FE0032507

CATREDOX
CATALYTIC & REDOX SOLUTIONS

Sustainable Aromatics Manufacturing from Methane via Oxidative Coupling and Aromatization

Kick Off Meeting

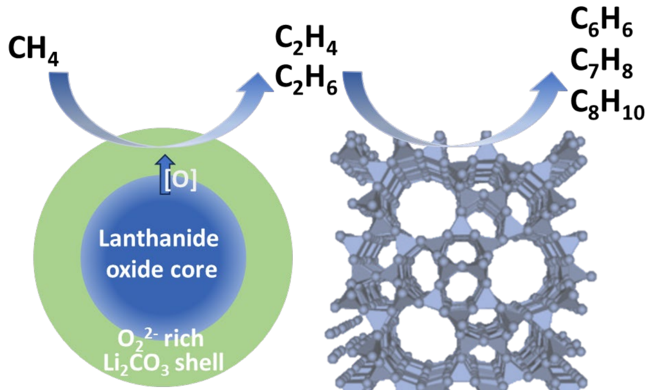
August 29th, 2024

NC STATE UNIVERSITY

Agenda/Outline

- Introductions
  - CatRedox, Luke Neal
  - NC State University, Fanxing Li
  - WVU, John Hu and Debangsu Bhattacharyya
  - Other Partners: Dan Rutherford, Jay Hewitt, JM
  - DOE NETL
- Overview and Background
- Tehcnial approach, scope of work and timeline
- Discussions

Overview: OC-DHA



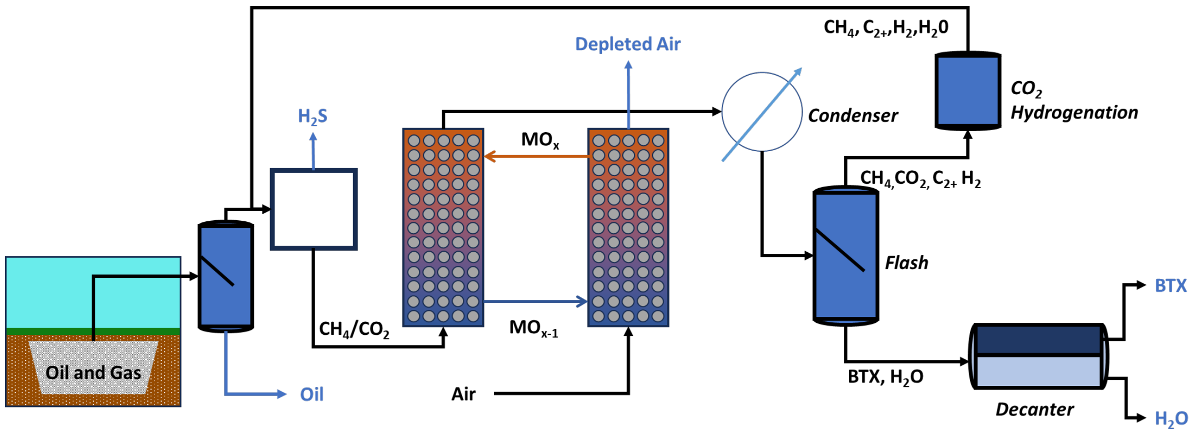
Core-shell OCM catalyst

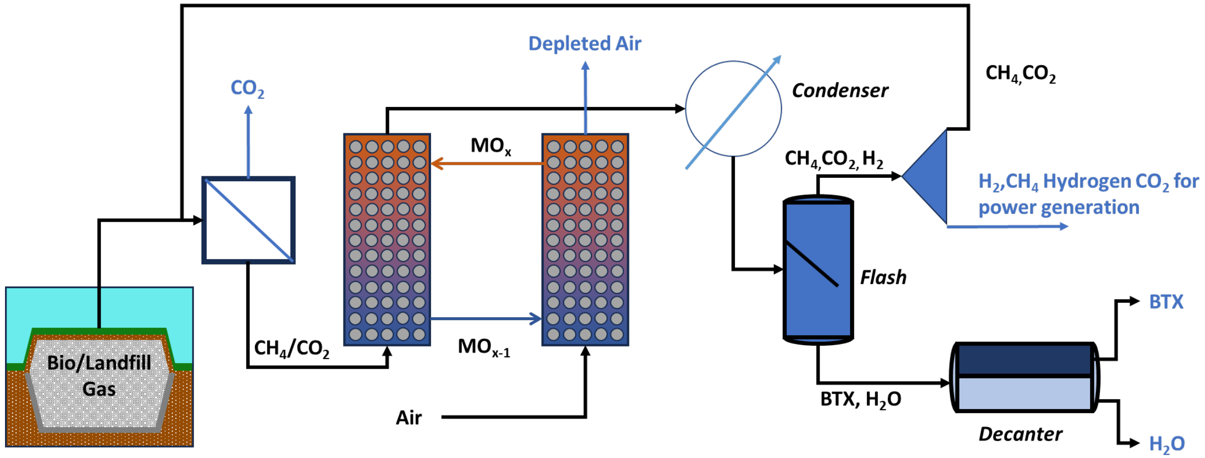
Metal-exchanged Zeolite DHA catalyst

$2CH_4+MO_x \rightarrow C_2H_6 + H_2O + MO_{x-1}$ Reaction 1a
$2CH_4+2MO_x \rightarrow C_2H_4 +2H_2O + 2MO_{x-1}$ Reaction 1b
$3C_2H_4 \leftarrow \rightarrow C_6H_6 + 3H_2$ Reaction 2
$MO_{x-1}+Air \rightarrow MO_x+N_2$ Reaction 3

- Stranded methane is converted into aromatics (BTX) in a 2-steps
  - CL-OCM (Rxn. 1 a&b): Methane is oxidatively coupled over a chemical looping catalyst to form ethane or ethylene
  - DHA (Rxn. 2): The C_2 products are reacted over a zeolite to form aromatics
- To close the chemical looping mass balance the CL-OCM catalyst is regenerated in air (Rxn 3)
- The OCM/regeneration steps provide heat allowing for autothermal operation.
- The hydrogen byproduct can be used to hydrogenate CO_2 to improve ultimate yields
- The feasibility of the chemical looping OC-DHA catalyst was recently validated in DOE-NETL funded project and NCSU and WVU (DE-FE0031869: PM Anthony Zammerilli)

Technology advantages





- 1. Simplified feedstock preparation; The OC-DHA redox catalyst will simultaneously convert C$_1$-C$_3$ components in shale or bio/landfill gas.
- 2. Increased single pass yield and productivity; existing DHA is limited by thermodynamics with 8% single pass CH$_4$ conversion at 650 °C vs 75% CH$_4$ conversion for CL-OCM within a single pass. Aromatic yields of ~15% have been demonstrated;
- 3. Simplified product separation and recycle scheme; OC-DHA results in an easy-to-separate product slate consisting of liquids (aromatics and water) and gas (gaseous alkanes and alkenes with small amount of CO$_x$ and unconverted H$_2$).
- 4. High robustness; The cyclic process periodically regenerates the catalysts.

Background: Previous Project

Core-Shell Oxidative Aromatization Catalysts for Single Step Liquefaction of Distributed Shale Gas

Fanxing Li (PI)

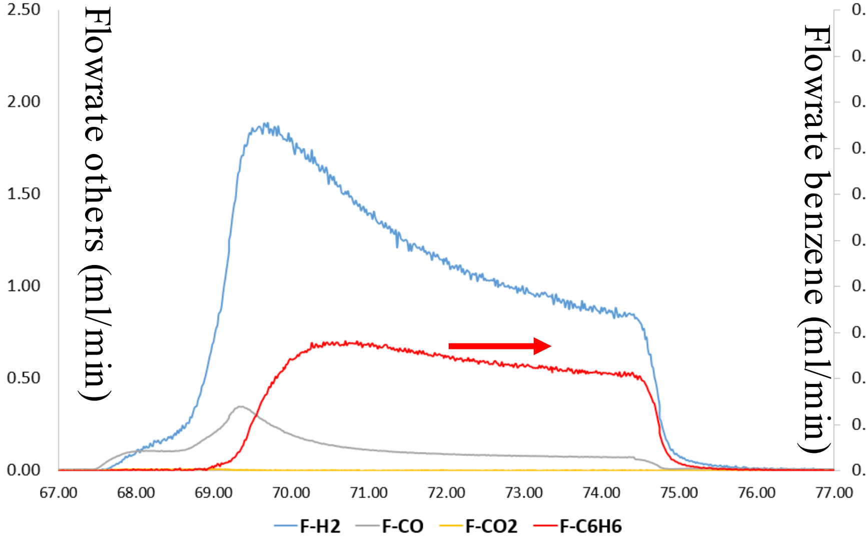
NC State University

Project Partners: West Virginia University, Lehigh University, Susteon Inc. and Shell

