

Two Dimensional Model of a Catalytic Plate Reactor for Methane Steam Reforming using Different Kinetic Mechanisms

Mayur Mundhwa

PhD student

Dr. Christopher Thurgood (RMC)

Dr. Brant Peppley (FCRC)

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KEY POINTS

- Developed the steady state two dimensional mathematical model of a Catalytic Plate Reactor (CPR)
- Studied the effects of co- and counter-current flow on the conversion of methane
- Studied the different kinetic schemes of methane steam reforming
- Studied the effect of inlet H₂ concentrations on the reaction rate profile

INTRODUCTION

- Catalytic Plate Reactor (CPR) is the well known portable reactor design for the coupling of endothermic (e.g. Steam Reforming of Methane) and exothermic (e.g. Combustion of Methane) reactions
- To design such reactor requires the knowledge of temperature distribution within the reactor
- It is difficult to measure the temperature inside the micro area of such reactor
- Therefore, to evaluate not only local temperature distribution but the whole reactor performance in terms of conversion and concentration distribution, accurate predictive models are necessary

INTRODUCTION

- Steam Reforming of Methane (SRM) is a well established industrial process for the production of syngas ($\text{CO} + \text{H}_2$)
- Different kinetic mechanisms are published to understand the driving force behind SRM process
- Three kinetic schemes are implemented in this model for the comparative study of their rate profiles under the same operating conditions
- Reaction kinetics used in this study are:
 - (1) Xu and Froment
 - (2) Hou and Hughes
 - (3) Wei and Iglesia

Steam Reforming of Methane

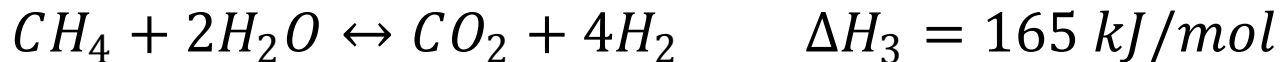
Methane steam reforming reaction



Water gas-shift reaction:



