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solutions that transform

U.S. DEPARTMENT OF ENERGY

DE-FE0031909

Dehydration Membrane Reactor for Production of Valuable Chemicals from CO_2 and H_2

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2023 Carbon Management Research Project Review Meeting

August 28 – September 1, 2023

GTI Energy: 80-year history of turning raw technology into practical energy solutions

GTI ENERGY

World-class facility in Chicago area

500+
Enterprise Employees

Across the entire energy value chain

CCUS is one of GTI strategic focus areas

- **Carbon conversion**
  - **FE0031909**: Membrane reactors for conversion of CO_2 to fuels/chemicals
- **Carbon capture**
  - **FE0031946**: Engineering scale facilitated transport membrane
  - **FE0031598**: Bench-scale GO-based membrane
  - **FE0032215**: Nano-confined Ionic liquid membrane
  - **FE0031630**: Solvent-based ROTA-CAP
  - **FE0031730**: Size-sieving adsorbent
- **Carbon dioxide removal (CDR)**
  - **FE0031969**: Trapped small amines in capsules
- **Carbon transport and storage**
  - **FE0032239**: CarbonSAFE Phase II

Project overview

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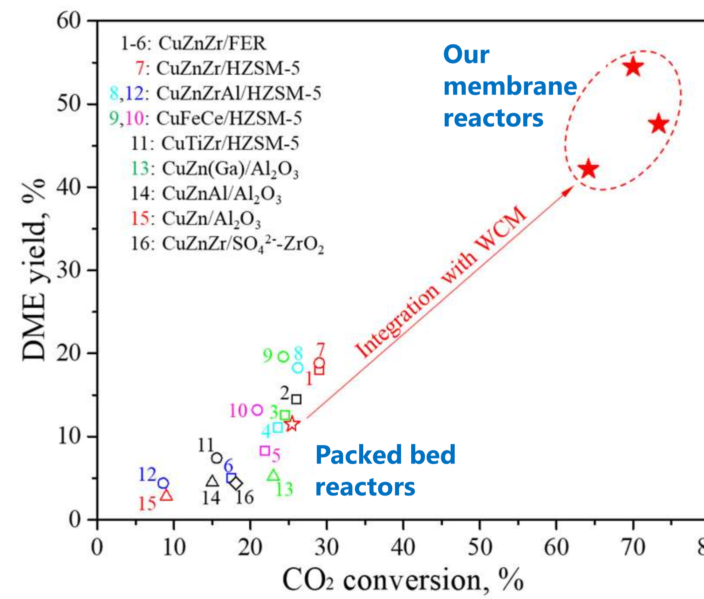
- **Background**: Membrane reactor DME production successfully developed through an ARPA-E project (DE-AR0000806)
- **Current project objective**: Develop membrane reactor for production of valuable chemicals from CO_2 and H_2
  - Target product: liquefied petroleum gas (LPG)
- **Performance period**: 1/1/21 – 3/31/25
- **Total funding**: \$1,269,664 (DOE: \$1.0 MM, cost share: \$269,664)
- **Goal:** CO_2 conversion >50%, LPG yield >45%
- **Team**:

Member	Roles
GTI ENERGY solutions that transform	• Project management and planning • Parametric and deactivation tests • Techno-economic and life-cycle analyses
UB	• Membrane and membrane reactor development
Missouri S&T; Washington University in St. Louis	• Catalyst development



- $2CO_2 + 6H_2 \leftrightharpoons CH_3OCH_3 + 3H_2O$
- CO_2 conversion and DME yield significantly greater than packed bed reactors reported in the literature

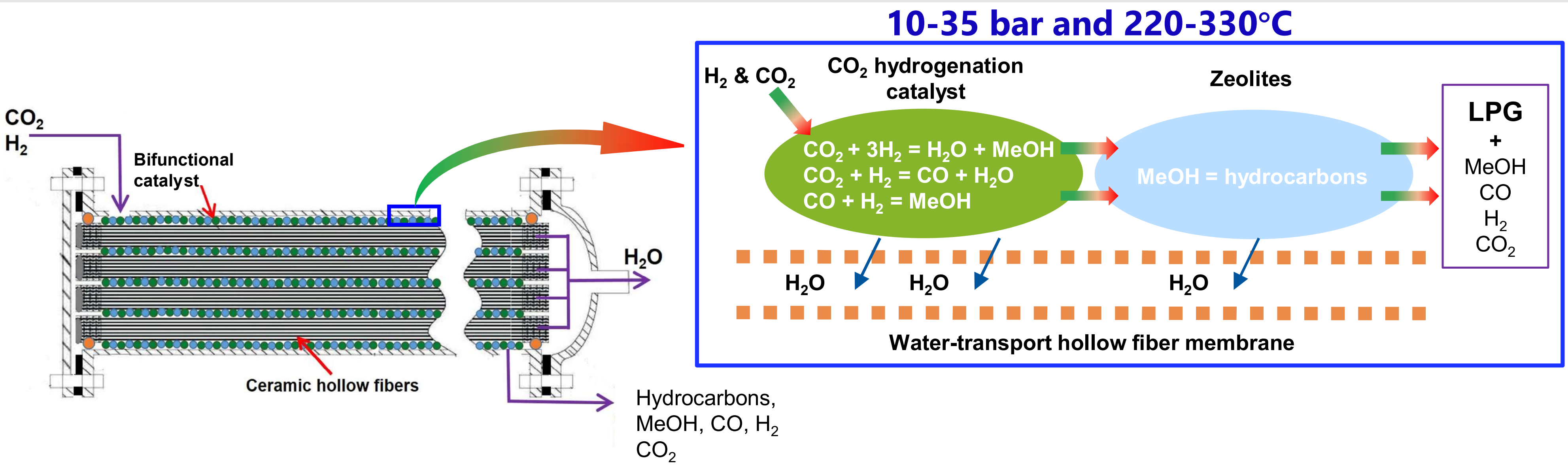
DME: dimethyl ether; LPG: liquefied petroleum gas