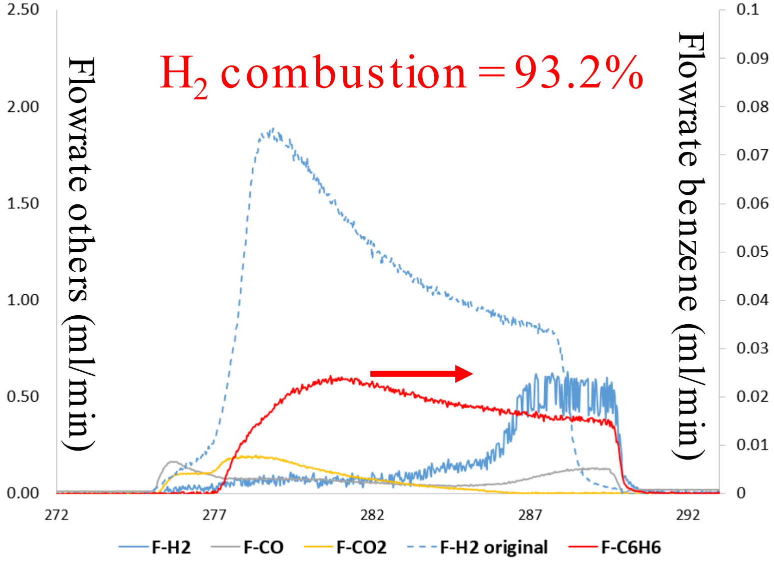
DOE/NETL Project Manager: Anthony Zammerilli

Summary of Project Progress – DHA + SHC +DHA sequential bed

DHA
single bed

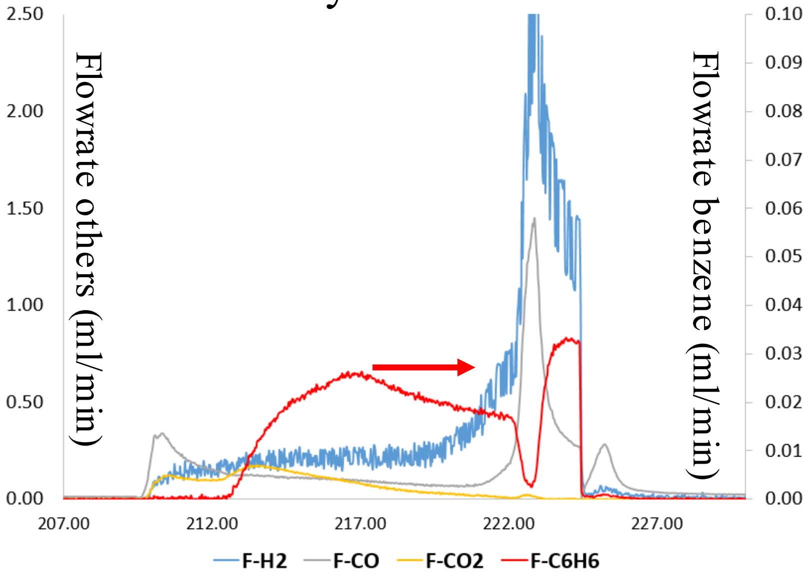


DHA+SHC
2-layer bed



H_2 combustion = 93.2%

DHA+SHC+DHA
3-layer bed



- $Na_2WO_4/CaMnO_3$ leads to H_2 combustion = 93.2%.
- CO by-product is also combusted into CO_2.
- Benzene formation rate is barely affected.

- H_2O formed in the SHC bed deactivates benzene formation from the 2nd DHA bed.
- 2nd DHA bed starts to form benzene only when the SHC bed is fully consumed of active lattice oxygen.

DHA → SHC → H_2O Removal → DHA

~40% yield increase but a very complex process configuration

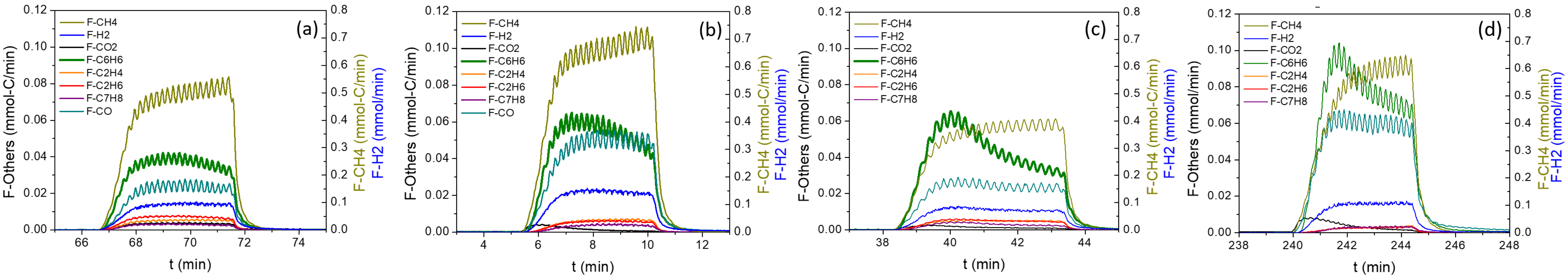
Summary of Project Progress – Further Improvement OCM+DHA Catalyst

Alternative approach :

