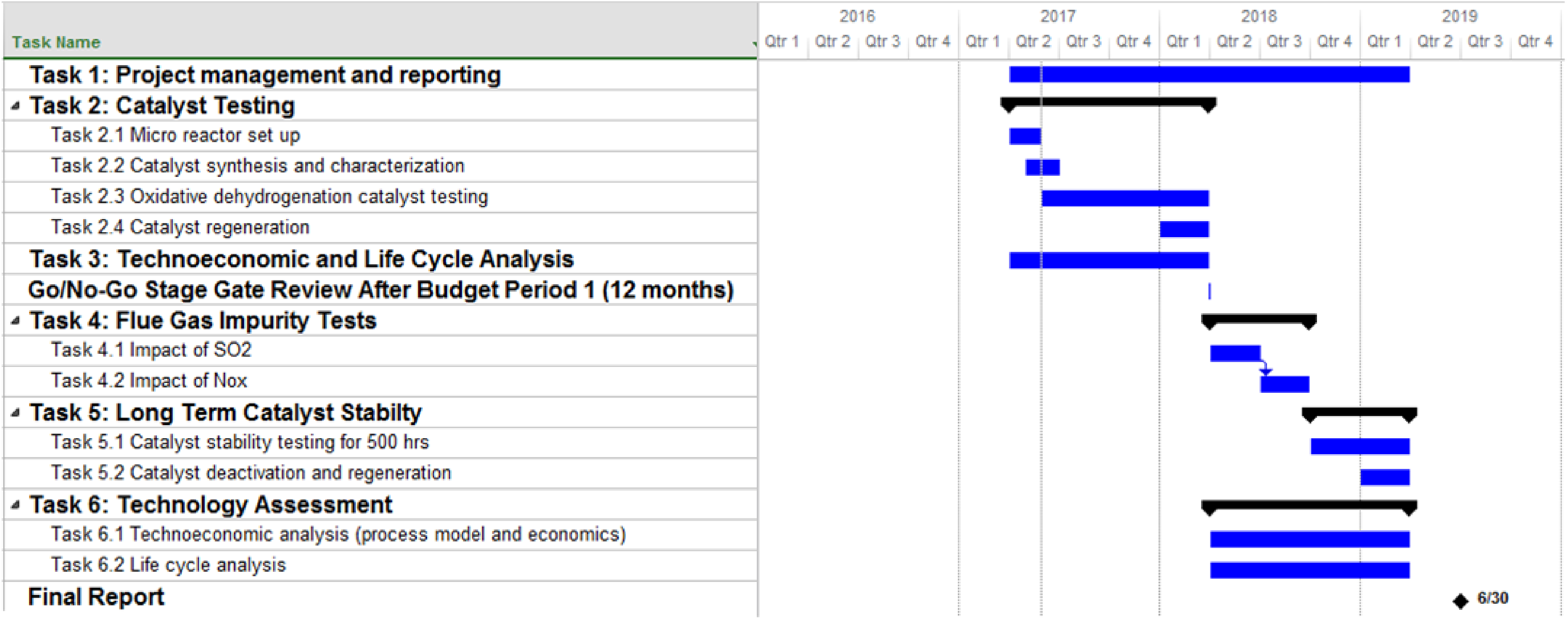
Participants and Roles

Southern Research: Lab-scale reactor system design and commissioning, Product analysis, Catalysis Synthesis and Characterization, Catalyst Deactivation studies, Reports and deliverables.

ARTC (Consultant): Guidance on catalyst design, testing and industrial requirements for integration with utility and petrochemical sectors especially with respect to easy retrofits and early adoption opportunities.

Southern Company: Guidance on flue gas characteristics, composition, heat integration with coal fired plant and opportunities to use other CO_2 streams within plant.

Project schedule and task summary



Task Name
Task 1: Project management and reporting
Task 2: Catalyst Testing
Task 2.1 Micro reactor set up
Task 2.2 Catalyst synthesis and characterization
Task 2.3 Oxidative dehydrogenation catalyst testing
Task 2.4 Catalyst regeneration
Task 3: Technoeconomic and Life Cycle Analysis
Go/No-Go Stage Gate Review After Budget Period 1 (12 months)
Task 4: Flue Gas Impurity Tests
Task 4.1 Impact of SO2
Task 4.2 Impact of Nox
Task 5: Long Term Catalyst Stabilty
Task 5.1 Catalyst stability testing for 500 hrs
Task 5.2 Catalyst deactivation and regeneration
Task 6: Technology Assessment
Task 6.1 Technoeconomic analysis (process model and economics)
Task 6.2 Life cycle analysis
Final Report

- ➢ Six tasks, two budget periods.