The rising need for LPG

- Global LPG production ~330 million tonnes in 2022
- The Europe LPG market was roughly 42 million tonnes in 2021, and is expected to grow to 59 million tonnes by 2027
- Nearly 2% of the U.S. energy needs are supplied LPG
- LPG is an economically efficient, cooking energy solution already used by over 2.5 billion people worldwide

LPG: liquefied petroleum gas

Technology description

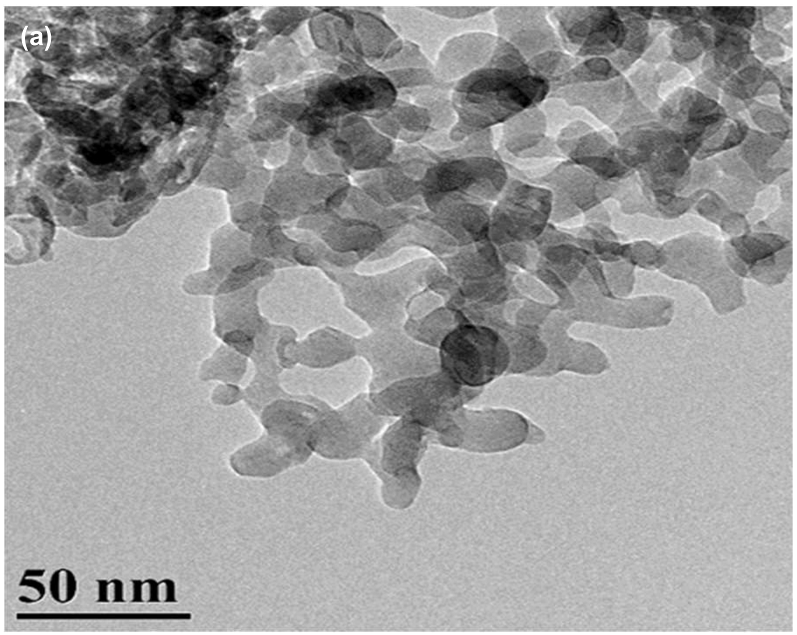


- One-step process with bifunctional catalyst intensifies a process that would otherwise require multiple steps:
  - Methanol synthesis: $CO_2 + 3H_2 \leftrightharpoons CH_3OH + H_2O$ — Catalyst 1: $CuO/ZnO/Al_2O_3$ based
  - LPG synthesis: MeOH ⇋ hydrocarbon pool ⇋ LPG — Catalyst 2: Pd-zeolite β based
- Na^+-gated membrane (***Science***, vol. 367, pp. 667, 2020) removes water *in situ*, shifting the equilibrium towards product formation

Catalyst Development

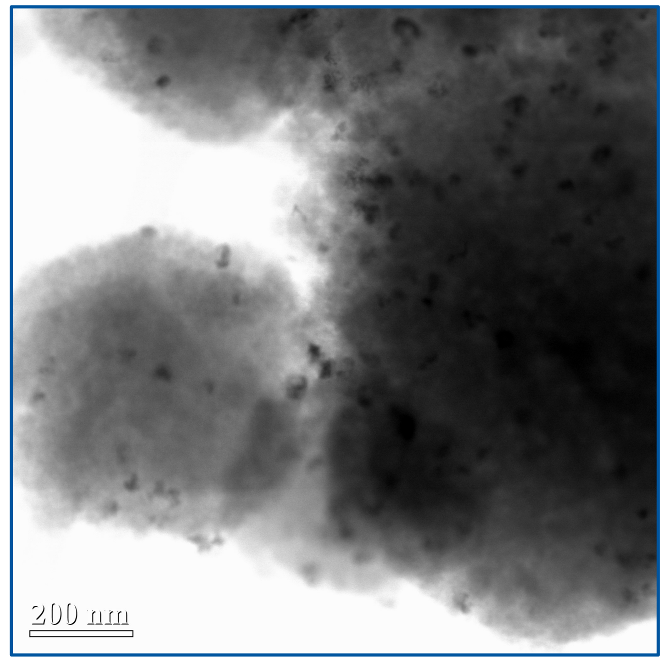
Bifunctional catalyst developed for LPG synthesis

Zirconium (Zr) modified $CuO/ZnO/Al_2O_3$ (CZZA) for the 1st reaction – methanol synthesis



TEM image: uniform nanoscale particles (~15 nm)

Pd-zeolite β catalyst prepared for the 2nd reaction – LPG synthesis



TEM image: Pd particle size ~5.4 nm

CZZA: Zirconium (Zr) modified $CuO/ZnO/Al_2O_3$; TEM: Transmission Electron Microscopy

Bench-mark LPG synthesis with packed bed reactor: LPG yield of 11% when using bifunctional catalyst

- **Reaction temperature**: 300 °C
- **Pressure**: 20 bara
- **Bifunctional catalyst**: 0.5 g CZZA and 1 g Pd-β zeolite
  - Pd content in Pd-β zeolite catalyst: 0.032 wt.%
- **Reaction products**: CO, CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, i-C_4H_{10}, C_5+, CH_3OH, DME
- **Results**:

CO_2 conversion	31%
Hydrocarbons selectivity	46%
LPG selectivity	35%
LPG yield	11%

LPG: liquefied petroleum gas; CZZA: Zirconium (Zr) modified $CuO/ZnO/Al_2O_3$; DME: dimethyl ether