Methane oxidative coupling → C2+ Dehydroaromatization (DHA) →

Surface promoted mixed oxide

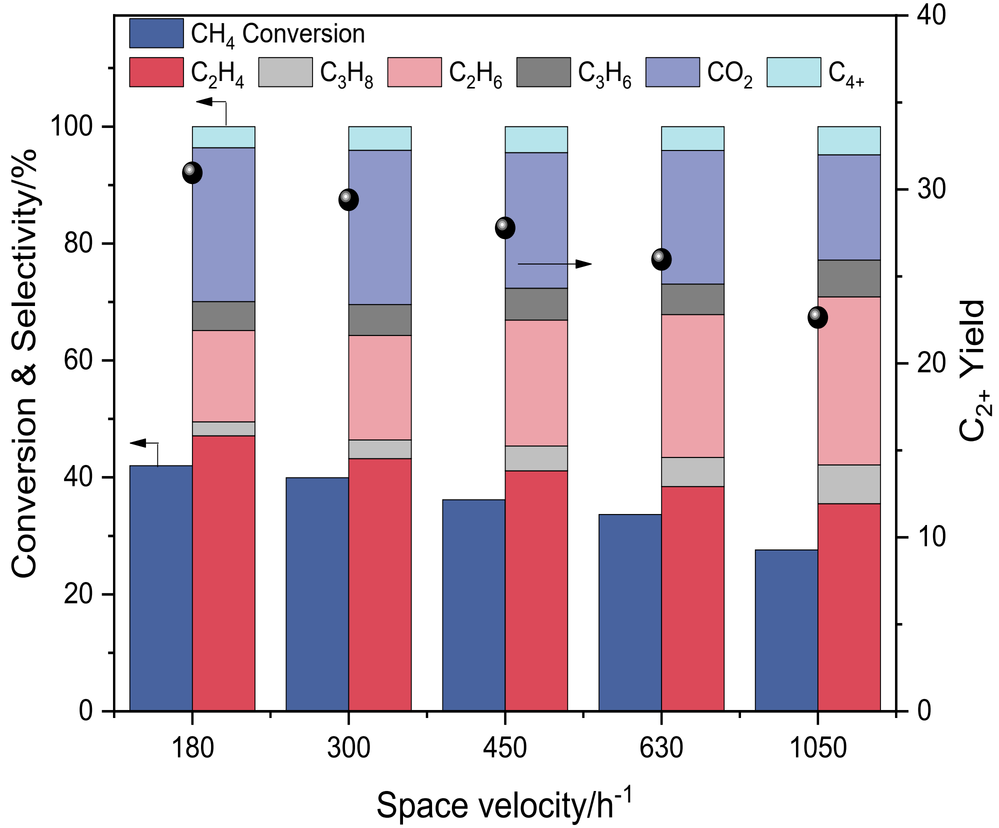
Ga/ZSM based catalyst

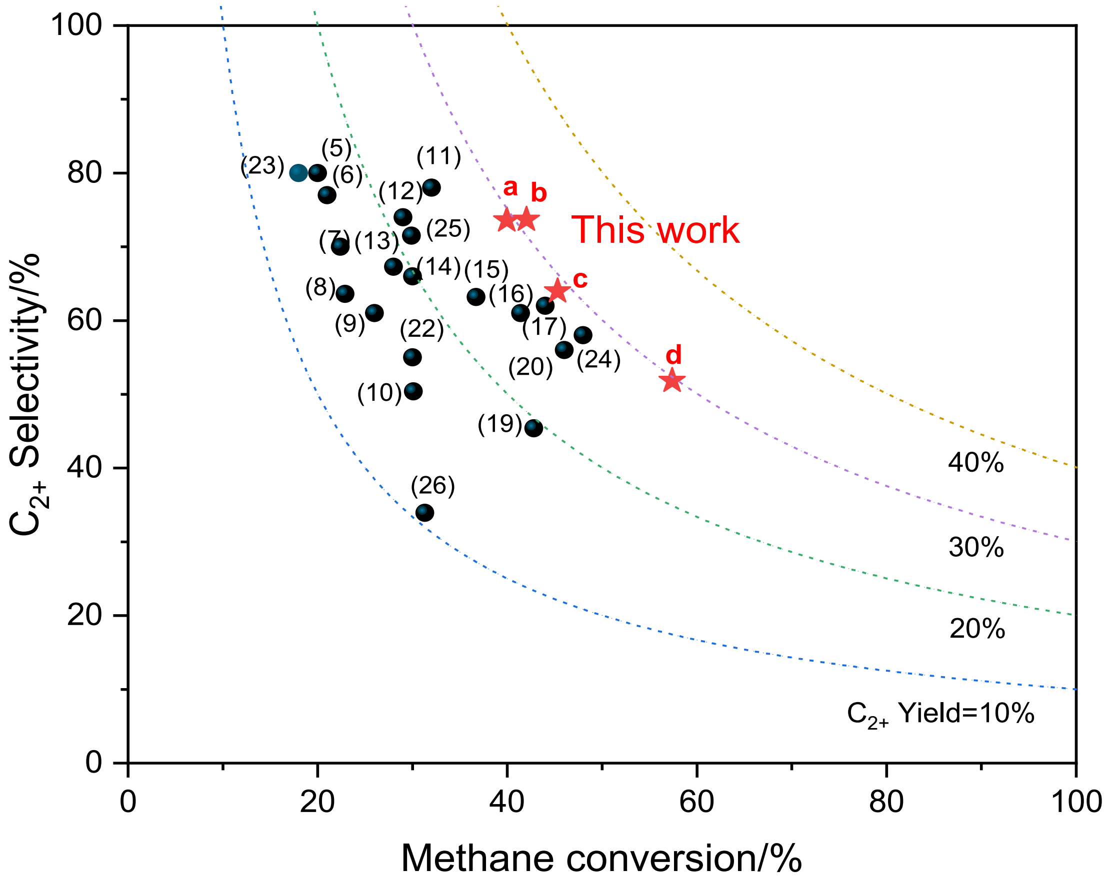


Methane DHA tests in OCM+DHA route at 700^{o}C (a) without H_2-pretreatment, (b) with H_2-pretreatment and 720^{o}C (c) without H_2-pretreatment (d) with H_2-pretreatment.

Combining OCM with DHA shows promising aromatic yield

Summary of Project Progress – OCM Catalyst Optimization





Our recently developed CL-OCM redox catalyst showed 30+% single pass C2+ yield

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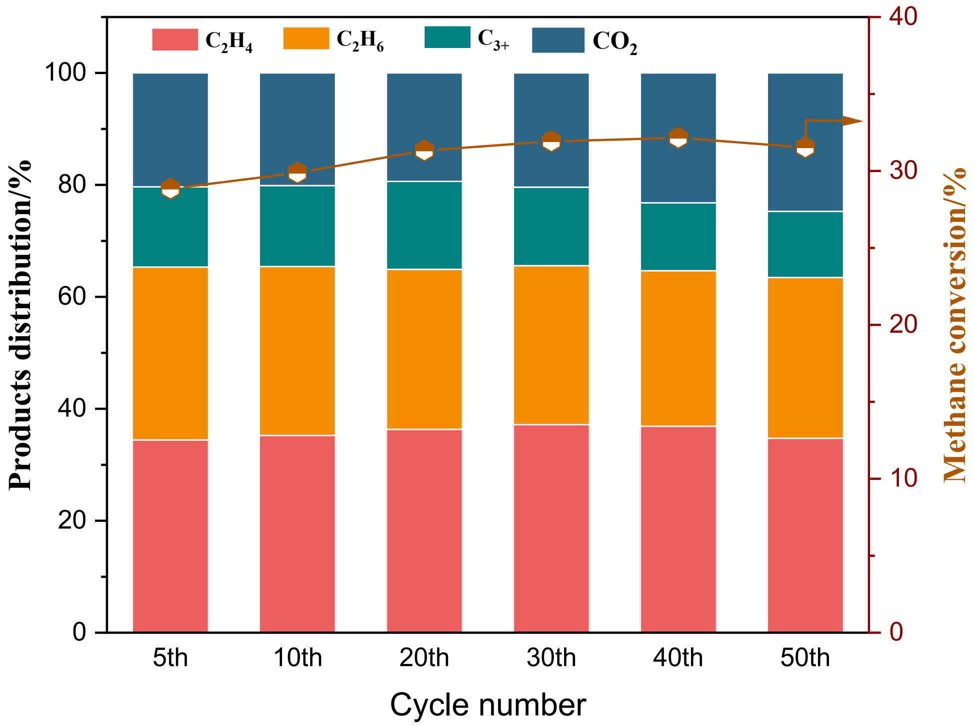
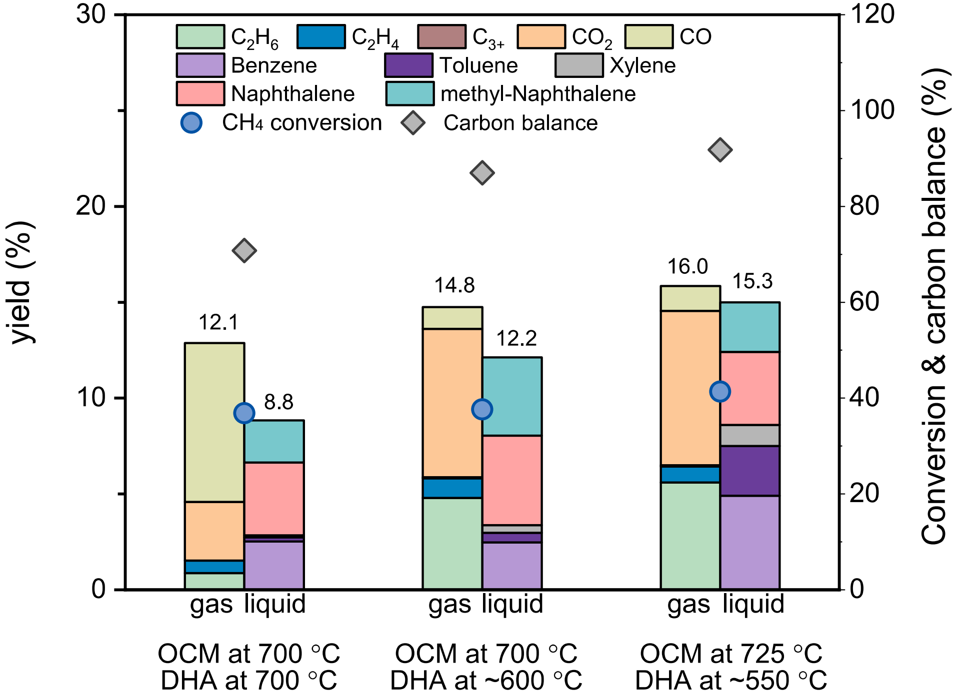
Summary of Project Progress – OCM Catalyst Stability and OCM+DHA Performance



