Technology Development for Carbon Capture and Conversion

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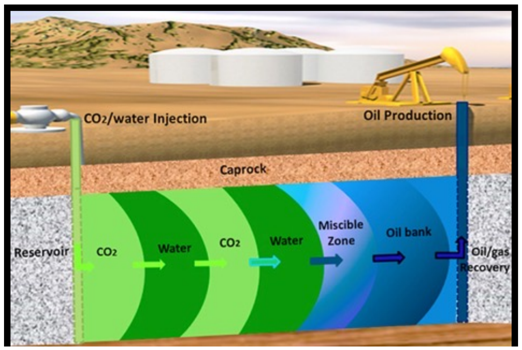
The Tale of Two Terms

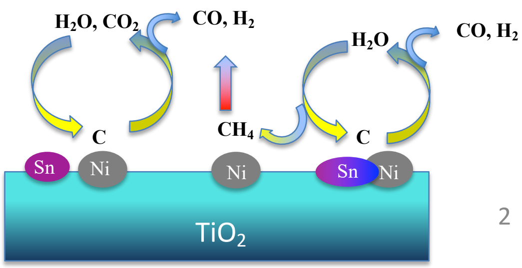
Near Term

- Carbon Capture
  - Higher CO_2 comp streams
  - Amine absorption
- Carbon Utilization
  - Enhanced Oil Recovery

Longer Term

- Carbon Capture
  - Lower CO_2 comp streams
  - Ionic Liquid absorption, pressure swing adsorption
- CO_2 Conversion
  - Tri-reforming
  - Photocatalytic conversion





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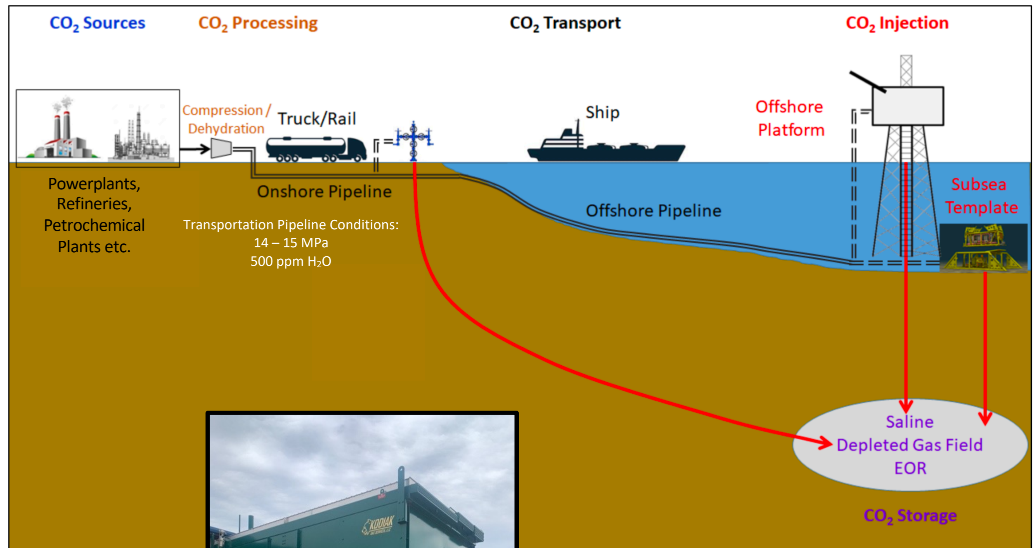
Carbon Capture and Storage (CCS)

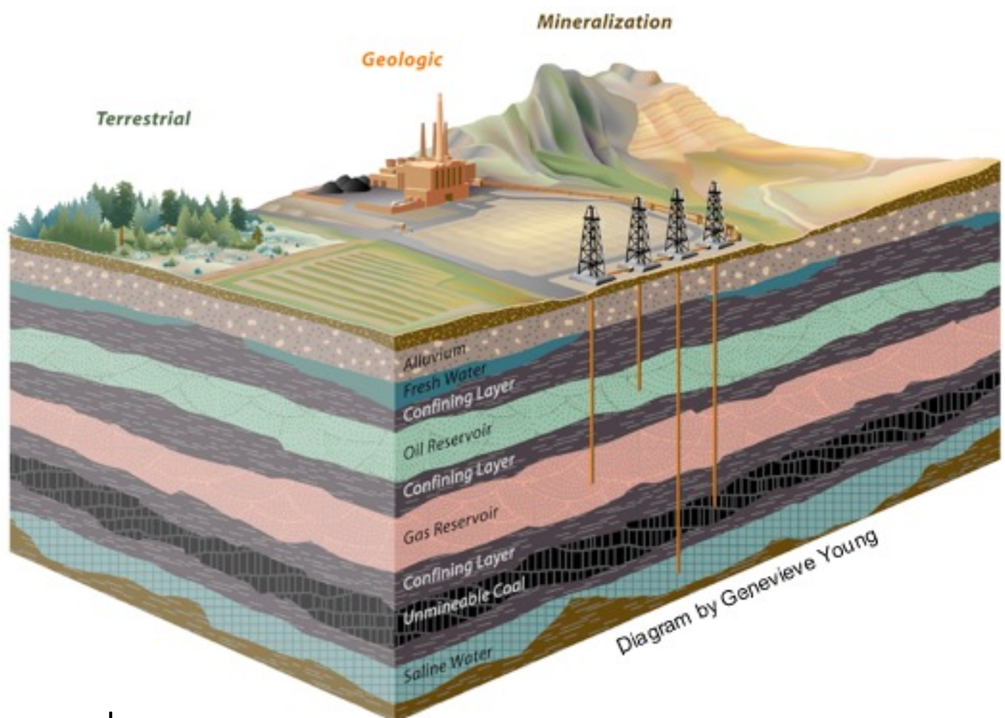


Deep Underground Storage

Gulf of Mexico Partnership for Offshore Carbon Storage (GoMCarb)

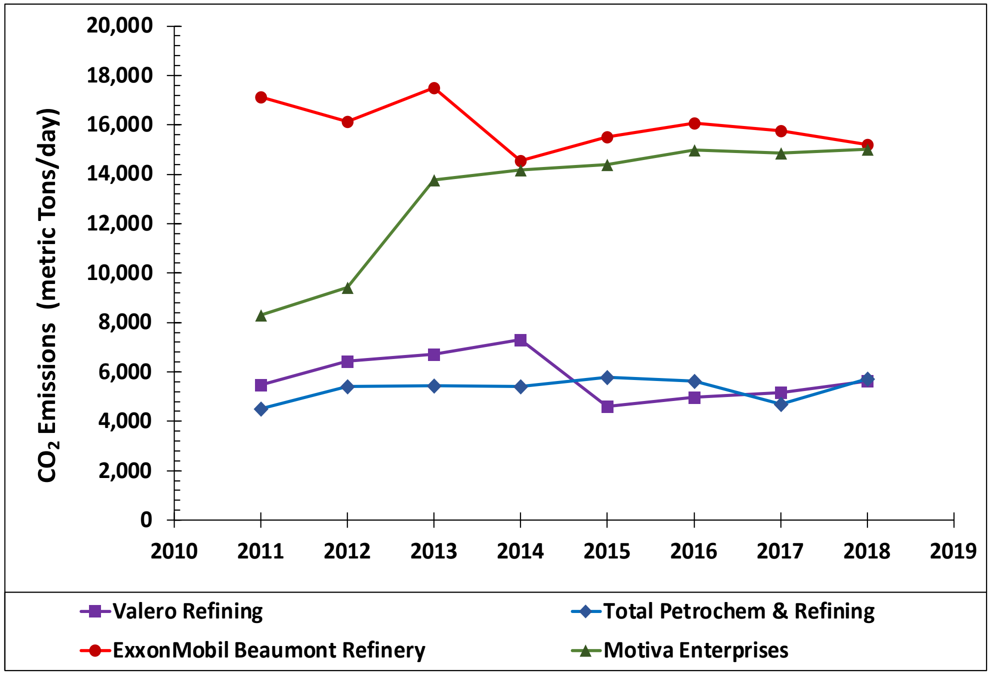
Why Store in Gulf of Mexico?

