2018 NETL CO_2 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

SOUTHERN RESEARCH

8/20/2018

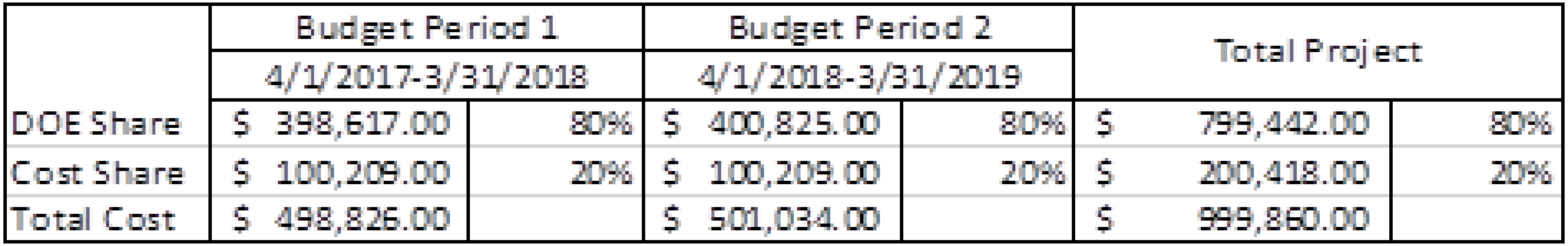
Principal Investigator: Amit Goyal
Co-Principal Investigator: Jadid Samad
DOE FPM: Sai Gollakota

Project overview

Goal: Develop novel nano-engineered catalysts for the production of ethylene (main product) and CO (Secondary product) from natural gas derived ethane and coal fired flue gas CO_2.

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	

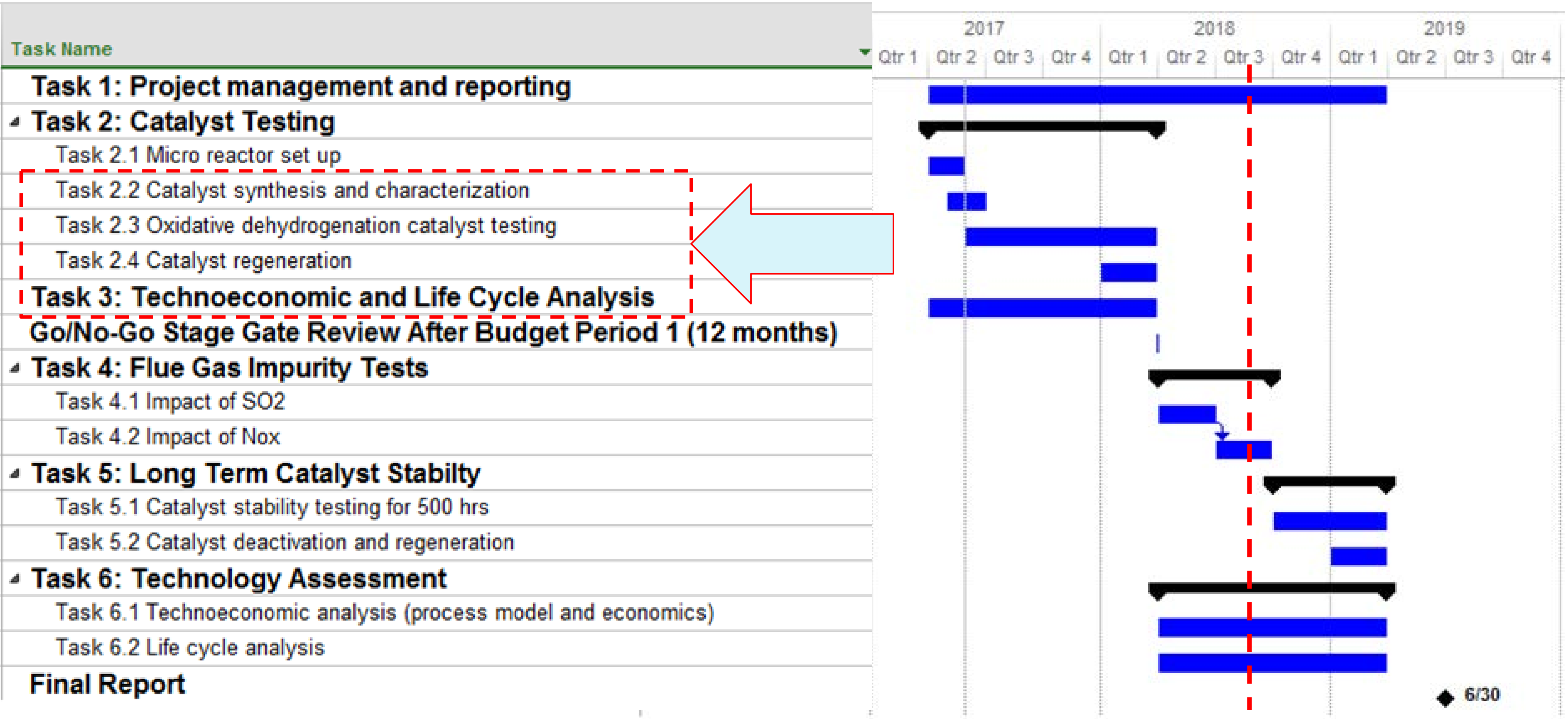
Participants and Roles

***Southern Research (prime)*:** Lab-scale reactor system design and commissioning, Product analysis, Catalysis Synthesis, characterization and Deactivation studies, Reports.

Catalyst consultant: Guidance on catalyst design, testing and industrial requirements for integration with utility and petrochemical sectors.

Utility 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.

Why ethylene ?

❑ Great target platform chemical due to-

  ❑ Large production volume (150 million tons/year)