Task description and Progress/plans

Start of Budget Period (BP) 1

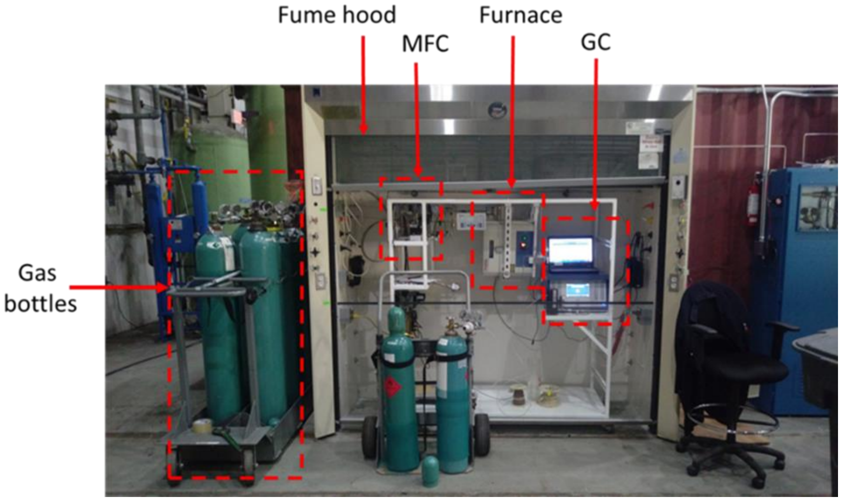
Task 1: Project management and reporting

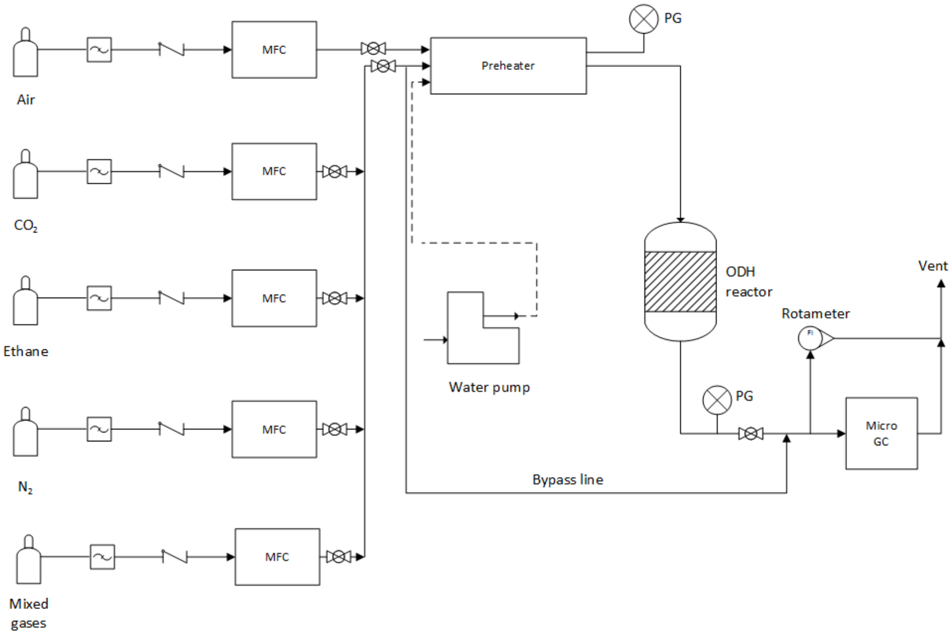
- ☐ Revised Project Management Plan (PMP) upon award; updated periodically as necessary - Completed
- ☐ Regular updates to/discussions with project participants for coordination/scheduling – Biweekly phone call meetings
- ☐ ***Kick-Off Meeting upon award***; additional Project Review Meetings as appropriate - Completed
- ☐ Quarterly Technical, Financial, and Other Reports to DOE/NETL – First Quarterly report submitted
- ☐ Papers at national conferences – 2017 NETL CO2 capture project review meeting
- ☐ Final Technical/Scientific Report

Task description and Progress/plans

Task 2: Catalyst testing

Task 2.1 Microreactor setup





Photograph of skid

Lab scale ODH skid schematic

- Task completed. Fully operational skid fabricated.

