

**PARTICLE-RESOLVED SIMULATIONS
OF FLUID FLOW, TRANSPORT
PROCESSES AND DEACTIVATION
FOR GAS-PHASE CATALYTIC
REACTIONS**

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PARTICLE-RESOLVED SIMULATIONS OF FLUID FLOW, TRANSPORT PROCESSES AND DEACTIVATION FOR GAS-PHASE CATALYTIC REACTIONS

by

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Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the



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*Dedicated to my wife (Vaenil Mathi K) and daughter
(Avira K V).*

Certificate

This is to certify that the thesis entitled ”**Particle-resolved Simulations of Fluid Flow, Transport Processes and Deactivation for Gas-phase Catalytic Reactions**”, being submitted by **Karthik G. M.** to the Indian Institute of Technology Delhi, is worthy of consideration for the award of the degree of **Doctor of Philosophy** and is a record of the original bonafide research work carried out by him under my guidance and supervision. The results contained in the thesis have not been submitted in part or full, to any other University or Institute for the award of any degree or diploma.

I certify that he has pursued the prescribed course of research.

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Abstract

Packed bed reactors (PBR) are commonly used in the chemical process industries to perform gas-phase catalytic reactions (e.g., methane steam reforming (MSR)) due to their high surface area to volume ratio offered by the catalyst particles of different sizes and shapes that are randomly placed inside these reactors. Fluid flows over the catalyst particles, reactions and heat transfer take place simultaneously on the external (particle-scale) and internal (pore-scale) surfaces of the particles. Particle shape influences the local fluid flow (in the vicinity of the particle) and therefore the pressure drop (ΔP), heat transfer and reaction performance of PBR. This is even more crucial for PBR with low tube-to-particle diameter ratio (< 10) as in MSR where the confining walls also influence the local fluid flow. Therefore, the performance of PBR can be improved by understanding the complex interactions between the particle shapes and the surrounding flow field.

Common particle shapes (e.g., spheres and cylinders) have been widely studied in the literature using particle-resolved CFD simulations. However, there is a lack of information in the literature on the impact of particle shape on reactor performance and also on the choice of optimal particle shape for a particular catalytic process. Also, a reasonable method to simulate the transient catalyst deactivation process which includes the changes in the particle properties and the effect of particle shape on catalyst deactivation is still lacking. In addition, there is a lack of information in the literature on the application of monolith and foam structure as bulk catalyst which can offer significant advantages compared to the conventional pellets. Apart from that, a validation of particle-resolved CFD simulations with detailed particle-scale measurements under the turbulent flow conditions, in particular, the effect of different turbulence models on the particle-scale flow predictions is still lacking.

In the present thesis, particle-resolved CFD simulations are performed in a packed bed with different particle shapes to understand and to quantify the effect of particle shape on the ΔP , dispersion, heat transfer, effectiveness factor and reactant conversion using the MSR reactions. Also, a modified ΔP correlation is developed for different particles shapes considered in the present work. Later, the work is extended to other industrial catalytic reactions with varying extents of heat/mass transfer limitations to demonstrate a computational approach for selection of optimal catalyst shape for a particular catalytic reaction. In addition, a method to simulate the transient catalyst deactivation process which includes the change in particle properties is demonstrated using propane dehydrogenation (PDH) reactions, and the method is used to understand the impact of particle shape on catalyst deactivation. Further, numerical investigations are performed to understand the performance of monolith and foam as bulk catalyst against conventional pellets using the MSR reactions, and on catalyst deactivation using the PDH reactions.

Apart from that, a comparison of the particle-scale PIV measurements with the corresponding particle-resolved CFD simulations (using the SST $k - \omega$ model) is performed in a packed bed under the turbulent flow conditions. Later, the particle-resolved CFD simulations with different turbulence models (standard $k - \varepsilon$, SST $k - \omega$, SSG Reynolds-stress, BSL Reynolds-stress and LES WALE) are validated with the PIV measurements to understand the influence of different turbulence models on the particle-scale flow predictions. In addition, numerical investigations are performed in a packed bed to understand the influence of different turbulence models on the heat transfer and reaction performance using the MSR reactions. The methodology presented in this thesis can be applied to different particle shapes and industrial catalytic reactions and thereby aid the development of optimal particle shape for a particular catalytic reaction to improve the reactor performance.