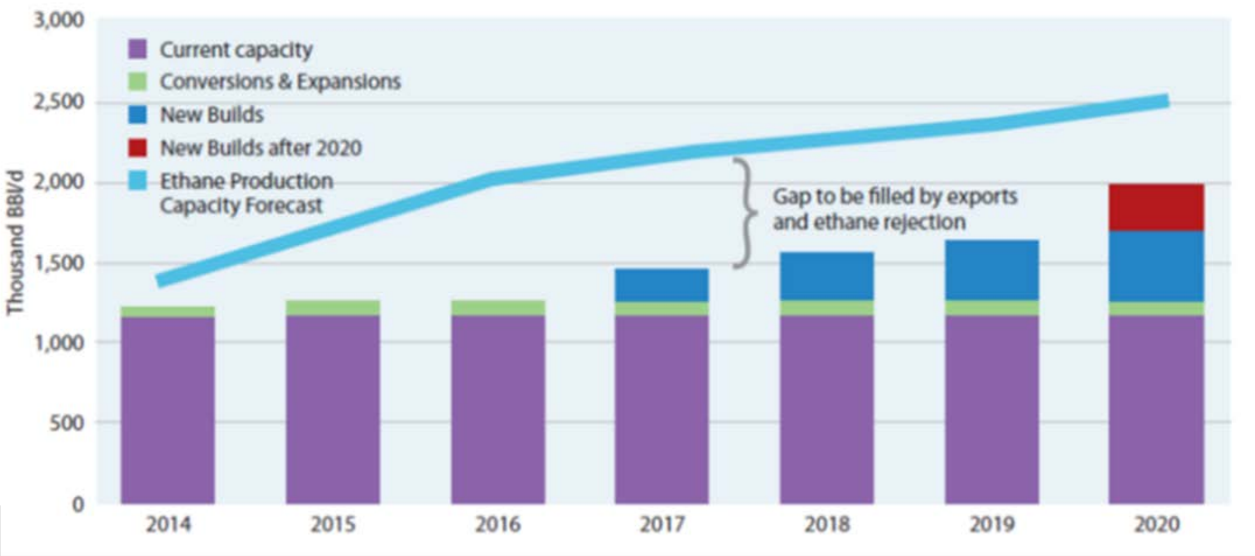
  ❑ Large energy consumption (5 quadrillion BTU/year)

  ❑ Large CO_2 emission during production (180-200 million tons/year)

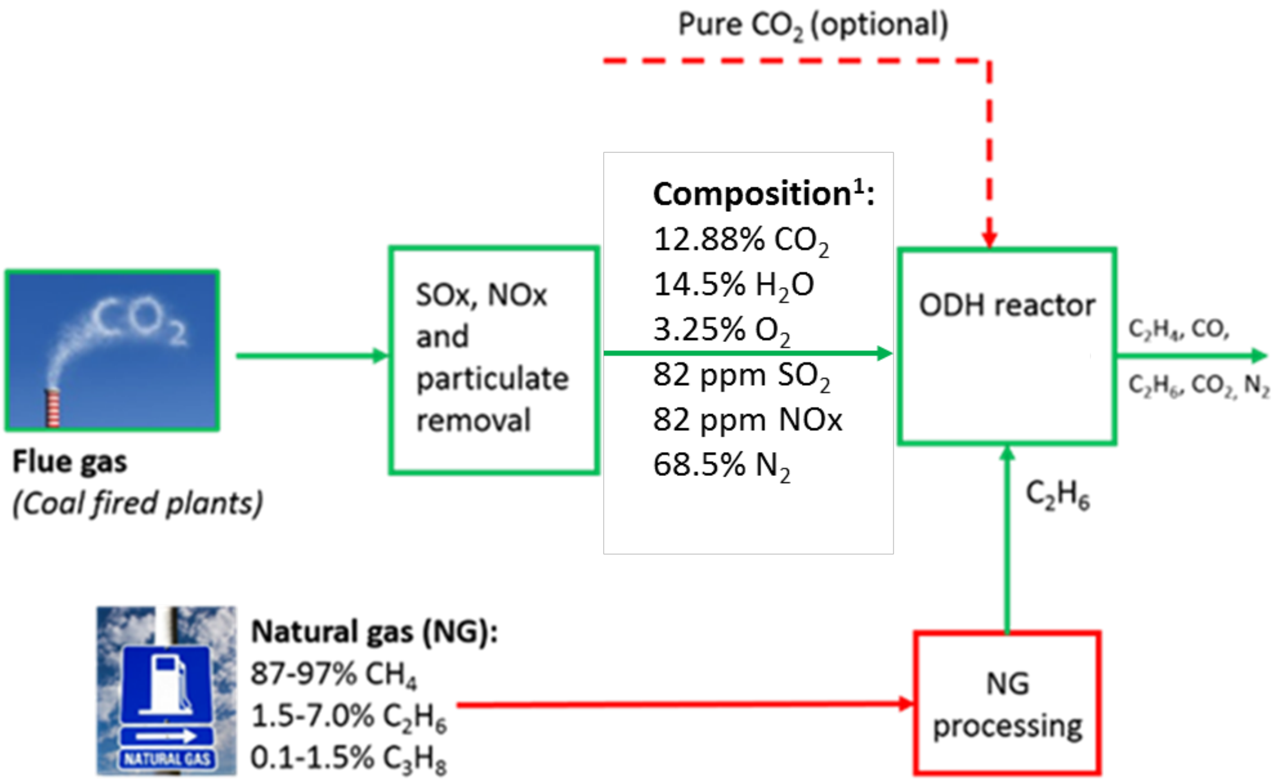
❑ Surplus ethane available in the U.S. is a low cost feedstock for ethylene production.

➢ Potential for CO_2 utilization in an otherwise CO_2 emitting process

➢ Even small reduction of energy usage will have large impact due to large scale.



Commercial embodiment



Pure CO_2 (optional)

Flue gas
(Coal fired plants)

SOx, NOx and particulate removal

Composition[1]:
12.88% CO_2
14.5% H_2O
3.25% O_2
82 ppm SO_2
82 ppm NOx
68.5% N_2

ODH reactor

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

- ☐ Produces ethylene and CO, two highly desirable platform chemicals
- ☐ Direct environmentally regulated flue gas utilization with option to use captured CO_2

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[1] Cost and Performance Baseline for Fossil Energy Plants, Volume 1a: Bituminous Coal (PC) and Natural Gas to Electricity, Revision. (https://www.netl.doe.gov/File%20Library/Research/Energy%20Analysis/Publications/Rev3Vol1aPC_NGCC_final.pdf)

Chemistry of the process

- **Oxidative dehydrogenation (ODH) reaction:**

$$C_2H_6 + CO_2 = C_2H_4 + CO + H_2O \quad \Delta H^\circ = 134 \text{ kJ/mol.}$$

- CO_2 acts as a mild oxidant in the ODH process. Oxidation power: O_2 (105) > H_2O (3) > CO_2 (1) > H_2 (0.003)

- **Side reactions involve some other notable CO_2 consuming reactions-**

  - $C_2H_6 = C_2H_4 + H_2$, $CO_2 + H_2 = CO + H_2O$, $CO_2 + C = 2CO$

  - $C_2H_6 + 2CO_2 = 4CO + 3H_2$, $C_2H_6 + 2CO_2 = CH_4 + CO + H_2O$

  - Moles CO_2 converted/moles C_2H_4 produced will be > 1.0 due to side reactions.