Membrane and Membrane Reactor Development

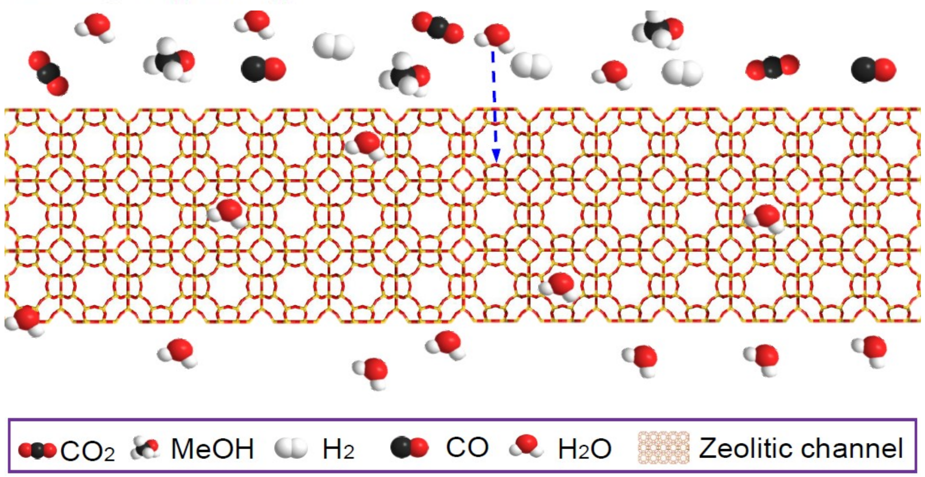
Breakthrough development of Na^+-gated, nanochannel membrane for dehydration

Science

Na^+-gated water-conducting nanochannels for boosting CO_2 conversion to liquid fuels

Huazheng Li, Chenglong Qiu, Shoujie Ren, Qiaobei Dong, Shenxiang Zhang, Fanglei Zhou, Xinhua Liang, Jianguo Wang, Shiguang Li and Miao Yu

Science **367** (6478), 667-671.
DOI: 10.1126/science.aaz6053

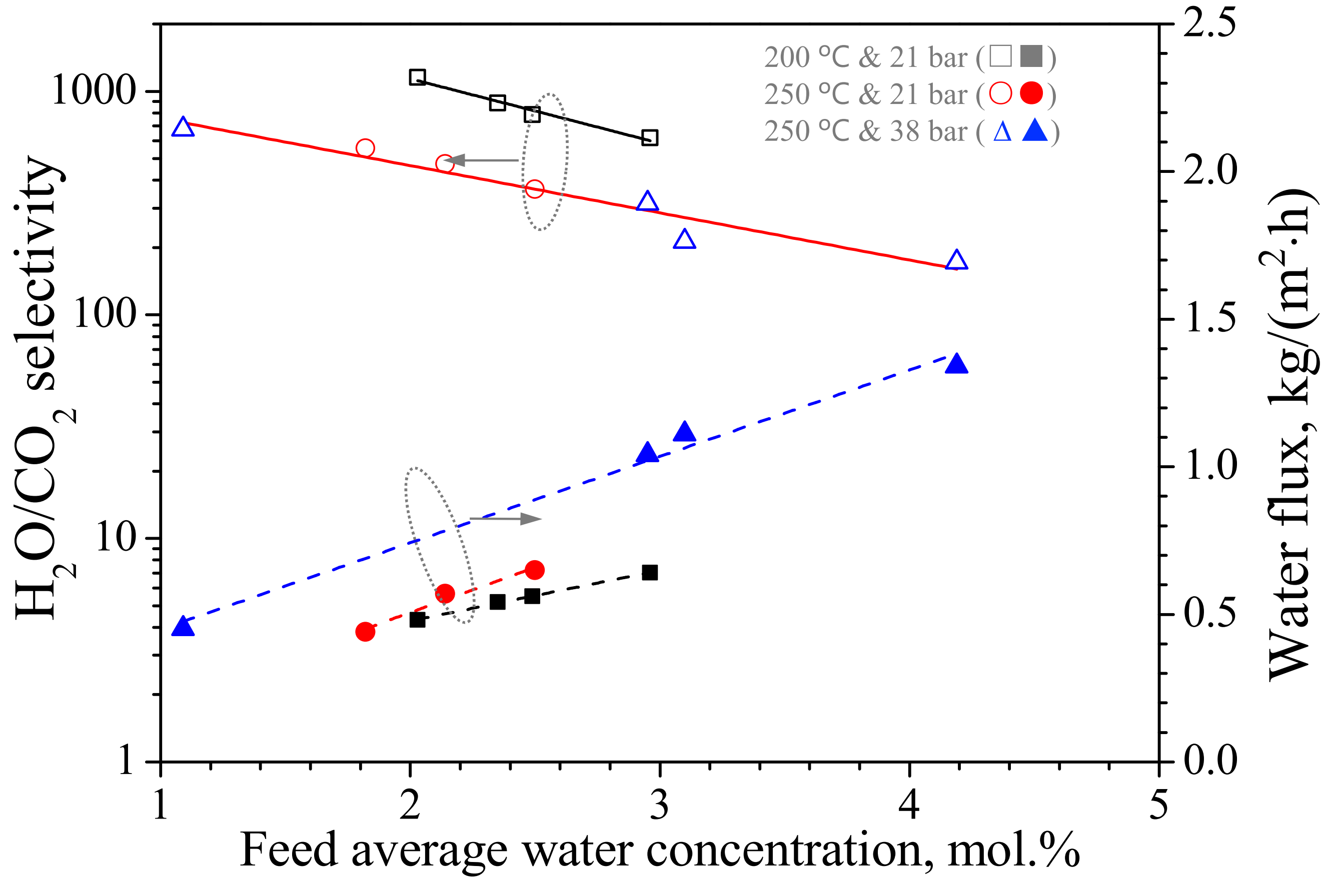


Na^+ neutralizes the negatively charged NaA framework and position inside zeolite nanocavities, allowing fast transport of small H_2O molecules, whereas blocking the permeation of larger molecules, such as H_2, CO_2, CO, and methanol

Kinetic diameters:

