Field-Scale Testing of the Thermocatalytic Ethylene Production Process Using Ethane and Actual Coal-Fired Flue Gas CO_2

DE-FE0031713

Joel Cassidy, Chanse Appling, & Jadid Samad

Founded in 1941

Team ~ 400
Divisions - 4

Private 501(c)(3) non-profit CRO

Discovered 7 FDA approved Cancer drugs

Sustainable Chemistry and Catalysis – New Processes and catalysts for production of chemicals/fuels

U.S. Department of Energy

Carbon Utilization Virtual Project Review Meeting
August 31st, 2021

Project Overview: Funding Profile

	Total (02-01-2019 to 11-30-2021)	
	DOE funds	Cost Share
Southern Research	$1,319,410	$350,500
ARTC	$35,200	$0
NCCC	$45,000	$0
8 Rivers LLC	$99,832	$24,958
Total ($)	$1,499,442	$375,458
Total Cost Share %		20%

Project Overview: Timeline

Task Name	Start	End	Resource
Task 1: Project management and reporting	Fri, 02/01/19	Sun, 02/28/22	SR
Task 2: Field scale preparation and testing	Fri, 02/01/19	Sun, 06/30/19	SR
Task 2.1: Catalyst scale up	Fri, 02/01/19	Sun, 03/31/19	SR
Task 2.2: Catalyst testing in a lab scale reactor	Mon, 04/01/19	Sun, 06/30/19	SR
Task 3 : Technology maturation plan	Mon, 07/01/19	Wed, 07/31/19	SR
Task 4: Procurement and integration of actual flue gas with skid	Thu, 08/01/19	Fri, 01/31/20	SR/NCCC
Task 4.1 Field scale skid preparation and transportation to the host site	Thu, 08/01/19	Mon, 09/30/19	SR
Task 4.2 Integration with the host site and commissioning of the skid	~~Tue, 10/01/19~~ Mon, 12/07/20	~~Fri, 01/31/20~~ Fri, 04/30/21	SR/NCCC
Task 4.3 Development of a baseline ASPEN simulation model	Mon, 09/30/19	Fri, 01/31/20	SR
Task 5: Continuous operation using actual flue gas	~~Sat, 02/01/20~~ Mon, 05/03/21	~~Mon, 11/30/20~~ Tue, 11/30/21	SR/NCCC
Task 6. Techno-economic and life cycle/ technology gap analysis	Wed, 12/01/21	Mon, 02/28/22	SR

Project Overview: Objectives of the Field Scale Study

- Scale up (~100x) synthesis of nano-engineered catalysts
- Validate performance of scaled up catalysts using laboratory scale reactor
- Integrate field scale skid with host site's post-combustion facility for direct actual flue gas derived CO_2 access. (Task 4.2)
- Process simulation with post reaction separation and capital cost estimation.
- Test the catalysts for stability under optimized process condition for an extended period of time. (Task 5)
- Techno-economic and life cycle assessment for potential commercialization of the process.

