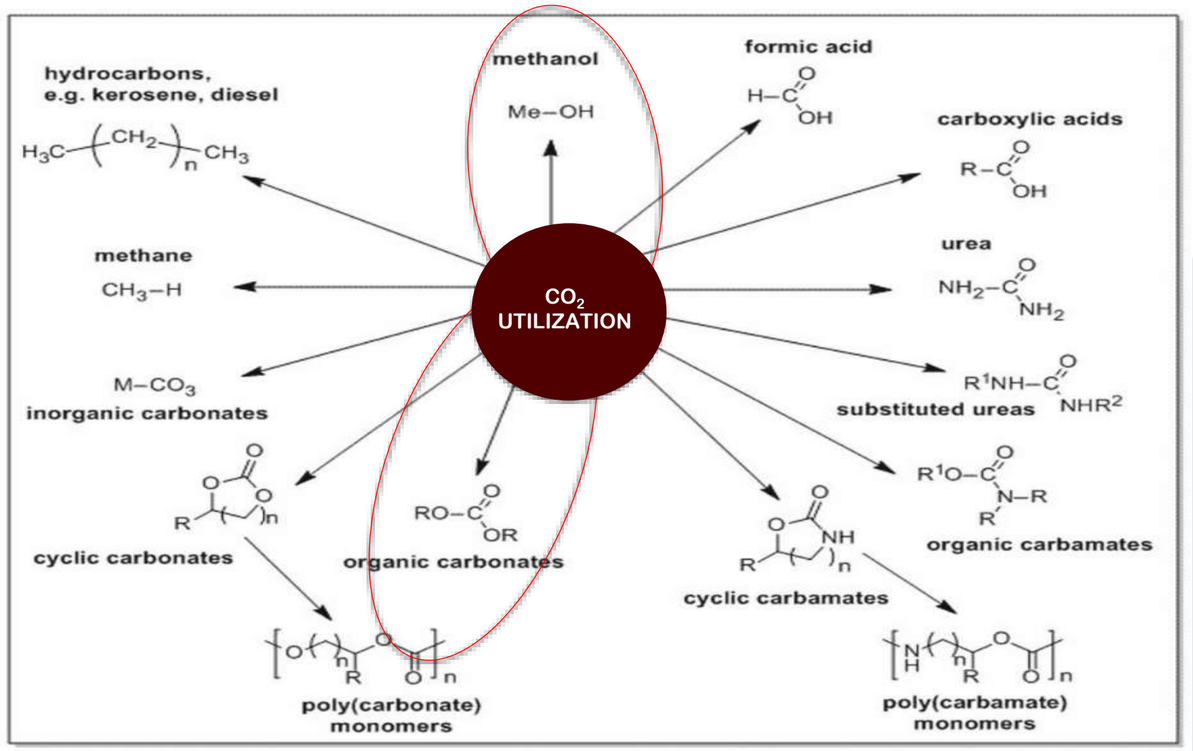
GAS & FUELS RESEARCH CENTER
TEXAS A&M ENGINEERING EXPERIMENT STATION

ORYX GTL
ORYX GTL Gas-to-Liquid Excellence Program

# Direct Synthesis of Dimethyl Carbonate (DMC) from Methanol and $CO_2$

# $CO_2$ Utilization Routes




## DMC synthesis by CO2

$$2CH_3OH(l) + CO_2(g) \leftrightarrow CO(OCH_3)_2(l) + 2H_2O(l)$$

**Main uses of DMC:**

- **DMC is a versatile non toxic solvent**
- **Used as solvent in polycarbonate and PU industry**
- **Used as fuel additive for gasoline/diesel**
- **DMC can boost density and RON of the GTL fuels**

| name | abbrev | MW | mp (°C) | bp (°C) | $d_{20°C}$ (g/cm$^3$) | vapor pressure at 37.8 °C (mmHg) | lower heating value (MBtu/gal) | wt % O |
|---|---|---|---|---|---|---|---|---|
| dimethyl carbonate | DMC | 90 | 1 | 90 | 1.069 | 81 | 55.6 | 53.3 |