Task description and Progress/plans

Task 2: Catalyst testing

Task 2.2 Catalyst synthesis and characterization

- ☐ Catalyst formulation

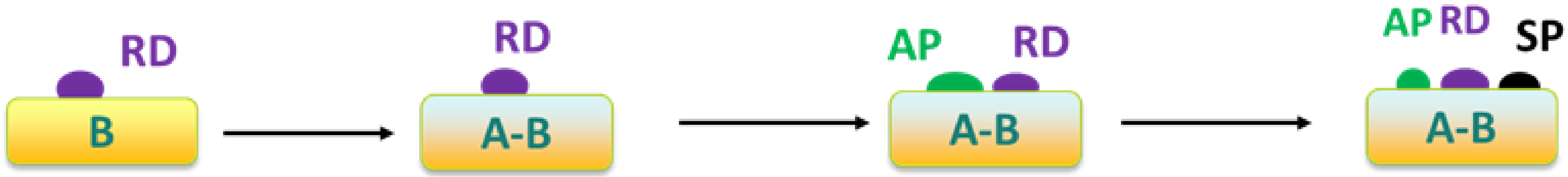
Functionality	ID	Purpose
Redox	**RD**	Ethane and CO_2 activation
Acid-base	**A-B**	H abstraction, CO_2 activation, ethylene desorption
Activity promoter	**AP**	Higher ethane and CO_2 conversion
Selectivity promoter	**SP**	Higher ethylene selectivity

- ☐ Careful balance of each functionality important.
  - Study catalytic performance using one component at a time.

Task description and Progress/plans

Task 2: Catalyst testing

Task 2.2 Catalyst synthesis and characterization (Contd)



B - fixed
RD- varies

RD - fixed
A-B- varies

RD - fixed
A-B - fixed
AP - varies

RD - fixed
A-B - fixed
AP – fixed
SP - varies

Catalyst formulation strategy

- Catalyst optimization to identify best compositions for –
  - Lowest onset Temperatures for ethane and CO_2
  - Maximum yield of ethylene
  - Lowest selectivity to undesired products (e.g., CH_4)

Task description and Progress/plans

Task 2: Catalyst testing

Task 2.2 Oxidative dehydrogenation catalyst testing

Temperature Programmed Surface Reaction (TPSR)

- While reactor skid was being fabricated and readied for operation, a series of catalysts synthesized and tested in an TPSR apparatus.
- Rapid, fully automated small scale analysis to compare catalytic behavior mainly to determine onset temperatures for ethane and CO2 activation.
- For better comparison following parameters were kept constant during catalytic study –
    - Pretreatment/activation temperature, ramp and flows
    - Catalyst mass
    - Space velocity
    - Inlet gas partial pressures

