Computational Fluid Dynamics based design of a novel reactor technology for oxidative coupling of methane

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The chemical industry today

Raw Materials

Products

Cracker

(source: 2011 BP Statistical Review)

(source: CMAI 2012)

(source: CMAI 2012)

New trends in olefin production

Abundancy of cheap methane from shale gas and stranded gas
→ Develop processes to **valorize methane** to higher hydrocarbons

**Syngas / MeOH**

Avoid syngas

**Oxidative Coupling of Methane**

Avoid intermediates

Success for implementation will require:
- Breakthrough in catalysis, reactor design, separation processes
- Fundamental technology development
- Industry / government / academic partnerships
Oxidative Coupling of Methane (OCM)

Recent history

- **1982** Keller and Bhasin: pioneering work
- **2008** DOW Chemical awards “methane challenge grants”
- **2013** Small firms are developing technology for converting natural gas to fuel and chemicals
- **April 2015** Siluria Technologies announces successful start-up of demonstration plant for OCM

Key challenges

- Strongly **exothermic** reaction(s)
- Inverse relationship between C2 hydrocarbon selectivity and CH₄ conversion: **low C2 yields**

Reactor design!
Reactor design for OCM

**Conventional Fixed Bed**
- Methane
- Oxygen
- Ethane
- Ethylene

**OCM Reaction Section:**
\[2\text{CH}_4 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2\text{O} + \text{heat}\]

**Ethane Conversion Section:**
\[\text{C}_2\text{H}_6 + \text{heat} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\]

**Limitations:**
- Thermal control of the reactor is difficult:
- Potential formation of hotspots

**Advantages:**
- Better heat and mass transfer

**Static Fluidized Bed**
- Drag force
- Gravitational force

**Riser/Circulating Fluidized Bed**

**Limitations:**
- Limited slip velocities (~ 1 m s\(^{-1}\))
- Entrainment of particles at high gas flow rates
Reactor design for OCM

Centrifugal instead of gravitational force field → Process intensification

**Advantages:**
- Dense particle bed
- High gas feed flow rates
- Higher slip velocity → better heat & mass transfer

**Limitation:**
- Mechanical moving parts (abrasion)

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**limitations:**
- Limited slip velocities (~ 1 m s⁻¹)
- Entrainment of particles at high gas flow rates
Gas-Solid Vortex Reactor (GSVR)

**Advantages:**
- Dense particle bed
- High gas feed flow rates → *high throughput* operation
- Higher slip velocity → *better heat & mass transfer*

GSVR emerges as an excellent reactor choice to demonstrate the OCM process.
GSVR Research at LCT (Laboratory for Chemical Technology)

Cold flow unit  Hot flow unit  Reactive unit

Optimize GSVR for OCM… A lot of degrees of freedom!
- Operating conditions (temperature, pressure, \( \text{CH}_4/\text{O}_2 \) ratio)
- Bed density, solid loading, particle diameter
- Gas-phase residence time (flow rate)
- Type of catalyst (!)
Comparison of catalysts using a simple isothermal plug flow reactor model, which is an ideal representation of an isothermal fixed bed reactor

\( \text{La}_2\text{O}_3/\text{CaO} \) (Stansch, 1997) – \( \text{Mn}/\text{Na}_2\text{WO}_4/\text{SiO}_2 \) (Dan espayeh, 2009)

Comprehensive 10-step kinetic model

(1 gas-phase, 9 catalytic reactions)

\( \text{Sr}/\text{La}_2\text{O}_3 – \text{Sn-Li}/\text{MgO} \) (Alexiadis, 2014)

Detailed microkinetic model developed at the LCT

(39 gas-phase, 26 catalytic reactions)

Remark

Homogeneous and heterogeneous reactions simultaneously \( \Rightarrow \) Two space times

For the presented simulations, the bed density has been kept constant (40%) and only the gas phase residence time has been varied
For the investigated conditions, the Sr/La$_2$O$_3$ catalyst is most interesting.