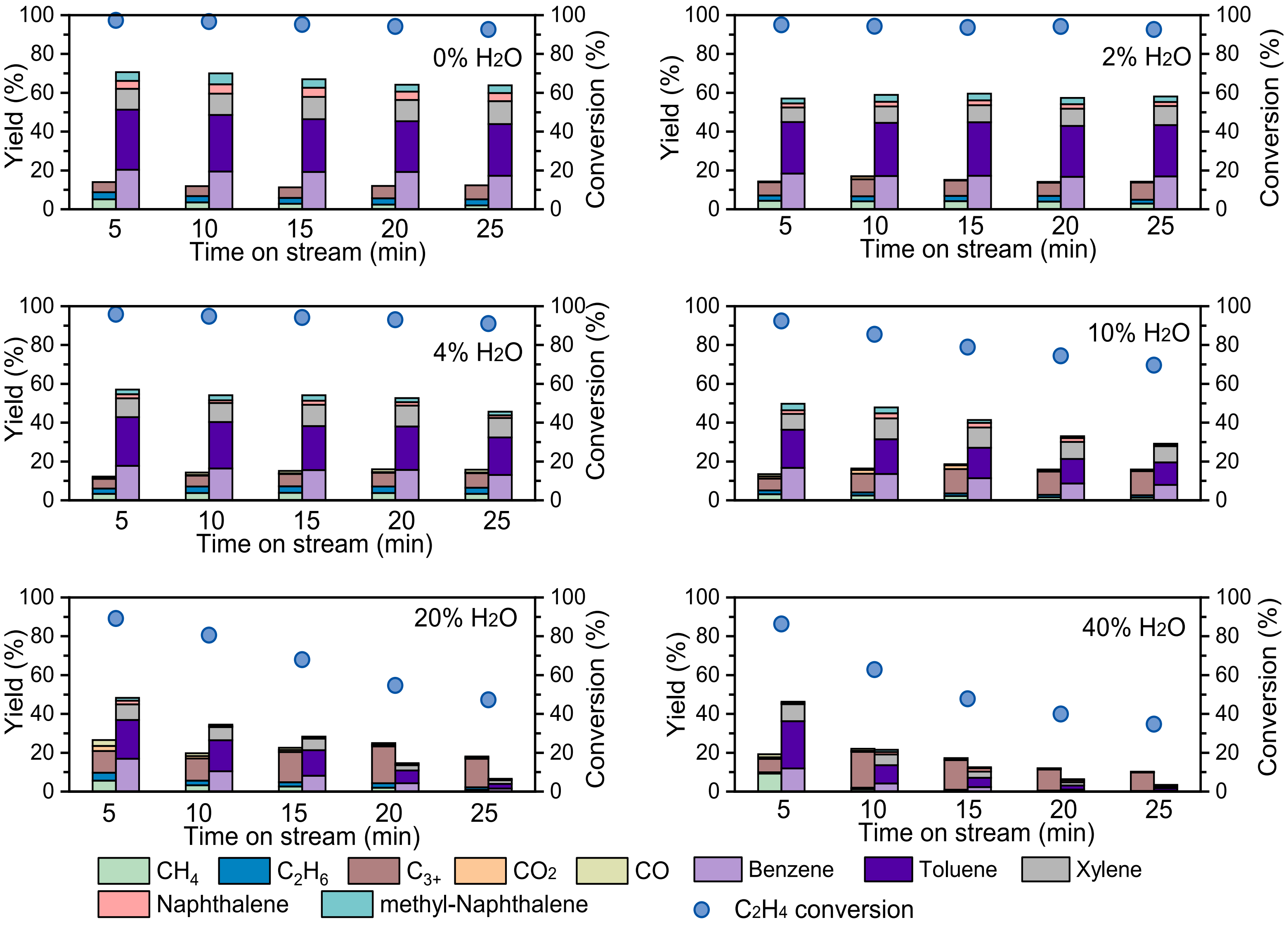


- OCM catalyst with core-shell structure enabled 30.9% C2+ yield and 42.7% methane conversion.
- OCM catalysts remained stable during the cycling test for over 50 cycles (~500 mins overall reaction time)

- OCM+DHA reached the aromatic yield milestone of 15%, nearly doubling the optimal yield from state-of-the-art methane DHA catalysts.

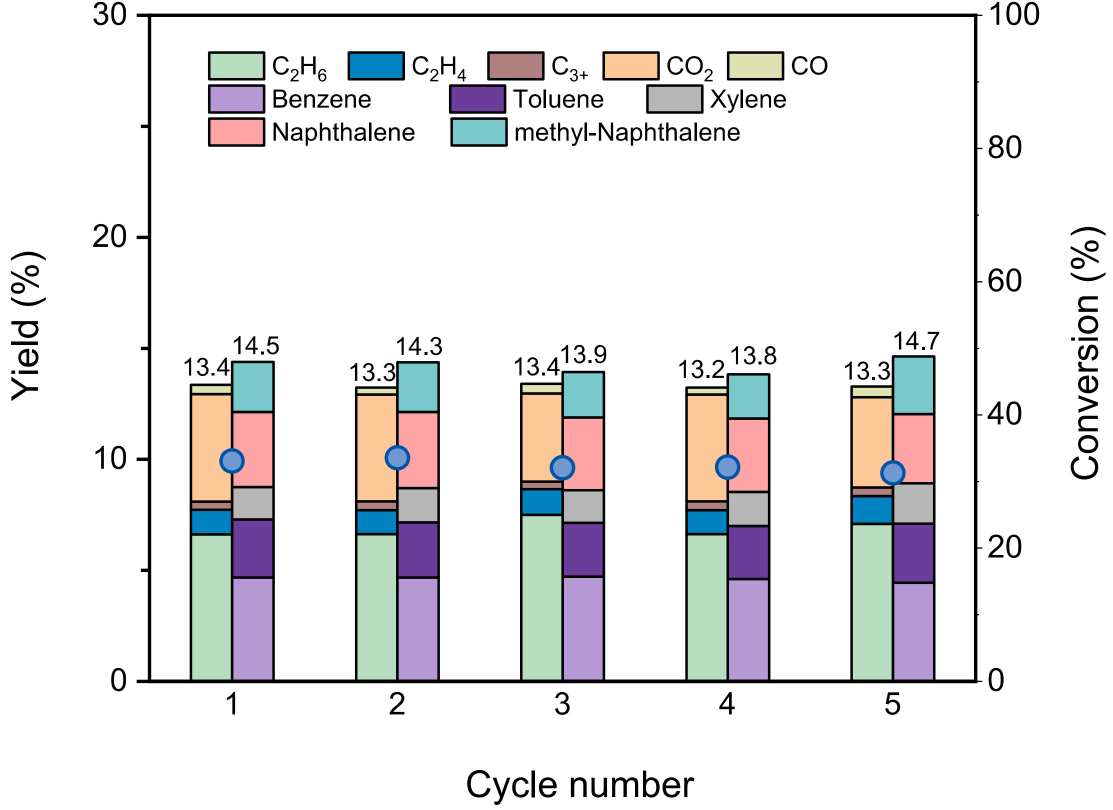
Milestone 5.1 : 15% single pass aromatics yield was achieved

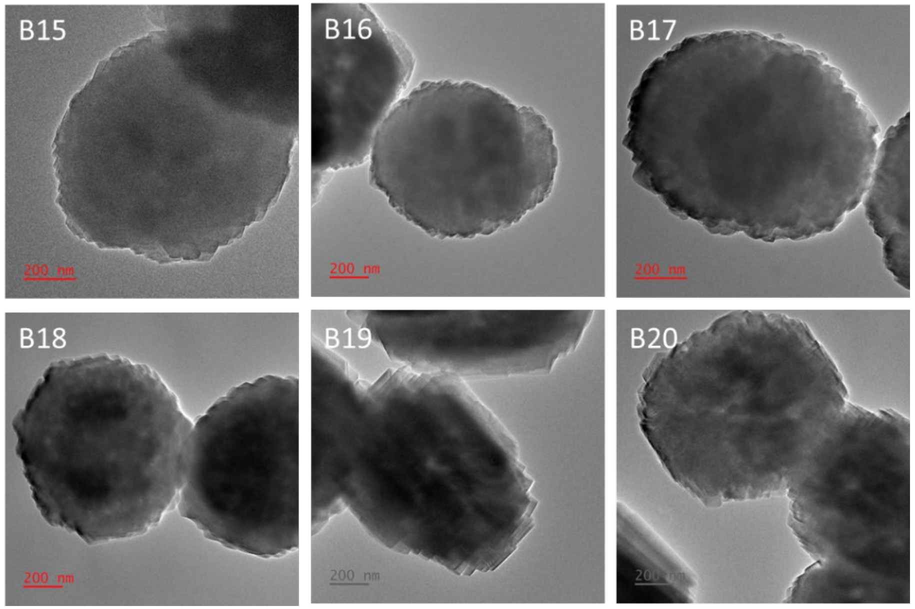
Summary of Project Progress – OCM+DHA Stability



- Increased amount of water can deactivate the DHA catalyst.
- The current OCM reaction has 15-25% water as the side product.