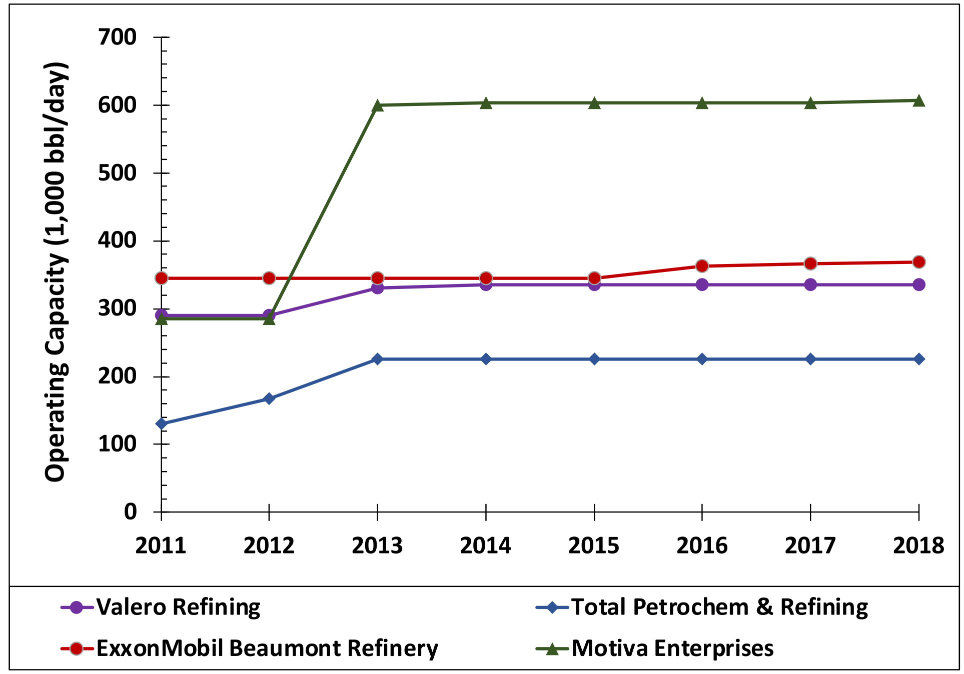
- Well studied geology
- Industrial CO_2 emission sources
- Large volume, low risk
- Industrial sources close to transportation facilities
- Existing Capture and transportation
- Commercial EOR to offset costs