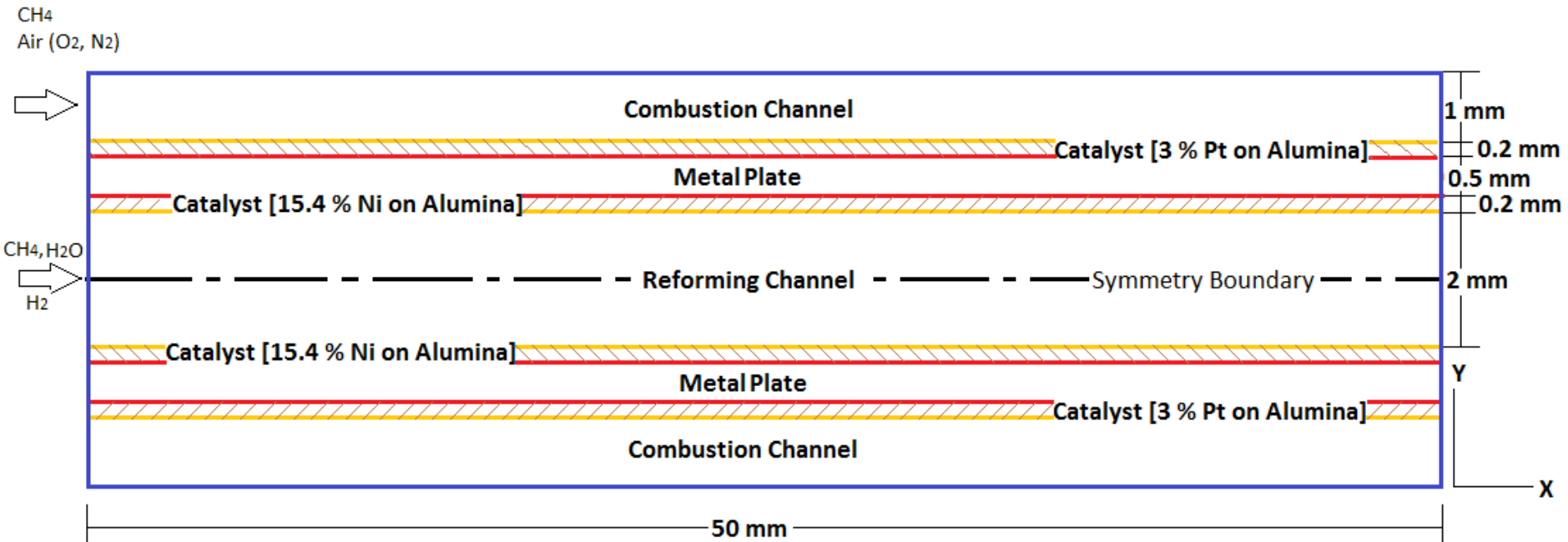
Reverse Methanation Reaction



Combustion Reaction of Methane



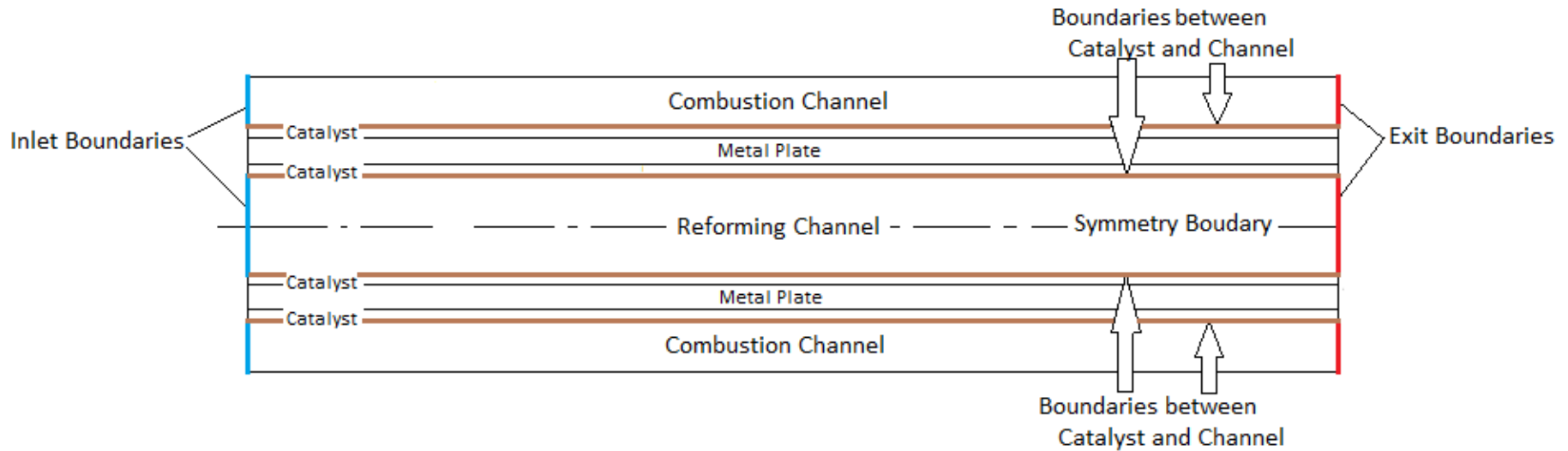
SCHEMATIC VIEW OF CPR



ASSUMPTIONS

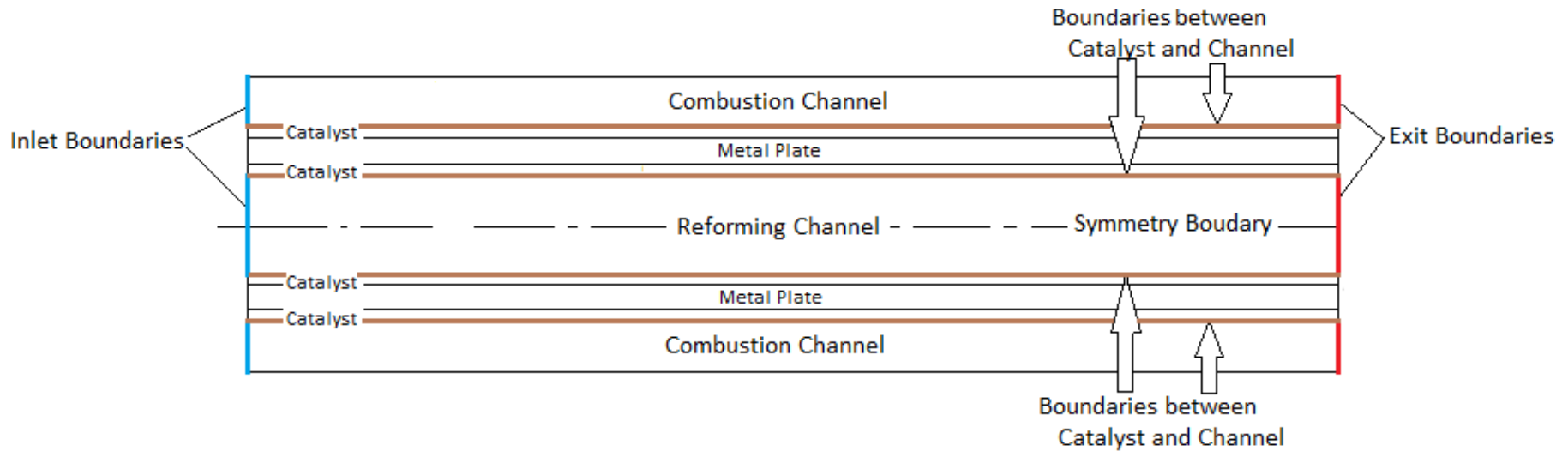
- Ideal gas law
- All the reacting species are in gaseous form
- Reactions occur only inside the catalyst surface bed
- No convection through catalyst surface bed
- Inlet feed must contains small amount of H_2
- Total oxidation of CH_4 to H_2O and CO_2 in combustion channel

MASS & MOMENTUM CONSERVATION



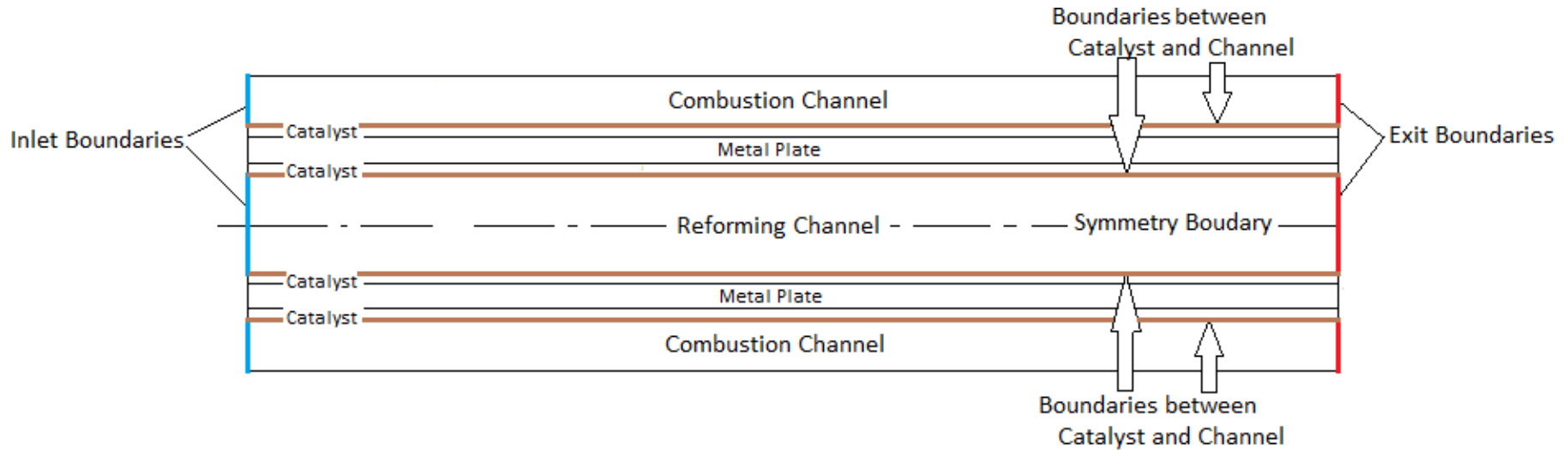
Reforming and Combustion Channels	
Subdomain Settings	Boundary Settings
$\nabla \cdot (\rho_{mix} \mathbf{u}) = 0$ (No Source Term)	Input $\mathbf{u} \cdot \vec{n} = u_0$
$\rho_{mix} (\mathbf{u} \cdot \nabla)$ $= \nabla[-pI + \eta_{mix} (\nabla \mathbf{u} + (\nabla \mathbf{u})^T)]$	Output $P = P_{exit}$
	Boundary between catalyst surface and channel $\mathbf{u} \cdot \vec{n} = 0$ (no slip boundary)