Summary of Project Progress – OCM+DHA Stability and Catalyst Scalability

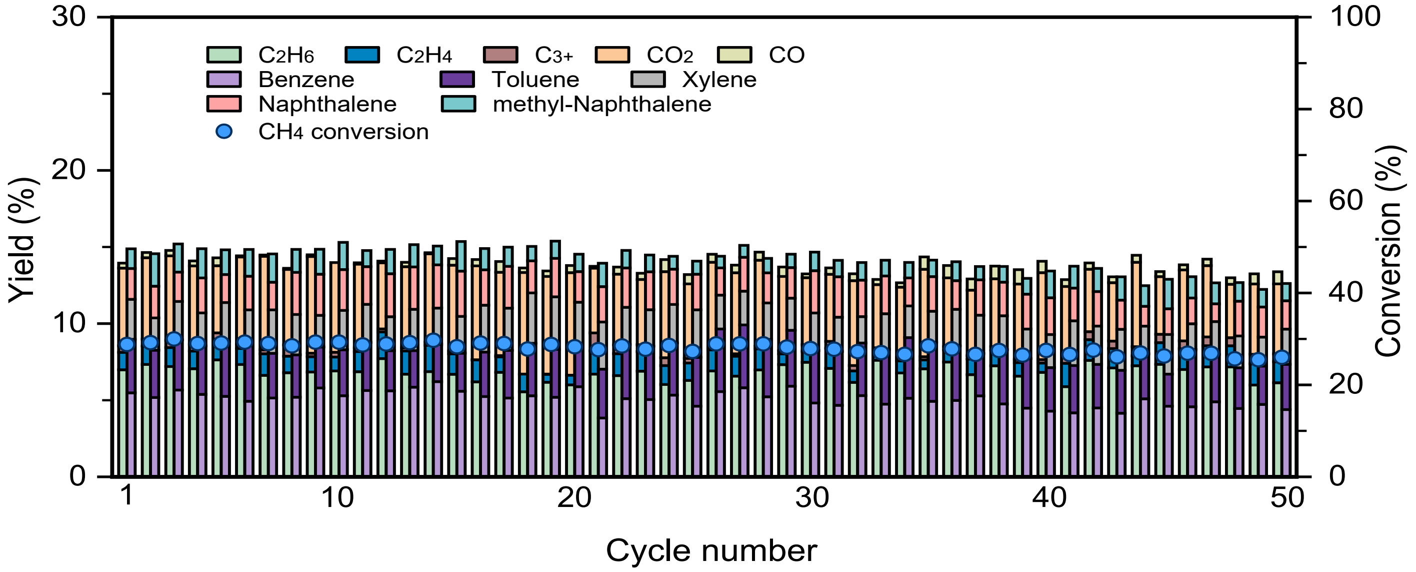


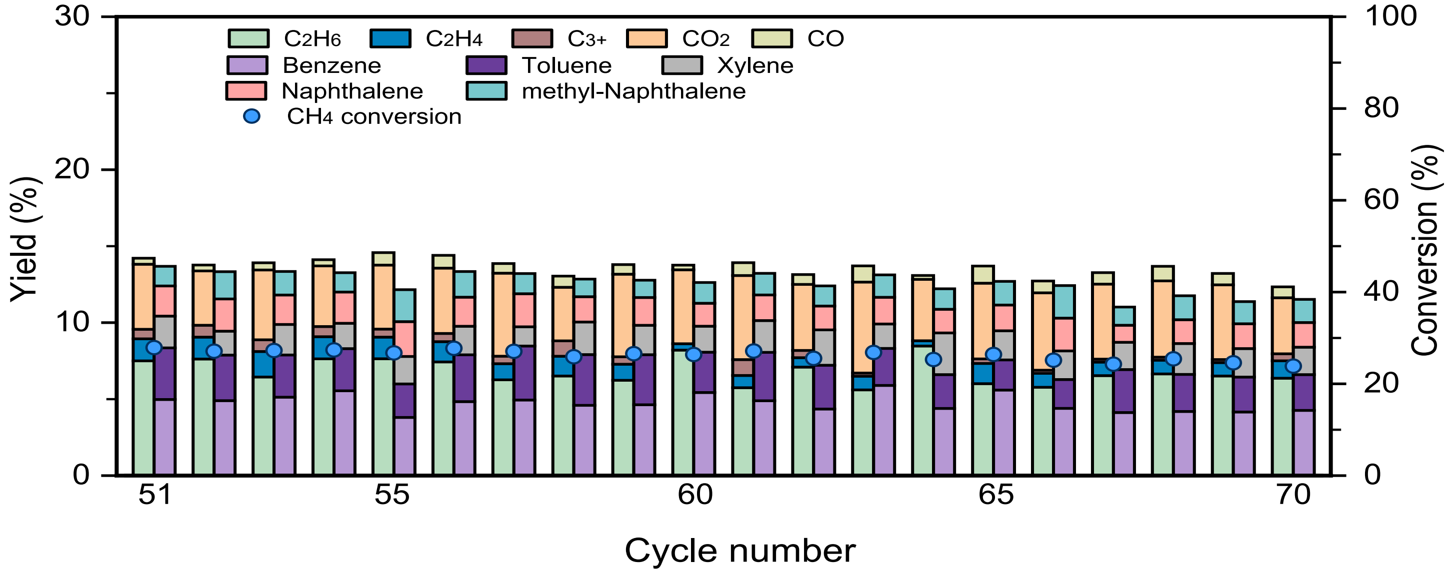


- ~15% single pass aromatic yield with almost no deactivation can be achieved by O_2-oxidation for OCM and H_2-reduction for DHA as the regeneration setup.

- SEM showed the synthesized DHA catalysts were highly repeatable.
- We validated the scale-up synthesis from 5g, 8g, 10g, and 20g with repeatable performance.

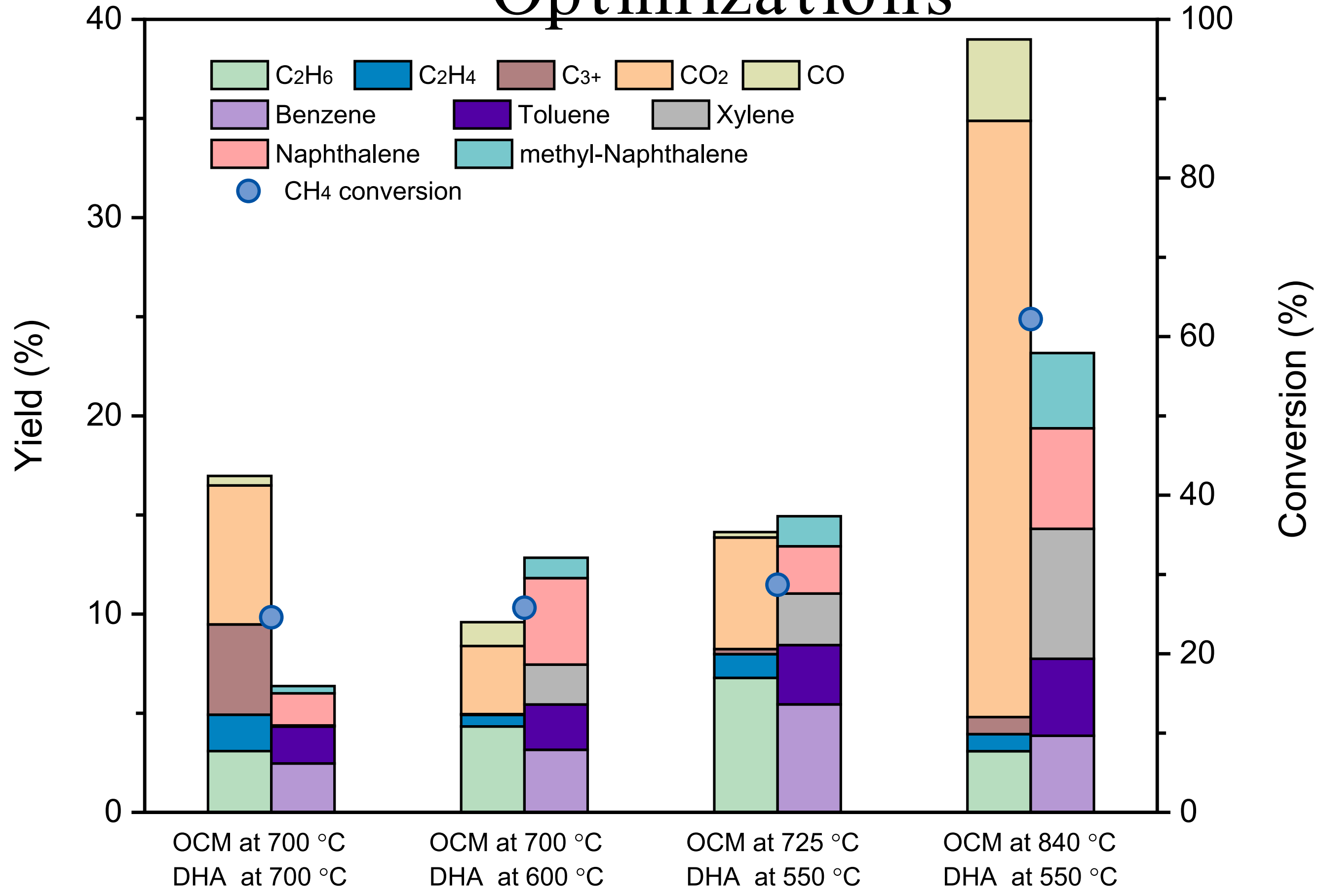
Summary of Project Progress – Long-Term Testing





Tasks 6.2 and 6.3: 100-hour catalyst testing completed. Slight deactivation of the catalyst observed, with aromatics yield dropping from 14.7% to 11.6%; OCM catalyst sintering and reactor pressure increase was observed.

