The Oxidative Coupling of Methane: a Kinetic Model

by
Lauryn Holgado

Adviser: Prof. Srinivas Rangarajan

Lehigh University

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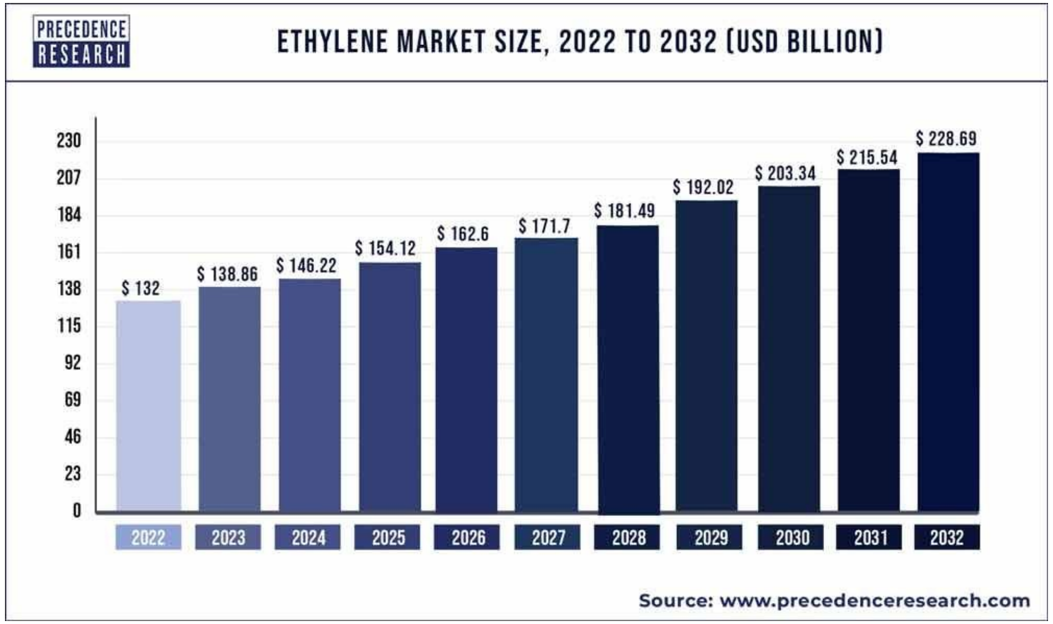
Natural Gas and Ethylene Production

- Low-carbon solutions: conversion of natural gas to useful chemicals.
- Increasing natural gas production.
    - 2022: 28.6 trillion cubic feet (Tcf) shale gas produced in the U.S. (79% of total U.S. dry natural gas production).[1]



1. U.S. Energy Information Administration. (accessed 2023-12-06)

Kinetic Model[2]

- 39 gas-phase reactions
- 14 surface reactions
- 33 species (gas-phase, surface, free radicals, inert gas)

2. SUN, J.; THYBAUT, J.; MARIN, G. Microkinetics of Methane Oxidative Coupling. *Catalysis Today* **2008**, *137* (1), 90–102. DOI:10.1016/j.cattod.2008.02.026.

Python Script

- $$V\frac{dC_A}{dt} = \begin{bmatrix} S^{gas} \\ S^{surf} \end{bmatrix} \begin{bmatrix} r^{gas} \cdot V_{gas} \\ r^{surf} \cdot cat\_SA \end{bmatrix}$$

$$\frac{d\theta}{dt} = S^{surf}\, r^{surf}$$

$$[*] = \sigma - \sum_i [\theta_i]$$

V = total volume [m^3]
V_{gas} = gas volume [m^3]
C_A = gas phase species concentration matrix [mol m^{-3}]
S = reaction matrix (gas or surface)
r = rate expression (gas or surface) [mol m^{-3} s^{-1} or mol m^{-2} s^{-1}]
σ = active site density [mol m^{-2}]
cat_SA = catalyst surface area [m^2]
θ = adsorbed species concentration matrix [mol m^{-2}]

- Solve a system of ODEs
- solve_ivp
- Method: 'BDF' (backward differentiation formula)
- Example inpu

Gas Phase Rate Constants

The forwards rate constant was calculated using the Arrhenius equation. The equilibrium constant relation was used in order to determine the backwards rate constant.

$$k_f = A_f \, exp(-\frac{E_a^f}{RT})$$

$$k_b = \frac{k_f}{K}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

$$\Delta G^o = - RTlnK$$

A_f = pre-exponential factor [1/s or m^3/mol s or m^6/mol^2 s]

E_a^f = activation energy [kJ/mol]

K = equilibrium constant

Surface Reaction Rate Constants

For adsorption steps, the following equation was used:

$$k = \frac{S_o}{\sigma^n}\sqrt{\frac{RT}{2\pi M}}$$

S_o = the initial sticking probability

σ = the density of active sites [mol/m^2]

n = reaction order

M = the molar mass [kg/mol]