ENERGY CONSERVATION



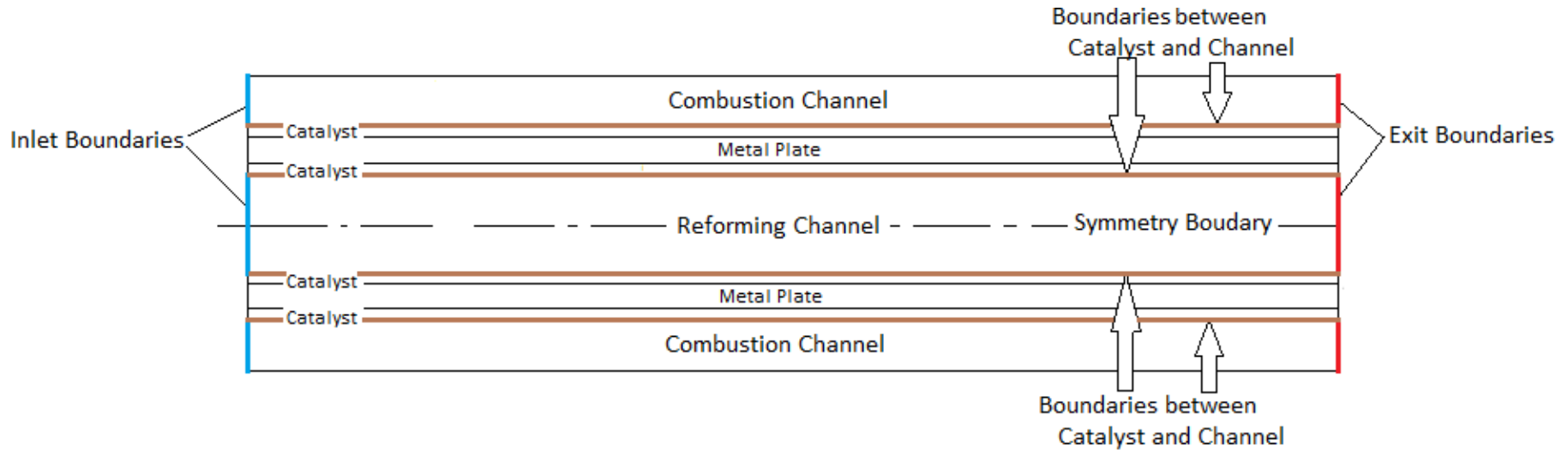
Subdomain Settings	Boundary Settings
Reforming Channel $\nabla \cdot (-k_{sr} \nabla T) = -\rho_{mix} C_{p, sr} u \cdot \nabla T$	Inlet Boundary $T = T_{in}$
Combustion channel $\nabla \cdot (-k_c \nabla T) = -\rho_{mix} C_{p, c} u \cdot \nabla T$	Exit Boundary $\vec{n} \cdot (-k_{sr \text{ or } c} \nabla T) = 0$
Metal Plate $\nabla \cdot (-k_{plate} \nabla T) = 0$	Walls (Thermal Insulation) $-\vec{n} \cdot (-k \nabla T) = 0$