- H_2O: 0.265 nm
- H_2: 0.289 nm
- Methanol: 0.36 nm
- CO_2: 0.33 nm

Membrane showed high flux and selectivity for dehydration of $H_2O/CO_2/CO/H_2$/methanol mixture

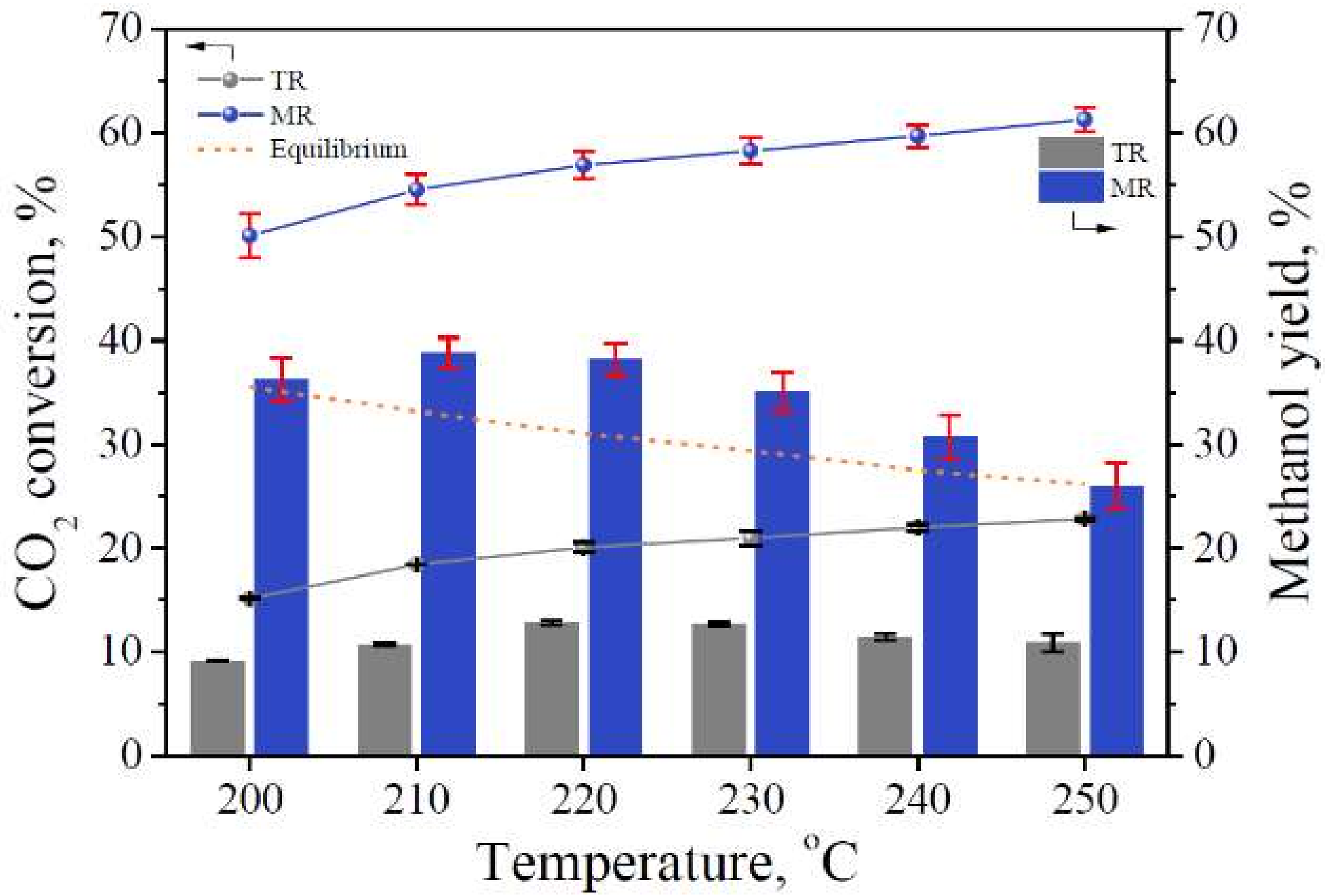


- **Other selectivities**
  - H_2O/H_2 >190
  - H_2O/CO >170
  - $H_2O/MeOH$ >80

Kinetic diameters:

- H_2O: 0.265 nm
- H_2: 0.289 nm
- CO_2: 0.33 nm
- Methanol: 0.36 nm

Membrane reactor methanol synthesis (first reaction): superior performance to packed bed