http://www.beg.utexas.edu/gccc/research/gomcarb

Evaluation of Annual CO_2 Emissions from Refineries

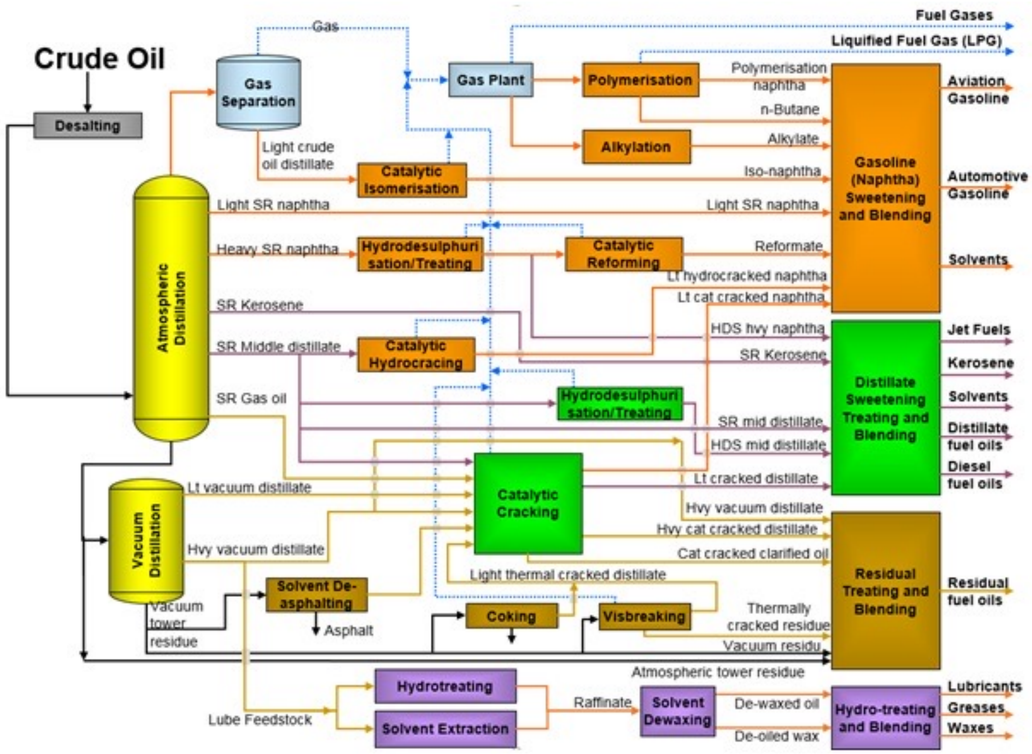


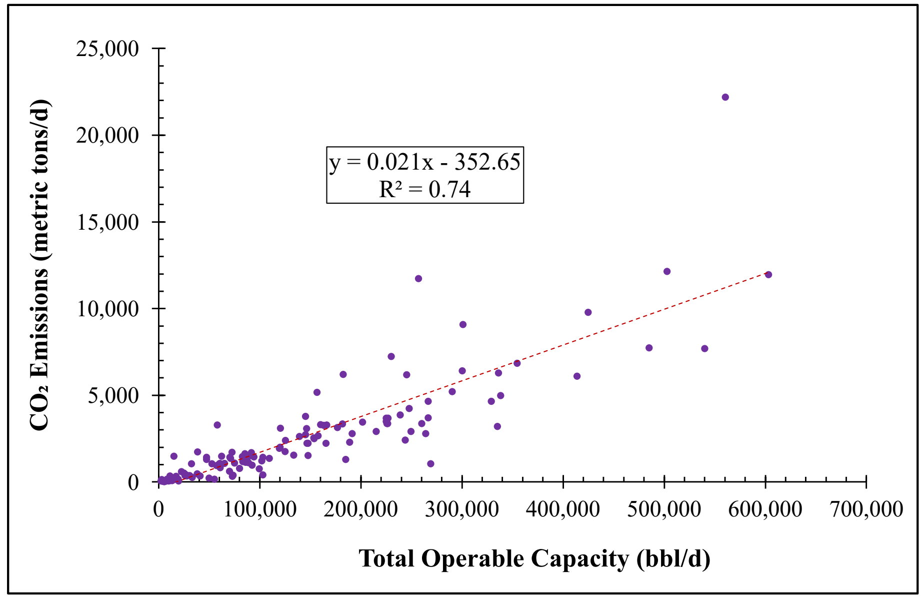


Data Sources:
Refinery Capacity Report,
U.S. Energy Information Administration

Data Sources:
FLIGHT
United States Environmental Protection Agency

CO_2 Emissions vs Operating Capacity

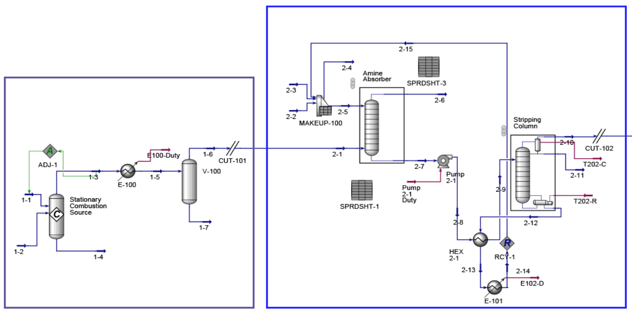


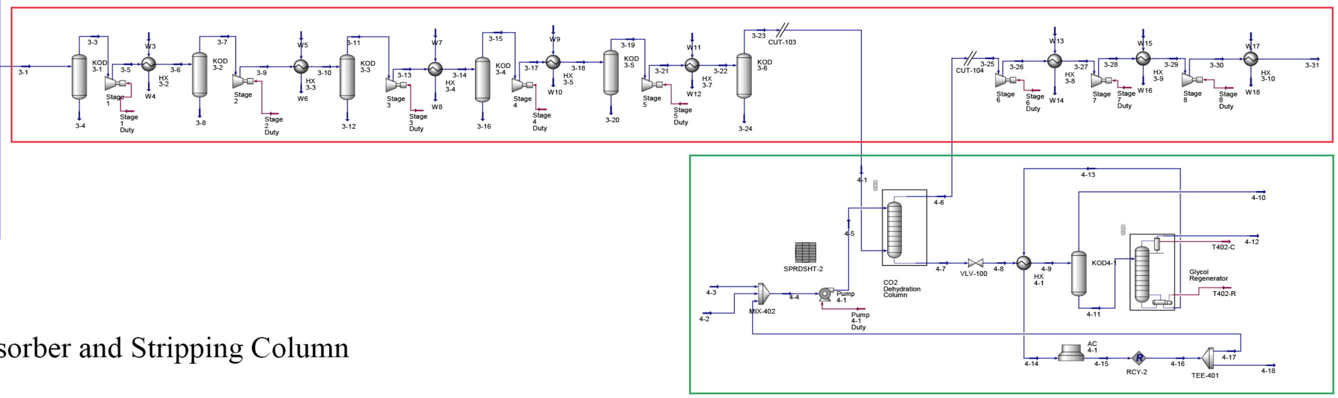


Carbon Capture and Storage (CCS)

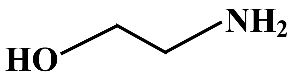
(Process simulation from waste flue gas to pipeline quality)

10 – 15 wt% CO_2 and 1 atm → **CO_2 w/ 500 ppm water and 130 atm**



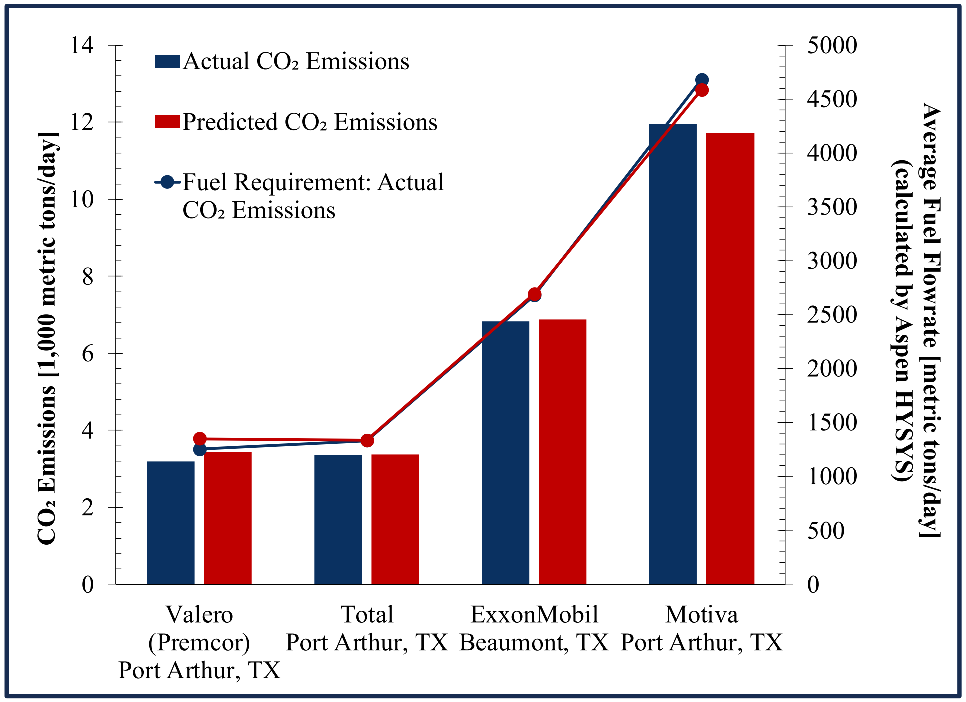


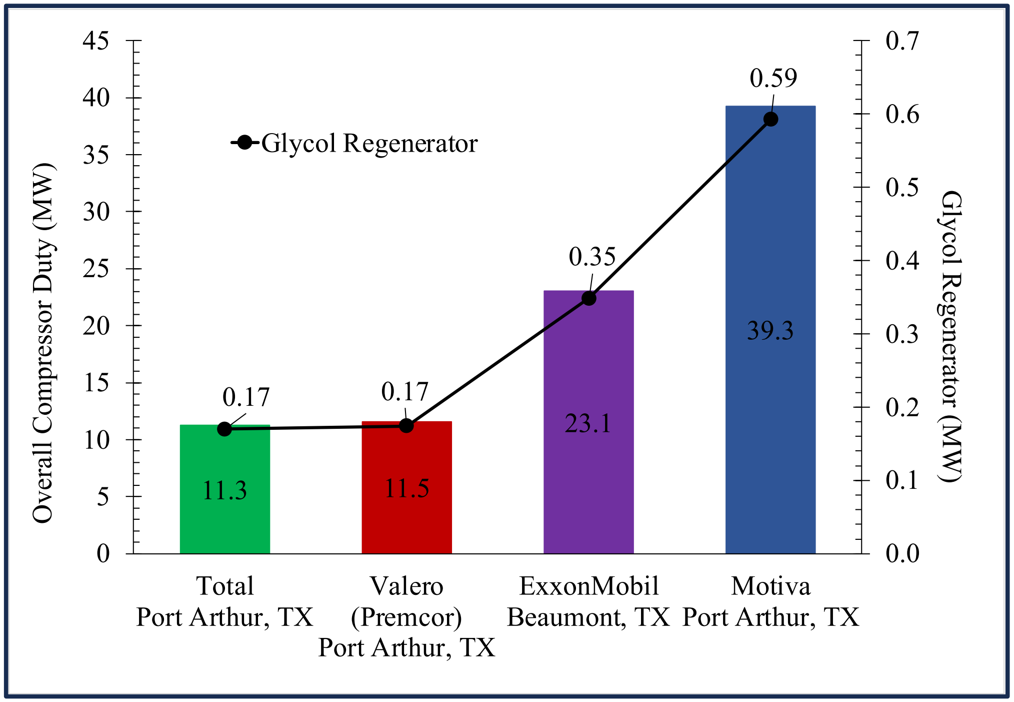
- CO_2 Generation – Combustion Reaction
- CO_2 Capture using Amine (MEA) – Amine Absorber and Stripping Column
- CO_2 Compression
- CO_2 Dehydration using TEG – CO_2 Dehydration Column and Glycol Regenerator