ENERGY CONSERVATION



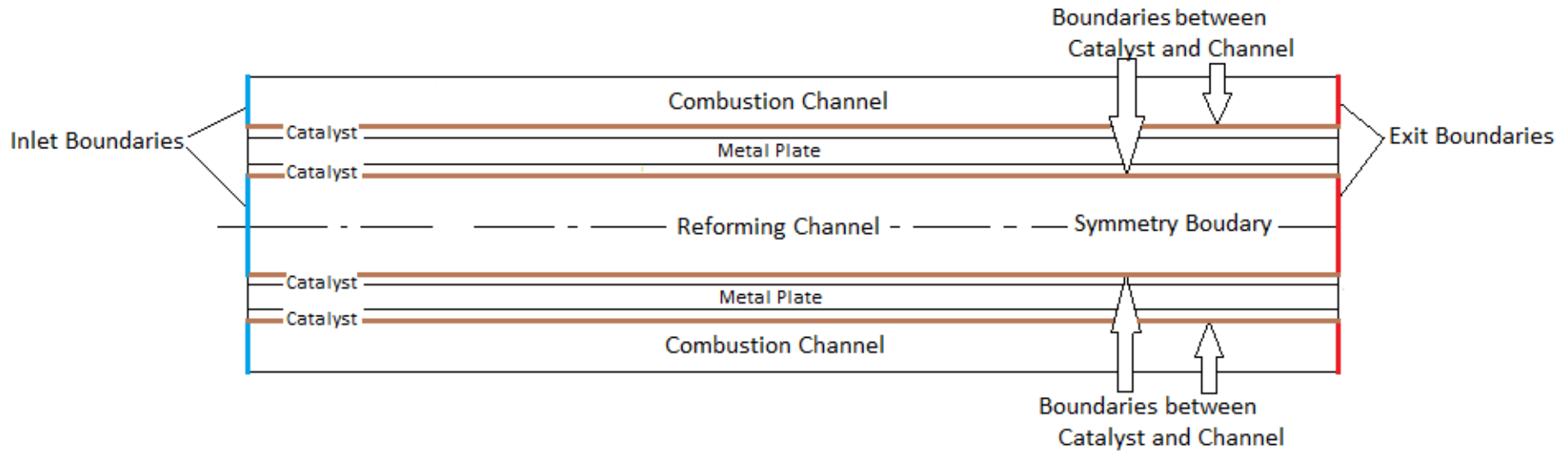
Subdomain Settings	Boundary Settings
<p>Reforming catalyst $\nabla \cdot (-k_{cat}^{sr} \nabla T) = R_1 \Delta H_1 + R_2 \Delta H_2 + R_3 \Delta H_3$</p> <p>Combustion catalyst $\nabla \cdot (-k_{cat}^c \nabla T) = R_c \Delta H_c$</p>	<p>Internal boundaries between catalyst and channels $\vec{n} \cdot (q_1 - q_2) = 0;$ where $q_1 = -k_{sr \text{ or } c} \nabla T + \rho_{mix} C_{p, sr \text{ or } c} u \cdot \nabla T;$ $q_2 = -k_{cat} \nabla T$</p>
	<p>Internal boundaries between catalyst and metal plate $\vec{n} \cdot (q_1 - q_2) = 0;$ where, $q_1 = -k_{cat} \nabla T;$ $q_2 = -k_{plate} \nabla T$</p>

SPECIES CONSERVATION



Subdomain Settings	Boundary Settings
<p>Reforming & Combustion channel</p> $\nabla \cdot (-D_{i,k} \nabla C_i) + u \cdot \nabla C_i = 0$	<p>Input Boundary</p> $C_i = C_{i0}$
<p>Reforming catalyst</p> $\nabla \cdot (-D_{eff,i,k} \nabla C_i) = \theta_{1,i} R_1 + \theta_{2,i} R_2 + \theta_{3,i} R_3$ <p>$\theta_{j,i}$ is the stoichiometric coefficient of the i species in the j reaction</p>	<p>Exit Boundary</p> $\vec{n} \cdot (-D_{i,k} \nabla C_i) = 0$

SPECIES CONSERVATION



Subdomain Settings	Boundary Settings
<p>Combustion catalyst</p> $\nabla \cdot (-D_{eff,i,k} \nabla C_i) = \theta_{c,i} R_c$ <p>$\theta_{c,i}$ is the stoichiometric coefficient of the i species in the combustion reaction.</p>	<p>Boundaries between catalyst surfaces and channels</p> $\vec{n} \cdot (N_{i,1} - N_{i,2}) = 0;$ $N_{i,1} = D_{i,k} \nabla C_i + u C_i \text{ and}$ $N_{i,2} = D_{eff,i,k} \nabla C_i$

$$D_{i,k} = \frac{0.00143 T^{1.75}}{PM_{i,k}^{1/2} [(\sum v)_i^{1/3} + (\sum v)_k^{1/3}]^2},$$

$$D_{eff,i,k} = \frac{\varepsilon}{\tau} \left[\frac{1}{D_{i,k}} + \frac{1}{D_{i,k}^K} \right]^{-1} \quad D_{i,k}^K = 97 R_p \sqrt{\frac{T}{M_{i,k}}}$$

Xu & Froment Kinetics

$$R_1 = \frac{k_1}{p_{H_2}^{2.5}} \left(p_{CH_4} p_{H_2O} - \frac{p_{H_2}^{2.5} p_{CO}}{K_{e1}} \right) \times \frac{1}{DEN^2}$$

$$R_2 = \frac{k_2}{p_{H_2}} \left(p_{CO} p_{H_2O} - \frac{p_{H_2} p_{CO_2}}{K_{e2}} \right) \times \frac{1}{DEN^2}$$

$$R_3 = \frac{k_3}{p_{H_2}^{3.5}} \left(p_{CH_4} p_{H_2O}^2 - \frac{p_{H_2}^4 p_{CO_2}}{K_{e3}} \right) \times \frac{1}{DEN^2}$$

$$DEN = 1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + \frac{K_{H_2O} p_{H_2O}}{p_{H_2}}$$

$$k_j = k_{j0} \exp\left(-\frac{E_j}{R_g T}\right) \quad K_i = K_{i0} \exp\left(-\frac{\Delta H_i}{R_g T}\right)$$

As we can see that the partial pressure of H₂ is in denominator, so if we don't consider the small amount of H₂ in inlet feed, the reaction rate goes to infinite at the inlet of the reactor.