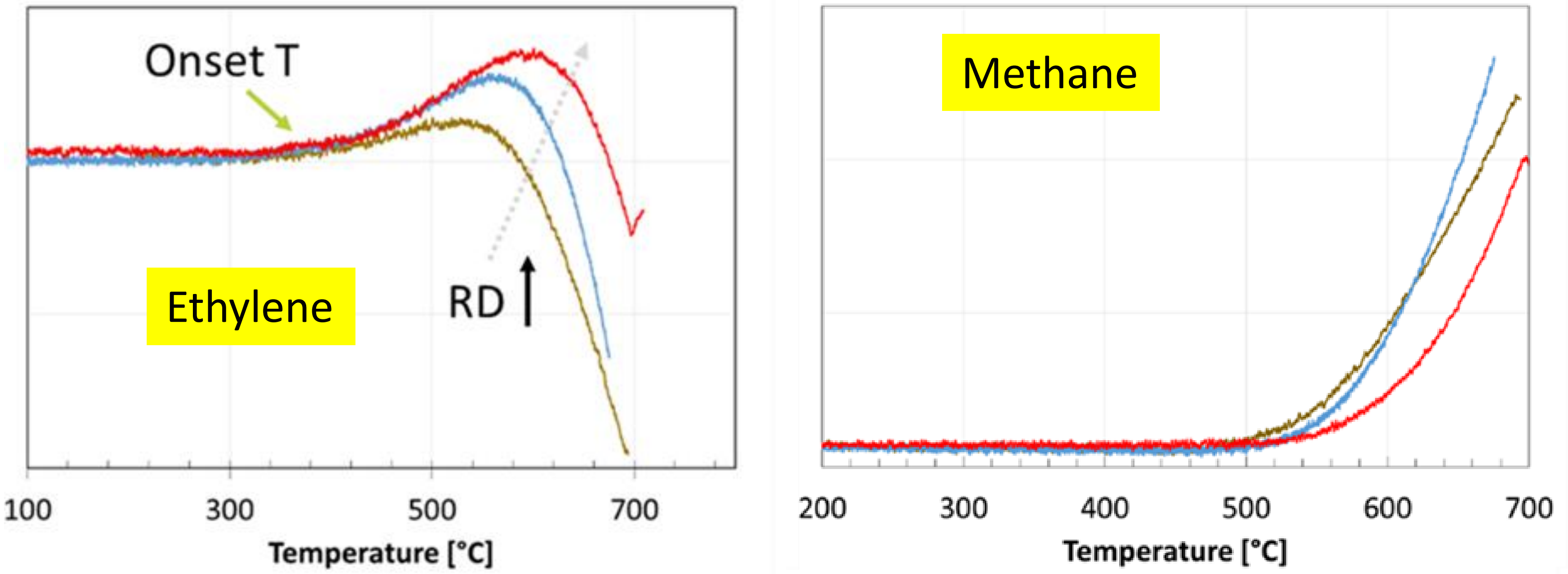
Task description and Progress/plans

Task 2: Catalyst testing

Task 2.2 Catalyst synthesis and characterization (Contd)

Effect of Redox (RD) functionality

(RD-B catalysts)



- As RD **increases** -
  - Onset temperatures ↑↓
  - At higher temperature (higher conversion), ethylene ↑, methane ↓