From simulations at different temperature:
- residence time $\sim$ 20-50 ms $\Rightarrow$ 10-25% methane conversion, 5-15% C2 yield
Non-ideal behavior of the GSVR

The GSVR is fundamentally different from a fixed bed reactor, hence it cannot be modeled by an ideal plug flow reactor model.

Get information about the non-ideal behavior by constructing the residence time distribution.

✓ Scaled residence time distribution from tracer experiment/simulation.

GSVR can be modeled as a combination of a plug flow reactor and CSTR.

*PFR = Plug Flow Reactor, CSTR = Continuously Stirred Tank Reactor
Adiabatic reactor operation

Non-ideal behavior is important during adiabatic reactor operation!

Thermal control of the reactor!
Formation of hotspots unavoidable in fixed bed reactor (PFR)

CSTR characteristics
→ better mixing
→ delay / smoothing of hot spots

*PFR = Plug Flow Reactor, CSTR = Continuously Stirred Tank Reactor

GSVR behavior somewhere in this region

CH$_4$/O$_2$=4, T=923K, p=1.1bara, $\epsilon_b$=0.6, Sr/La$_2$O$_3$
Adiabatic reactor operation

Non-ideal behavior is important during adiabatic reactor operation!

Thermal control of the reactor!
Formation of hotspots is possible in a fixed bed reactor (PFR).

CSTR characteristics
→ better mixing
→ delay / smoothing of hot spots

WANTED: CFD SIMULATIONS

*PFR = Plug Flow Reactor, CSTR = Continuously Stirred Tank Reactor
Non-reactive CFD simulations

Example: optimize design / conditions for stable bed formation
(N₂ feed: 10 g/s, 923 K; catalyst particles: 2300 kg/m³, 16 g total)

Bubbling bed not optimal for OCM
⇒ Increase particle diameter OR increase number of inlet slots

Stable bed
Non-reactive CFD simulations

Nitrogen feed: 10 g/s, 923 K
Catalyst particles: 2300 kg/m³, 16 g, ø1 mm
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Catalyst particles: 2300 kg/m³, 16 g, ø1 mm

Mean gas-phase residence time in the bed: ~1 ms

With simulated conditions: very low gas phase residence times in the bed (probably too low to obtain significant conversions and yields for OCM)
Reactive CFD simulations

La$_2$O$_3$/CaO catalyst
Stansch kinetics: 10-step mechanism

Very low C2 selectivity and CH$_4$ conversion

CH$_4$/O$_2$ feed: ratio 4, 10 g/s, 923 K
Catalyst particles: 2300 kg/m$^3$, 16 g, $\phi$1 mm

Selectivity too low → Use different catalyst / kinetic model
Reactive CFD simulations

State-of-the-art catalysts can reach C2 selectivity ~ 80%

\[ \text{CH}_4 \text{ conversion} \quad \text{C2 selectivity} \quad \text{Gas temperature} \]

- CH\(_4\)/O\(_2\) feed: ratio 4, 10 g/s, 873 K
- Catalyst particles: 2300 kg/m\(^3\), 16 g, \(\varnothing\)1 mm

- Conversion low (~3%) → Increase residence time
- Non-uniform temperature profile → Increase number of inlet slots
Reactive CFD simulations

Number of inlet slots influences bed uniformity

CH$_4$/O$_2$ feed: ratio 4, 10 g/s, 873 K
Catalyst particles: 2300 kg/m$^3$, 16 g, $\varnothing$1 mm

Increasing the number of inlet slots increases bed uniformity

- Less bypassing of the bed: higher conversion and C2-yields
- More uniform temperature profile
Conclusions

• New reactor technology for OCM: gas-solid vortex reactor (GSVR)
  – Uniform, dense particle beds
  – High gas throughput
  – Very good heat transfer and mixing

• A PFR+CSTR model can be used as a quick screening tool for catalysts and operating conditions

• CFD simulations are required to design and optimize the GSVR
  *Residence times need to be increased to obtain acceptable CH$_4$ conversions and C2 yields.*
  *Adjust design (number of inlet slots) to improve uniformity and increase yields.*
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Thank you for your attention!

Any questions?