- Inherent ability of CO_2 to remove coke: $CO_2 + C = 2CO$

Task description and Progress/plans

Task 2: Catalyst testing

Task 2.2 Catalyst synthesis and characterization

- ☐ **Catalyst recipe screening**
  - ☐ Four different recipes
  - ☐ Finding preferred preparation steps to obtain
    - ☐ Critical surface attributes
    - ☐ Critical phases of oxides

Task description and Progress/plans

Task 2.2 Catalyst synthesis and characterization

- ☐ **Catalyst screening**
  - ☐ Temperature Programmed Surface Reaction (TPSR) used to screen components for low temperature ethane activation and high ethylene selectivity

Functionality	ID	Purpose	Observed roles
Redox	RD	Alkane and CO_2 activation	Alkane and CO_2 activation
Acid-base	A-B	H abstraction, CO_2 activation, ethylene desorption	Support, interaction with other components
Activity promoter	AP	Higher alkane/CO_2 conversion	Higher alkane/CO_2 conversion
Selectivity promoter	SP	Higher ethylene selectivity	CO_2 activation, Coke resistance
Catalyst nomenclature		RD-B, RD-SP-A-B, RD-SP-AP-A-B etc	

Task description and Progress/plans

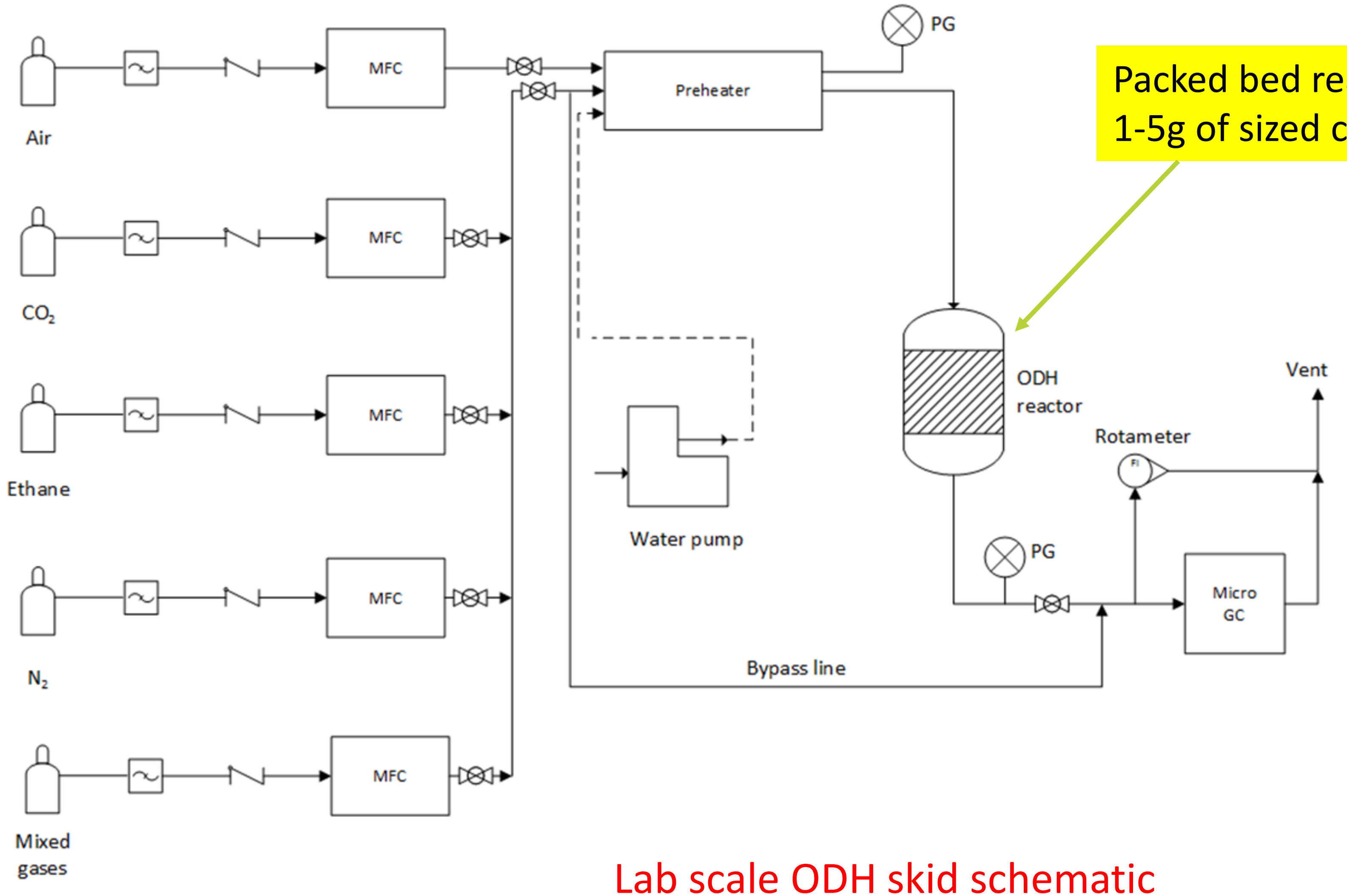
Task 2.3 Oxidative dehydrogenation catalyst testing

CO_2 concentrations cases

- **Dilute (flue gas) CO_2**
  - Coal fired flue gas contains ~12-14% CO_2 with high N_2 content
  - Feed comprised of 15% (ethane and CO_2) with remaining 85% N_2
  - Used in long term catalyst testing

- **Concentrated (Captured) CO_2**
  - CO_2 captured from coal fired flue gas has high purity (95% or higher)
  - Only ethane and CO_2 used as feed (<5% N_2 as internal standard)
  - High ethane partial pressure in feed allows accelerated catalyst performance and stability screening and comparison