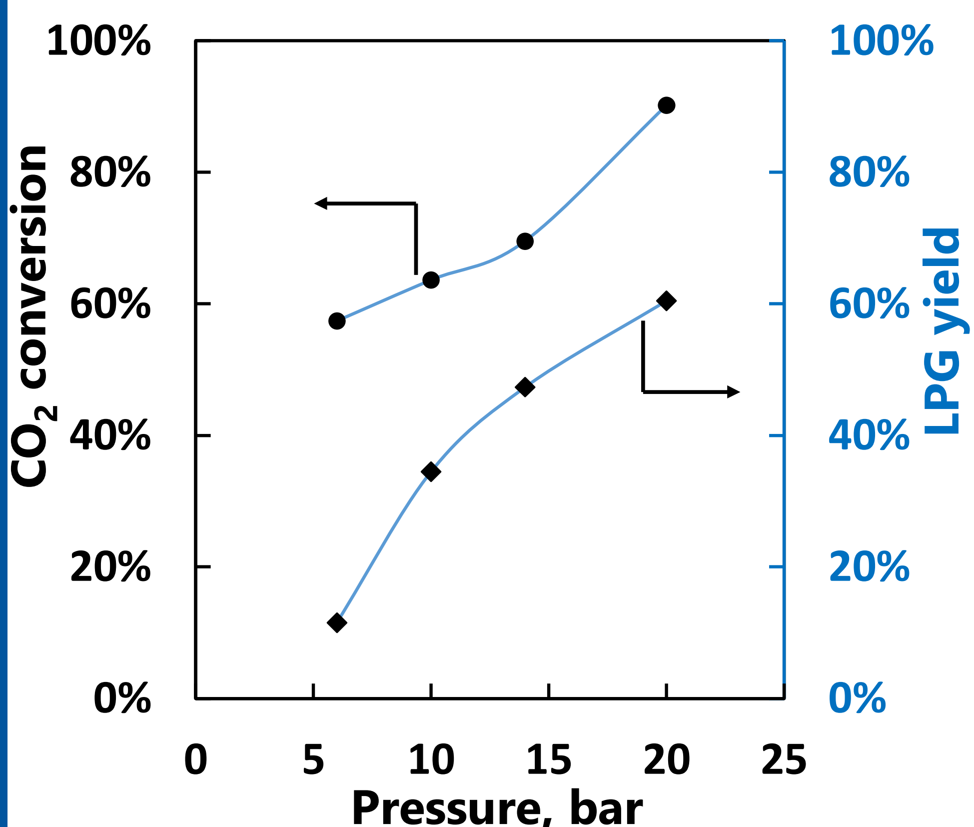


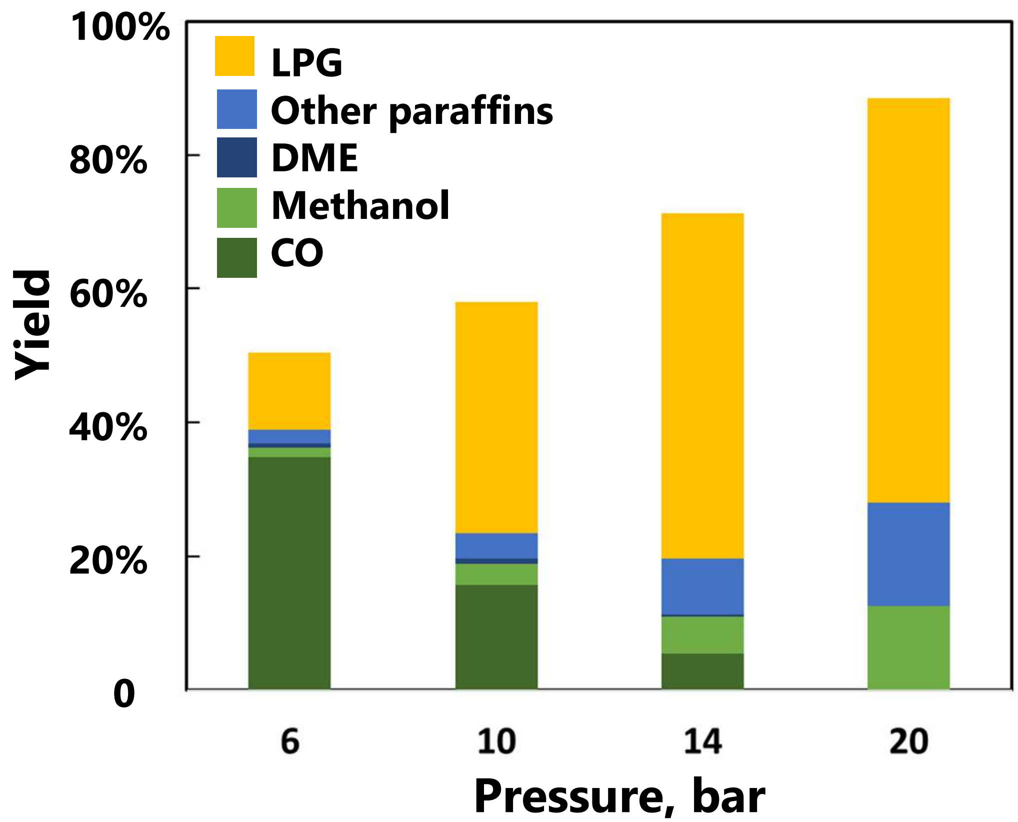
- **Compared to a traditional packed bed reactor without membrane, both CO_2 conversion and methanol yield increased 3 times in membrane reactor**

TR: traditional packed bed reactor; MR: membrane reactor

Membrane reactor LPG synthesis using bifunctional catalyst: high CO_2 conversion, high LPG selectivity and yield

300 °C, H_2/CO_2 ratio = 5:1, W/F = 23.5 g(cat)/(mol/h)