*Blue texts indicate NCCC tests

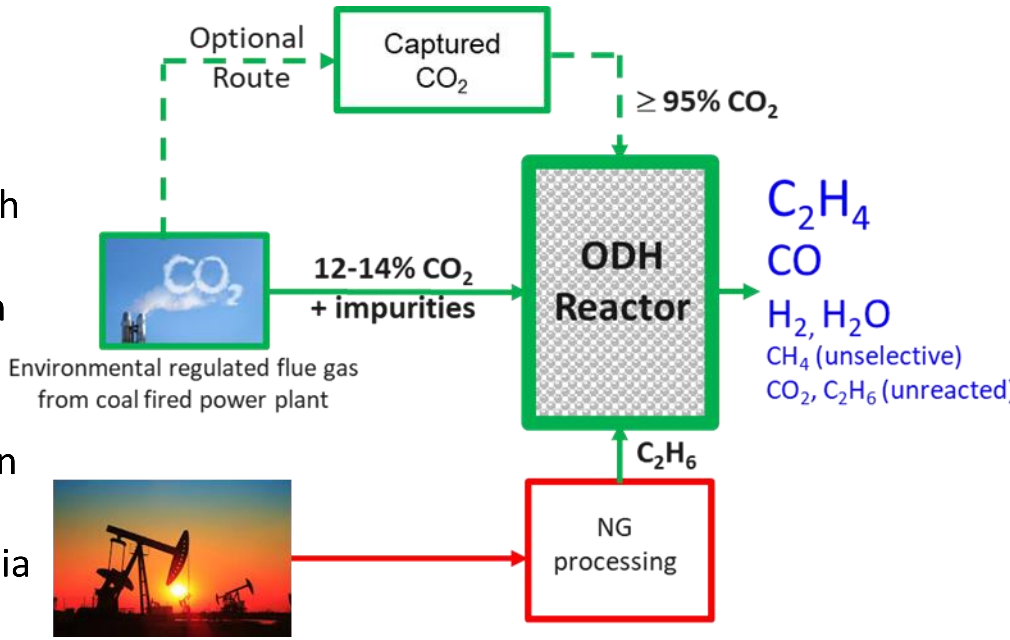
Technology Background

Thermo-catalytic ethylene production using ethane and CO_2 *(CO_2-ODH)*

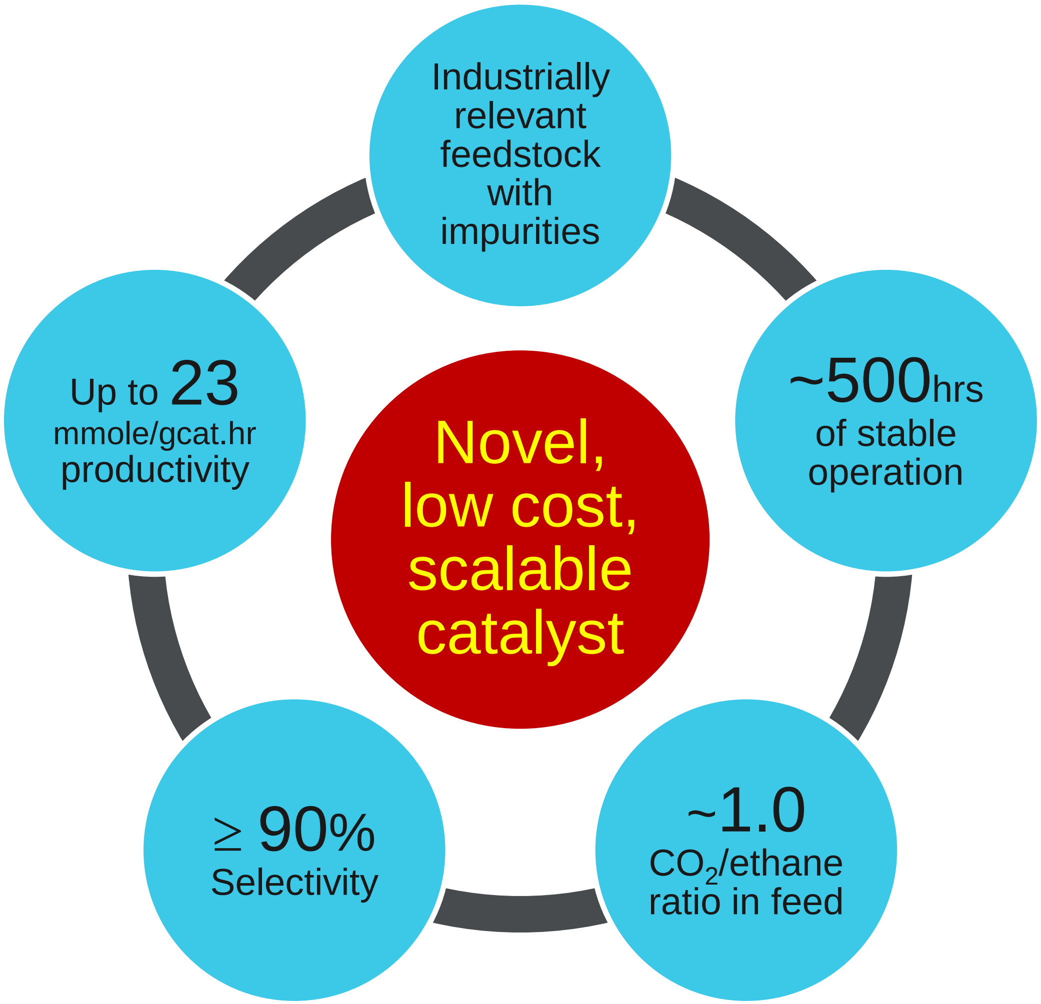
Oxidative dehydrogenation (ODH): $C_2H_6 + CO_2 \rightarrow C_2H_4 + CO + H_2O$

Advantages over *commercial steam cracking (SOA)*

- ✓ At least **150°C** lower operating temperature
- ✓ Catalytic process that **utilizes CO_2** and **eliminates** use of **H_2O and external reductants (e.g., H_2) or strong oxidant (e.g., O_2)**
- ✓ Process adaptable to different CO_2 streams with impurities
- ✓ Reduced process footprint due to high reaction selectivity
- ✓ Co-production of CO-rich syngas
- ✓ With co-product utilization, production cost can be lowered to SOA cost
- ✓ **50%** or more overall GHG emission reduction via direct CO_2 conversion



Innovation



Validation Using Two Relevant CO_2 Concentrations:

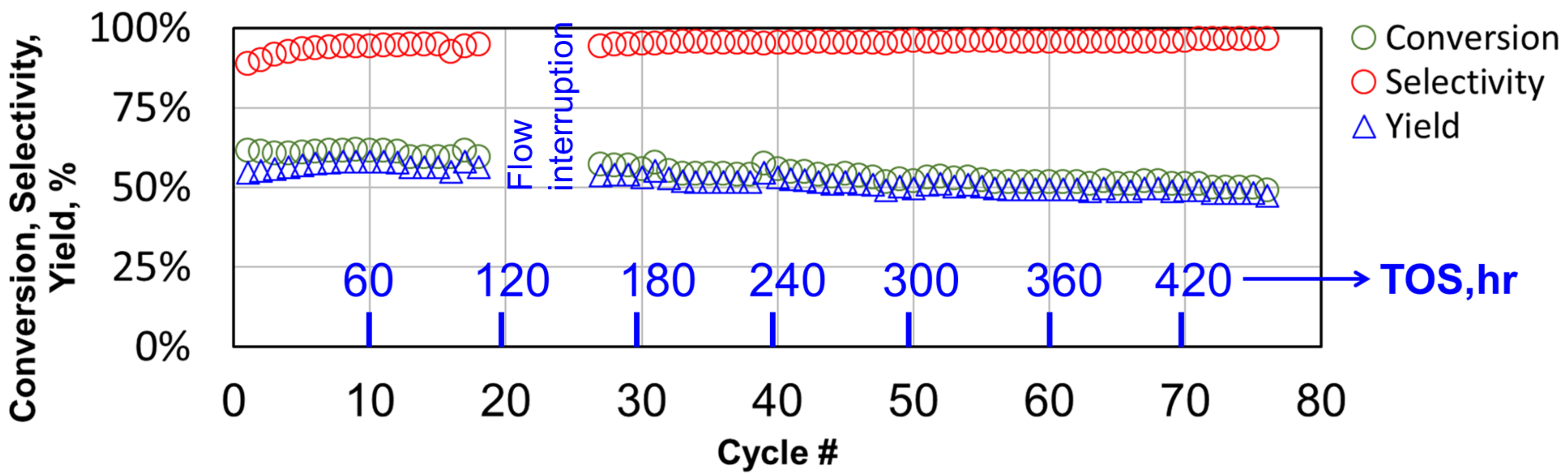
FG: Environmentally Regulated Flue Gas (**12-14% CO_2, balance N_2 + impurities**)