Task description and Progress/plans

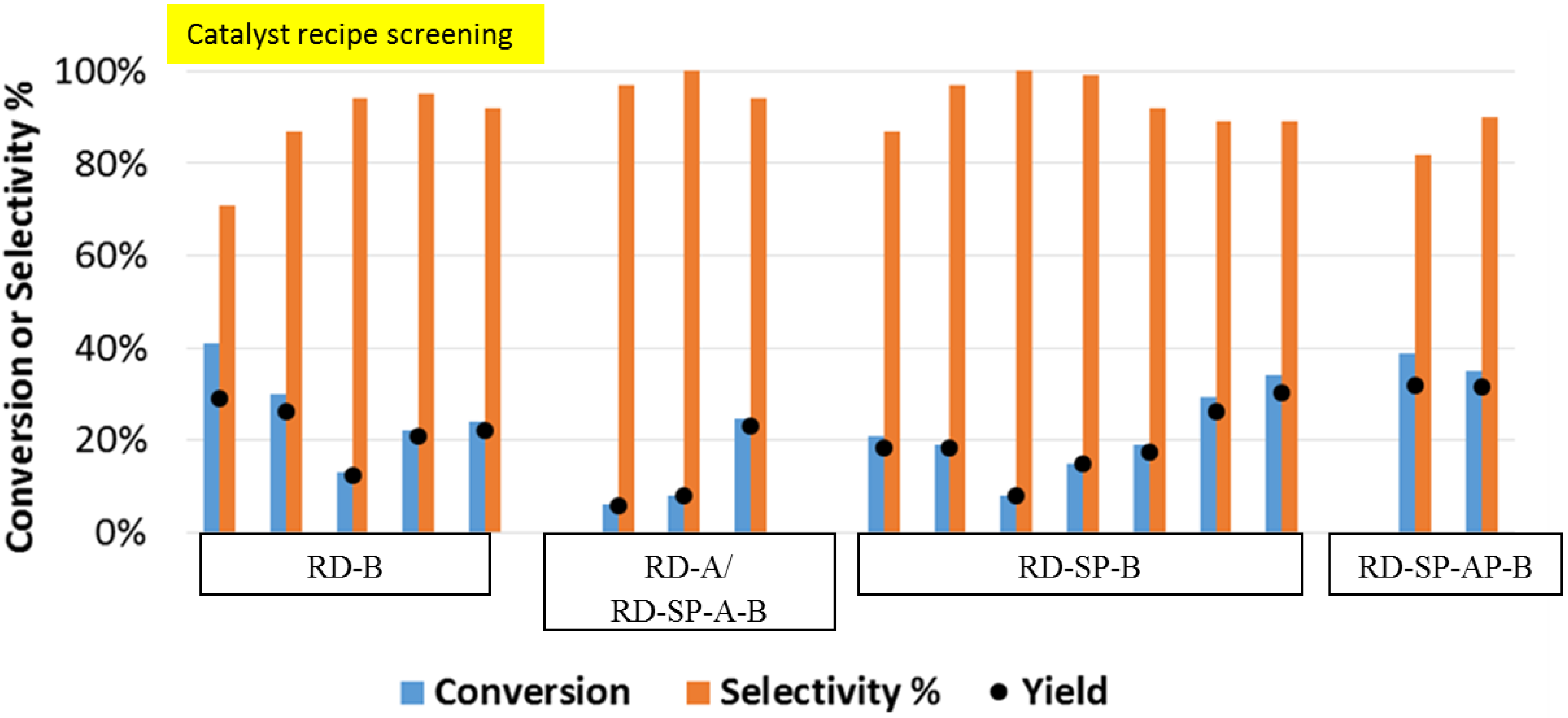


Packed bed reactor
1-5g of sized catalyst

Lab scale ODH skid schematic

Task description and Progress/plans

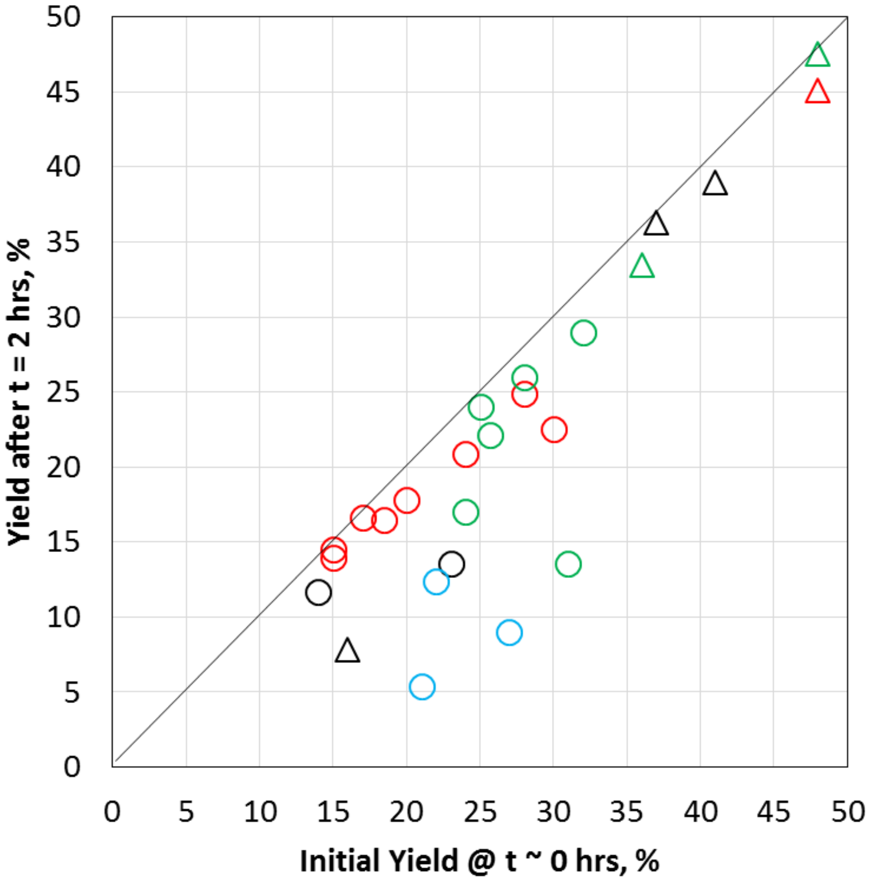
Catalyst screening summary



Catalyst optimization at specific condition (SV, T, P, Ratio of feed)