REACTION KINETICS

Hou & Hughes Reforming Kinetics

$$R_1 = k_1 \left(\frac{p_{CH_4} p_{H_2O}^{0.5}}{p_{H_2}^{1.25}} \right) \left(1 - \frac{p_{H_2}^3 p_{CO}}{K_{p1} p_{CH_4} p_{H_2O}} \right) \times \frac{1}{den^2}$$

$$R_2 = k_2 \left(\frac{p_{CO} p_{H_2O}^{0.5}}{p_{H_2}^{0.5}} \right) \left(1 - \frac{p_{H_2} p_{CO_2}}{K_{p2} p_{CO} p_{H_2O}} \right) \times \frac{1}{den^2}$$

$$R_3 = k_3 \left(\frac{p_{CH_4} p_{H_2O}}{p_{H_2}^{1.75}} \right) \left(1 - \frac{p_{H_2}^4 p_{CO_2}}{K_{p3} p_{CH_4} p_{H_2O}^2} \right) \times \frac{1}{den^2}$$

$$den = 1 + K_{CO} p_{CO} + K_{H_2} p_{H_2}^{0.5} + \frac{K_{H_2O} p_{H_2O}}{p_{H_2}}$$

$$k_j = k_{j0} \exp\left(-\frac{E_j}{R_g T}\right)$$

$$K_i = K_{i0} \exp\left(-\frac{\Delta H_i}{R_g T}\right)$$

Wei & Iglesia Reforming Kinetics

$$R_n = R_f(1 - \varphi)$$

Where, $R_f = k_f p_{CH_4}$, and

$$\varphi = \frac{p_{CO} p_{H_2}^3}{p_{CH_4} p_{H_2O} K_{EQ}}$$

In the above kinetic scheme, R_f is the forward rate of decomposition of CH_4 and water Gas Shift is in equilibrium with the net rate of reaction (R_n)

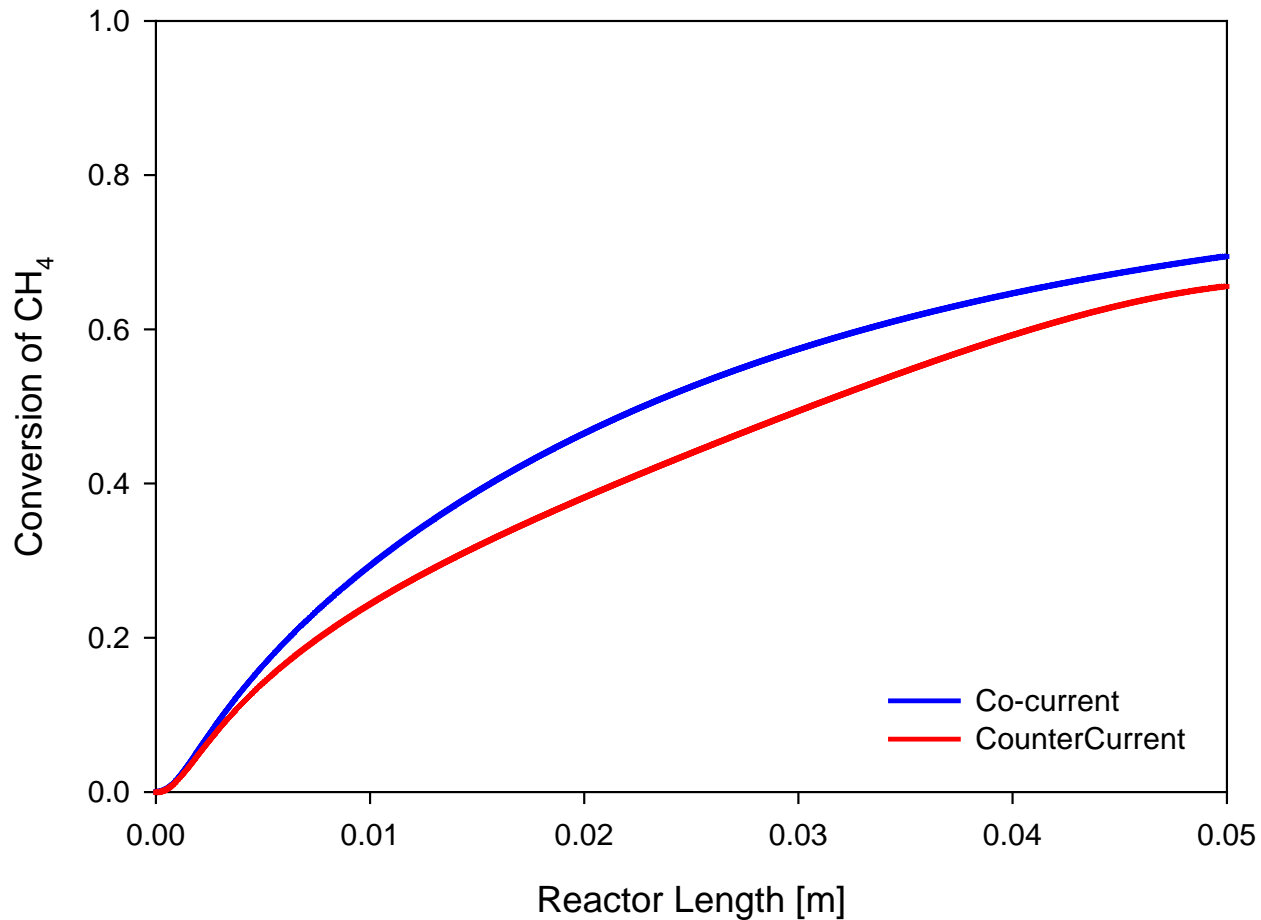
Combustion Kinetic

$$R_c = k_c p_{CH_4}$$

INLET FEED CONDITIONS

Gas Phase	Reforming channel	Combustion channel
Co-current flow		
Compositions (mole fractions)		
Steam to Carbon Ratio	3.0	
CH ₄	0.2499	0.075
H ₂ O	0.7498	0
H ₂	2.499e-4	--
CO	0	--
CO ₂	0	0
O ₂	--	0.1942
N ₂	--	0.7308
Pressure (Pa)	101325	101325
Feed Temperature (K)	800	800
Inlet average velocity (m/s)	0.8	0.8