CAP: Captured CO_2 (**>95% CO_2, balance N_2**)

Catalyst addresses key commercialization issues

Laboratory Scale Results

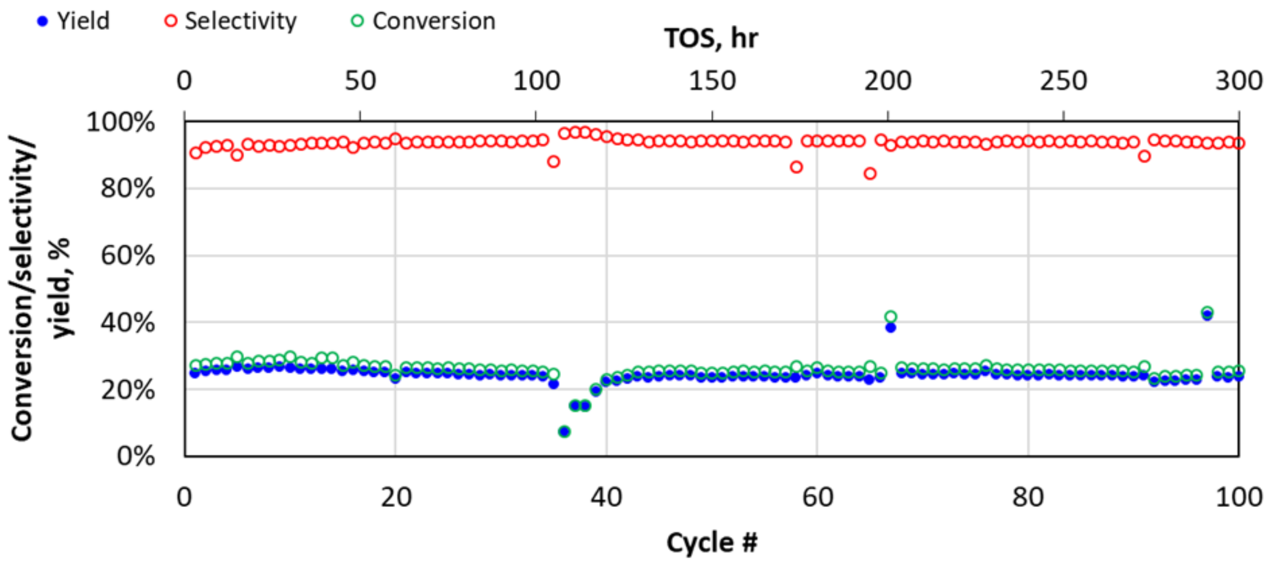
Long Term Stability (FG-case)



- **Cycle** = 5-7hr continuous run followed by 1hr air regeneration
- **Feed:** CO_2:ethane ~1.5, 80ppm SO_2, 80ppm NO (**FG** case)
- Stable performance during 76-cycle (~500hr) testing.

Laboratory Scale Results

Long Term Stability (CAP-case)



- ❑ **Cycle** = 2-3hr continuous run followed by 1hr air regeneration
- ❑ Stable performance during 100-cycle (~300hr) testing.

Technical Approach

Work Plan

- Total 1000-hr of total testing using **two actual** CO_2 streams (**FG & CAP**)
  - For flue gas stream testing the feed may vary between coal and natural gas flue gas.
  - During integration with the test facility, the flue gas feed was modified to accept feed from the coal unit as well as the newly installed natural gas boiler. This will allow for testing to proceed in the event of an outage or other shutdown of the coal fed boiler.

Flow rates for different CO_2 test cases

Test Case	Max. flow rate (L/min)				Ethane vol% in feed	Testing duration (hrs)
	Cap. CO_2	Flue gas	C_2H_6	Total Max.		
CAP	10	N/A	5.0	15	≥ 20%	500
CFG	N/A	11.5	0.5	12	≤ 10%	500
NFG	N/A	7.31	2.4	9.7	≤ 20%	-

Actual CO_2 composition

	Actual Composition (vol%)
FG	14% CO_2, 4.5% O_2, 68.5% N_2+Ar, 13% H_2O, < 1ppm SO_2, ~ 50ppm NO
CAP	> 99.5% CO_2, balance N_2

Technical Approach (cont.)

