

MODELING THE RECUPERATIVE COUPLING OF EXOTHERMIC AND ENDOTHERMIC REACTIONS IN COMPACT ETHANOL REFORMERS

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by

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THESIS CERTIFICATE

This is to certify that the thesis entitled '**Modeling the Recuperative Coupling of Exothermic and Endothermic Reactions in Compact Ethanol Reformers**' submitted by **Ms. Tejas Puneet Kaur Sidhu** to the Indian Institute of Technology-Delhi for the award of degree of **Doctor of Philosophy (PhD)** is a bona fide record of research work carried out by her under my supervision. The contents of this thesis have not been submitted to any other Institute or University for the award of any degree or diploma.

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ABSTRACT

Global energy requirements are increasing day by day at a significant rate, and this demand is being primarily met by fossil fuels like natural gas, coal, and fractions of petroleum. On one hand, there is a threat of depletion of the finite fossil energy resources; on the other hand, there is an equally imminent threat of global warming through non-judicious burning of fossil energy. Hydrogen has been suggested as an attractive and clean energy carrier depending on how it is produced, and serves as a remedy to the depletion of fossil fuels and the associated environmental concerns. Aside from the major applications of hydrogen in the chemical, foods and refining industries, it can be used in fuel cells to power vehicles, as well as for other stationary and non-stationary applications.

“On-board” or “distributed” processing of fuel to produce hydrogen, on demand, seems like an obvious concept, but is often not viable because of the fact that fuel reforming is endothermic, and energy needs to be supplied to the reforming reactor in a way so as to offset the drop in reactor performance due to the “cooling” induced by the reaction. One way of offsetting this issue is to create a heat-integrated design. However, such designs have exothermic and endothermic fronts that move in time and space, and hence the problem is non-trivial. Effective design of such reactors require knowledge of the time and space movements of such fronts. Thus, the final "success" of this technology will depend largely on modeling, understanding and control of temperature excursions from the steady state situation.

In this thesis, such process concepts are evolved using mathematical modeling of the ethanol steam reforming reactor, to produce hydrogen in a compact reformer under dynamic operation.

In the first part of the study, various spatio-temporal evolutions of temperature and conversions in the reaction zones were explored through models developed for recuperative heat exchange and process integration. Further, a design alternative was investigated for the effective transport of heat. The species flow in exothermic section was shifted in order to study its impact on temperature fronts. The extensive modeling work revealed the way in which the temperature fronts were expected to evolve, and how that affected the design alternatives. Alternate designs by conducting the reforming reaction in monolith microreactors, rather than packed beds, was also evolved. A design parameter ‘volumetric reactor activity’ to define an optimal extruded and washcoated monolith configuration was given.

To have a complete picture of the ethanol steam reforming at the reactor level, catalyst deactivation was also accounted. Several alternative inlet feed configuration schemes (distributed feed) and recycle scheme were also explored.

सार

वैश्विक ऊर्जा आवश्यकताओं को दिन-प्रतिदिन एक महत्वपूर्ण दर से बढ़ाया जा रहा है, और यह मांग मुख्य रूप से प्राकृतिक गैस, कोयले और पेट्रोलियम के अंश जैसे जीवाश्म ईंधन से मिलती है। एक ओर, परिमित जीवाश्म ऊर्जा संसाधनों की कमी का खतरा है; दूसरी तरफ, जीवाश्म ऊर्जा के गैर-न्यायी जलाने के माध्यम से ग्लोबल वार्मिंग का एक समान आसन्न खतरे है। हाइड्रोजन को एक आकर्षक और स्वच्छ ऊर्जा वाहक के रूप में सुझाया गया है कि यह कैसे तैयार किया जाता है, और जीवाश्म ईंधन की कमी और संबंधित पर्यावरणीय चिंताओं के उपाय के रूप में कार्य करता है। रसायन, खाद्य पदार्थ और शोधन उद्योगों में हाइड्रोजन के प्रमुख अनुप्रयोगों के अलावा, यह ईंधन कोशिकाओं में बिजली के वाहनों के साथ-साथ अन्य स्थिर और गैर-स्थिर अनुप्रयोगों के लिए इस्तेमाल किया जा सकता है।