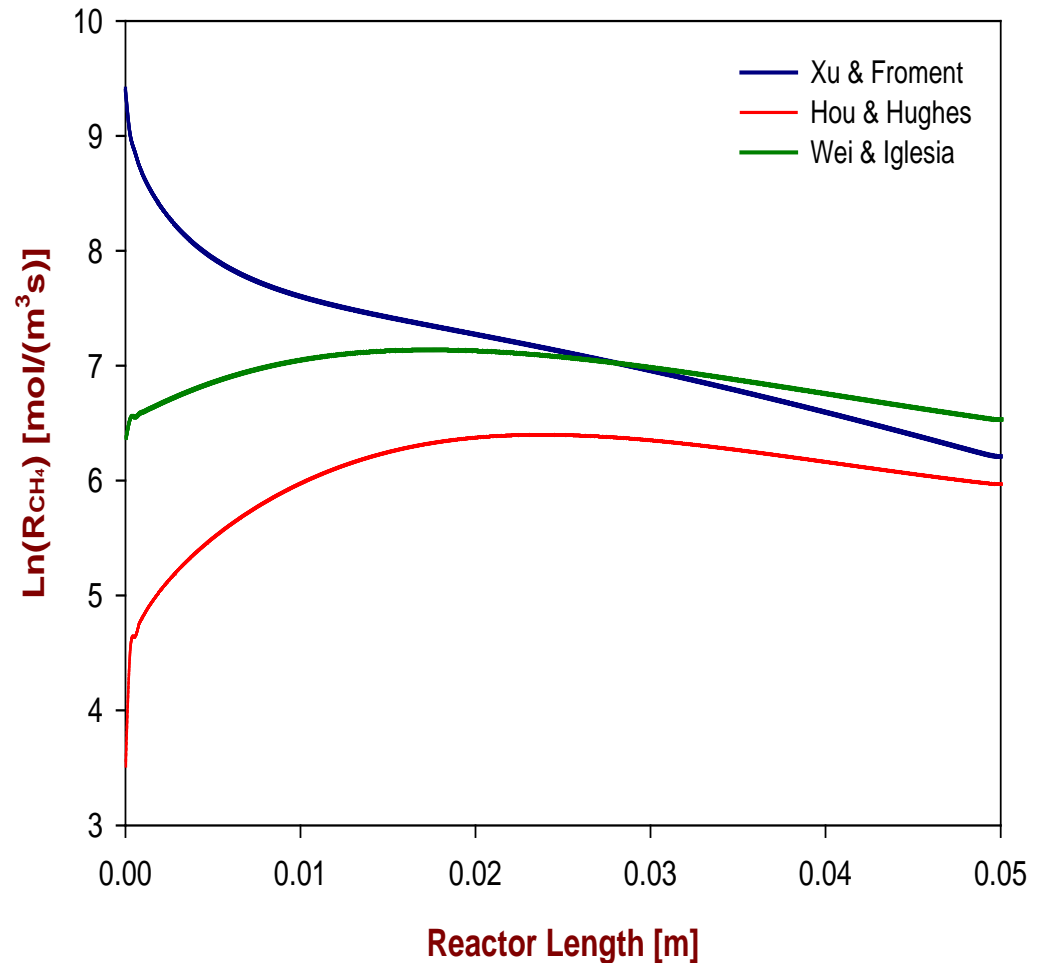
CONVERSION [CO- AND COUNTER CURRENT]



Xu and Froment Kinetic Scheme

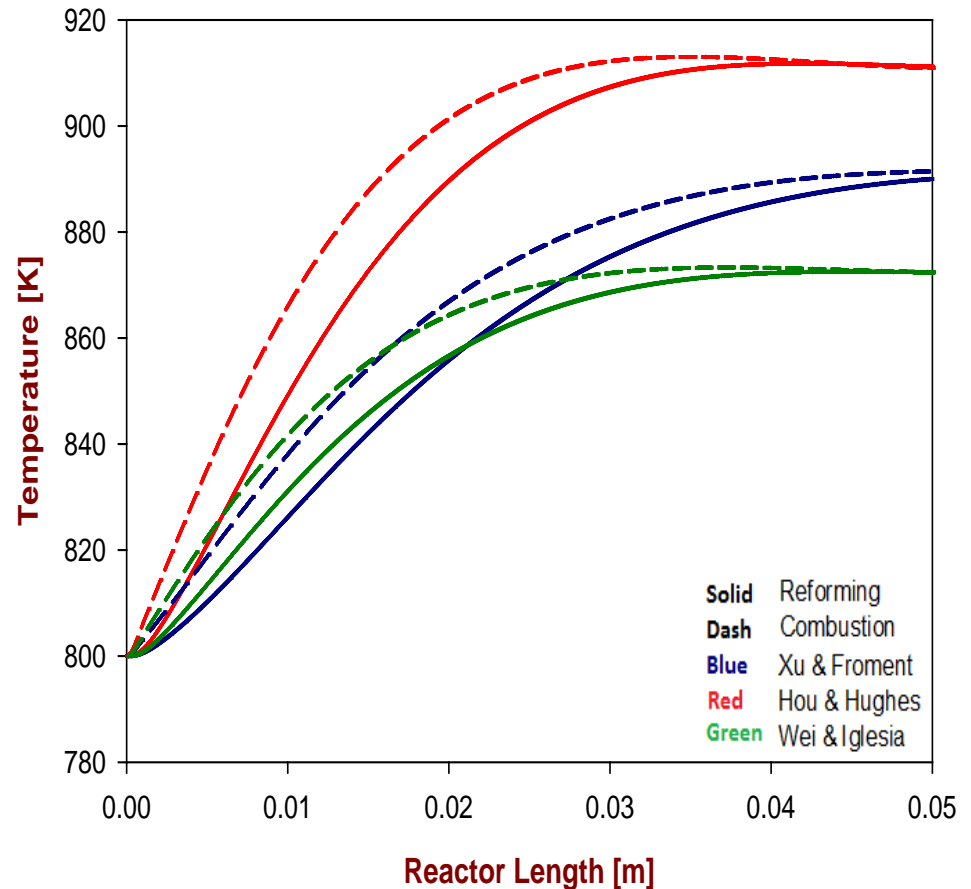
- Highest rate of reaction is demonstrated by Xu & Froment's kinetics, however Wei & Iglesia's rate of reaction is higher than Xu & Froment's one before the exit of the reactor.