- Critical check outs prior to actual operation
  - Empty reactor tube fed with N_2 (temperature set point on preheater and reactor furnace, Feed analysis, GC calibration check),
  - Flow (Process and GC gases) and temperature profile (5-point TC)
  - Pressure difference across the bed
  - Periodic data collection and performance assessment on an pre-formulated excel spreadsheet

Technical Approach (cont.)

Catalytic Run Steps

1. **Pretreatment**: Activation at 650°C and atmospheric pressure under N_2

Cycle (3-8hrs)

2. **Reaction** run at 650°C: Ethane + FG/CAP + N_2 (optional) + SO_2 (optional)
3. **Purge**: N_2 only at 650°C
4. **Regeneration**: air at 650°C
5. **Purge**: N_2 only at 650°C

6. Repeat 2-5

Reaction – Endothermic – Temperature drop

Regeneration – Exothermic – Temperature increase

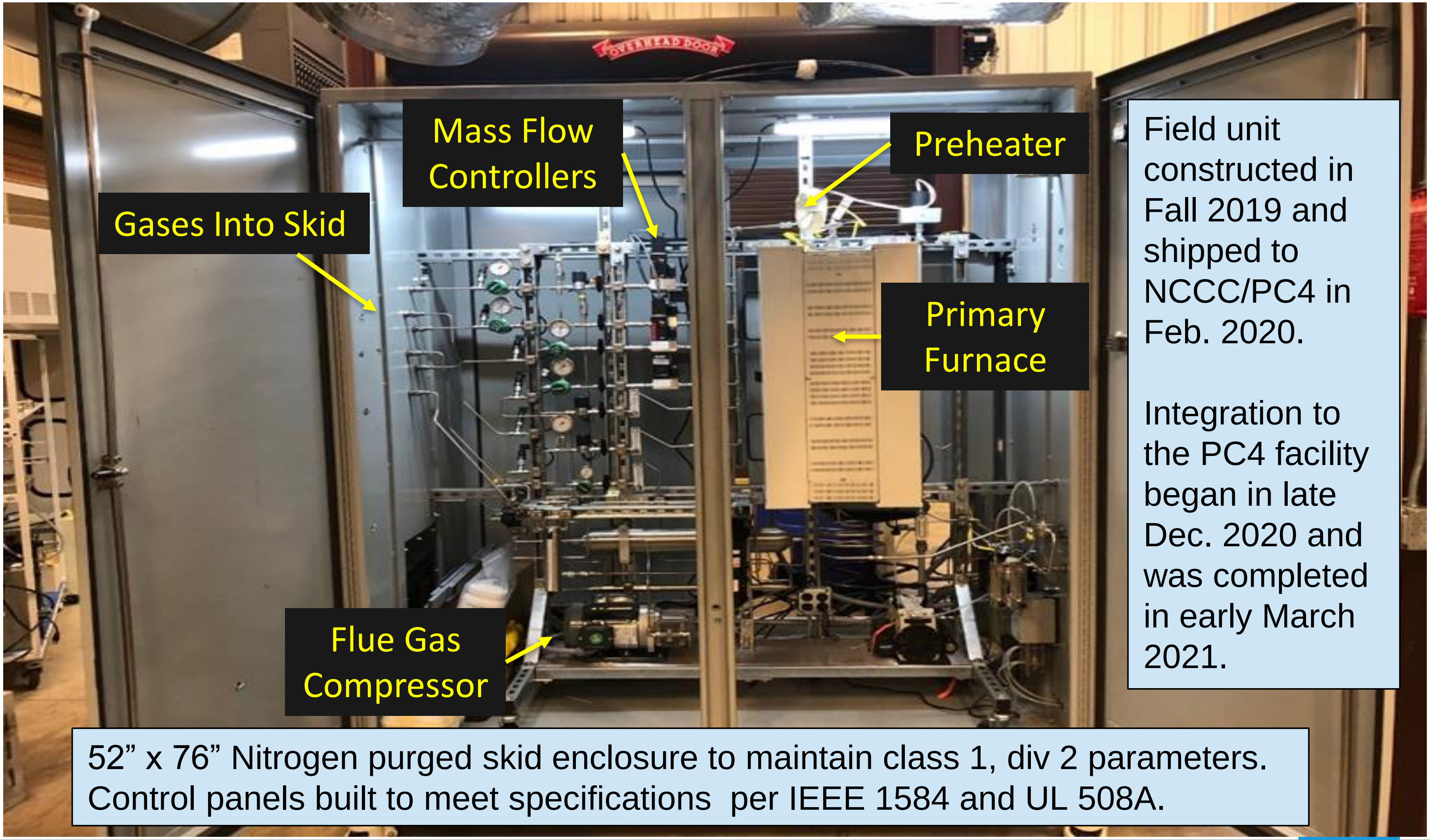
Success Criteria

Decision Point	Date	Success Criteria
Go/No-Go Decision Point: Scaled up catalyst performance validated	01/31/2020	2 catalysts with at least 48% (direct flue gas utilization) or 32% (captured CO_2) per pass yield
Technical Decision Point: TEA and LCA to determine ethylene production cost and net CO_2 reduction	02/28/2022	Final cost of ethylene compared with conventional ethylene production and lower than \$0.5/kg. Overall net CO_2 reduction > 40%

Technical Risks/Mitigation Strategies

Description of Risk	Probability	Impact	Response/Mitigation
Technical Risks:			
Process does not achieve anticipated conversion, yield upon catalyst scale up	Low	Med	Performance of scaled up catalysts will be first validated in an existing laboratory scale reactor prior to use in field scale. SR has prior experience catalyst synthesis and scale up through other projects
Flue gas impurities impact conversion or cause catalyst deactivation	Medium	High	SR is conducting laboratory scale study to evaluate the impact of specific impurities of flue gas. SR will also use captured CO_2 from actual flue gas as an alternative feedstock to direct flue gas utilization. Impurity levels in captured CO_2 is significantly lower.
Techno-economic analysis demonstrates poor economics because of technical integration issues	Low	Med	Preliminary model design with laboratory scale testing data show positive economics and life cycle benefits. Two different CO_2 options and catalyst options provide TE/LCA flexibility.