मांग पर, हाइड्रोजन का उत्पादन करने के लिए "ऑन बोर्ड" या "वितरित" प्रसंस्करण की प्रक्रिया एक स्पष्ट अवधारणा की तरह दिखती है, लेकिन इस तथ्य की वजह से अक्सर व्यवहार्य नहीं होता है कि ईंधन सुधार करना एंडोस्टर्मी है, और सुधार रिएक्टर को ऊर्जा की आपूर्ति की जानी चाहिए एक तरह से प्रतिक्रिया से प्रेरित "शीतलन" के कारण रिएक्टर प्रदर्शन में गिरावट को ऑफसेट करने के लिए। इस मुद्दे को ऑफसेट करने का एक तरीका एक गर्मी-एकीकृत डिजाइन बनाना है हालांकि, इस तरह के डिजाइनों में एक्सओथेरमिक और एंडोथेरमिक मोर्चों होते हैं जो समय और स्थान पर जाते हैं, और इसलिए समस्या क्षुद्र है। ऐसे रिएक्टरों के प्रभावी डिजाइन को ऐसे मोर्चों के समय और अंतरिक्ष आंदोलनों के बारे में ज्ञान की आवश्यकता होती है। इस प्रकार, इस तकनीक का अंतिम "सफलता" स्थिर स्थिति की स्थिति से मॉडलिंग, समझ और तापमान भ्रमण के नियंत्रण पर काफी हद तक निर्भर करेगा।

इस काम में, गतिशील ऑपरेशन के तहत एक कॉम्पैक्ट सुधारक में हाइड्रोजन का उत्पादन करने के लिए, एथेनॉल स्टीम रिएक्टर सुधार करने के गणितीय मॉडलिंग का उपयोग करके इस तरह की प्रक्रिया अवधारणाएं विकसित की जाती हैं।

अध्ययन के पहले भाग में, प्रतिक्रिया क्षेत्रों में तापमान और रूपांतरण के विभिन्न स्थानिक-अस्थायी विकास ने शोधनशील गर्मी विनिमय और प्रक्रिया एकीकरण के लिए विकसित मॉडल के माध्यम से पता लगाया गया। इसके अलावा, गर्मी के प्रभावी परिवहन के लिए एक डिजाइन विकल्प की जांच की गई। एक्स्टोमायमिक खंड में प्रजातियों के प्रवाह को तापमान मोर्चों पर इसके प्रभाव का अध्ययन करने के लिए स्थानांतरित किया गया था। व्यापक मॉडलिंग कार्य ने जिस तरह से तापमान के मोर्चों के विकास की उम्मीद की थी, और कैसे डिजाइन विकल्प को प्रभावित किया पैक बेडों की बजाय, मोनोलिथ माइक्रोएरेक्टर्स में सुधार की प्रतिक्रिया का आयोजन करके वैकल्पिक डिजाइन भी विकसित हुए थे। एक इष्टतम निकला हुआ और उबका हुआ मोनोलिथ विन्यास को परिभाषित करने के लिए एक डिजाइन पैरामीटर 'वोल्यूमेट्रिक रिएक्टर गतिविधि' दिया गया था।

रिएक्टर स्तर पर सुधार में इथेनॉल स्टीम की एक पूरी तस्वीर रखने के लिए, उत्प्रेरक निष्क्रिय करने का भी जवाब दिया गया था। कई वैकल्पिक इनलेट फीड विन्यास योजनाएं (वितरण फीड) और रीसायकल स्कीम का भी पता लगाया गया।

CONTENTS

	Page
ACKNOWLEDGEMENTS	i
ABSTRACT	iii
CONTENTS	v
LIST OF FIGURES	ix
LIST OF TABLES	xv
NOMENCLATURE	xvii
 CHAPTER 1: Introduction	 1
1.1. Scope	1
1.2. Overview	1
1.3. Motivation for research	9
1.4. Research objectives	11
1.5. Organization of thesis	11
References	12
 CHAPTER 2: Background	 21
2.1. Scope	21
2.2. Coupling of exothermic and endothermic reactions	21
2.2.1. Reactors for recuperative coupling	22
2.3. Production of hydrogen from ethanol	27
2.3.1. Available technologies for producing hydrogen	28
2.3.2. Experimental work on steam reforming of ethanol	30
2.3.3. Modeling work on steam reforming of ethanol	31
2.4. Catalyst deactivation	34
2.5. Roadmap of this thesis	36
References	37
 CHAPTER 3: Process and kinetic modeling	 47
3.1. Introduction	47
3.2. Process model	47
3.3. Kinetic parameters estimation	48