Summary of Project Progress – Further Catalyst Optimizations

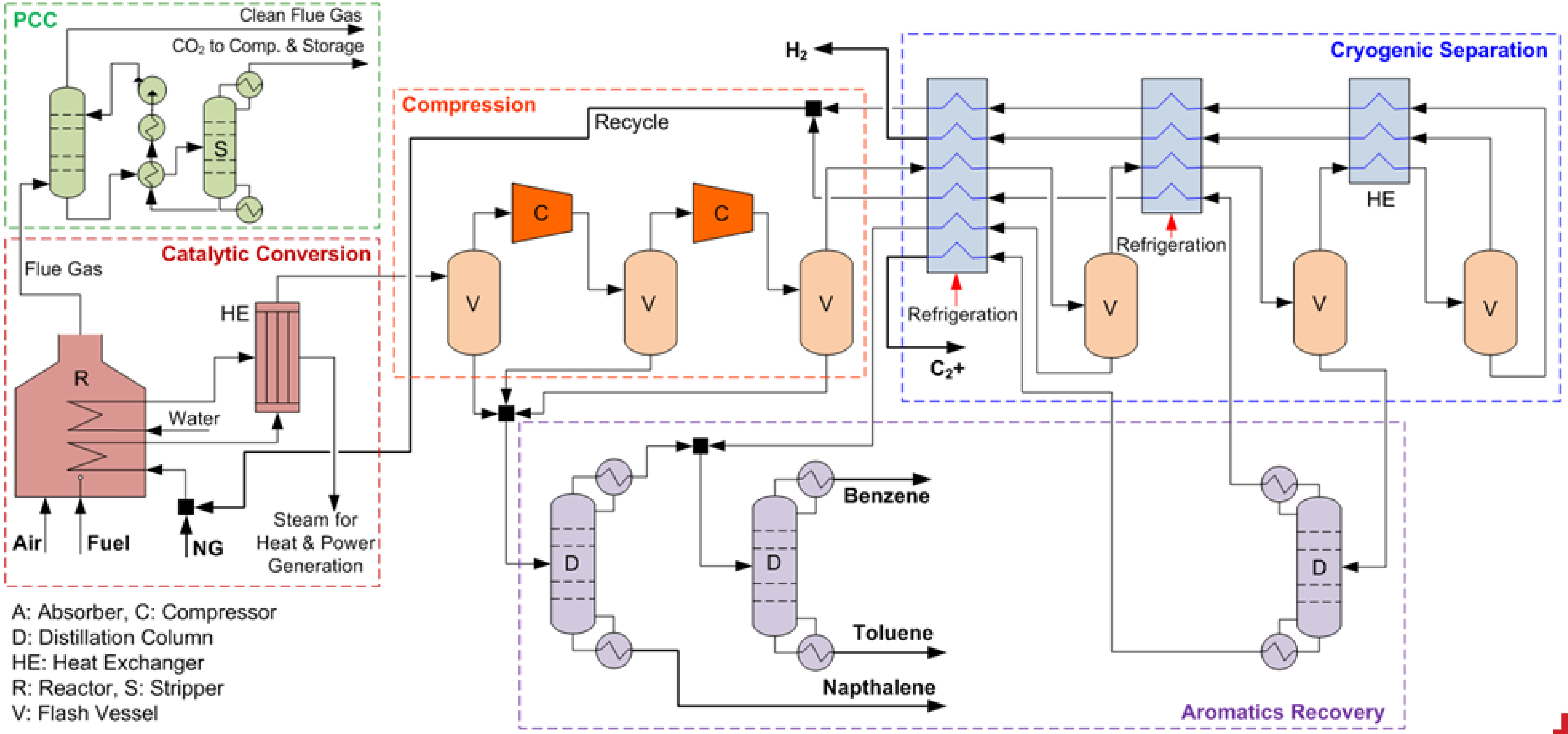


An improved CL-OCM catalyst formulation led to 23.2% single-pass yield. The new catalyst formulation also shows great potential to be highly stable.
State-of-the-art methane DHA yield is ~8%.

Preliminary TEA/LCA

Model of the Base Case Process

- For comparing the economics and environmental footprint of the OC-DHA process with a base case process, a menthane DHA process from the open literature* is adopted by including a post-combustion capture process using Cansolv to obtain similar environmental footprint as the OC-DHA process.

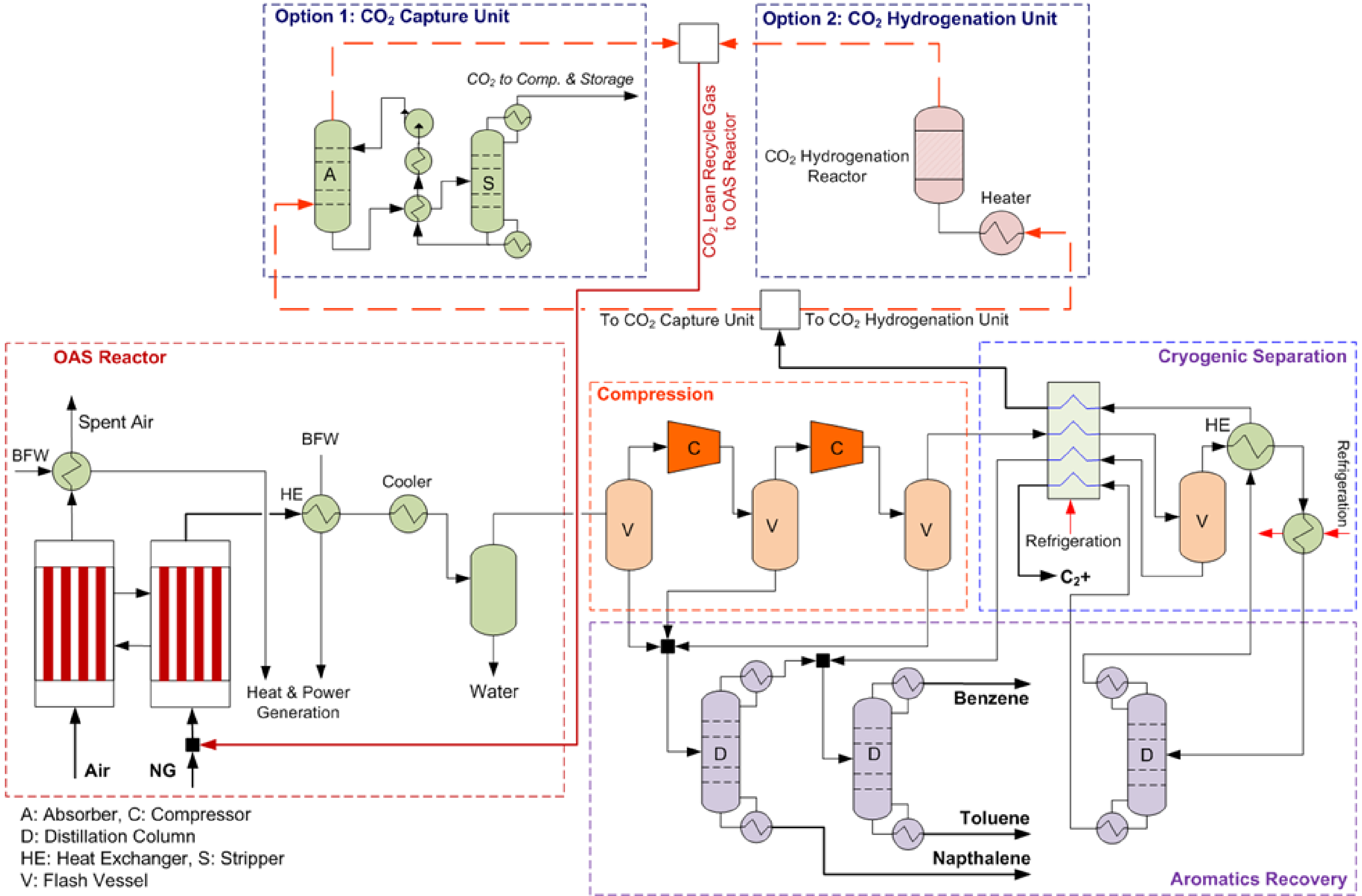


A: Absorber, C: Compressor
D: Distillation Column
HE: Heat Exchanger
R: Reactor, S: Stripper
V: Flash Vessel

*Huang & Maravelias, "Synthesis and Analysis of Nonoxidative Methane Aromatization Strategies", *Energy Technol*. 2020, 8, 1900650

Model of the OC-DHA Process

- The OC-DHA process leads to about 65% reduction in CO_2 compared to the base case due to higher yield of aromatics. For additional CO_2 removal, two options are considered:
  - Option 1: CO_2 capture using Cansolv- amount of CO_2 to be captured is about 35% of what is needed for the base case.
  - Option 2: CO_2 utilization- CO_2 selectively reacts with residual H_2 in the recycle stream producing HCs, which can then be converted to aromatics in the DHA reactor. Option 2 is considered to be the best case scenario for the screening TEA.
  - Both options achieve near 100% capture/conversion of CO_2 overall.