Task description and Progress/plans

Catalyst screening by stability



RD-B ✗

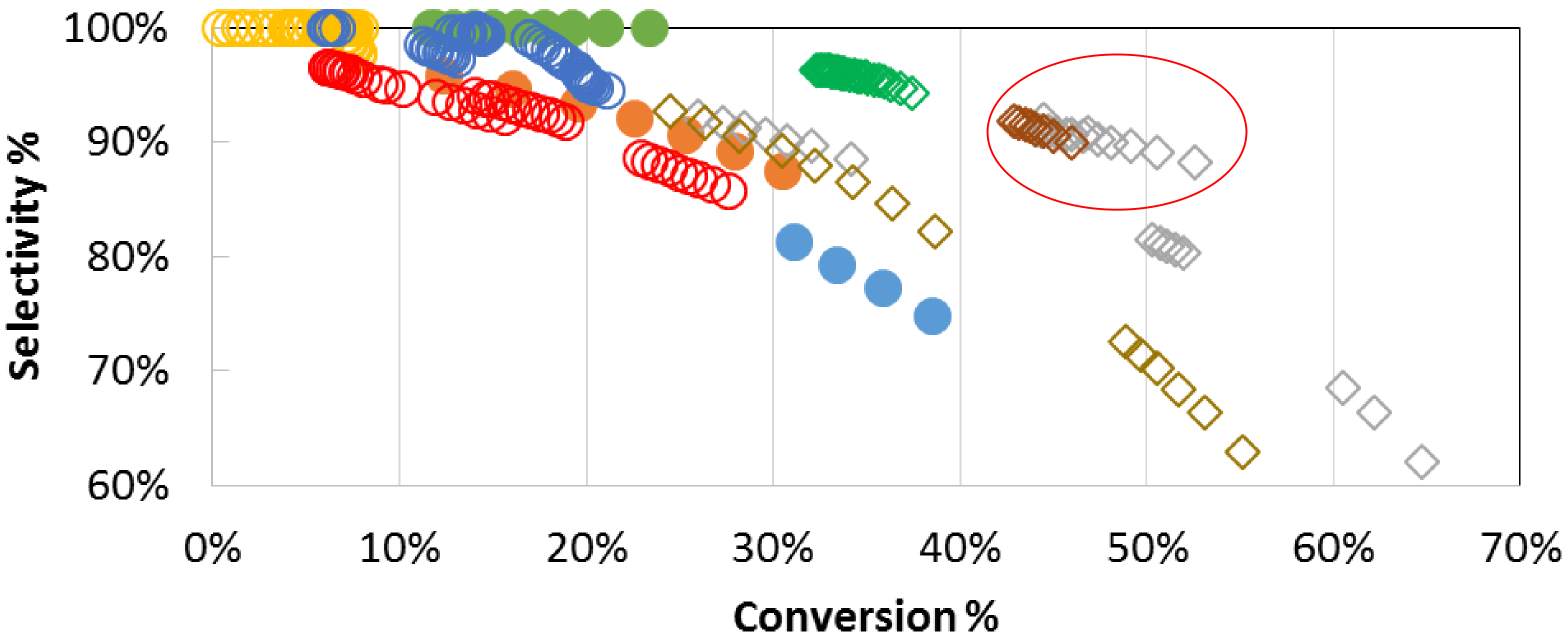
RD-SP-B ✓

RD-SP-A-B ✓

RD-SP-AP-B ✓

Task description and Progress/plans

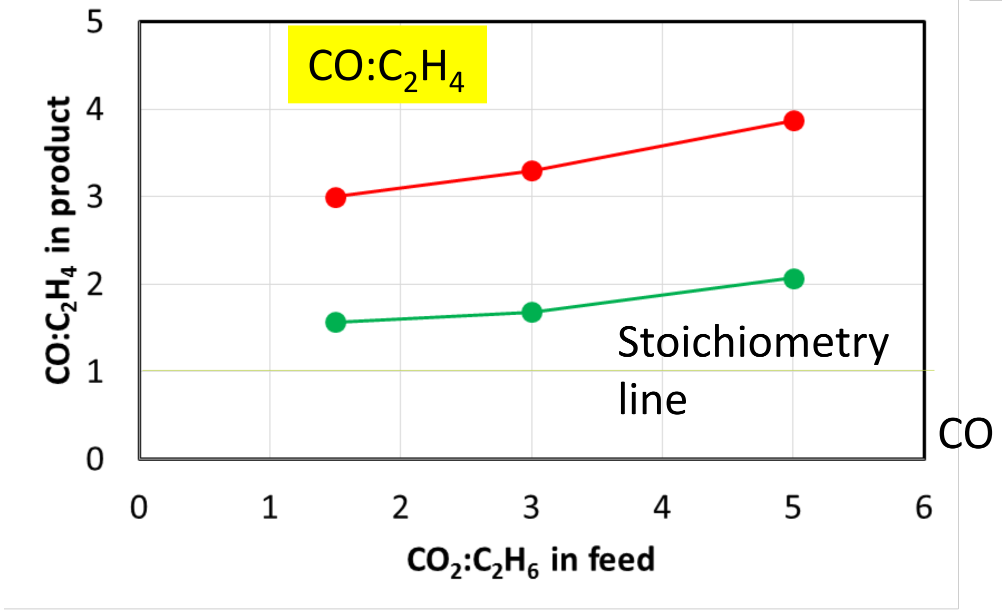
Conversion vs. selectivity (progress over time)

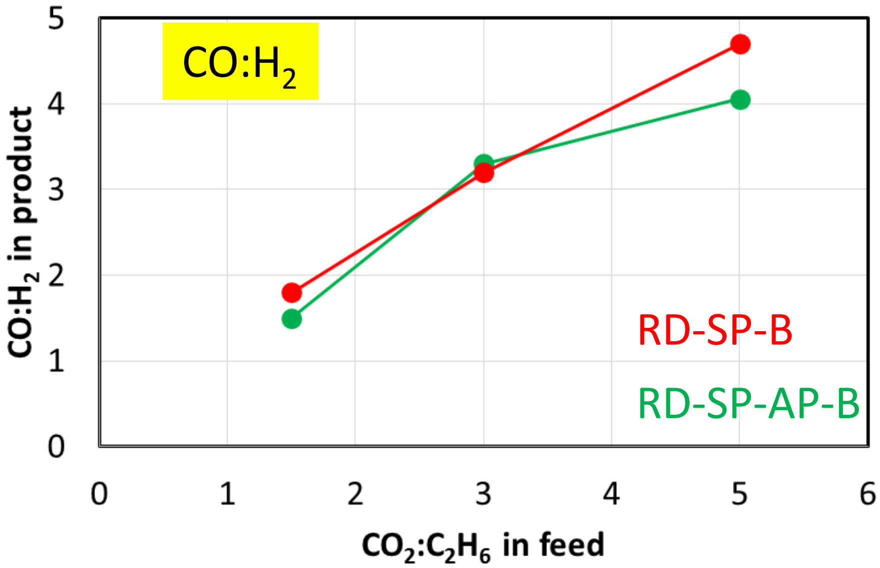


Task description and Progress/plans

CO_2 consumption and secondary product evolution

Overall reaction: $C_2H_6 + CO_2 = C_2H_4 + CO + H_2O$





$C_2H_6 = C_2H_4 + H_2$

$CO_2 : C_2H_6$ ↑
In feed

→

$CO_2 + H_2 = CO + H_2O$, $CO_2 + C = 2CO$

$C_2H_6 + 2CO_2 = 4CO + 3H_2$

↑

Task description and Progress/plans

Catalyst	**Concentrated (Captured) CO_2**		**Dilute (flue gas) CO_2**	
	Max. C_2H_4 yield (per pass), %	*Max. Productivity* (mmole C_2H_4/gcat.hr)	*Max. C_2H_4 yield* (per pass), %	Max. Productivity (mmole C_2H_4/gcat.hr)
RD-B	29	26	-	-
RD-SP-B	30	20	48	5.5
RD-SP-AP-B	32	23	48	7.8
RD-SP-A-B	23	14	41	4.7

- ☐ Yields are higher in dilute case primarily due to lower partial pressure of ethane in feed
- ☐ Ethylene productivity reduces with feed dilution