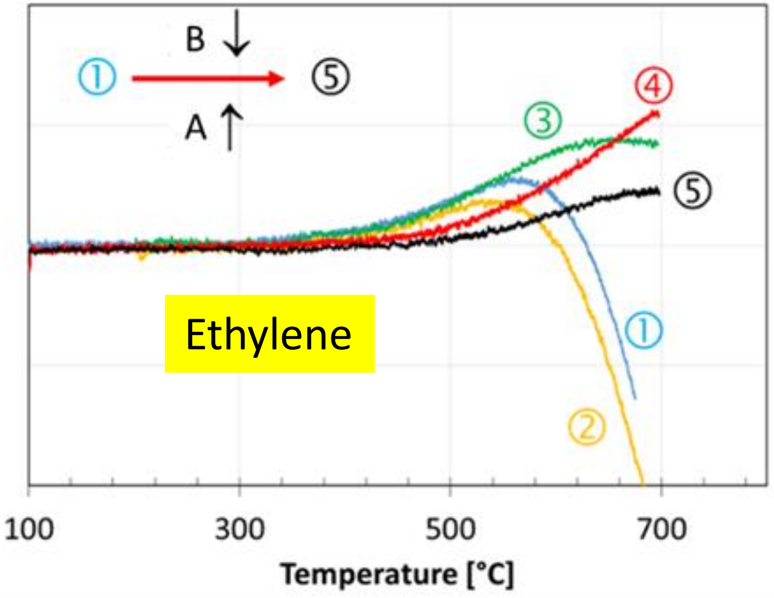
Task description and Progress/plans

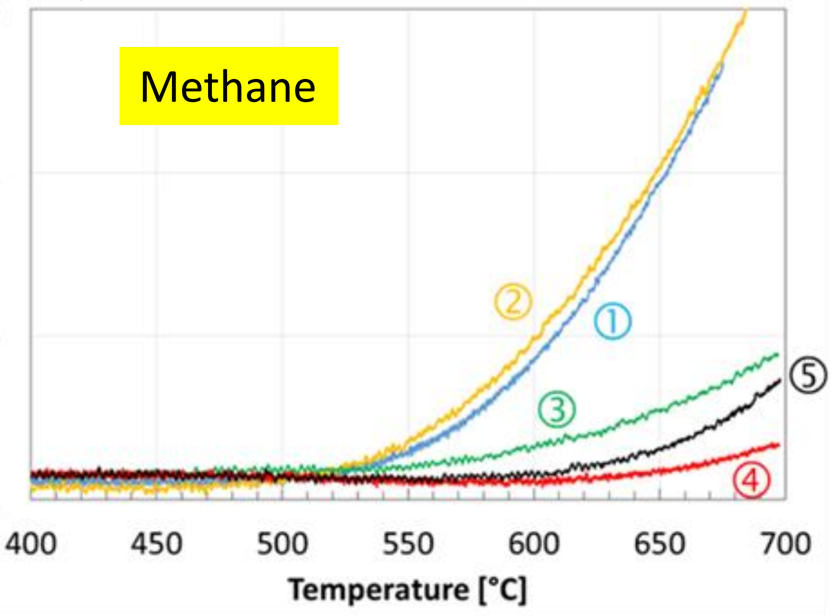
Task 2: Catalyst testing

Task 2.2 Catalyst synthesis and characterization (Contd)

Effect of Acidic (A)-Basic (B) functionality

(RD-A-B catalysts)





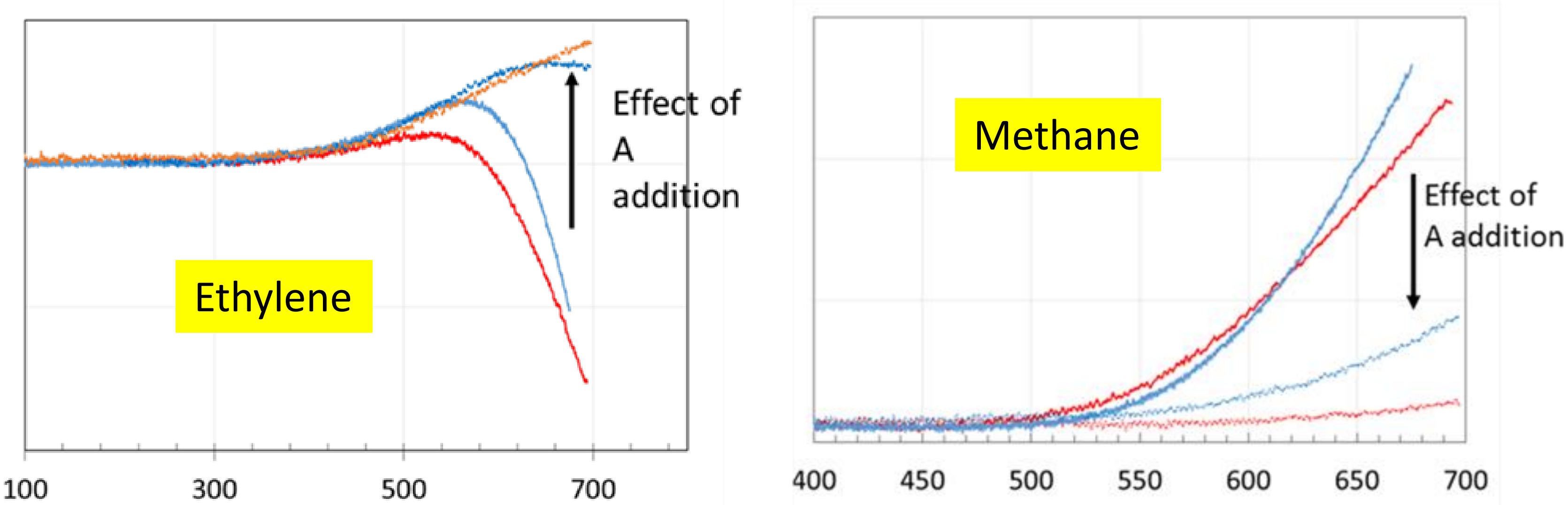
- As A **increases and B decreases** -
  - Onset temperatures ↑
  - At higher temperature (higher conversion), ethylene ↑, methane ↓

Task description and Progress/plans

Task 2: Catalyst testing

Task 2.2 Catalyst synthesis and characterization (Contd)

Effect of Acidic (A) component on RD-B catalysts



- With small A addition on the RD functionality-
    - Onset temperatures ↑↓
    - At higher temperature (higher conversion), ethylene ↑, methane ↓