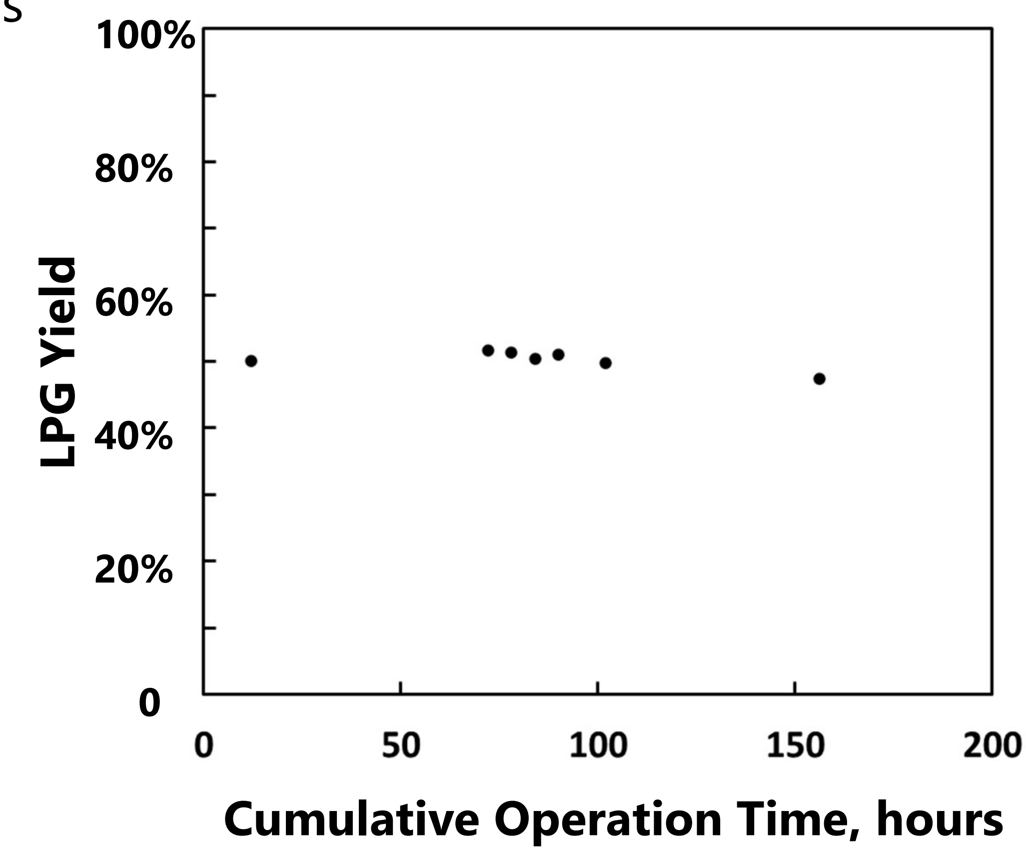


W/F = wight of catalyst / flow rate of the feed stream; LPG: liquefied petroleum gas; DME: dimethyl ether

Good stability

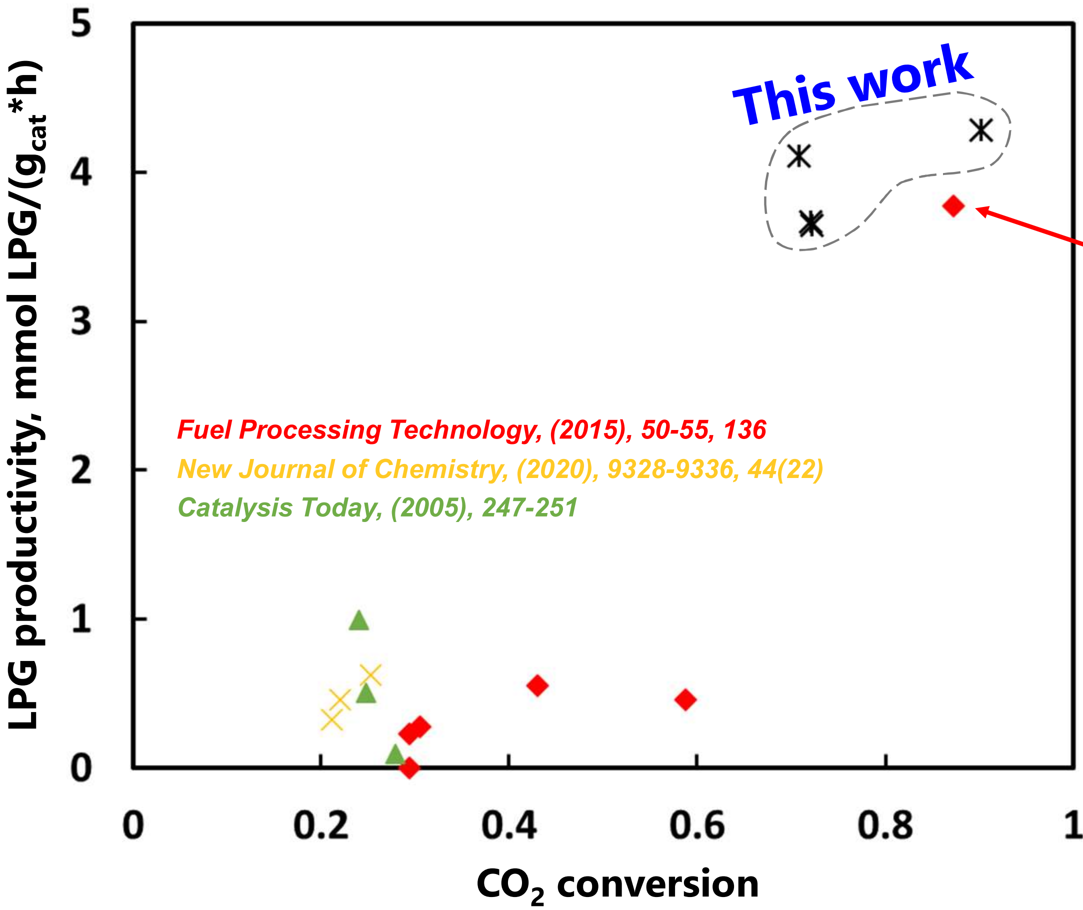
- The system has been tested for ~2 months (~6 hours/day when operated; standby at 200 °C in H_2 when not operated)
- "Standard" operating conditions repeated occasionally during systematic evaluation to investigate the stability

Standard Operating Conditions	
W/F, g(cat)/(mol/h)	23.5
Pressure, bara	14
H_2/CO_2 molar ratio	5:1
Temperature, °C	300