Monoethanolamine (MEA)

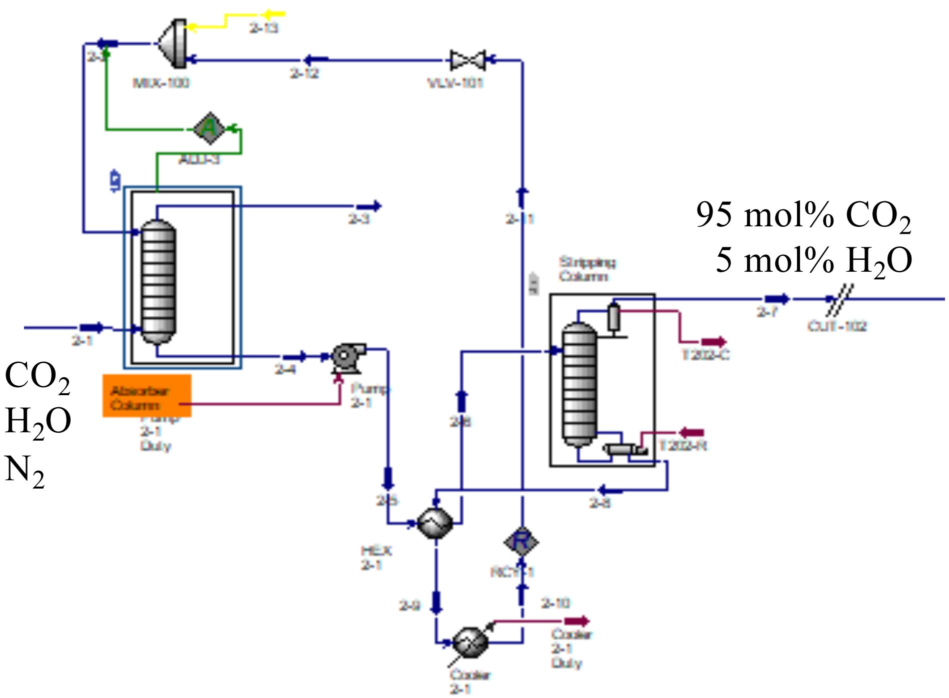
Process Simulation: Actuals vs Predicted





Madugula, et al. (2020) Chem. Eng. J. Advances, 100162.

Carbon Capture Using Cyclic Absorption/Stripping



10 – 15 mol% CO_2
8 – 10 mol% H_2O
75 – 85 mol% N_2

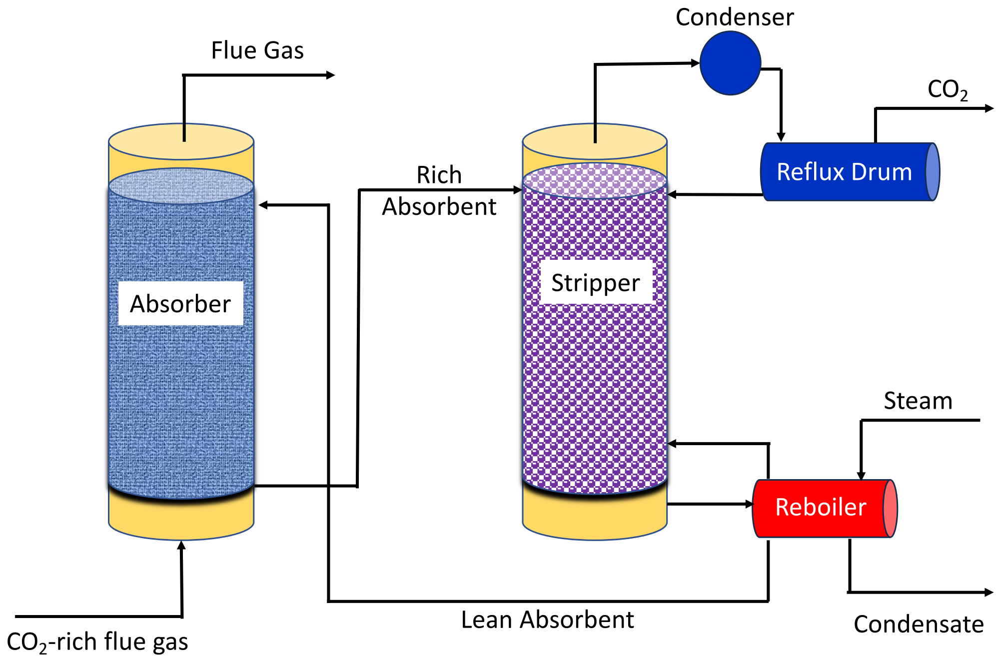
95 mol% CO_2
5 mol% H_2O

Amine Absorbents

+ **Established chemistry**
+ **Established technology**
+ **Industry ready**

- **High energy demand**
- **Amine degradation**
  - **Temperature**
  - **O_2, SOx, NOx**

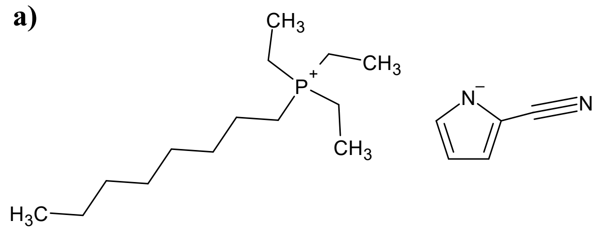
Capturing of Flue Gases (10 – 15 wt% CO_2)



- **Amines**
  - **Current Technology**
  - **High regeneration costs**
  - **Produces VOCs**
  - **Poisoned by contaminants**
- **Ionic Liquids**
  - **Lower regeneration costs**
  - **No VOCs**
  - **High viscosities**
  - **Poisons (??)**

Aprotic Heterocyclic Anion Ionic Liquids (AHA- IL)

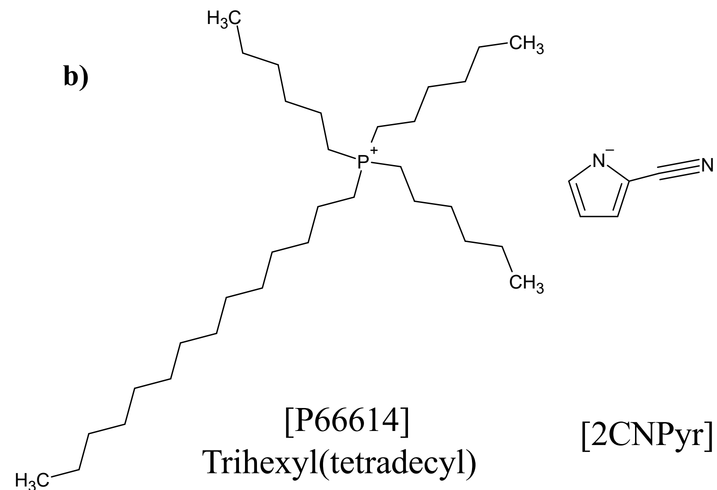
a)



[P2228]
Triethyl(octyl) phosphonium

[2CNPyr]
2-Cyanopyrrolide

b)