Current Progress - Field Testing Skid

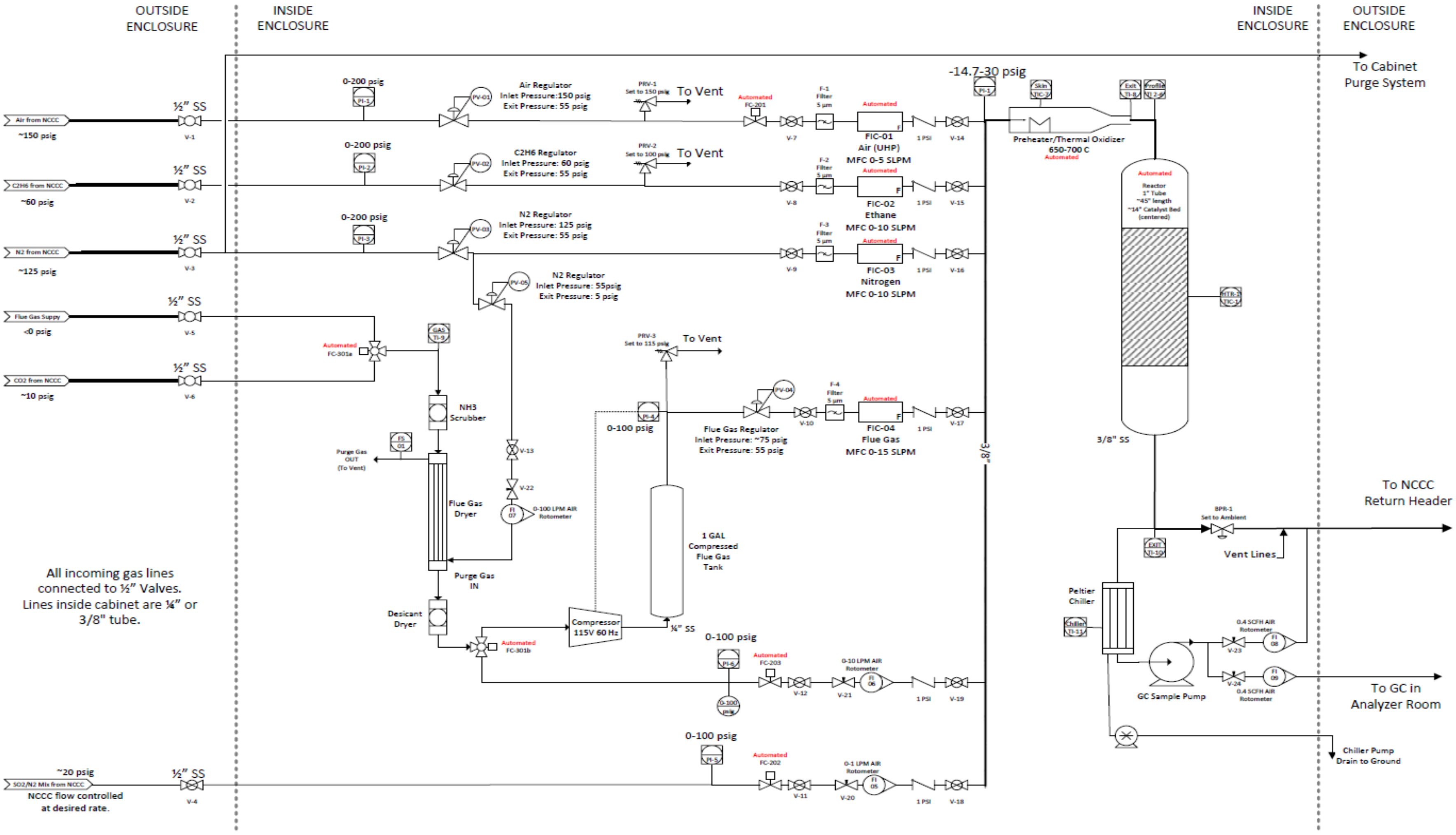


Field unit constructed in Fall 2019 and shipped to NCCC/PC4 in Feb. 2020.

Integration to the PC4 facility began in late Dec. 2020 and was completed in early March 2021.

52” x 76” Nitrogen purged skid enclosure to maintain class 1, div 2 parameters. Control panels built to meet specifications per IEEE 1584 and UL 508A.