सार

पैकड बेड रिएक्टर (PBR) का उपयोग आमतौर पर रासायनिक प्रक्रिया उद्योगों में गैस-चरण उत्प्रेरक प्रतिक्रियाओं (उदाहरण के लिए, मीथेन स्टीम रिफॉर्मिंग (MSR)) के लिए किया जाता है, जो विभिन्न आकारों और आकारों के उत्प्रेरक कणों द्वारा पेश किए जाने वाले वॉल्यूम अनुपात के लिए उनके उच्च सतह क्षेत्र के कारण होता है। कि इन रिएक्टरों के अंदर बेतरतीब ढंग से रखा जाता है। द्रव उत्प्रेरक कणों पर प्रवाहित होता है, जिसे अभिक्रियाएँ और ऊष्मा स्थानांतरण कणों के बाह्य (कण-स्केल) और आंतरिक (छिद्र-स्केल) सतहों पर एक साथ होते हैं। कण आकार स्थानीय द्रव प्रवाह (कण के आसपास के क्षेत्र) को प्रभावित करता है और इसलिए दबाव ड्रॉप (ΔP), गर्मी हस्तांतरण और पीबीआर की प्रतिक्रिया प्रदर्शन प्रभावित होती है। एमएसआर की तरह कम ट्यूब-टू-पार्टिकल व्यास अनुपात (<10) के साथ पीबीआर के लिए यह और भी अधिक महत्वपूर्ण है, जहां सीमित दीवारें स्थानीय तरल प्रवाह को भी प्रभावित करती हैं। इसलिए, कण आकार और आसपास के प्रवाह क्षेत्र के बीच परस्पर की प्रक्रिया को समझकर पीबीआर के प्रदर्शन में सुधार किया जा सकता है।

आम कणों के आकार (जैसे, गोले और सिलिंडर) का व्यापक रूप से कण-हलित सीएफडी सिमुलेशन का उपयोग करके साहित्य में अध्ययन किया गया है। हालांकि, रिएक्टर प्रदर्शन पर कण आकार के प्रभाव और एक विशेष उत्प्रेरक प्रक्रिया के लिए इष्टतम कण आकार की पसंद पर साहित्य में जानकारी की कमी है। इसके अलावा, क्षणिक उत्प्रेरक निष्क्रियकरण प्रक्रिया को अनुकरण करने के लिए एक उचित विधि जिसमें कण गुणों में परिवर्तन शामिल हैं और उत्प्रेरक निष्क्रियकरण पर कण आकार के प्रभाव में अभी भी कमी है। इसके अलावा, थोक उत्प्रेरक के रूप में मोनोलिथ और फोम संरचना के आवेदन पर साहित्य में जानकारी का अभाव है जो पारंपरिक छरों की तुलना में महत्वपूर्ण लाभ प्रदान कर सकता है। इसके अलावा, अशांत प्रवाह की स्थिति के तहत विस्तृत कण-स्केल माप के साथ कण-हलित सीएफडी सिमुलेशन, विशेष रूप से, कण-स्केल प्रवाह भविष्यवाणियों पर विभिन्न अशांति मॉडल के प्रभाव में अभी भी कमी है।

वर्तमान थीसिस में, कण-हलित सीएफडी सिमुलेशन को अलग-अलग कण आकार के साथ पैक बेड में प्रदर्शन किया जाता है ताकि एमएसआर प्रतिक्रियाओं का उपयोग करके, ΔP , फैलाव, गर्मी हस्तांतरण, प्रभावशीलता कारक और प्रतिक्रियाशील रूपांतरण पर कण आकार के प्रभाव को दर्शाया गया है। इसके अलावा, वर्तमान कार्य में एक संशोधित ΔP कोरिलेशन विभिन्न कणों के आकृतियों के लिए विकसित किया गया है। बाद में, कार्य को अन्य औद्योगिक उत्प्रेरक प्रतिक्रियाओं के लिए विस्तारित किया जाता है, जिसमें किसी विशेष उत्प्रेरक प्रतिक्रिया के लिए इष्टतम उत्प्रेरक आकार के चयन के लिए कम्प्यूटेशनल दृष्टिकोण प्रदर्शित किया गया है। इसके अलावा, क्षणिक उत्प्रेरक निष्क्रियकरण प्रक्रिया को अनुकरण करने के लिए एक विधि जिसमें कण गुणों में परिवर्तन शामिल है उसे प्रोपेन डिहाइड्रोजनेशन (पीडीएच) प्रतिक्रियाओं का उपयोग करके दिखाया गया है जिसे इसको विधि उत्प्रेरक निष्क्रियकरण पर कण आकार के प्रभाव को समझने के लिए उपयोग किया जाता है। इसके अलावा, एमएसआर प्रतिक्रियाओं का उपयोग करते हुए पारंपरिक उत्प्रेरक के खिलाफ मोनोलिथ और फोम के प्रदर्शन को समझने के लिए संख्यात्मक जांच की जाती है जिसे पीडीएच प्रतिक्रियाओं का उपयोग करके उत्प्रेरक निष्क्रियता पर भी समजा जा सकता है।