A: Absorber, C: Compressor
D: Distillation Column
HE: Heat Exchanger, S: Stripper
V: Flash Vessel

Key Differences in the Separation Section and Plant Scale

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- Base case process requires low cryogenic temperature (about -167°C) for separating H_2 from unreacted CH_4 before recycling the unreacted CH_4 back to the reactor.
- For the OC-DHA process, the lowest temperature in the cryogenic separation section is -72°C as most of the H_2 is converted in the DHA reactor, thus leading to considerable energy savings.
- For the breakeven price of benzene for the base case, the smallest plant capacity (i.e., base capacity) considered is about 200 times larger than that considered for the OC-DHA (i.e., 50 bbl/day of aromatics for the OC-DHA process vs about 9500 bbl/day of aromatics for the base capacity of the base case process). This is due to considerably poorer economics of the base case process with further decrease in the plant capacity.
- As the target of the proposed process is modular scale application, capacity of the OC-DHA process is not increased.

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Economic Model

- The economics for the base case model is based on the literature* but updated by considering the capital and operating costs for CO_2 capture based on the NETL baseline studies (Case B31B.95).
- The base case process has steep increase upon reduction of plant capacity mainly due to the poor economics of the reactor furnace at small scale and the refrigeration section for separation of CH_4 from H_2 in the base case process requiring very low cryogenic temperature (-167°C). It should be noted that neither the reactor furnace nor that extreme refrigeration requirement exists in the OC-DHA process.
- Other economic parameters are listed below:
  - Capital recovery factor is 12.4%: 20-year payback, 11% IRR
  - 90% annual availability: 330 days a year
  - Natural gas price: \$3/MMBTU or \$0.132/kg with 20,000 BTU/lb energy density
  - Reference price of benzene: \$650/tonne or \$2.21/gallon
  - OAS process scheme produces power, which is expected to suffice the power requirement of this section based on the current estimates.
  - Capital and operating costs of the CO_2 capture units are based on specific costs (i.e., \$/tonne or \$/tonne/h) obtained from NETL baseline studies (Case B31B.95).

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*Huang & Maravelias, "Synthesis and Analysis of Nonoxidative Methane Aromatization Strategies", *Energy Technol*. 2020, 8, 1900650

Screening TEA

Values in MW (unless otherwise noted)	**Base Case***	**OC-DHA****
Inlet Flows		
Natural Gas (Feed Stream)	1400.0	1355.0
Outlet Flows		
Benzene	334.5	339.0
Toluene	15.5	14.8
Naphthalene	456.4	460.0
Hydrogen	681.5	0.0
Heating Duty	**679.1**	**195.3**
Cooling Duty	**260.0**	**145.3**
Electricity		
Compression	168.3	62.8
Refrigeration	285.5	96.7
Generation (HRSG, Regen, etc.)	-191.6	-159.5
Net Work Required	**262.2**	**0.0**
Fuel Credits		
Hydrogen	681.5	0.0
Fuel Gas	25.7	18.1
Excess Heat (i.e., Exotherms)	0.0	23.6
Capital Cost ($/bbl of aromatics/day)	165,670	110,231
Cost for CO_2 capture ($/tonne)[a]	59.9	59.9 for Option 1 or N/A for Option 2
Breakeven Price for Benzene ($/kg) 95% CO_2 abated[b]	**1.01 (best), 1.63 (base)**	**0.744** for Option 1 and **0.69** for Option 2
Reduction in Cost of Benzene with Respect to Base Case	-	**25.6%** for Option 1 and **30.9%** for Option 2 wrt best **54.3%** for Option 1 and **57.6%** for Option 2 wrt best

*base case is from literature; ** unless otherwise mentioned results presented are for Option 1; a 95% CO_2 is captured for the base case, for both options of OC-DHA, similar amount of CO_2 as the base case is released, b for the base case, the base plant capacity is about 200 times larger than what is considered for the OC-DHA while the best case for the base case is when the plant capacity becomes about 1200 times that of OC-DHA.

Preliminary LCA

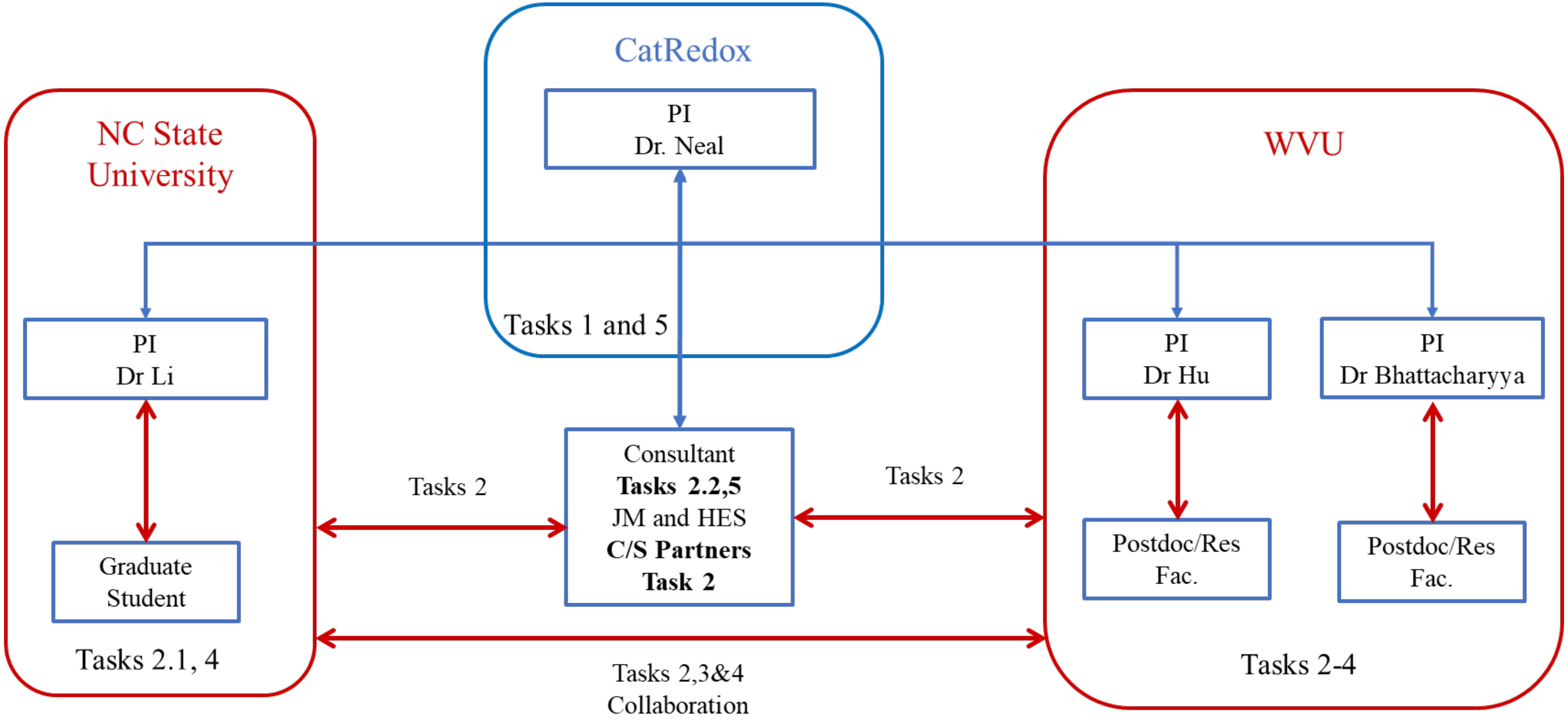
- A GHG-only preliminary LCA is conducted.
- Electricity is assumed to be green (i.e., fully produced by renewable resources or by using bio-methane or similar sources without GHG emission) and the refrigeration and cooling duties are driven by electricity.
- The base case process releases 5.7 kg CO_2/kg benzene by considering only CO_2 released in the flue gas of the reactor furnace. There would be also additional CO_2 released due to decoking when the coke formed (about 5 wt% yield) in the non-oxidative process is burnt. This extra CO_2 is not considered in the screening LCA for simplicity.
- In absence of either Option 1 or Option 2, the OC-DHA process would lead to about 65% CO_2 reduction compared to the base case.
- While both options lead to near 100% removal/conversion of CO_2 in the recycle loop, a small amount of CO_2 is obtained from the top of the distillation column that separates benzene from toluene along with a small stream of light gases. Considering combustion of that light gas along with the small amount of CO_2 due to purge from the recycle loop, both options lead to emission of about 0.21 kg CO_2/kg benzene (i.e., slightly lower than the base case with 95% CO_2 capture).