- Though higher reactant concentration at the inlet section, Hughes and Iglesia's scheme demonstrated lower rate of reaction compared to the center section of the reactor

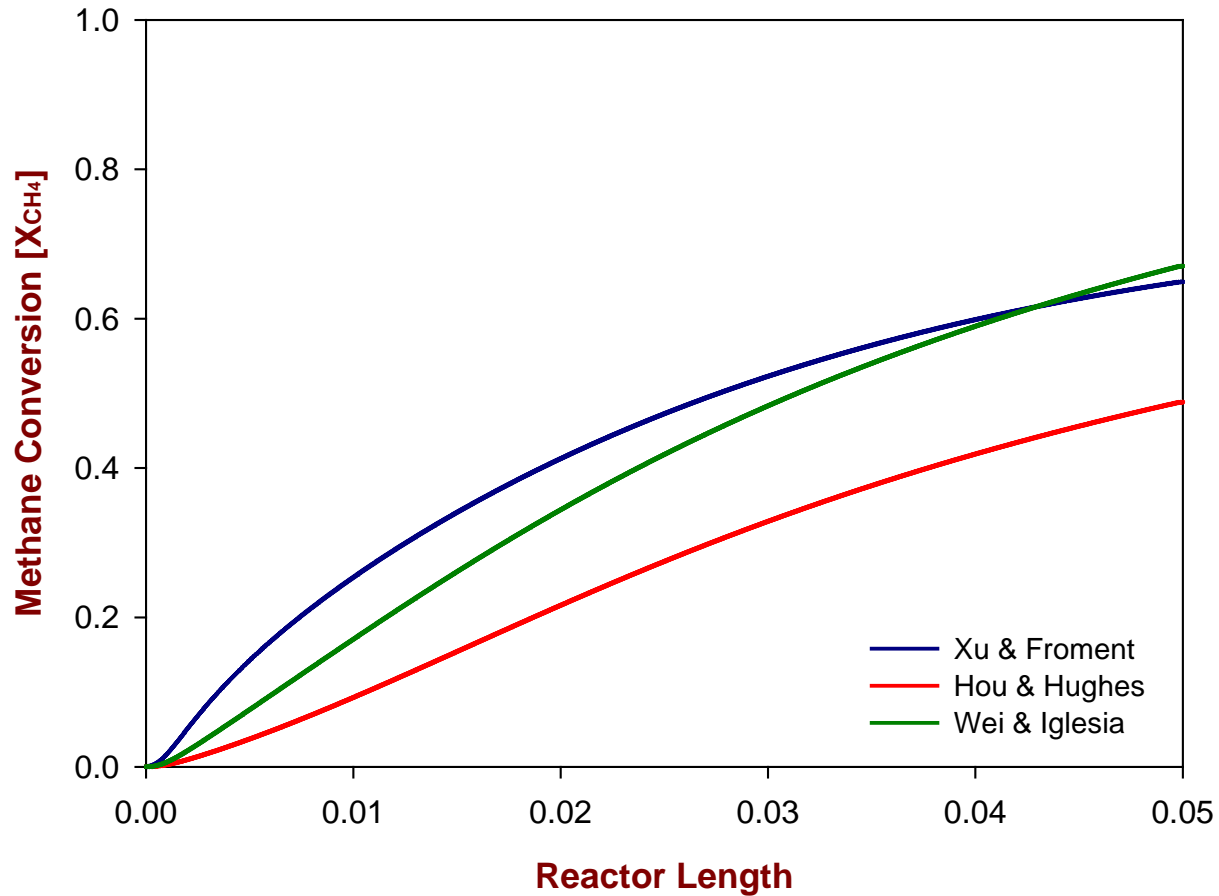


TEMPERATURE PROFILES

It is evident due to the lower rate of reaction, the higher temperature profile in the case of Huo & Hughes compared to the other two kinetics.