[P66614]
Trihexyl(tetradecyl) phosphonium

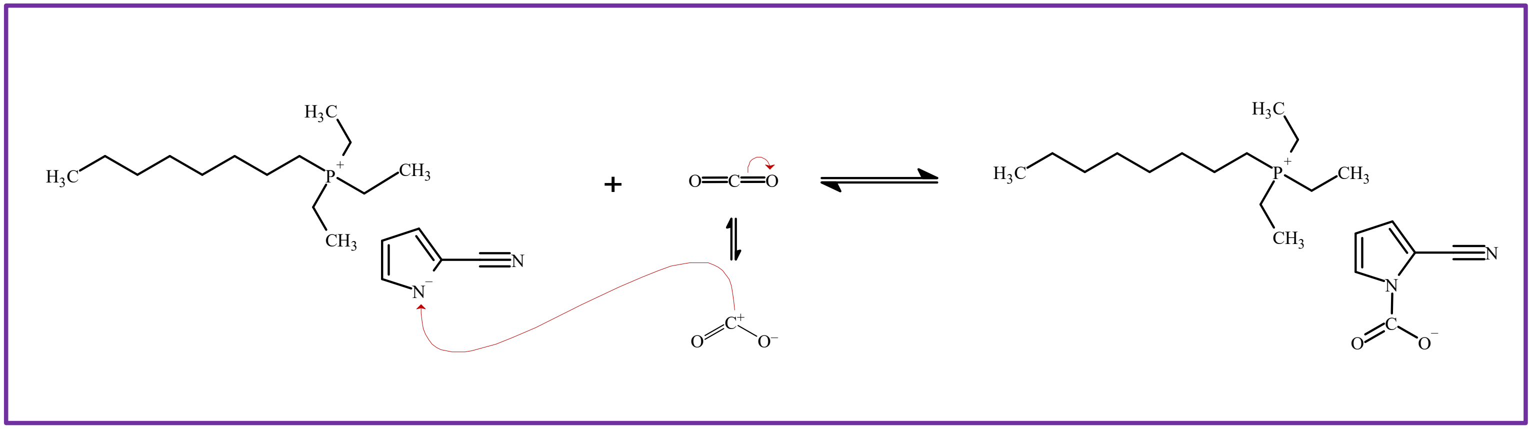
[2CNPyr]
2-Cyanopyrrolide

Henry's Law:

$$P_{CO2} = y_{CO2}P = x_{CO2}H(T)$$

Viscosity ↑, Diffusivity ↓
Temperature ↑, Viscosity ↓
Temperature ↑, Capacity ↓

Chemisorption Mechanism

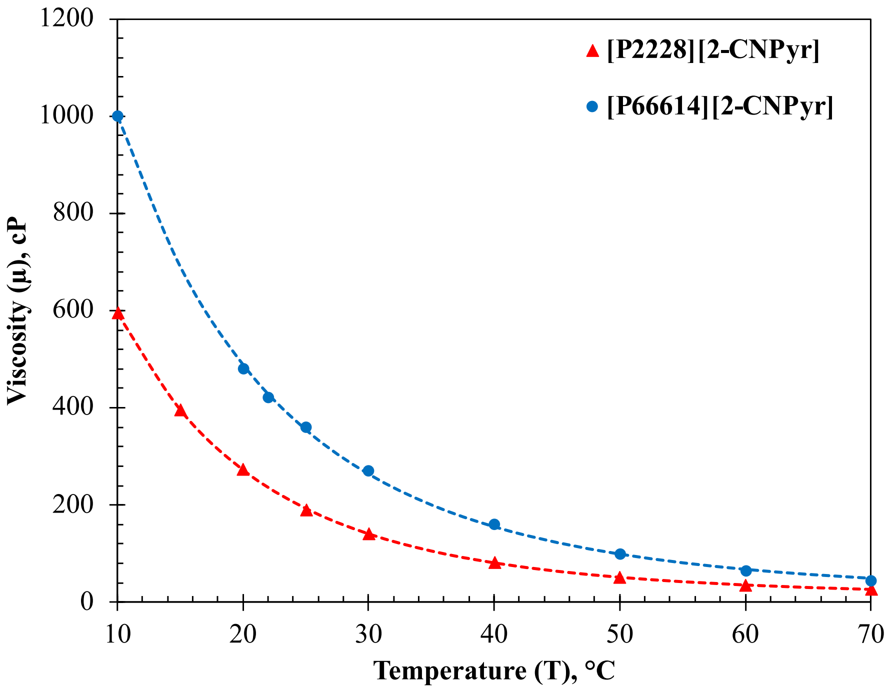


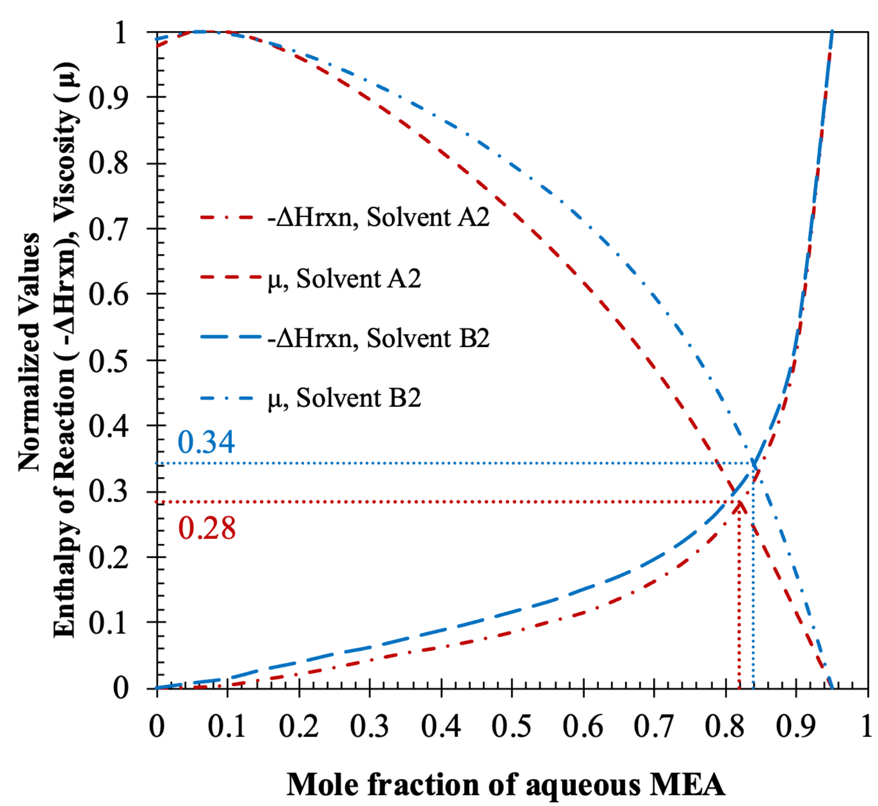
$$\ln(K_H) = A_{H,i} + \frac{B_{H,i}}{T}$$

$$\ln(K_{eq}) = \frac{\Delta S}{R} + \left(\frac{-\Delta H^0_{chem}}{RT}\right)$$

$$\ln(K_{eq}) = A_{K,i} + \frac{B_{K,i}}{T}$$

IL/MEA Hybrid Solvent





Solvent A: [P2228][2-CNPyr]
Solvent B: [P66614][2-CNPyr]

CO_2 - Birth, Death, and Reuse

$CO_2 + H_2O$ —Catalyst→ $CO + H_2$ → Diesel, Methanol, DME, Alcohols

Thermo-Chemical

- ✓ Dry Reforming
  $CO_2 + CH_4 \rightarrow CO + H_2$
- ✓ Tri-Reforming
  $CO_2 + CH_4 + H_2O \rightarrow CO + H_2$