इसके अलावा, पीआईवी माप और सुलझे-कण सीएफडी सिमुलेशन (एसएसटी $k-\omega$ मॉडल का उपयोग करके) के की तुलना अशांत प्रवाह स्थितियों के तहत एक की गयी है। बाद में, अलग-अलग टर्बुलेंस मॉडल (मानक $k-\epsilon$, एसएसटी $k-\omega$, एसएसजी रेनॉल्ड्स-स्ट्रेस, BSL रेनॉल्ड्स-स्ट्रेस और LES WALE) के साथ किए गए CFD सिमुलेशन को अलग-अलग टर्बुलेंस मॉडल के प्रभाव को समझने के लिए PIV मापों के साथ मान्य किया जाता है। इसके अलावा, MSR प्रतिक्रियाओं का उपयोग करके गर्मी हस्तांतरण और प्रतिक्रिया प्रदर्शन पर विभिन्न अशांति मॉडल के प्रभाव को समझने के लिए संख्यात्मक जांच की गयी है। इस थीसिस में प्रस्तुत पद्धति को विभिन्न कण आकार और औद्योगिक उत्प्रेरक प्रतिक्रियाओं पर लागू किया जा सकता है जो इस तरह रिएक्टर के प्रदर्शन को बेहतर बनाने के लिए एक विशेष उत्प्रेरक प्रतिक्रिया के लिए इष्टतम कण आकार के विकास में सहायता करता है।

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Nomenclature

Symbols

\bar{t}	Mean residence time, s
\bar{U}	Fluid velocity, m/s
\widehat{C}_p	Fluid specific heat capacity, $J/kg.K$
$\widehat{C}_{p,s}$	Particle specific heat capacity, $J/kg.K$
A_s	Particle surface area, m^2
$C_{C,t-1}$	Accumulated carbon at the end of previous timestep, mol/m^3
$C_{C,t}$	Accumulated carbon for the current timestep, mol/m^3
C_i	Species concentration in i^{th} species in fluid domain, mol/m^3
$C_{s,i}$	Species concentration in i^{th} cell inside particle volume, mol/m^3
$C_{s,i}^s$	Species concentration in i^{th} cell on particle surface, mol/m^3
D	Axial diffusion coefficient, m^2/s
d_h	Hydraulic diameter of inlet cross-section, m
D_i	Mass diffusivity of i^{th} species due to molecular transport in fluid domain, m^2/s
d_p	Particle diameter, m
d_t	Tube diameter, m
d_{hole}	Hole diameter of 7-hole pellets, m
$D_{K,i}$	Knudsen diffusivity of i^{th} species in particle domain, m^2/s

$d_{p,avg}$	Mean particle diameter, m
$d_{p,piv}$	PIV seeding particle diameter, m
$D_{s,eff,i}$	Effective mass diffusivity of i^{th} species in particle domain, m^2/s
$D_{s,i}$	Mass diffusivity of i^{th} species due to molecular transport in particle domain, m^2/s
$D_{t,i}$	Mass diffusivity of i^{th} species due to turbulent transport in fluid domain, m^2/s
h	Specific static enthalpy, J/kg
k	Turbulent kinetic energy, m^2/s^2
$K_{eq,i}$	Equilibrium rate constant of i^{th} reaction
K_i	Adsorption constant of i^{th} species
k_i	Rate constant of i^{th} reaction
$L_{bed,glass}$	Bed height packed with glass particles, m
$L_{bed,hydrogel}$	Bed height packed with hydrogel particles, m
L_{bed}	Bed height, m
L_p	Particle height, m
L_t	Tube height, m
M_i	Molecular mass of i^{th} species, $kg/kmol$
P	Fluid pressure, Pa
P_i	Partial pressure of i^{th} species, Pa
Pr_t	Turbulent Prandtl number
Q_{sink}	Particle heat sink, W
R	Universal gas constant, $J/mol.K$
r_j	Reaction rate of j^{th} reaction, $mol/m^3.s$
$r_{j,0}$	Reaction rate of j^{th} reaction at time $t = 0$ s, $mol/m^3.s$
$r_{j,t}$	Reaction rate of j^{th} reaction at time t , $mol/m^3.s$
Re_p	Particle Reynolds number