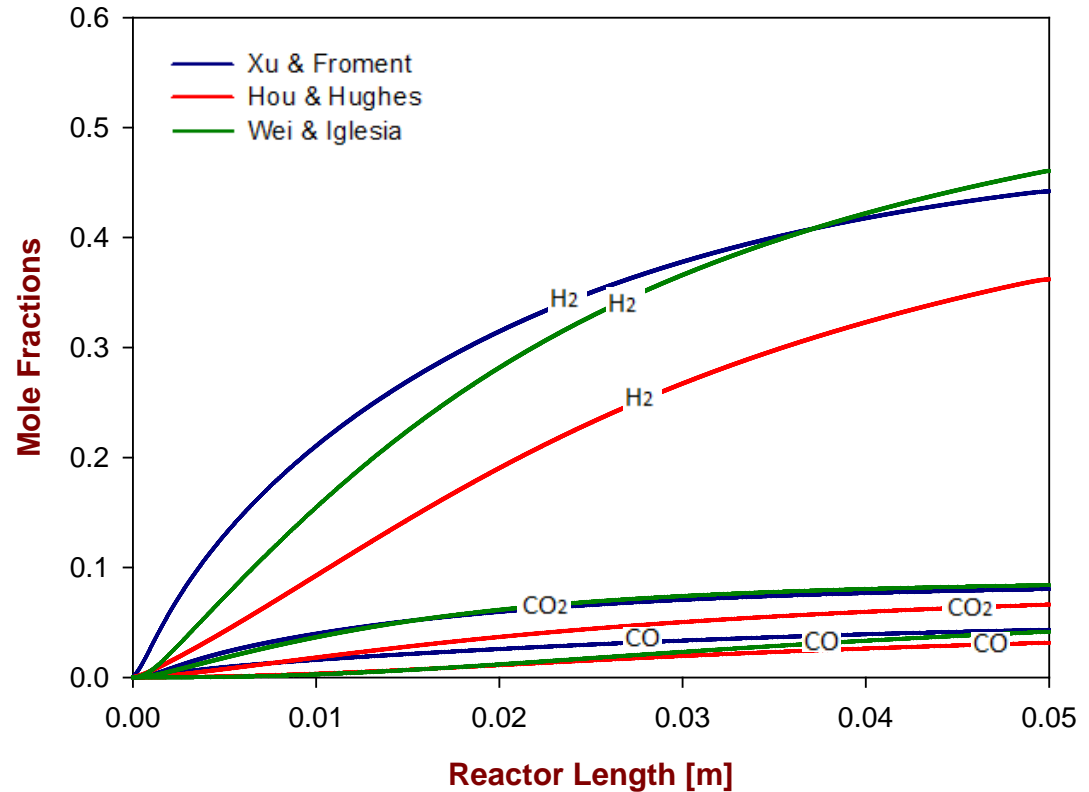


CONVERSION PROFILES



CONCENTRATION PROFILES

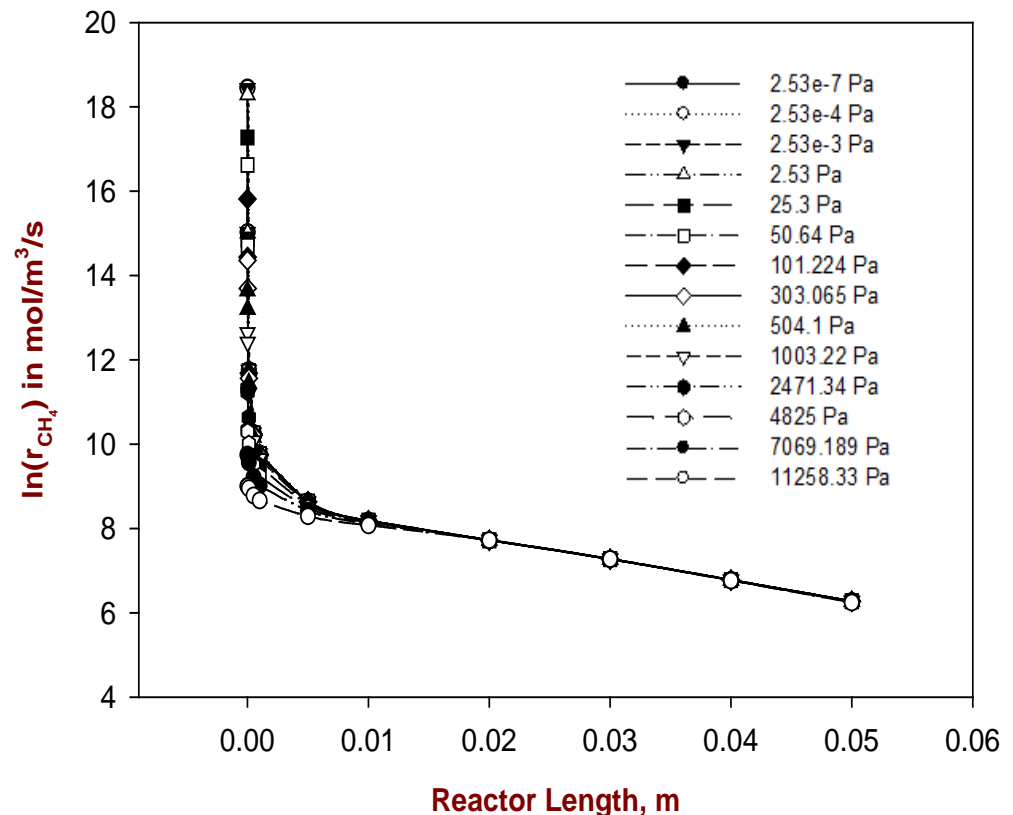
Though there is a difference between the rate of reactions of Xu & Froment and Wei & Iglesia, no significant difference is found in the exit compositions; but in the case of Hou & Hughes, they differ significantly compared to Froment and Iglesia due to the lower rate of reaction



EFFECT OF INLET H_2 ON REACTION RATE

A significant change is found in the rate at the inlet section of the reactor due to different Inlet concentration of H_2 , however no significant changes are observed after the inlet section.

Inlet p_{H_2} varies from $2.53e-7$ Pa to 11250 Pa



Xu & Froment Kinetic Scheme

COMMENTS

- Among three reforming reaction kinetics studied, highest rate of reaction is demonstrated by Xu & Froment's kinetics, however Wei & Iglesia's rate of reaction is higher than Xu & Froment's one before the exit of the reactor.
- Hou & Hughes's kinetic scheme has the lowest rate of reaction compared to the other two kinetics.
- Though there is a difference between the rate of reactions of Xu & Froment and Wei & Iglesia, no significant differences are found in the exit compositions; but in the case of Hou & Hughes, they differ significantly compared to Froment and Iglesia due to the lower rate of reaction
- It is also evident due to the lower rate of reaction, the higher temperature profile in the case of Huo & Hughes compared to the other two kinetics.

FUTURE WORK

- Study the influence of reactor geometry
- Develop the 3D transient model of CPR



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THANK
YOU



COMMENTS & QUESTIONS?