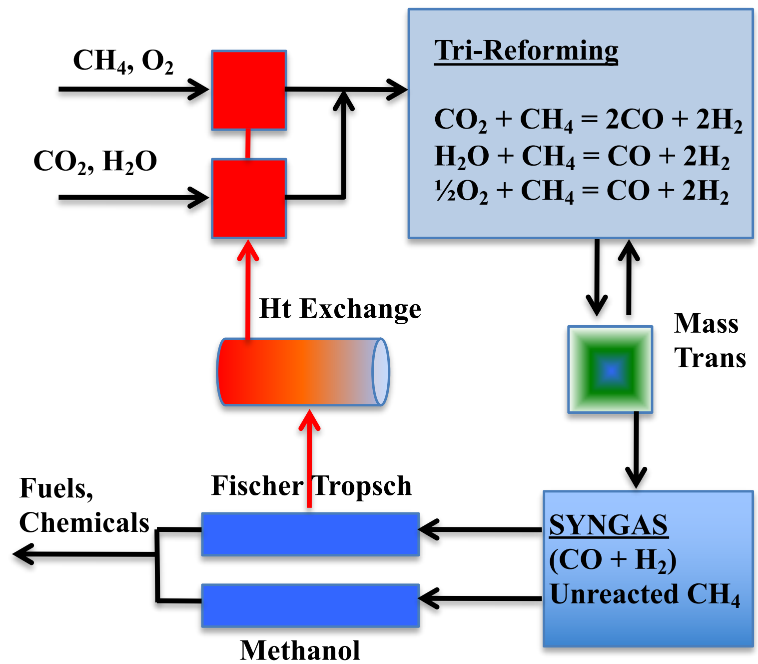
Non-thermo-Chemical

- ✓ Electrolytic
  $CO_2 + H_2O \rightarrow CO + H_2$
- ✓ Photocatalytic
  $CO_2 + H_2O \rightarrow CO + H_2 + HCs$

Tri-Reforming: Turning CO_2 into a Fuel

$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	$\Delta H = +247$ kJ/mol
$CH_4 + H_2O \rightarrow CO + 3H_2$	$\Delta H = +206$ kJ/mol
$CH_4 + ½ O_2 \rightarrow CO + 2H_2$	$\Delta H = - 36$ kJ/mol
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	$\Delta H = - 880$ kJ/mol
$CH_4 \rightarrow C + 2H_2$	$\Delta H = + 75$ kJ/mol
$2CO \rightarrow C + CO_2$	$\Delta H = -172$ kJ/mol
$C + CO_2 \rightarrow + 2CO$	$\Delta H = +172$ kJ/mol
$C + H_2O \rightarrow CO + H_2$	$\Delta H = +131$ kJ/mol
$C + O_2 \rightarrow CO_2$	$\Delta H = -394$ kJ/mol

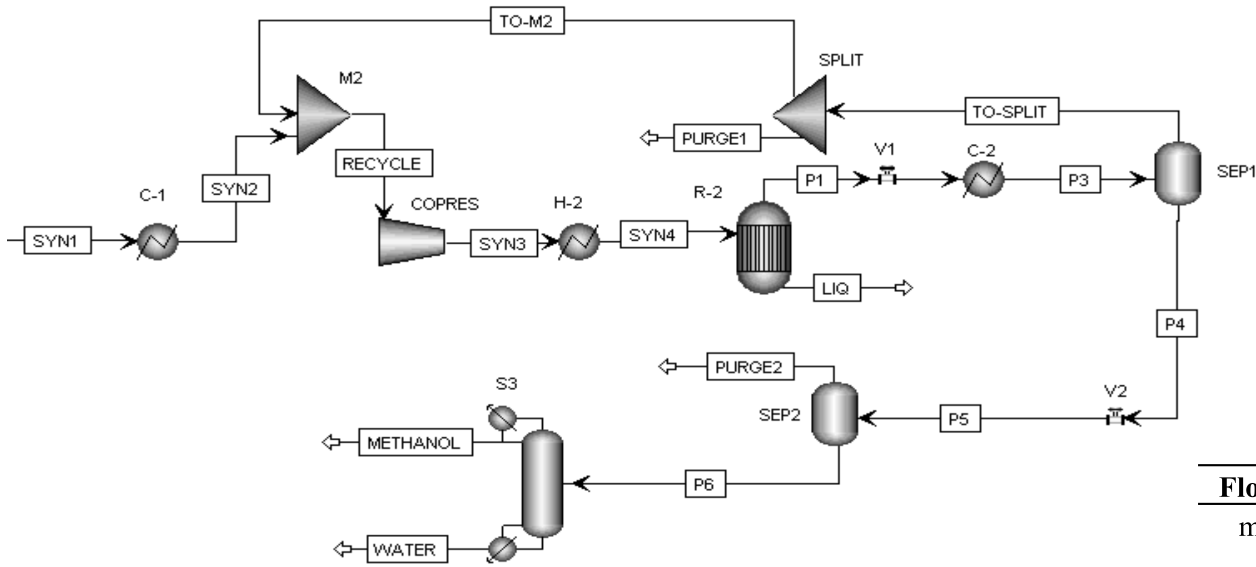
Conversion: 70% CO_2, 98% CH_4
$H_2/CO = 1.5 – 2.0$

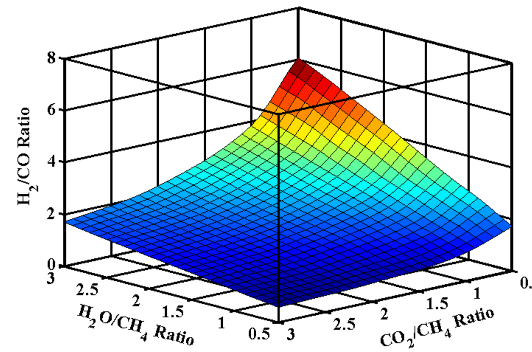


- Conversion and utilization of CO_2 without CO_2 separation from power plant
- Effective production of syngas with desired H_2/CO ratio for Fischer –Tropsch synthesis
- Reducing the possibility of carbon formation compared with dry reforming

Zhang et al. (2013) Int. J H2 Energy, 38, 13617-13630.
Zhang et al. (2014) Energy & Fuels, 28, 2717-2726.
Zhang et al. (2014) Chem Eng & Tech, 37, 1493-1499.
Zhang et al. (2015) Fuel Proc Tech, 131, 37-46.

Combined Methanol Synthesis and Tri- Reforming





Flowsheet Element	Parameter	Value
methanol reactor	temperature (°C)	220
	pressure (bar)	50
sep1	temperature (°C)	25
	pressure (bar)	24
sep2	temperature (°C)	25
	pressure (bar)	10
S3 (Radfrac)	Number of stages	19
	Feed stage	11
	Reflux ratio	1.5
	Distillate to feed ratio	0.988

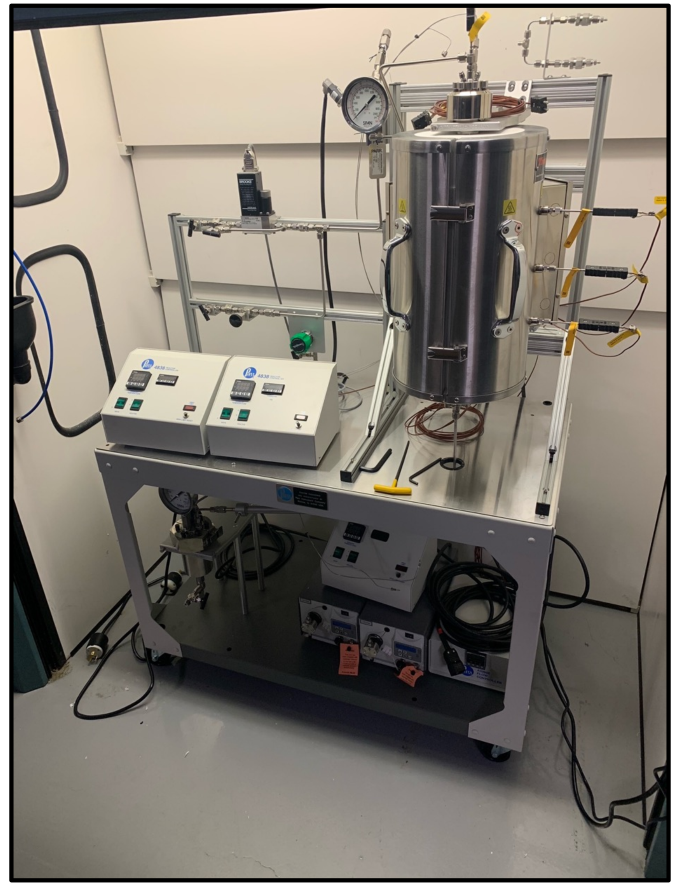
$CO + 2H_2 \rightarrow CH_3OH$ ΔH = - 91 kJ/mol