Task description and Progress/plans

Task 2: Catalyst testing

Task 2.2 Catalyst synthesis and characterization (Contd)

Catalyst ID	Surface area (m_2/g)	Onset T for ethylene formation	Onset T for unselective formation
RD-B-1	107	400	500
RD-B-2	166	400	500
RD-B-3	148	400	540
RD-A-1	188	460	600
RD-A-B-1	128	400	575
RD-A-B-2	130	400	500
RD-A-B-3	124	400	650
RD-B-A-1	182	425	650

Summary of onset temperatures for activation on different catalysts

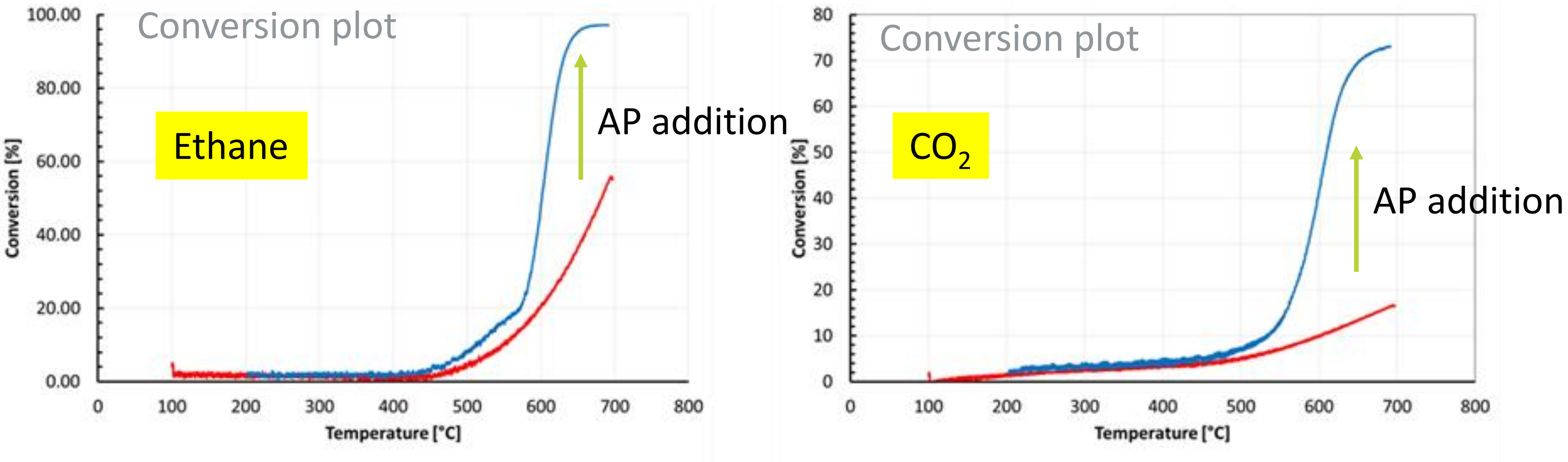
Task description and Progress/plans

Task 2: Catalyst testing

Task 2.2 Catalyst synthesis and characterization (Contd)

Effect of Activity Promoter (AP)

(RD-A-B-AP catalysts)



Red – “AP free” analog

Blue – With AP functionality

- Inclusion of AP functionality drastically improves conversion – requires further optimization