Technical Approach

Technical Approach

- Process Modeling and Techno Economic Analysis
  - The preliminary ASPEN+ model will be evaluated and refined. Literature review and stakeholder outreach will be used to update TEA parameters.
  - The cost of a commercial-scale DHA plant will be estimated and the potential ROI will be estimated.
- Life Cycle Analysis
  - Process modeling will be used to update the cradle-to-gate GHG emissions by using International Standards Organization (ISO) 14040/14044 standards.
- Experimental Process Data Collection and TEA/LCA Driven Experimental Validation
  - Previous experimental data will be evaluated for completeness and used as the basis for process modeling.
  - A limited amount of experimental data will be collected in cases where there are gaps in available data/conditions.
- EH&S Risk Assessment, Gap Analysis, and Project Planning
  - A high-level screening hazardous operations review will be done by the project team to identify potential hazards in the conceptual plant and develop mitigation strategies.
  - Based upon the conceptual plant design, TEA, LCA, and stakeholder outreach will be conducted to identify remaining gaps that need to be addressed in phase 2 and beyond.
  - These gaps will be integrated into project planning and detailed scope of work for phase 2.

Organization Structure



Perceived Risk	Probability	Impact	Overall	Mitigation/Response Strategy
Financial Risks:				
Over/insufficient budget	Low	Med	Low	High experience with projects of similar scope. Experience in identifying such potential overruns early and communicating potential changes in scope to the funding agency.
Cost/Schedule Risks:				
Insufficient Personnel in time for project	Low	High	Low	PI groups currently possess personnel needed for project
Delay of tasks	Low	Med	Low	Logical progression of tasks
Technical/Scope Risks:				
Insufficient OC-DHA Performance	Med	Med	Med	Early Identification with development of phase 2 technical scope to overcome limitations
EH&S Risks:				
Potential Hazardous Process	Low	Med	Low	All project activities are expected to be within existing EPA permits and existing lab safety guidelines. Any new processes will be discussed through the respective institutions' EH&S departments in accordance with existing policy.
External Factor Risks:				
Unexpected external factor(s) and influences	Low	Med	Low	Understanding of costs, schedules, and interactions will allow recovery plans to be defined; 2) Previous project management experience will allow quick decision-making and necessary prioritization

Task 1.0 - Project Management and Planning

- Subtask 1.1 Project Management Planning: The Recipient shall update the Project Management Plan 30 days after award and as necessary throughout the project to accurately reflect the current status of the project

- Subtask 1.2 – Technology Maturation Plan: The Recipient shall develop a Technology Maturation Plan (TMP) that describes the current technology readiness level (TRL) of the proposed technology/technologies, relates the proposed project work to maturation of the proposed technology, describes the expected TRL at the end of the project, and describes any known post-project research and development necessary to further mature the technology. The initial TMP is due 90 and final TMP should be submitted 90 days prior to project completion.”

Task 2.0 – Process Modeling and Techno-Economic Analysis and

- Subtask 2.1 – Conceptual Plant Design Refinements and ASPEN Modeling: The proposed conceptual design for the screening study will be re-evaluated. In the current conceptual design, two options are presented for CO2 abatement through conversion/capture of CO_2. The team will study alternative technologies that can be considered as the base case. To this end, methane to methanol via syngas followed by methanol to aromatics can be a possible base case
- Subtask 2.2 – Technoeconomic Analysis: Capital cost information will be updated by using the results from the updated Aspen simulation. Conventional equipment items will be costed using the database in Aspen Process Economic Analyzer. Costing estimates of the OC-DHA materials and OC-DHA reactors will be refined. The catalyst cost will be estimated through the cost of precursors and heuristics for tolling (third-party production) of catalyst synthesis. The reactors will be costed through sizing followed by consideration of costs due to the materials of composition and applying fabrication factors for the main vessel, and costing of the individual components.

Task 3.0 – Life Cycle Analysis

- Preliminary GHG-only LCA will be revised to prepare the preliminary cradle-to-gate LCA by using the updated information from task 2 and by including updated information of process, energy and material inputs. For this analysis, the proposed OC-DHA process integrated with other components such as those that will be evaluated as possible alternatives will be considered.
- The methodology established by the International Standards Organization (ISO) in ISO 14044 will be utilized for performing LCA studies, which comprise four phases: Goal and Scope, Life Cycle Inventory (LCI) analysis, Life Cycle Impact Assessment (LCIA) and Interpretation.
- The impact of GHGs will be calculated using 100-year global warming potentials. All the emissions will be converted into the carbon dioxide equivalent (kg CO_2 eq). to demonstrate a path to a net-zero carbon emissions industrial process. In addition to carbon, and energy and materials inputs, the results will include a thorough analysis of the impact of the process on criteria air pollutants.

Task 4.0 Experimental Process Data Collection and TEA/LCA Driven Experimental Validation

- Sufficient data exist to perform detailed process modeling
- However, it is anticipated that LCA and TEA optimization will identify potential optimal operating regimes that have not been tested.
- Limited experimental activities may be conducted to support the LCA and TEA by generating any additional data needed for TEA and LCA modeling efforts and preliminary validation of performance in identified operating regimes.
- Any such OCM and DHA materials can be tested alone or combined in existing laboratory reactors.

Task 5.0 EH&S Risk Assessment, Gap Analysis, and Project Planning

- Subtask 5.1 – EH&S Risk Assessment: The Process modeling and literature review/outreach to methane source will be used to identify the quality and nature of all product/waste streams of the system. This will include materials in any support unit operations identified, such as acid gas removal (e.g. a caustic wash). The safe transport of the BTX and naphthalene products will also be considered. A description of the various toxicological, flammable/explosive, and corrosive properties of the materials will be identified through literature review. A literature/database review will be used to identify potentially relevant health and safety mitigation strategies to reduce or eliminate any toxic byproducts will also be evaluated.
- Subtask 5.2 – Gap Analysis, and Project Planning: Based upon the conceptual plant design, TEA, LCA, and stakeholder research and outreach the technology will review for remaining gaps that need to be addressed in phase 2 and beyond. We will focus on identifying technical or market barriers to commercial adoption of the technology. Gaps that need to be bridged to push the system to 95% reduction in CO2 will also be identified These gaps will be integrated into project planning and detailed scope of work for phase 2.

Task / Subtask Number	Milestone Title & Description	Planned Completion Date	Verification Method
1.1	Project Management Plan - Update PMP and deliver to DOE 30 days after award.	8/31/2024	Submission by email
1.2	Initial Technology Maturation Plan (TMP) - Formulate initial TMP and deliver to DOE 90 days after award.	10/30/2024	Submission by email
2.1	Revised ASPEN model of OC-DHA and baseline processes	1/31/2025	Submission by email
2.2	Preliminary Techno-Economic Analysis (TEA) – Perform TEA and deliver to DOE 90 days prior to project completion.	5/2/2025	Submission by email
3.0	Preliminary Life Cycle Analysis (LCA) - Perform LCA and deliver to DOE 90 days prior to project completion.	5/2/2025	Submission by email
2.0	Oxygen-Based Process Data Table - Complete table and deliver to DOE 90 days prior to project completion.	5/2/2025	Submission by email
5.0	Technology EH&S Risk Assessment – Complete EH&S risk assessment and deliver to DOE 90 days prior to project completion.	5/2/2025	Submission by email
1.3	Study on workforce implications and related DEIA/Energy Equity	7/31/2025	Submission by email
5.1	Preliminary Pilot Unit design and sizing	7/31/2025	Submission by email
5.2	Technology Gap Analysis (TGA) – Perform TGA and deliver to DOE at the end of the technical period of performance.	7/31/2025	Submission by email
5.3	Phase 2 Application – Complete Phase 2 application and submit at the end of the technical period of performance.	7/31/2025	Submission to DOE through Grants.com

Upcoming/ Completed Tasks

- Project Management Plan - Update PMP and deliver to DOE 30 days after award.
  - Finalize
- Initial Technology Maturation Plan (TMP) - Formulate initial TMP and deliver to DOE 90 days after award.
  - Will be generated inline with template

Upcoming TEA and LCA tasks

- Task 2.0 – Process Modeling and Techno-Economic Analysis
  - Subtask 2.1 – Conceptual Plant Design Refinements and ASPEN Modeling: For achieving net-zero emission, the team will evaluate additional options as needed. Potential alternatives such as various AGR technologies will also be evaluated for Option 1. Heat integration and recovery will be reevaluated to improve the process efficiency. For reducing the compression cost in the product recovery section, studies will be considered leading to possible changes in the configuration. The preliminary ASPEN model will be refined by including these alternative options. Furthermore, the team will study alternative technologies that can be considered as the base case.
- Task 3.0 – Life Cycle Analysis
  - Preliminary GHG-only LCA will be revised to prepare the preliminary cradle-to-gate LCA by including updated information of process, energy, and material inputs.
  - LCA will be undertaken using ISO 14044 methodology with SimaPro.

Task group for TEA and LCA

- Professor Debangsu Bhattacharyya from WVU will lead the tasks on TEA and LCA.
- Dr. Emdadul Haque, Research Assistant Professor at WVU will work with Prof. Bhattacharyya for the TEA and LCA.

Discussion