$CO_2 + 3H_3 \rightarrow CH_3OH + H_2O$ ΔH = - 50 kJ/mol

$CO + 2H_2O \rightarrow CO_2 + H_2$ ΔH = - 41 kJ/mol

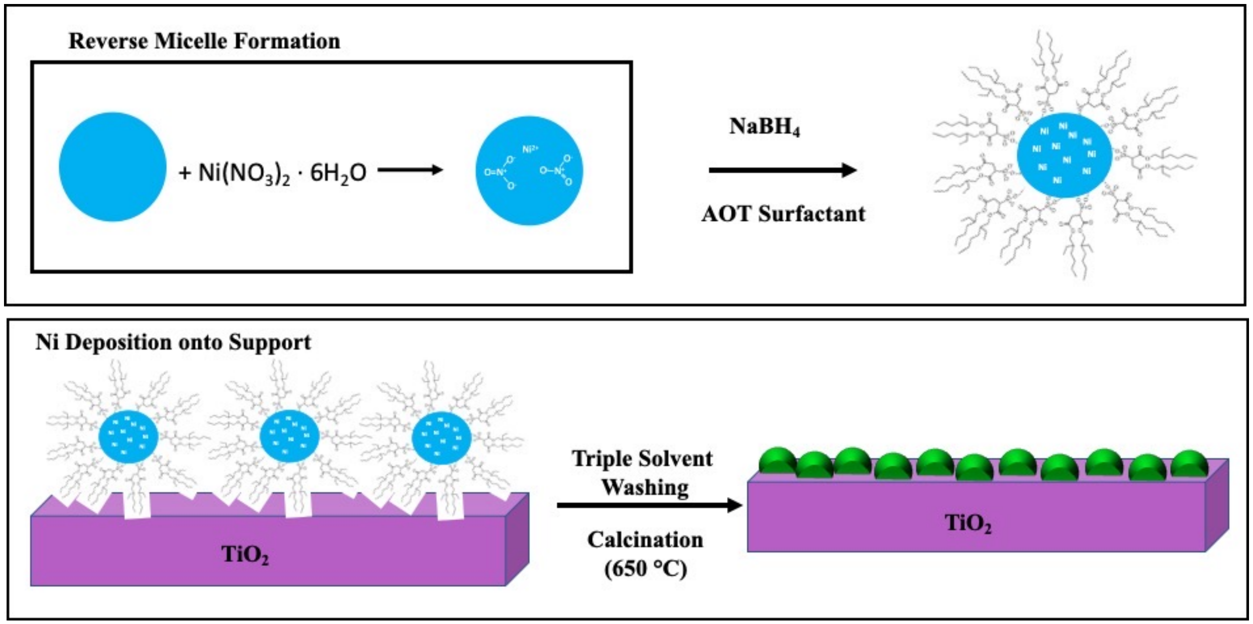
Tri-Reforming – Searching for the Right Catalyst

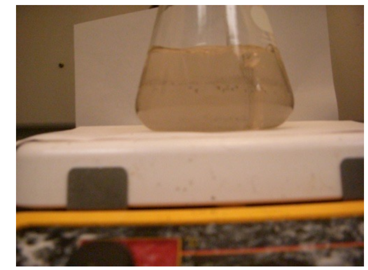
Catalyst	Reaction Conditions	% Conversions (H_2:CO ratio)	H2:CO Ratio
Ni/MgO	850°C, 1 atm	75% CO_2, 95% CH_4	1.5
Ni/MgO/CeZrO	850°C, 1 atm	70% CO_2, 93% CH_4	1.6
Ni/Mg_x Ti_{1-x}O	700-850°C, 1 atm	75% CO_2, 98% CH_4	2.0
NiO/YSZ/CeO_2	650-850°C, 1 atm	100% CO_2, 90% CH_4	1.67
Ni/Ce/ZrO_2	750°C, 3 atm	80% CO_2, 88% CH_4	1.2
Ni/SiO_2	750°C, 1 atm	91% CO_2, 31% CH_4	2.0
Ni-Mg/ß-SiC	750 °C, 1 atm	50% CO_2, 75% CH_4	1.5 – 2.0

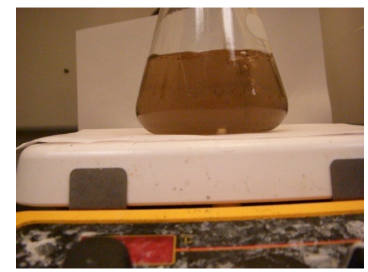


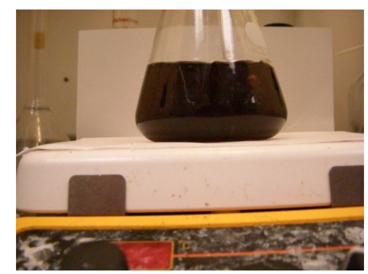
- **Need data under real conditions**
- **Catalyst and contaminants (NOx/SO_X)**

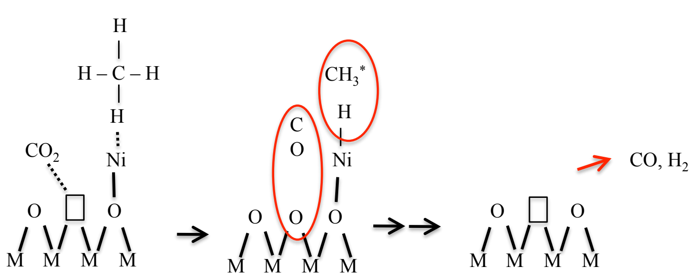
Tri-Reforming – Novel Catalyst Synthesis