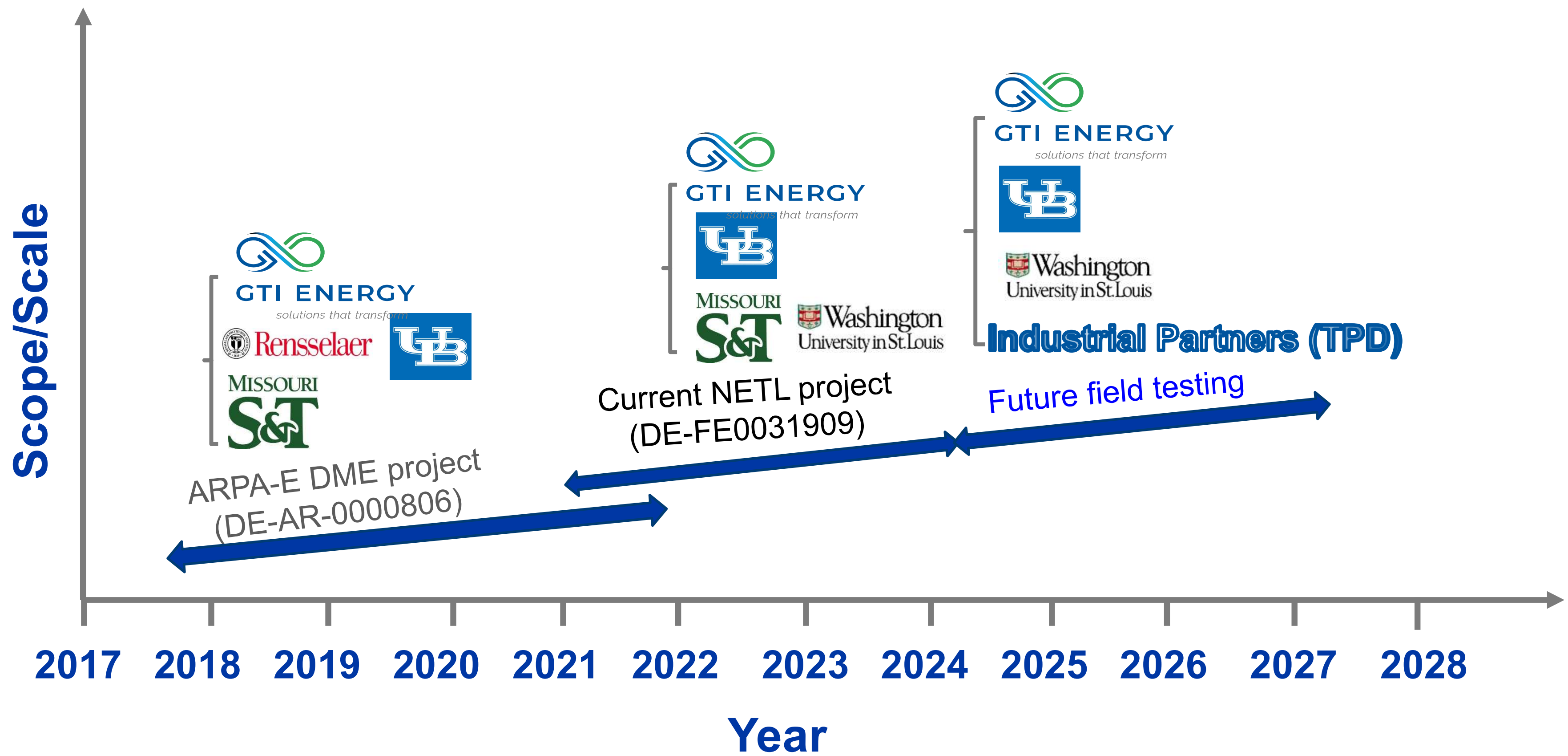
W/F = wight of catalyst / flow rate of the feed stream; LPG: liquefied petroleum gas

Literature comparison: superior performance to packed bed reactors for LPG synthesis



- Highest LPG productivity and CO_2 conversion of any work found in literature (CO_2 conversion to LPG)
- Only other competitive performance used a highly impractical configuration of **two** packed bed reactors with intercooling and reheating in between
  - 1st packed bed reactor: 260°C
  - Cooling to 0°C
  - Reheating from 0°C to 330°C
  - 2nd packed bed reactor: 330°C

Membrane reactor technology development path



Summary

- GTI and partners are developing a membrane reactor for production of valuable chemicals
  - Na^+-gated membrane removes water *in situ*, shifting equilibrium towards product formation
- First reaction (methanol synthesis): membrane reactor CO_2 conversion and methanol yield are 3 times greater than packed bed reactor
- One-step membrane reactor LPG synthesis using bifunctional catalyst: CO_2 conversion as high as 90% and LPG yield as high as 61%
  - Superior performance to packed bed reactors
  - Good stability