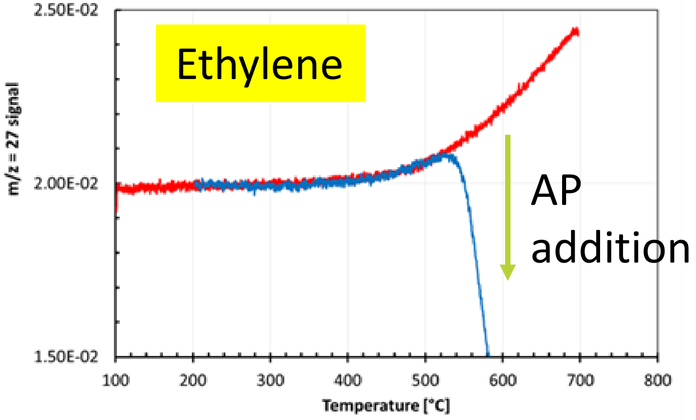
Task description and Progress/plans

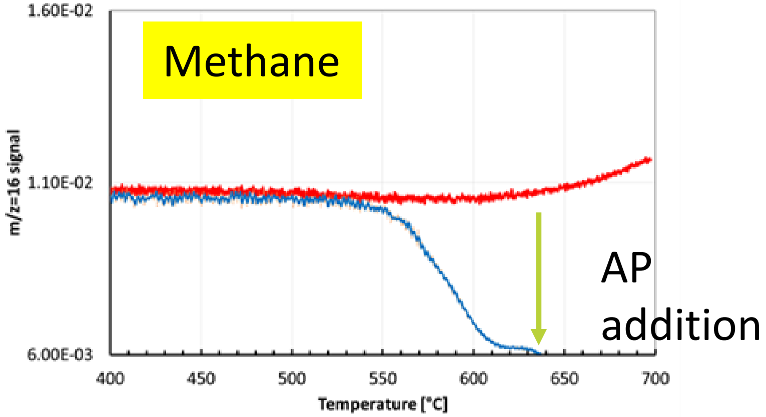
Task 2: Catalyst testing

Task 2.2 Catalyst synthesis and characterization (Contd)

Effect of Activity Promoter (AP)

(RD-A-B-AP catalysts)





- ➢ Inclusion of AP makes lowers ethylene selectivity and shows higher selectivity to dry reforming.

Task description and Progress/plans

Task 2: Catalyst testing

Task 2.3 Oxidative dehydrogenation catalyst testing

- **List of parameters –**
  - N_2 dilution
  - Space velocity
  - Temperature
  - CO_2/ethane ratio

- **Two sets of parameters based on their effect on catalytic performance -**
  - **Major parameters** –Maximum effect. Used for optimization
  - **Minor parameters** – Minimum effect. Generally maintained constant.

Task description and Progress/plans

Task 2: Catalyst testing

Task 2.3 Oxidative dehydrogenation catalyst testing

- **List of parameters –**
  - N_2 dilution - minor
  - Space velocity - major
  - Temperature - major
  - CO_2/ethane ratio – minor

- **Two sets of parameters based on their effect on catalytic performance -**
  - **Major parameters** –Maximum effect. Used for optimization
  - **Minor parameters** – Minimum effect. Generally maintained constant.

Task description and Progress/plans

Task 2: Catalyst testing

Task 2.4 Catalyst regeneration

- Catalyst deactivation.
- Coking (TGA analysis).
- Regeneration scheme.
    - Process condition (Temperature)
    - Gas flow (Air/CO_2)

Task description and Progress/plans

Task 2: Catalyst testing

- **Summary till date –**
  - Tested catalysts showed similar performance trend as determined from TPSR experiments
    - ➢ Reliable tool for rapid catalyst screening
  - Considerably truncated ranges of operating condition parameters
    - ➢ Resulted from thorough parameter effect study on reference catalysts
  - Challenges with respect to catalyst life
    - ➢ Nature and extent of coking determined
    - ➢ Regeneration at reaction temperature fully recovers catalyst functionality

Task description and Progress/plans

Task 3: Techno-economic lifecycle analysis

- ☐ Preliminary techno-economic analysis (TEA) and life cycle analysis (LCA).
- ☐ Initial conceptual design.
- ☐ These results will serve as a starting point and help guide the BP2 and the design of full commercial embodiment.

End of Budget Period (BP) 1

Task description and Progress/plans

Task 4: Flue gas impurity tests

- Screened catalysts exposed to flue gas impurities. Their compositions will be representative of flue gas compositions:
  - O_2
  - H_2O
  - SOx
  - NOx

Task 5: Long term stability

- Catalytic run for up to 500hrs using simulated gas stream containing flue gas impurities.

Task description and Progress/plans

Task 6: Technology assessment

- Techno-economic analysis
- Life cycle analysis
- Technology gap analysis
  - Identify major/critical components for the proposed process
  - Performance, Cost, Emissions, Market, and Safety Metric advantages
  - R&D gaps and TRL levels
  - Potential vendors for commercial equipment
- Recommended flue gas composition
- Recommended catalyst composition

Acknowledgement

This material is based upon work supported by the Department of Energy under Award Number DE-FE0029570.

Disclaimer

Questions/Comments?