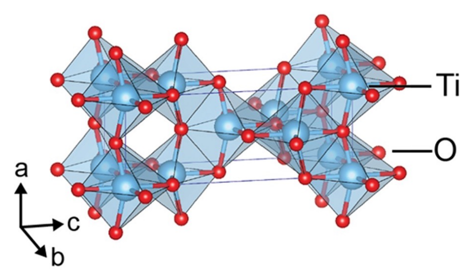






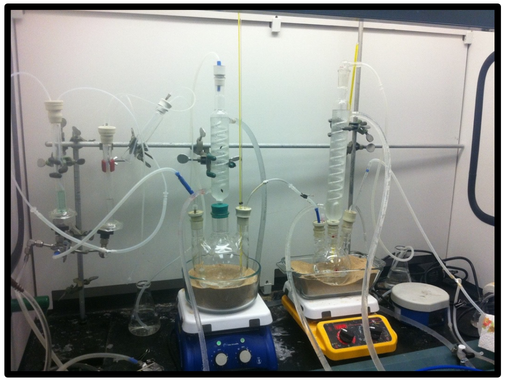


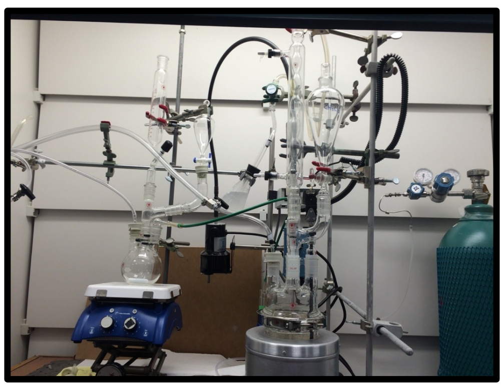




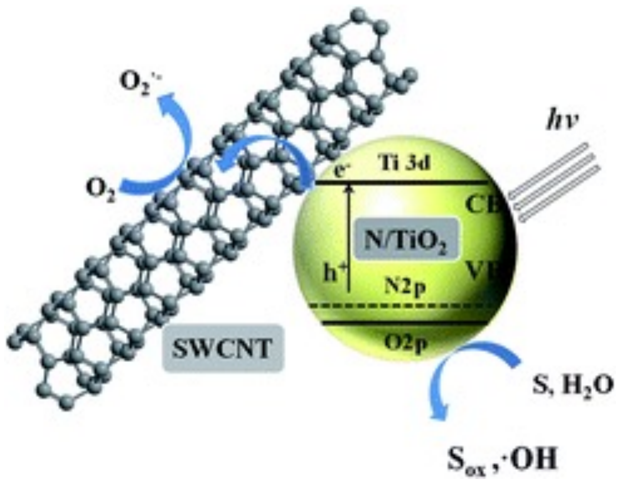
Piler et al. (2019) Chem. Eng. Com., 207, 537-548

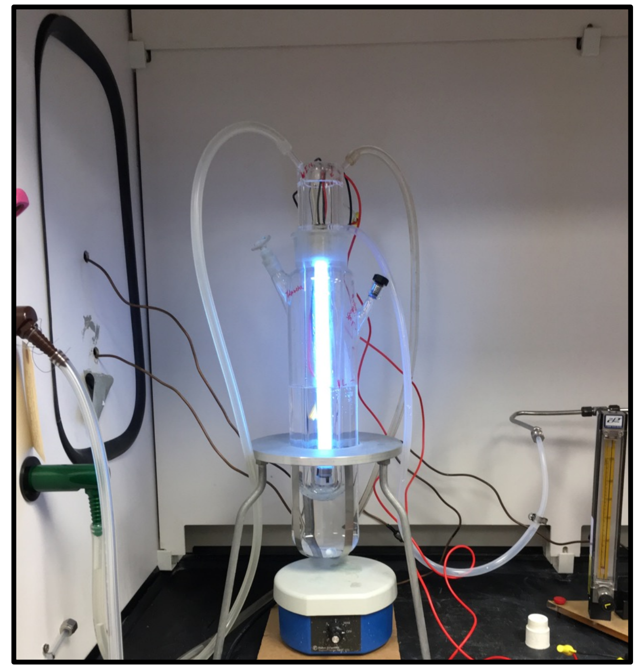
Photocatalytic Conversion of CO_2





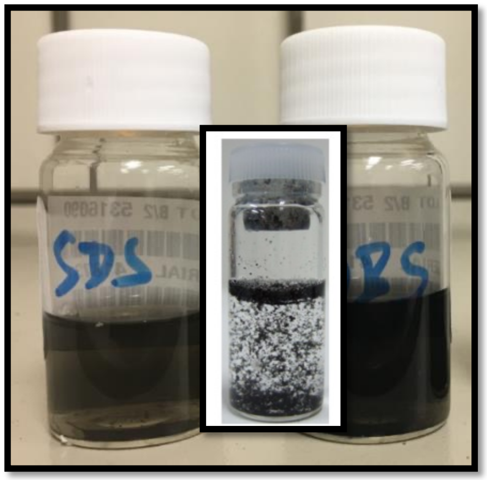
TiO_2-SWCNT Catalyst



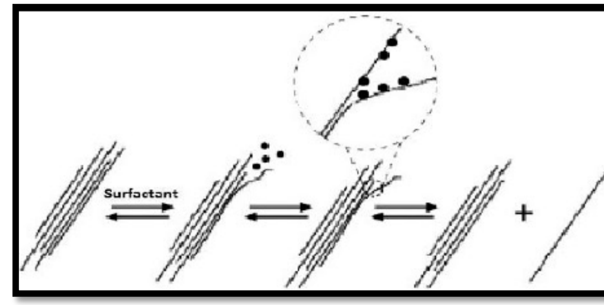


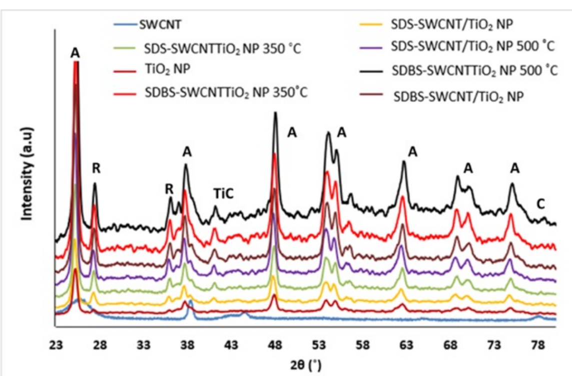
Piler et al. (2020) Mater. Letters, 278, 12810
Piler et al. (2020) Adv Catal., 66, Ch. 2

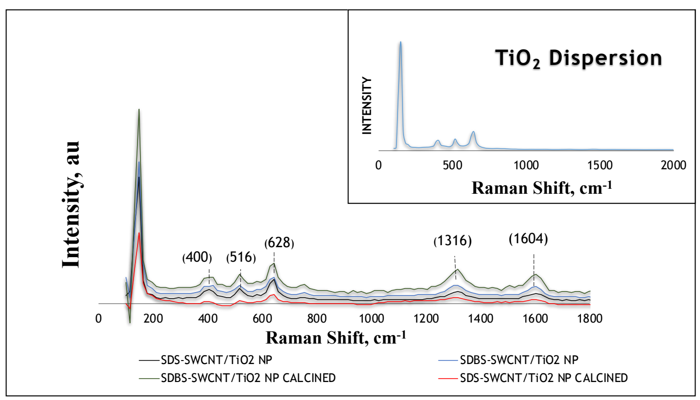
TiO_2 – SWCNT Photocatalyst

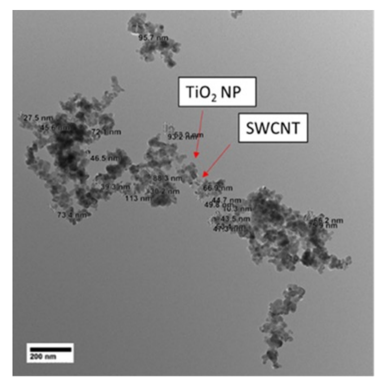


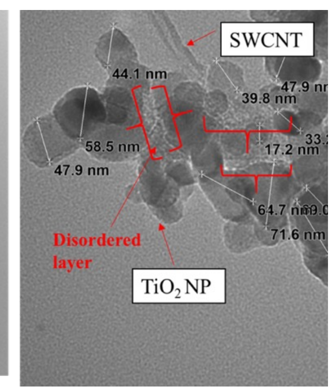
- Band gap reduction
- Longer electron – hole pair separation
- Enhanced adsorption of reactants (Such as CO_2, H_2O)











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GoMCarb

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