Third-Body Modeling

- Implemented third-body modeling using and inert (N_2) as the third body. Third body modeling is an integral part of this kinetic model.

$$A + B + M \rightleftharpoons AB + M$$
$$r_f = [A][B][M]k_f$$

Catalyst

Sn/Li/MgO

- BET surface area = 2800 m^2/kg
- Density = 2300 kg/m^3
- Porosity = 0.27
- Areal density = 1.14e-5 mol site/m^2

Assumed 100 mg of catalyst

- Catalyst surface area = 0.28 m^2

Conditions[3]

- T = 750°C, P = 130 kPa
- Runtime = 0.0124 seconds
- CH4 initial fraction = 0.1
- $CH_4/O_2 = 2$
- $[CH_4]_o = 1.54$ mol/m³
- $[O_2]_o = 0.77$ mol/m³
- $[N_2]_o = 12.5$ mol/m³
- Reactor volume = 3.27e-5 m³
- Gas volume = 3.19e-05 m³
- Weight of Catalyst/Flowrate = 2 kg s/mol

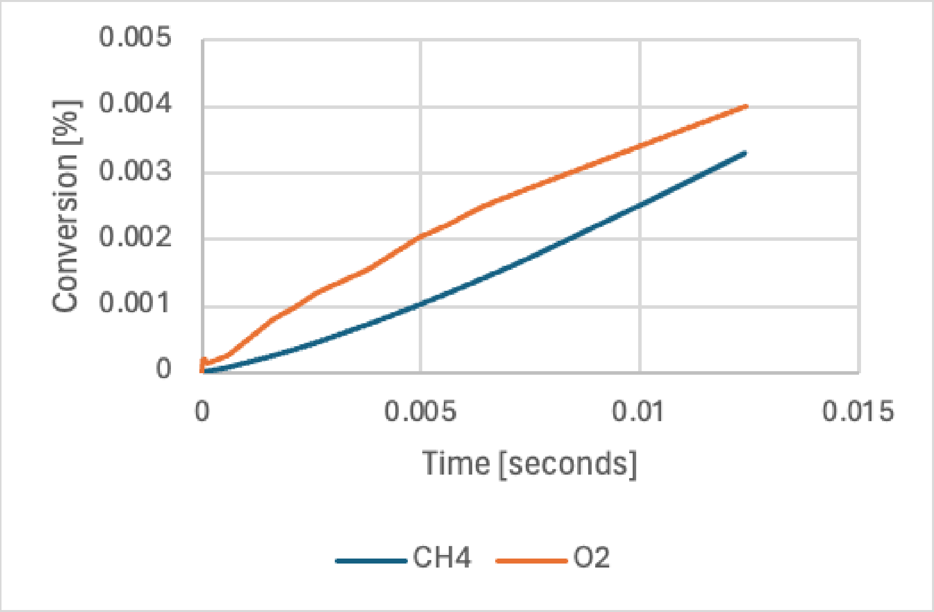
3. Couwenberg, P. M.; Chen, Q.; Marin, G. B. Kinetics of a Gas-Phase Chain Reaction Catalyzed by a Solid: The Oxidative Coupling of Methane over Li/MgO-Based Catalysts. *Industrial & Engineering Chemistry Research* **1996**, *35* (11), 3999–4011. DOI:10.1021/ie9504617.

Conversion

- Very little conversion of both CH_4 and O_2
  - Maximum conversion of CH_4 = 3.31e-5%
  - Maximum conversion of O_2 = 4.01e-5%

$$Conversion = \frac{C_{i,o} - C_{i,t}}{C_{i,o}} \times 100$$

$C_{i,t}$ = concentration of species i at time t
$C_{i,o}$ = initial concentration of



Yield

- Very little yield for all species

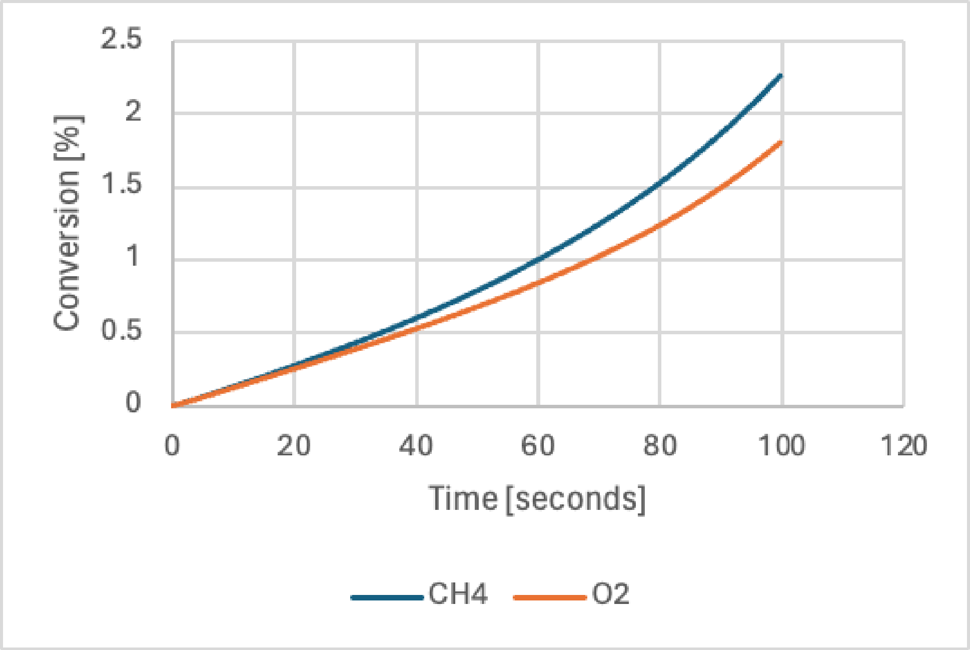
$$yield = \frac{num\_mol\_CH4 \times C_{i,t}}{C_{CH4,o}} \times 100$$