Current Progress - Field Test Unit P&ID



NCCC Specific Timeline

Task Name	Start	End	Resource
Task 4.2 Integration with the host site and commissioning of the skid	~~Tue, 10/01/19~~ Mon, 12/07/20	~~Fri, 01/31/20~~ Fri, 04/30/21	SR/NCCC
Skid Delivery to NCCC/PC4	02/2020	02/2020	SR/NCCC
Program delayed due to COVID site access restrictions	03/2020	12/2020	-
Skid Integration with host site at PC4	12/2020	03/2021	SR/NCCC
Skid commissioning at host site at PC4	03/2021	04/2021	SR
Task 5 Continuous operation using actual flue gas	~~Sat, 02/01/20~~ Mon, 05/03/21	~~Mon, 11/30/20~~ Tue, 11/30/21	SR/NCCC
Flue Gas Testing (Coal/Natural Gas)	05/2021	07/2021	SR/NCCC
Captured CO2 Testing	08/2021	11/2021	SR/NCCC

NCCC Testing Phase Overview

Task 4.2 Integration with the host site and commissioning of the skid

- Adherence to industrial codes on skid
- Participation in the HAZOP study
- Arranging location of potential site for skid operation
- Share with SR the available actual CO_2 characteristics

Task 5. Continuous operation using actual flue gas

- Supply of gases (Flue gas, captured CO_2, N_2, air)
- Operational and analytical support, if needed

ASPEN Simulation Model Development

- Models have been completed for both direct flue gas (DFG) and captured CO_2 (CAP) utilization cases.
- Separation schemes considered in the model are at or near commercial stage (TRL 6 or higher). This includes cryogenic separation, sorbent based PSA separations etc.
- Separation scheme steps:
  - CO_2 separation: CO_2 is removed because it can freeze at low temperature in heat-exchange and fractionation equipment. CO_2 concentration in the overhead stream of the CO_2 separation are typically below 0.2ppm.
  - CO/C_2H_4 separation: Depending on the concentration of CO and C_2H_4 in the product stream, a pressure swing adsorption (PSA) or cryogenic distillation based system has been applied. With the applied scheme, a final C_2H_4 purity of 99.8% and CO purity of 98% were achieved.
  - C_2 splitter: This tray type distillation column involves separation between ethane and ethylene widely used in commercial steam cracking process and commonly referred to as "C_2 splitter".

Techno-Economic Analysis

CAPITAL COST		
Total permanent Investment incl. land & startup	$719,620,184	$410,602,298
Capital depreciation (20-year Straight)	**$33,488,711**	**$18,008,873**
OPERATING COST (Annual)		
Raw materials	$132,510,437	$162,707,271
Utility	$49,979,844	$46,138,987
Catalyst cost	$4,225,285	$3,968,254
Fixed cost	$22,396,600	$12,779,096
General expense	$61,285,541	$64,999,975
TOTAL OPERATING COST (ANNUAL)	**$270,397,706**	**$290,593,584**
OTHER PRODUCTION COST (ANNUAL)		
Intermediate CO2 separation	$36,960,000	$72,299,400
CO+C2H4 separation	$181,779,115	$35,165,686
Post production CO separation	-	
TOTAL PRODUCTION COST (Annual)	**$522,625,533**	**$416,067,542**
Cost of ethylene production	**$411/MT**	**$302/MT**

DFG: Production capacity: 500,225 MT/year Ethylene – 772,575 MT/year CO

CAP: Production capacity: 500,000 MT/year Ethylene – 879,142 MT/year CO

Future Plans

- **Complete ongoing project**
  - Complete a cumulative 1000-hr testing on field scale
  - Update TEA/LCA

- **Recommendations for future research include -**
  - Other sources of real CO_2 wastes: Concentration/Purity
  - Product processing and separation
  - Process scale up with separation
  - Co-product utilization

Summary

- Developed Technology
  - Nano-engineered mixed oxide catalyst
  - Thermocatalytic process
    - Utilizes CO_2
    - Produced ethylene at lower temperatures than SotA
- Prior Work
  - Lab-scale testing with over 500 hours of catalyst run time proven
  - Highly selective and notable conversions
  - Brought to TRL-4
- Current Work
  - Testing at TRL-5 at a power plant
  - Three options of CO2 feed to test versatility

Acknowledgement

This material is based upon work supported by the Department of Energy under Award Number DE-FE0031713

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Thank you!

Questions/Comments?