Re_t	Tube Reynolds number
Re_{bed}	Bed Reynolds number
S	Strain rate, $1/s$
S_h	Heat source or sink due to chemical reactions, W/m^3
S_i	Species formation or consumption due to chemical reactions, kg/m^3
$S_{C,t-1}$	Rate of carbon formation at the end of previous timestep, $mol/m^3.s$
$Sc_{t,i}$	Turbulent Schmidt number of i^{th} species
T	Fluid temperature, K
T_s	Particle temperature, K
$T_{s,i}$	Temperature in i^{th} cell inside particle volume, K
$T_{s,i}^s$	Temperature in i^{th} cell on particle surface, K
U_s	Superficial fluid velocity, m/s
V_i	Fluid velocity in i^{th} direction, m/s
V_s	Particle volume, m^3
v'_i	Fluid velocity fluctuations in i^{th} direction, m/s
X_{CH_4}	CH_4 conversion, %
Y_i	Mass fraction of i^{th} species in fluid domain
$Y_{s,i}$	Mass fraction of i^{th} species in particle domain

Greek symbols

α	Catalyst deactivation constant, m^3/mol
$\alpha_{i,j}$	Stoichiometric coefficient of i^{th} species in j^{th} reaction
$\Delta C_{C,\Delta t}$	Carbon formed during the previous timestep, mol/m^3
ΔH_j	Enthalpy of j^{th} reaction, kJ/mol
ΔP	Pressure drop, Pa
ϵ_s	Particle porosity
ϵ_{bed}	Bed porosity
$\epsilon_{s,0}$	Particle porosity at time $t = 0$ s

$\epsilon_{s,t}$	Particle porosity at time t
η_i	Effectiveness factor for i^{th} reaction
λ	Fluid thermal conductivity due to molecular transport, $W/m.K$
λ_s	Particle thermal conductivity, $W/m.K$
λ_t	Fluid thermal conductivity due to turbulent transport, $W/m.K$
$\lambda_{s,eff}$	Effective thermal conductivity in particle domain, $W/m.K$
μ	Fluid viscosity, $Pa.s$
μ_t	Turbulent viscosity, $Pa.s$
ω	Turbulence eddy frequency, Hz
$\overline{\overline{\tau}}_t$	Turbulent stress tensor, N/m^2
$\overline{\tau}$	Viscous stress tensor, N/m^2
ρ	Fluid density, kg/m^3
ρ_s	Particle density, kg/m^3
σ	Standard deviation
τ_s	Particle tortuosity
ε	Turbulence eddy dissipation, m^2/s^3
Ω	Vorticity, $1/s$
φ_s	Particle sphericity
$\varphi_{s,c}$	Corrected particle sphericity

Acronyms

ADM	Axial Dispersion Model
CFD	Computational Fluid Dynamics
DEM	Discrete Element Method
DME	DiMethyl Ether synthesis
DNS	Direct Numerical Simulation
FPS	Frames Per Second
MSR	Methane Steam Reforming
LDA	Laser Doppler Anemometry
LES	Large Eddy Simulation
MeOH	Methanol synthesis
MRI	Magnetic Resonance Imaging
NRMSD	Normalised Root Mean Squared Deviation
PBR	Packed Bed Reactor
PDF	Probability Density Function
PDH	Propane DeHydrogenation
PIV	Particle Image Velocimetry
PMMA	PolyMethyl MethAcrylate
RBD	Rigid Body Dynamics
RI	Refractive Index

RSM	Reynolds Stress Model
RTD	Residence Time Distribution
SST	Shear Stress Transport
STV	Surface area To Volume
TPD	Tube to Particle Diameter
WGS	Water Gas Shift