num_molCH4 = moles of CH4 required to produce species i
$C_{i,t}$ = concentration of species i at time t
$C_{CH4,t}$ = initial concentration of CH4

Species	Maximum Yield [%]
Ethane (C_2H_6)	2.69e-3
Ethylene (C_2H_4)	5.71e-7
Acetylene (C_2H_2)	3.23e-11
Propane (C_3H_8)	5.32e-12
Propylene	4.92e-11

Increase Runtime

- Modify rate constants to create a less stiff reaction network
- Increased the runtime to 100 seconds



Maximum conversion of CH_4 = 2.27%

Maximum conversion of O_2 = 1.82%

Species	Maximum Yield [%]
Ethane (C_2H_6)	1.46
Ethylene (C_2H_4)	0.346
Acetylene (C_2H_2)	6.30e-4
Propane (C_3H_8)	1.53e-9
Propylene (C_3H_6)	0.029

Future Directions

- Increase the amount of catalyst
- Model different types of reactors (PFRs, CSTRs, etc.)\
- Model UV-PIMS
- Compare to experimental data

Thank you!

Gas Phase Reactions

C2H5•+M⇌C2H4+H•+M
C2H5•+O2⇌C2H4+HO2•
C2H4+O2⇌C2H3•+HO2•
C2H4+H•⇌C2H3•+H2
C2H4+OH•⇌C2H3•+H2O
C2H4+CH3•⇌C2H3•+CH4
C2H4+OH•⇌CH3•+CH2O
C2H3•+M⇌C2H2+H•+M
C2H3•+O2⇌C2H2+HO2•
C2H3•+O2⇌CH2O+CHO•
C2H5•+CH3•⇌C3H8
C3H8+H•⇌C3H7•+H2
C2H4+CH3•⇌C3H7•
C3H7•⇌C3H6+H•
O2+H•⇌OH•+O•
O2+H•+M⇌HO2•+M
HO2•+HO2•⇌O2+OH•+OH•
H2O2+M⇌OH•+OH•+M
C2H6⇌C2H5•+H•

CH4+O2⇌CH3•+HO2•
CH4+H•⇌CH3•+H2
CH4+O•⇌CH3•+OH•
CH4+OH•⇌CH3•+H2O
CH4+HO2•⇌CH3•+H2O2
CH3•+O2⇌CH3O•+O•
CH3•+O2⇌CH2O+OH•
CH3•HO2•⇌CH3O•+OH•
CH3•+CH3•+M⇌C2H6+M
CH3O•+M⇌CH2O+H•+M
CH2O+OH•⇌CHO•+H2O
CH2O+HO2•⇌CHO•+H2O2
CH2O+CH3•⇌CHO•+CH4
CHO•+M⇌CO+H•+M
CHO•+O2⇌CO+HO2•
CO+HO2•⇌CO2+OH•
C2H6+H•⇌C2H5•+H2
C2H6+OH•⇌C2H5•+H2O
C2H6+CH3•⇌C2H5•+CH4
C2H5•+HO2•⇌CH3•+CH2O+OH•

Catalytic Reactions

O2+2S1⇌2OADS1
CH4+OADS1⇌CH3+OHADS
C2H4+OADS1⇌C2H3+OHADS1
C2H6+OADS1⇌C2H5+OHADS1
2OHADS1⇌H2OADS1+OADS1
H2OADS1⇌H2O+S1
CH3+OADS1⇌CH3OADS1
CH3OADS1+OADS1⇌CH2OADS1+OHADS1
CH2OADS+OADS⇌HCOADS+OHADS1
HCOADS1+OADS1⇌COADS1+OHADS1
COADS1+OADS1⇌CO2ADS+S1
CO+S1⇌COADS1
CO2+S1⇌CO2ADS1
4HO2→3O2+2H2O