

CFD Analysis and Optimization of CH₄ Pyrolysis in Commercial Hot Wall Chemical Vapor Deposition Reactor



Thesis submitted in partial fulfillment
for the award of the degree

Doctor of Philosophy

By

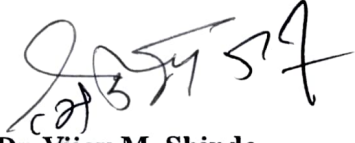
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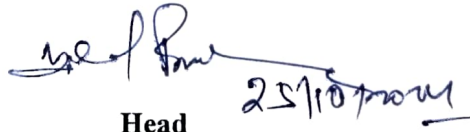
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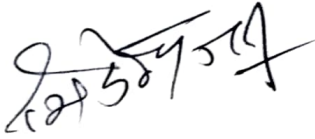
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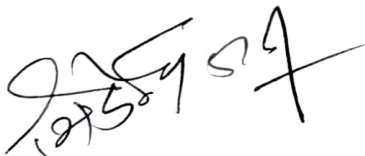

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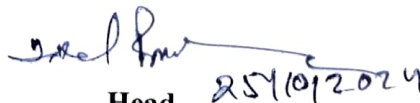
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Acknowledgement

In the grand tapestry of this doctoral journey, I find myself weaving words of gratitude, and at the forefront stands Dr. Vijay M. Shinde, a mentor par excellence. His guidance has been more than academic; it has been a poetic dance of enlightenment. Like a master potter, he molded my academic clay, quoting the verses of Kabir Das, "गुरु कुम्हार शिष कुंभ है, गढ़ि गढ़ि काढ़ै खोट। अन्तर हाथ सहार दै, बाहर बाहै चोट ॥," sculpting not just a researcher but a person of integrity and accountability. To him, I owe not only my academic growth but also the lessons of life. I am indebted to Dr. Shinde not only for his scholarly contributions but also for creating an environment that fostered personal and professional growth. His lessons extended beyond the laboratory, teaching me the art of integrity and the importance of surrounding oneself with a supportive community.

I extend my sincere thanks to Dr. S. S. Rao and Dr. Anurag Kamal for their unwavering mental support, helping me remain resilient through difficult times. Their words of encouragement were a source of strength for me.

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Lastly, I extend my heartiest thanks to all my well-wishers, whose constant motivation and encouragement were the driving forces that propelled me towards the completion of this thesis.


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Nomenclature

\vec{u} : velocity (m/s)	x^{mol} : mole fraction of species
A: pre-exponential factor in the Arrhenius equation	$x_{i,\text{inlet}}^{\text{mol}}$: inlet mole fraction of i^{th} species
b: constant	x^{wt} : mass fraction of species
C: hyperparameter	x: independent variable (predictor)
C_p : specific heat (kJ/kg)	x^{scaled} : the scaled value of the data point
D^{m} : mass diffusivity (m^2/s)	x_{B} : best vertex
D^{T} : thermal diffusivity (m^2/s)	x_{c1} : inside the compression point
E: activation energy (kcal/mol)	X_{c2} : outside the compression point
F_{B} : body force (N/kg)	X_{G} : good vertex
g: acceleration due to gravity (m/s^2)	x_{M} : middle point
h: enthalpy (kJ/kg)	X_{W} : worst vertex
h_{w} : heat transfer coefficient ($\text{J}/\text{m}^2\text{sK}$)	X_{R} : reflection point
h_i^0 : Standard heat of formation (kJ/kg)	y: dependent variable (response)
I: unit matrix	y_1 : local deposition rate ($\text{kg}/\text{m}^2\text{s}$)
J^{h} : energy diffusive flux (w/m^2)	y_2 : local uniformity index
J: mass diffusive flux ($\text{kg}/\text{m}^2\text{s}$)	y_1^{upper} : upper limit deposition rate ($\text{kg}/\text{m}^2\text{s}$)
k_{eff} : effective thermal conductivity ($\text{W}/\text{m.K}$)	<i>Greek symbols</i>
MAE: mean square error	ρ : density of gas mixture (kg/m^3)
M: molecular weight (kg/mol)	τ : stress tensor (N/m^2)
Min (x_n): minimum value of x_n	μ : gas viscosity (Pa.s)
Max (x_n): maximum value of x_n	α : weight for deposition rate
η : outward unit normal	β : weight for deposition rate
N_{r} : total number of surface reaction	β_{T} : exponential temperature factor
P: pressure (Pa)	ω : model coefficient
P_0 : initial pressure (Pa)	ε : acceptable margin of error

\hat{R} : total production rate of species by chemical reaction (kg/m ³ .s)	ϵ : emissivity factor
R^2 : coefficient of regression	ξ : slack variable
R_i : molar rate of production of i th species (mol/m ³ s)	σ : Stefan-Boltzmann constant (W/m ² K ⁴)
RMSE: root mean square error	<i>Subscripts</i>
s: total area of the substrate (m ²)	i: i th species
(s): surface sites	j: j th species
t: time (s)	k: k th data point
T: temperature (K)	n: total number of data points
T _a : atmospheric temperature (K)	r: r th reaction
T ₀ : initial reactor temperature (K)	<i>Superscript</i>
T _{ref} : reference temperature (K)	^: estimated value
T _s : substrate temperature (K)	-: mean value
T _w : reactor wall temperature (K)	w: wall surfaces

Description of non-dimensional numbers

The influence of various operational parameters on the flow behaviour in the CVD reactor and the film growth performance was studied using multiple dimensionless numbers. The ratio of inertial force to viscous force is given as the Reynolds number (Re):

$$\text{Re} = \frac{\rho u D}{\mu}$$

Where ρ is the density of the gas,

u is the gas flow velocity,

D is the reactor diameter and

μ is the dynamic viscosity of the gas.

All simulations satisfy the laminar flow condition (Re < 2100). The Grashof number (Gr) is defined as the ratio of buoyant force to the viscous force experienced by the fluid particle, which correlates with thermally induced convective fluid heat and mass transport.

$$\text{Gr} = \frac{\rho^2 g h^3 (T_s - T_o)}{T_o \mu^2}$$

T_s and T_o represent the substrates and the gas mixture's entrance temperature, respectively, while h represents the vertical distance measured from the spinning shaft. Furthermore, the buoyancy-to-inertia ratio, Gr/Re^2 , quantifies the relative strength of natural vs forced convection. Natural convection flow would be dominated by a high Gr/Re^2 ratio, resulting in poorer film uniformity due to increased recirculations in the reactor. To obtain a consistent film growth rate, however, the operating conditions and reactor geometry must be carefully chosen. The rotational Reynolds number Re_ω based on reactor diameter assesses the forced convection effects caused by substrate rotation and is defined as:

$$\text{Re}_\omega = \frac{\rho \omega D^2}{4\mu}$$

ω is the rotation of the substrate. The Prandtl number (Pr) is defined as the ratio of momentum to thermal diffusivity.

$$Pr = \frac{C_p \cdot \mu}{k}$$

A low Prandtl number indicates that thermal diffusion has taken precedence over momentum diffusion, resulting in a higher heat transfer rate due to conduction rather than convection. The Peclet number (Pe) is the ratio of heat transfer rate due to convection to heat transfer rate owing to conduction and is stated as:

$$Pe = Pr \cdot Re = \frac{\rho u D C_p}{k}$$