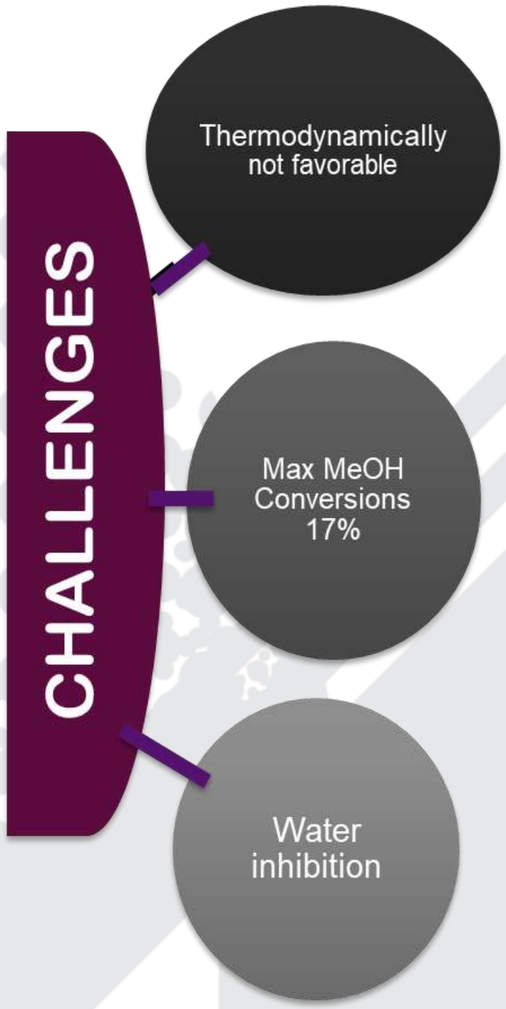
Table 6. Range of Alkyl Carbonate Gasoline Blending Values at 3–5 vol %

| | RON | MON | approx $R + M/2$ |
|---|---|---|---|
| dimethyl carbonate | 125–131 | 100–109 | 116 |

Table 4. Range of Alkyl Carbonate Gasoline Blending Values at 10 vol %[a]

| | DMC | DEC |
|---|---|---|
| RON | 106–111 | 111 |

# Challenges with DMC synthesis




$$2CH_3OH + CO_2 \leftrightarrow CO(OCH_3)_2 + 2H_2O$$

- Pressure has a positive effect on conversion
- Temperature has negative effect on conversion
- Reaction temperature more than 120 $^oC$ decreases MeOH conversion
- Water scavengers can help increase the conversion
- 2,2-dimethoxypropane (DMP) and dicyclohexylcarbodiimide (DCC) are reported (water scavengers)
- Reusability of scavengers and catalyst regeneration is a big concern and expensive
- Max MeOH conversion is 17% and DMC selectivity of 7%

# Objectives

**New process can be designed with :**

- **Cheap alternatives to 2-cyanopyradine for a sustainable option**
- **Use ion exchange resins as catalyst instead of metal oxide**
  - **Ion exchange resins can be operated in low temp range and high pressure**
  - **Catalyst regeneration is very economic and simple**
- **Optimized separation sequence developed in Hysys/Aspen Plus**
- **Incorporating new design by retrofitting a DMC plant in existing infrastructure in Qatar**
- **Utilizing MeOH and $CO_2$ to minimize C-footprint of Qatar**
- **Blending DMC with GTL Gasoline and Naphtha for a sustainable fuel mix for Qatar**

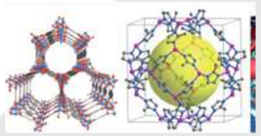
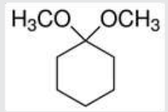
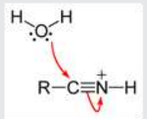
# Projected Project Flow

Synthesizing/identifying new catalysts



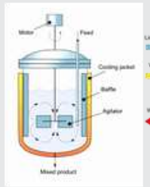
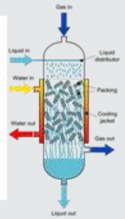
$CeO_2$, $ZrO_2$, Ion exchange resins

New Scavengers design

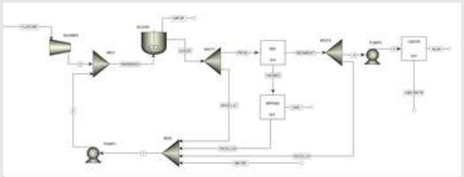
MOFs, Dimethyl ketals, Nitriles

Performance in batch reactor and flow reactor for scale up

Selectivity and Conversion

Techno economic analysis



ROI, CAPEX,$CO_2$ equivalence
Energy requirement

# Thank you