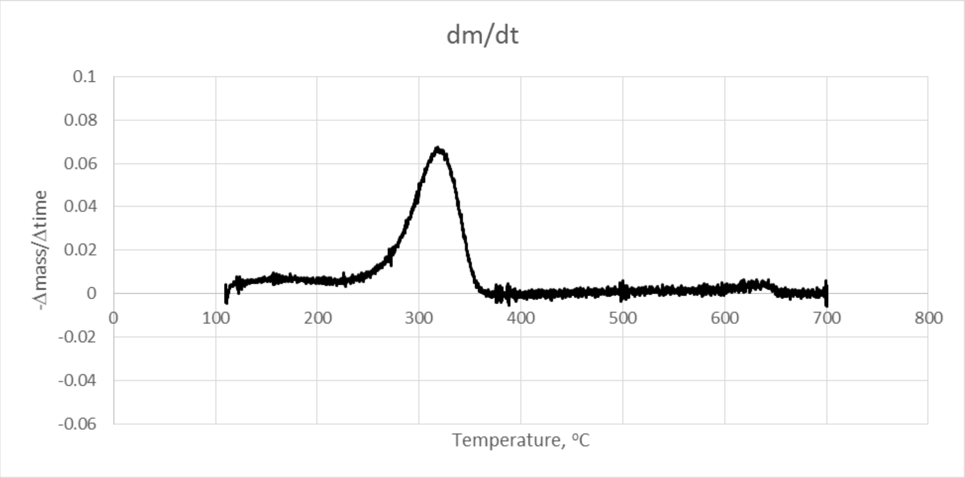
Task description and Progress/plans

Comparison with literature reports

- ☐ Inert gas content in feed specified to mimic captured and flue gas dilutions
- ☐ CO_2:C_2H_6 ratio in feed lowered to 1.5
- ☐ Ethylene productivity raised up to 26 mmoles/gcat.hr (literature < 20 mmole/gcat.hr)
- ☐ Long term, multiple cycle runs conducted to determine cycle to cycle reproducibility
- ☐ Examination of the impact of certain flue gas impurities is currently in progress

Task description and Progress/plans

Task 2.4 Catalyst regeneration



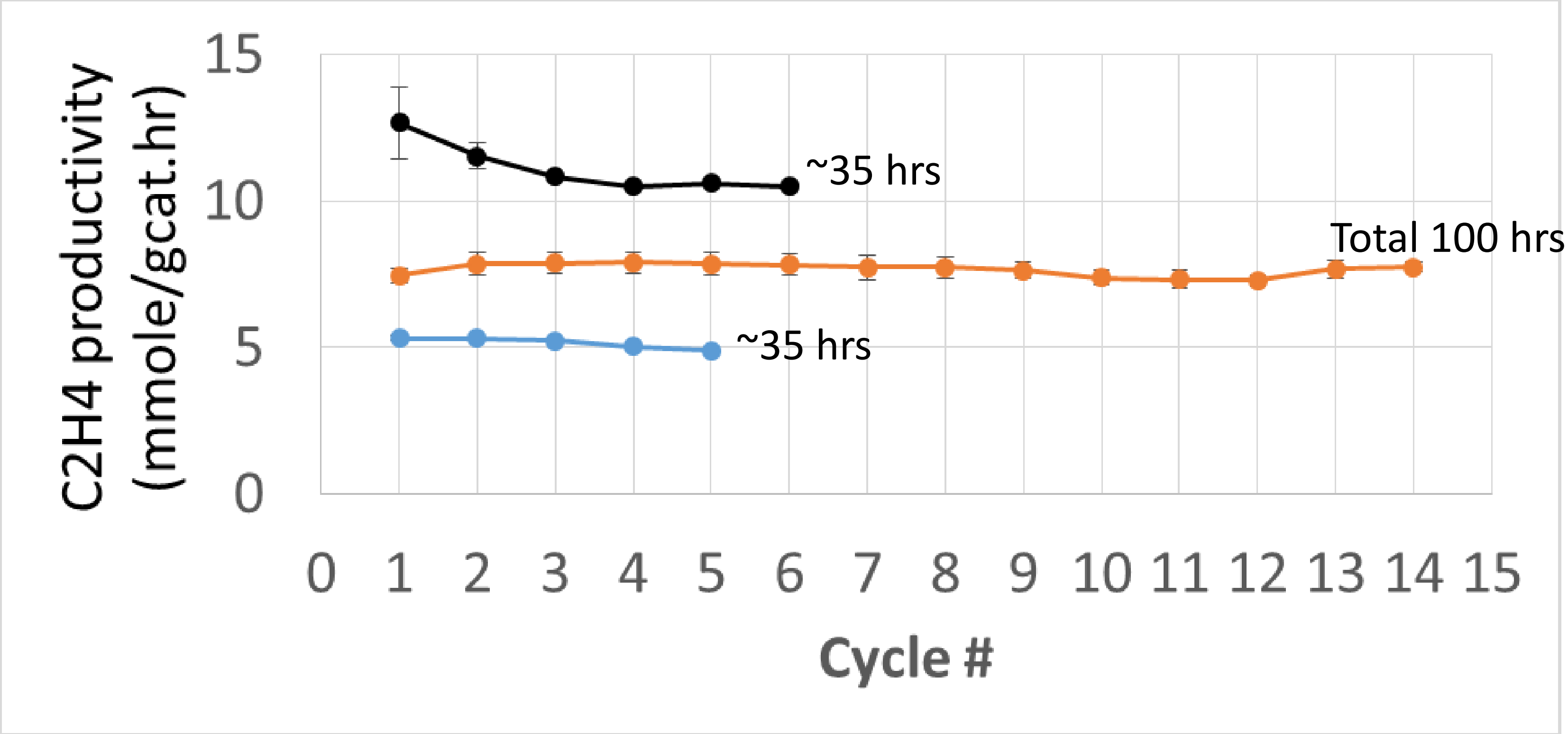
TGA plot: Coke burns off mostly ~300-350°C

(Catalyst regeneration @ reaction temperature ✓)

Catalytic run in cyclic mode:

ODH run (Cycle 1) --------> Regeneration @ reaction T ---------> ODH run (Cycle 2) ------>

Task description and Progress/plans



Continuous run time	5-7 hrs
Regeneration time @ reaction temperature	1 hr
Anticipated reactor occupancy	>80%

Task description and Progress/plans

Task 3: Initial Technoeconomic and life-cycle analysis

☐ **Assumptions/basis**

Coal-fired power plant	
Net power output (MW)	315
Type of coal	Bituminous
Boiler	PC subcritical
CO_2 emission (ton/MWh)[1]	0.8
Total CO_2 emission (ton/h)	253
Total CO_2 capture @ 90% (ton/h)	228
CO_2 capture process[2]	Shell Cansolv post-combustion CO_2 capture amine-based
CO_2 capture cost ($/ton)[2]	56.2
CO_2 avoided cost ($/ton)[2]	76
Plant life (years)	30

ODH plant	
Ethylene Production capacity, (ton/year)	790,000
CO_2:ethane ratio (feed)	5.0
CO_2 consumption (ton/ton ethylene)	2.4
Total CO_2 consumption (ton/hr)	228
Plant life (years)	30
Ethane price ($/ton)[3]	150
CO_2 price ($/ton)[4]	46

[4] Out of 76$/ton CO_2 avoided cost power plant shares $30/ton cost and the rest ($46/ton) is shared by proposed ethylene plant.