Acknowledgements

- Financial and technical support

DE-FE0031909

- DOE NETL: Andy Aurelio, Andrea McNemar and Andrew O'Palko

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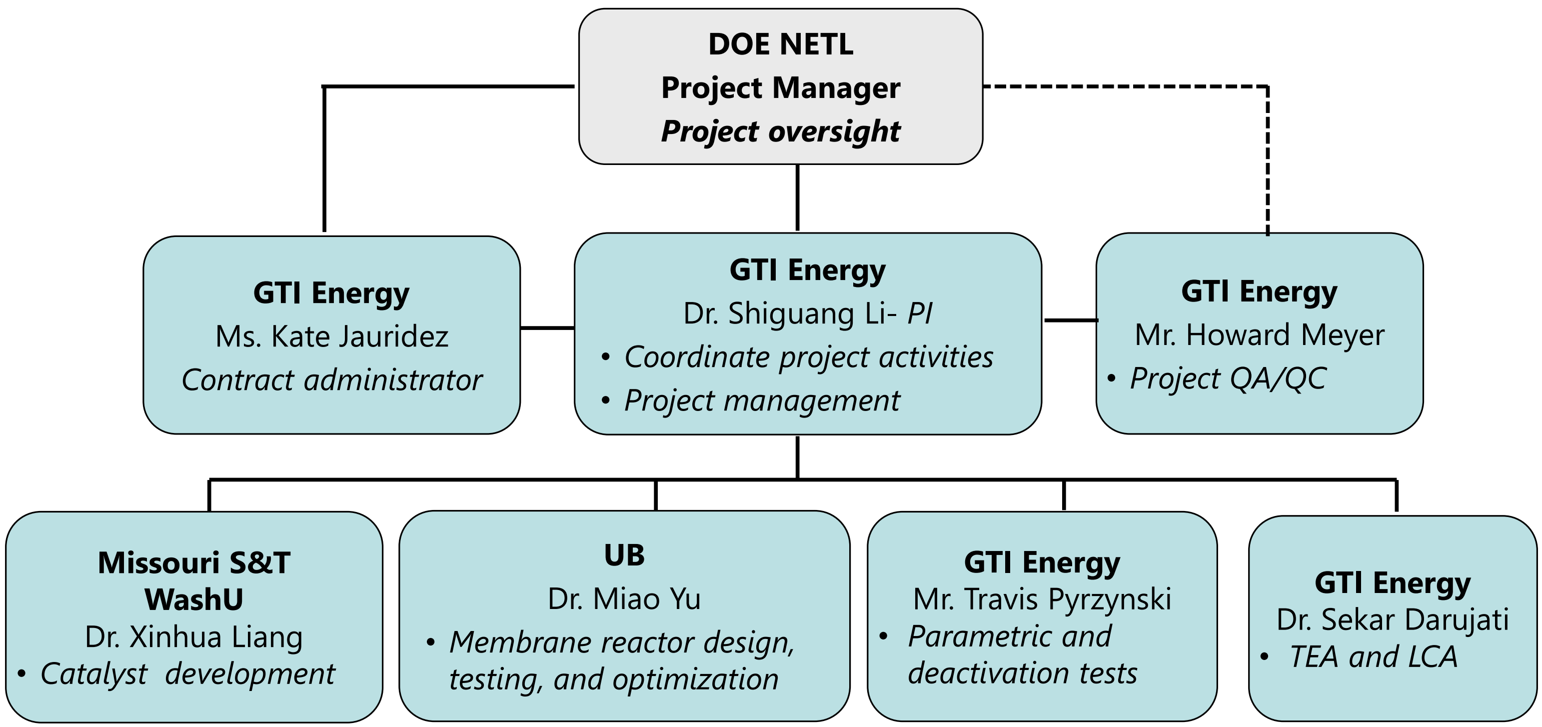
Appendix – Organization chart



Appendix – Gantt chart

ID	Task NO	SubT NO	MS	Task Name	Start	Finish
1	1.0			Project Management and Planning	Fri 1/1/21	Mon 3/31/25
2		1.01		Project Management Plan	Fri 1/1/21	Mon 3/31/25
3			M1.1	Submit updated Project Management Plan to DOE	Sun 2/28/21	Sun 2/28/21
4			M1.2	Complete Kickoff Meeting	Tue 3/30/21	Tue 3/30/21
5			M1.3	Submit technology maturation plan to DOE	Tue 3/30/21	Tue 3/30/21
6			M1.4	Submit Final Technical Report	Mon 6/30/25	Mon 6/30/25
7		1.02		Technology Maturation Plan	Fri 1/1/21	Mon 3/31/25
8	2.0			Preparation, characterization, and optimization of catalysts	Fri 1/1/21	Fri 3/31/23
9			M2.1	Ship >20 g of catalysts with BET surface area >100 m2/g to UB from MS&T	Wed 6/30/21	Wed 6/30/21
10	3.0			Sequential membrane reactor testing and optimization	Fri 1/1/21	Fri 3/31/23
11			M3.1	Achieve CO2 conversion >30%, hydrocarbon yield >25% at 200-350ºC and 10-35 bar	Fri 3/31/23	Fri 3/31/23
12	4.0			Catalyst optimization and catalytic performance evaluation	Sat 4/1/23	Sat 9/30/23
13		4.01		Catalyst optimization	Sat 4/1/23	Sat 9/30/23
14			M4.1	Complete development of CZZA-based catalyst with surface area > 100 m2/g, and palladium (Pd) loading ≥ 0.1 wt.% for the Pd-B zeolite catalyst	Sat 9/30/23	Sat 9/30/23
15		4.02		Catalytic performance evaluation of the optimized catalyst	Sat 4/1/23	Sat 9/30/23
16			M4.2	Achieve CO2 conversion >40%, hydrocarbon yield >15%, and LPG yield >7% at 220-350ºC and 10-35 bar in a fixed bed reactor; achieve CO2 conversion >80%, hydrocarbon yield >60%, and LPG yield >35% at 220-330ºC and 10-35 bar	Sat 9/30/23	Sat 9/30/23
17	5.0			Bifunctional membrane reactor testing and optimization	Sun 10/1/23	Sun 6/30/24
18			M5.1	Achieve CO2 conversion >85%, hydrocarbon yield >75%, and LPG yield >45% at 220-330ºC and 10-35 bar	Sun 6/30/24	Sun 6/30/24
19	6.0			Optimization of bifunctional catalyst for membrane reactor testing	Mon 7/1/24	Mon 3/31/25
20		6.01		Optimization of the catalyst	Mon 7/1/24	Mon 3/31/25
21		6.02		Catalytic performance evaluation of the optimized catalyst	Mon 7/1/24	Mon 3/31/25
22			M6.1	Achieve CO2 conversion >90%, hydrocarbon yield >80%, and LPG yield >45% at 220-330ºC and 10-35 bar using optimized catalyst and tested in membrane reactor	Tue 12/31/24	Tue 12/31/24
23	7.0			Membrane reactor parametric and deactivation tests	Tue 10/1/24	Mon 3/31/25
24			M7.1	Complete 100-500 hours continuous testing; achieve steady-state CO2 conversion >85%, LPG yield >45% at 220-330ºC and 10-35 bar	Mon 3/31/25	Mon 3/31/25
25	8.0			Detailed techno-economic and life-cycle analyses	Sun 12/1/24	Mon 3/31/25
26			M8.1	Issue Final TEA report with a Technology Gap Analysis	Mon 3/31/25	Mon 3/31/25
27			M8.2	Issue Final LCA report	Mon 3/31/25	Mon 3/31/25