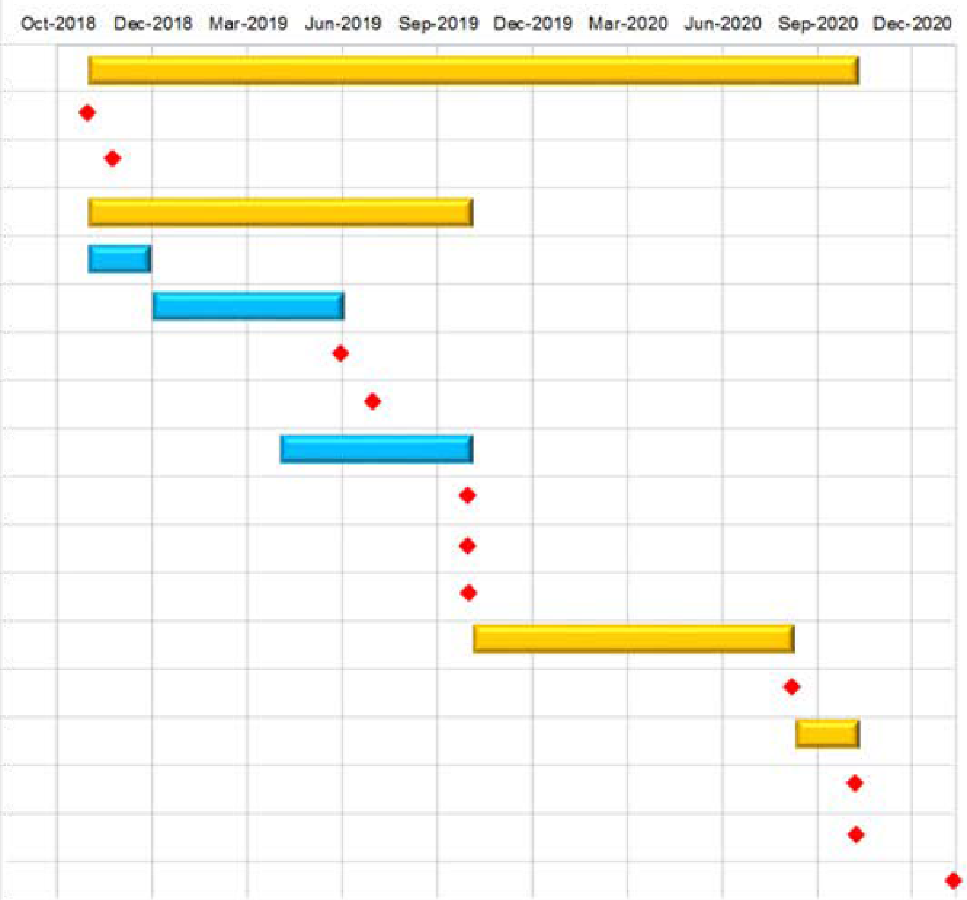
APPENDIX

Appx: Contact Personnel

- **Joel Cassidy** – PI
  - Interim Project Leader
  - jcassidy@southernresearch.org
- **Chanse Appling**
  - Process Engineer
- **Wes Wilson**
  - Sr. Process Technician
- **John Carroll** (*Southern Company*)
  - NCCC project coordinator and contact person
- **Jadid Samad** (*Consultant*)
  - Co-Inventor/Former Co-PI (Consulting with SR)

Appx: Gantt

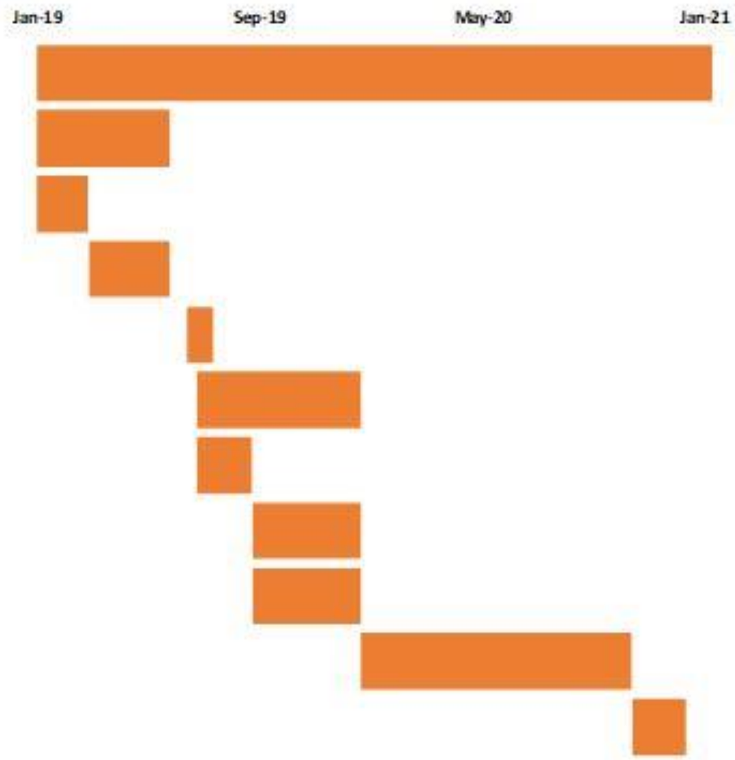
Task Name	Start	End	Resource
Task 1: Project management and reporting	Tue, 10/30/18	Thu, 10/29/20	SR
Milestone A	Tue, 10/30/18	Tue, 10/30/18	SR
Milestone B	Thu, 11/01/18	Thu, 11/01/18	SR
Task 2: Field scale preparation and testing	Tue, 10/30/18	Tue, 10/29/19	SR/NCCC/8R
Task 2.1: Catalyst scale up	Tue, 10/30/18	Sat, 12/29/18	SR
Task 2.2: Ethane ODH experiments	Sun, 12/30/18	Sat, 06/29/19	SR
Milestone C	Sat, 06/29/19	Sat, 06/29/19	SR
Milestone D	Mon, 07/29/19	Mon, 07/29/19	SR
Task 2.3: Procurement and integration of actual flue gas with skid	Tue, 04/30/19	Tue, 10/29/19	SR/NCCC/8R
Milestone E	Tue, 10/29/19	Tue, 10/29/19	SR
Milestone F	Tue, 10/29/19	Tue, 10/29/19	SR
Technical decision point (12-month)	Tue, 10/29/19	Tue, 10/29/19	SR
Task 3: Continuous operation using actual flue gas	Wed, 10/30/19	Sat, 08/29/20	SR/NCCC
Milestone G	Sat, 08/29/20	Sat, 08/29/20	SR
Task 4: Techno-economic and life cycle analysis	Sun, 08/30/20	Thu, 10/29/20	SR/8R
Milestone H	Thu, 10/29/20	Thu, 10/29/20	SR
Milestone I	Thu, 10/29/20	Thu, 10/29/20	SR
Milestone J	Fri, 01/29/21	Fri, 01/29/21	SR



Appx: Gantt-Updated

Table 1. Tasks and projected timeline.