1https://www.eia.gov/tools/faqs/faq.php?id=74&t=11

2Cost and performance baseline for fossil energy plants Volume 1a: Bituminous Coal (PC) and Natural gas to electricity Revision 3, DOE/NETL-2015/1723

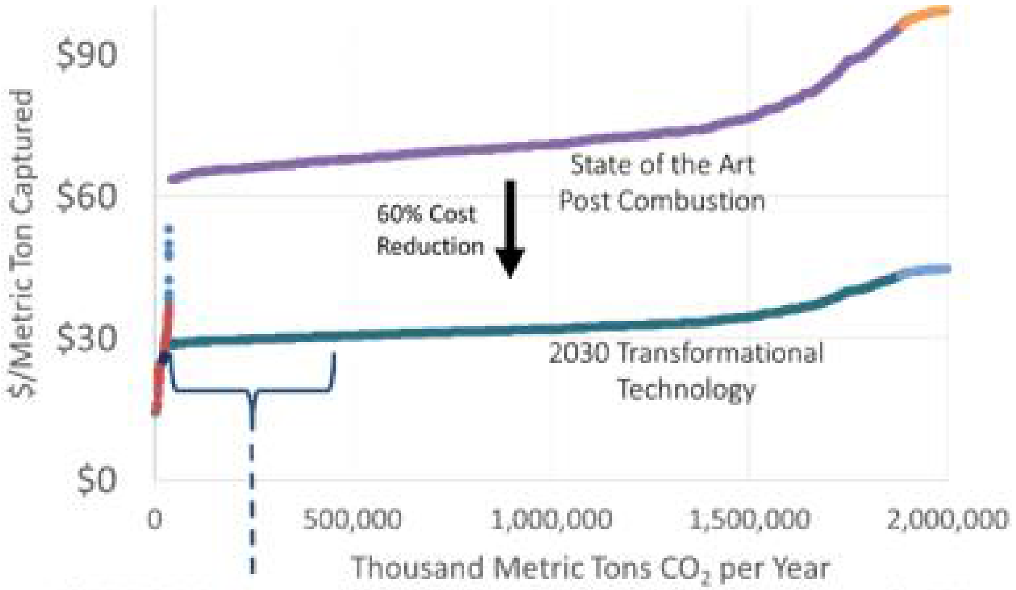
[3] http://marketrealist.com/2016/05/ethane-prices-fell-4-week-rally-impact-mlps/.
Accessed 12 Nov., 2016.

Task description and Progress/plans

Task 3: Initial Technoeconomic and life-cycle analysis

Supply Curve with Transformational Carbon Capture Technologies

Cost of Capture from Existing Sources



If RDD&D is successful, opportunity to capture approximately 400 million metric tons of CO$_2$ per year at roughly $30 per metric ton of CO$_2$

Carbon capture, utilization and storage: Climate change, economic competitiveness and energy security. DOE Report. August 2016.

Task description and Progress/plans

Task 3: Initial Technoeconomic and life-cycle analysis

Technology compared with baseline steam cracking (SC) in two different scenarios: (1) Direct utilization of flue gas as CO_2 source, (2) Use captured (95%) CO_2

Aspects	**SC (baseline)**	**Flue gas**	**Captured CO_2**
Raw materials	C_2H_6, steam (0.4lb/lb C_2H_6)	C_2H_6, N_2, CO_2	Ethane, CO_2
Raw material ($/ton ethylene)	270	250	358
Capex ($/ton ethylene)	45	67	34
Utility cost ($/ton ethylene)	108	161	113
Total production cost ($/ton ethylene)	423	480	505
Ethylene selling price ($/ton ethylene)[1]	978	978	978
By-product (CO or derivatives) sale to reach baseline profit ($/ton ethylene)	0	57	82
Net CO_2 avoided (ton/hr)	0	83	126
CO_2 avoidance cost for power plant ($/ton CO_2)	76	0	30

[1] http://www.platts.com/news-feature/2014/petrochemicals/pgpi/ethylene. 2016

Task description and Progress/plans

Task 3: Initial Technoeconomic and life-cycle analysis

Updated Preliminary LCA

Functional units: 1 kg ethylene and 2 kg CO

GHG emission flows: CO_2

Energy input flows: Methane combustion

Probable Plant location: Near Gulf coast or Pennsylvania

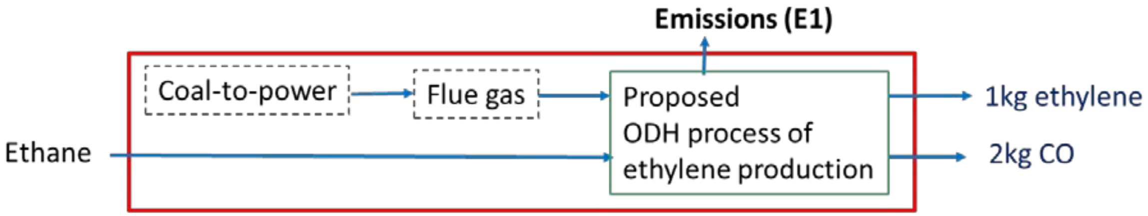
State of the art (SOA) alternative units: (i) Ethane steam cracking (Ethylene) and (ii) Coal gasification (CO as producer gas).

[1] http://www.platts.com/news-feature/2014/petrochemicals/pgpi/ethylene. Accessed 12 Nov., 2016.Accessed 12 Nov., 2016.

Task description and Progress/plans

Task 3: Initial Technoeconomic and life-cycle analysis

Scenario 1: Direct flue gas utilization



Emissions (E1)

Coal-to-power

Flue gas

Proposed ODH process of ethylene production

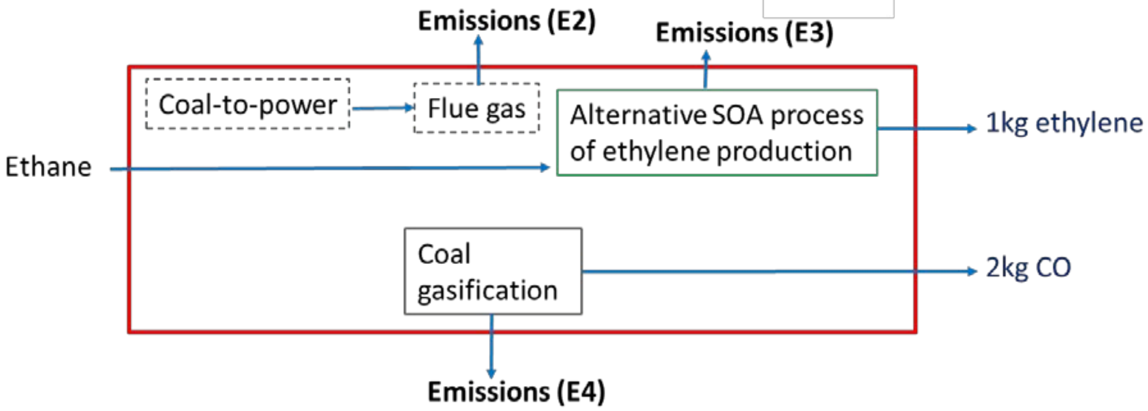
Ethane

1kg ethylene

2kg CO

E1 = 1.5kg/kg ethylene

SOA alternative case



Emissions (E2)