3.4.	Design calculations	53
3.5.	Physical model	55
3.6.	Feasibility analysis	56
3.7.	Summary	57
	References	58
	Appendix 3A	59
 CHAPTER 4: Coupling of ethanol steam reforming and ethanol combustion: Design driven by CFD Modeling		61
4.1.	Introduction	61
4.2.	One-dimensional pseudo-homogeneous model	61
4.2.1.	Steady state behavior	64
4.2.2.	Dynamic behavior	69
4.3.	Three-dimensional pseudo-homogeneous model	73
4.4.	Sensitivity analysis	83
4.4.1.	One-dimensional analysis	83
4.4.2.	Three-dimensional analysis	85
4.5.	Summary	89
	References	90
	Appendix 4A	90
	Appendix 4B	91
	Appendix 4C	92
 CHAPTER 5: Coupling of ethanol reforming and combustion in monolith reactors .		93
5.1.	Introduction	93
5.2.	Geometry optimization model	95
5.2.1.	Extruded monolith design	98
5.2.2.	Washcoated monolith design	104
5.3.	Three-dimensional modeling	110
5.3.1.	Extruded monoliths	113
5.3.2.	Washcoated monoliths	117
5.4.	Sensitivity analysis	120
5.4.1.	Extruded monoliths	120
5.4.2.	Washcoated monoliths	126
5.5.	Summary	131

References	132
Appendix 5A	134
CHAPTER 6: Modeling catalyst deactivation in ethanol steam reforming	135
6.1. Introduction	135
6.2. Kinetics	135
6.3. Model for catalytic deactivation with coking	136
6.3.1. Catalyst activity	137
6.3.2. Effective diffusivity	138
6.3.3. Significance of λ	140
6.4. Reactor model	141
6.5. Adiabatic reactor	143
6.6. Non-adiabatic reactor	151
6.7. Reactor efficiency	156
6.8. Summary	160
References	160
Appendix 6A	162
Appendix 6B	162
Appendix 6C	163
Appendix 6D	164
CHAPTER 7: Effect of recycle and distributed feed injection	165
7.1. Introduction	165
7.2. Product recycle	165
7.3. Distributed feed	167
7.4. Results and discussion	170
7.4.1. Product recycle	170
7.4.2. Distributed feed	174
7.5. Summary	186
References	187
CHAPTER 8: Summary, conclusions and recommendations	189
8.1. Coupling of ethanol steam reforming and combustion in packed bed reactors	189
8.2. Coupling of ethanol steam reforming and combustion in extruded monolith reactors	190

8.3.	Coupling of ethanol steam reforming and combustion in washcoated monolith reactors	191
8.4.	Effect of catalyst deactivation on the reactor performance	192
8.5.	Effect of product recycle and distributed feed injection	193
8.6.	Thesis accomplishments	193
8.7.	Recommendations for further work	194
VITA		195

LIST OF FIGURES

Figure		Page
1.1	Schematic of various methods of coupling exothermic and endothermic reactions.	7
2.1	Schematic diagram of recuperative coupled reactor.	22
2.2	Schematic diagram of the micro-reactor (Chen et al., 2016).	26
2.3	Schematic of micro-channel reformer (Bruschi et al., 2016).	32
2.4	Deactivation mechanisms (Moulijn et al., 2001; Wang et al., 2008).	34
3.1	Schematic diagram of a typical fuel processor.	47
3.2	Schematic diagram of experimental setup for ethanol steam reforming.	50
3.3	A comparison of experimental and predicted values of (a) Ethanol conversion and (b) Product selectivities.	52
3.4	Schematic diagram of the compact reformer geometry considered.	55
3.5	A quadrant of the reactor (Fig. 3.4) simulated.	55
3.6	Layout of the heat integrated reformer.	56
3.7	Desired ethanol conversion in combustion is varying with a fraction of ethanol entering reforming section for various ethanol conversions in reforming.	57
4.1	Representation of boundary conditions for the two flow configurations.	63
4.2	(a) Ethanol conversion and (b) Temperature variations as a function of axial distance for two types of the heat source.	65
4.3	(a) Ethanol conversion and (b) Temperature profiles along the axial distance when combustion act as the heat source (high combustion channel feed flow rate).	67
4.4	(a) Ethanol conversion and (b) Temperature profiles along the axial distance when combustion act as the heat source (low combustion channel feed flow rate).	68
4.5	(a) Ethanol conversion and (b) Temperature deviation profiles in reforming section as a function of dimensionless time and axial distance for co-flow configuration.	70
	(c) Temperature deviation in combustion section for co-flow configuration.	70