Task Name	Start	End	Resource
Task 1: Project management and reporting	Wed, 01/02/19	Sun, 01/31/21	SR
Task 2: Field scale preparation and testing	Wed, 01/02/19	Sat, 06/01/19	SR
Task 2.1: Catalyst scale up	Wed, 01/02/19	Fri, 03/01/19	SR
Task 2.2: Catalyst testing in a lab scale reactor	Sat, 03/02/19	Sat, 06/01/19	SR
Task 3 : Technology maturation plan	Sun, 06/02/19	Mon, 07/01/19	SR
Task 4: Procurement and integration of actual flue gas with skid	Tue, 07/02/19	Wed, 01/01/20	SR/NCCC/8R
Task 4.1 Field scale skid preparation and transportation to the host site	Tue, 07/02/19	Sun, 09/01/19	SR
Task 4.2 Integration with the host site and commissioning of the skid	Mon, 09/02/19	Wed, 01/01/20	SR/NCCC
Task 4.3 Development of a baseline ASPEN simulation model	Mon, 09/02/19	Wed, 01/01/20	SR/8R
Task 5: Continuous operation using actual flue gas	Thu, 01/02/20	Sun, 11/01/20	SR/NCCC
Task 6. Techno-economic and life cycle/ technology gap analysis	Mon, 11/02/20	Fri, 01/01/21	SR/8R



Appx: Pricing of Materials/Chemicals

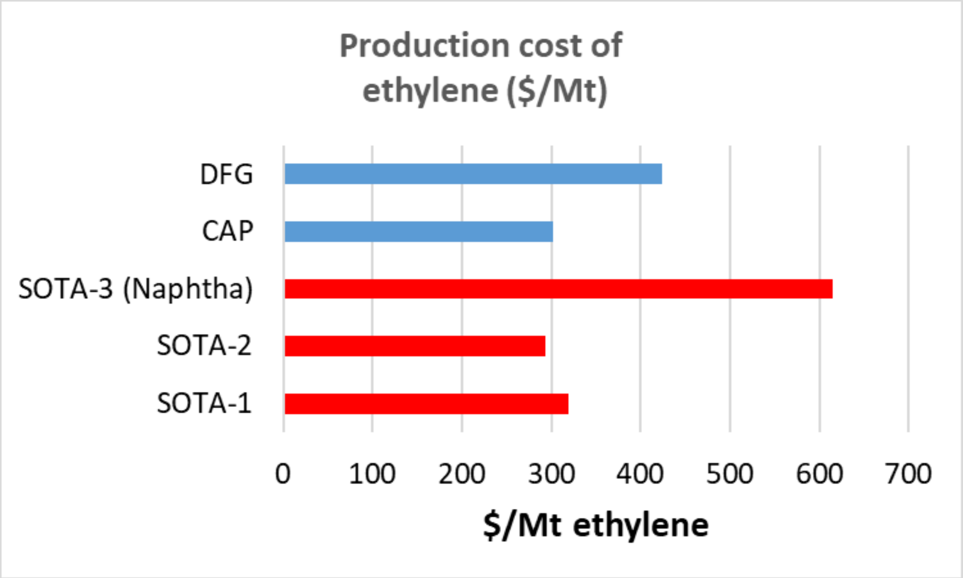
Material	Role	$/unit
Ethane	Raw material	$150/Mt
Flue gas	Raw material	$0.0/Mt
Captured CO_2	Raw material	$40/Mt
Natural gas	Utility	$3.1/ 10^3ft3
Steam	Utility	$3.0/klb

Ref:

1) Ethane price: http://marketrealist.com/2016/05/ethane-prices-fell-4-week-rally-impact-mlps/.
2) Natural gas: eia.gov
3) Steam: How to calculate true steam cost. US DOE. EERE

Appx: Cost of Production

Cost type	DFG	CAP
Total permanent investment[1]	$ 811,635,823	$ 410,602,298
Capital depreciation[2]	$ 35,987,442	$ 18,008,872
Annual operating Cost	$ 503,249,579	$ 398,058,669
Total production cost (annual)[3]	$ 539,237,021	$ 416,067,542
Ethylene production cost	**$0.424/kg**	**$0.302/kg**



TEA comparison

Production cost in CAP case is similar to the lowest SOTA[4] case

[1] Includes 25% contingency, 4% (of TDC) land and 10% (of TDC) start-up
[2] 20-year straight
[3] Includes capital depreciation, fixed and variable operating cost

[4] Yang, M., & You, F. (2017). Industrial & Engineering Chemistry Research, 56(14), 4038-4051.

Appx: Future Plans

- Transition technology from TRL 4/5 to TRL 6.
  - All necessary components of the technology will be integrated at a relevant environment at a substantially larger scale of 1 kg/hr which will amount to 10-20x scale up from the current field test scale.
  - Host site could be either a coal-fired utility plant or a natural-gas production plant.
  - Process simulation with necessary post-reaction separation will be demonstrated.
  - TEA study would be updated with actual separation and purification results.

Appx: Future Plans

- Further progression through TRL’s 7-9 would be achieved by:
  - Initial validation of system prototype in an operational environment.
  - All scaling issues relating to catalysis and separation will be address to obtain purity levels at 1 ton/hr production capacity.
  - Completing TRL 7 will inform further engineering design and enhancements to further develop TEA models that will support further commercialization decisions.
  - TRL 8 & 9 would eventually enable commissioning of a full scale plant and subsequent commercial operation.