Emissions (E3)

Coal-to-power

Flue gas

Alternative SOA process of ethylene production

Ethane

1kg ethylene

Coal gasification

2kg CO

Emissions (E4)

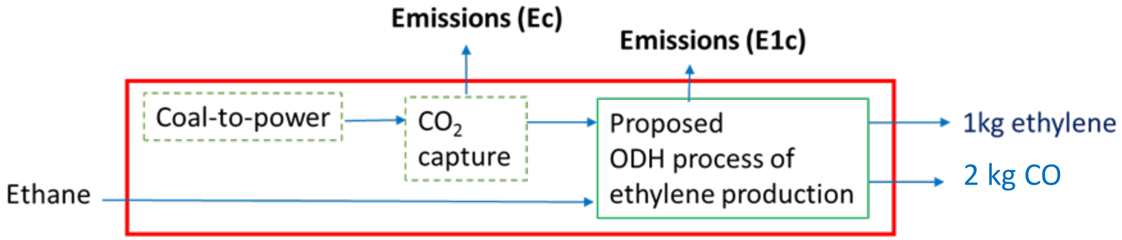
E2 = 0.8kg/kWh
E3 = 1.0 kg/kg ethylene
E4 = 0.8kg/2kg CO

$$\textbf{\% reduction in GHG emission} = \frac{E2+E3+E4-E1}{E2+E3+E4} = 42\%$$

Task description and Progress/plans

Task 3: Initial Technoeconomic and life-cycle analysis

Scenario 2: Captured CO_2 (95%) utilization



Emissions (Ec)

Emissions (E1c)

Coal-to-power

CO_2 capture

Proposed ODH process of ethylene production

Ethane

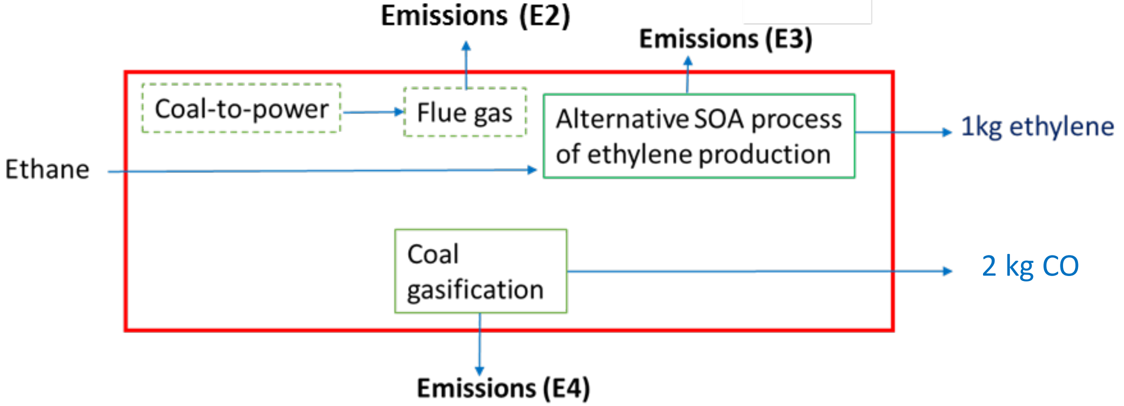
1kg ethylene

2 kg CO

Ec = 0.05kg/kWh

E1c = 1.05 kg/kg ethylene

SOA alternative case



Emissions (E2)

Emissions (E3)

Coal-to-power

Flue gas

Alternative SOA process of ethylene production

Ethane

1kg ethylene

Coal gasification

2 kg CO

Emissions (E4)

E2 = 0.8kg/kWh

E3 = 1.0 kg/kg ethylene

E4 = 0.8kg/2kg CO

% reduction in GHG emission= $\frac{E2+E3+E4-Ec-E1c}{E2+E3+E4}$=57%

Comparison with state of the art

Two competing processes – (1)Steam cracking (SC) and (2) Oxidative dehydrogenation by O_2 (ODH(O_2))

Aspects	**SC**	**ODH (O_2)**	**ODH (CO_2)**
Commercialization status	Commercial	Research	Research
Reactants	Steam	Air /O_2	CO_2
ΔH, kJ/mol	137	-105	134
Operating Temperature	750-900°C	<500°C	<700°C
CO_2 emission	Emission	Emission	Consumption
Major by-product(s)	C_1-C_4 alkanes/olefins	CO_2	CO
Catalyst	Steam	Expensive	Low cost
Chemical safety risk	Low	Highest	Lowest

Future work

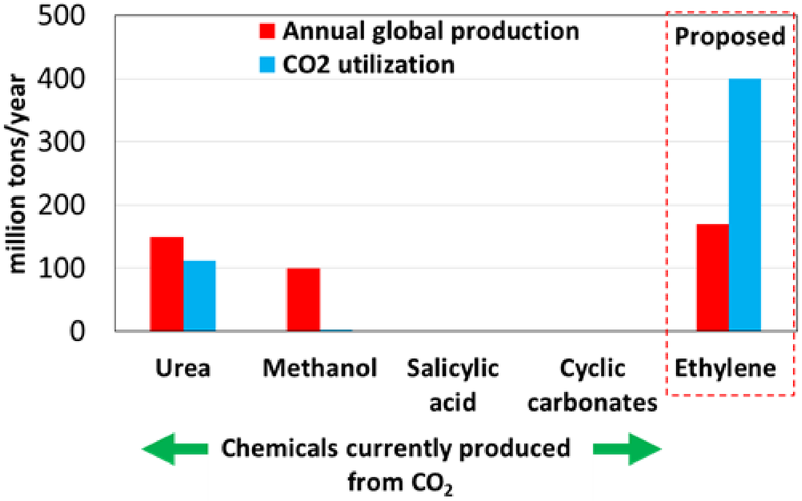
Remaining tasks-

- Impact of impurity testing (Task 4)
  - O_2, H_2O, SO_2, NOx (Determine recommended impurity levels)
- Long term catalyst testing for up to 500 hrs (Task 5)
- Technology assessment (Task 6)

Conclusion

Process advantages/promises

- Limits use of water in ethylene plant
- Reduces CO_2 avoidance cost to $30/ton
- CO_2 reduction via CO_2 conversion.
- Aligns favorably with recently passed carbon capture based legislature (45Q)
- Makes CO (platform chemical) as co product



Future consideration

- Separation of post-reaction raw gas stream
- Co-location of CO use with the available resources

Acknowledgement

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Disclaimer

Thank you!