4.6	(a) Ethanol conversion and (b) Temperature deviation profiles in reforming section as a function of dimensionless time and axial distance for counter-flow configuration.	71
	(c) Temperature deviation in combustion section for counter-flow configuration.	71
4.7	Temperature deviation profiles in reforming section as a function of time and axial distance (low combustion channel feed flow rate) for two configuration.	72
4.8	Physical model of the heat integrated reformer.	74
4.9	Temperature variation in reforming channel for the two flow configurations.	76
	(c) Temperature variation as a function of axial distance in the reforming channel at different radial locations.	77
4.10	Ethanol conversion variation in reforming channel for the two flow configurations.	78
	(c) Ethanol conversion variation as a function of axial distance in the reforming channel at different radial locations.	78
4.11	Temperature variation in combustion section for two flow configurations.	78
	(c) Temperature variation as a function of axial distance in the combustion channel at different radial locations.	79
4.12	(a) Average ethanol conversion and (b) Temperature profiles in the reforming and combustion sections.	80
4.13	Radial temperature variation at the exit of the reforming channel.	80
4.14	Compact multi tubular reformer design.	81
4.15	Radial temperature variation at the exit of reforming channel in the two multi-tubular flow configurations.	82
4.16	Temperature deviation in reforming section for two flow configurations by varying its inlet temperature.	83
4.17	Temperature deviation in reforming section for two flow configurations by varying its inlet velocity.	84
4.18	Temperature deviation in reforming section for two flow configurations by varying combustion channel inlet velocity.	85
4.19	Temperature variation along the axial distance in reforming section at different radial locations for its various inlet temperatures.	86

4.20	(a) Temperature and (b) Ethanol conversion variation along the axial distance in reforming section at different radial locations for its various inlet velocities in co-flow configuration.	87
4.21	(a) Temperature and (b) Ethanol conversion variation along the axial distance in reforming section at different radial locations for its various inlet velocities in counter-flow configuration.	89
5.1	Schematic representation of a single square channel of the monolith.	98
5.2	Surface plot of volumetric activity normalized by maximum as a function of hydraulic diameter and wall thickness.	99
5.3	(a) Ethanol conversion based on reactor volumetric activity as a function of wall thickness.	100
	(b) Variation of the open frontal area as a function of wall thickness.	100
	(c) Variation of the geometric surface area as a function of wall thickness.	101
	(d) Effectiveness factor based on reactor volumetric activity as a function of wall thickness.	101
5.4	(a) Ethanol conversions based on reactor volumetric activity as a function of hydraulic diameter.	102
	(b) Effectiveness factor based on reactor volumetric activity as a function of hydraulic diameter.	103
5.5	Geometries of washcoated cell, low catalyst loading on the left to high on the right side.	104
5.6	Plot of (a) Volumetric reactor activity (b) Effectiveness factor (c) Open frontal area (OFA) and (d) Geometric surface area (GSA) as a function of the ratio of catalyst area and cell area for different backbone thickness.	107
5.7	Plot of (a) Volumetric reactor activity and (b) Effectiveness factor as a function of the ratio of catalyst area and cell area for different hydraulic diameters of backbone.	108
	Plot of (c) Open frontal area (OFA) and (d) Geometric surface area (GSA) as a function of the ratio of catalyst area and cell area for different hydraulic diameters of backbone.	109
5.8	Different views of the monolith block with reforming channels and combustion channel surrounding the monolith.	110
5.9	(a) Ethanol conversion and (b) Temperature variation when hot gas used as a heat source.	114
	(c) Temperature variation in r - z plane.	114
5.10	Ethanol conversion variation for two flow configurations.	115

5.11	Temperature variation for (a) co-flow and (b) counter-flow configuration.	116
	Temperature variation in an r - z plane for (c) co-flow and (d) counter-flow configurations.	116
5.12	Reactant concentration field at the exit of a cell.	117
5.13	Ethanol conversion variation for two flow configurations.	118
5.14	Temperature variation for two flow configurations.	119
5.15	Temperature variation in an r - z plane for two flow configurations.	120
5.16	(a) Surface plot of volumetric activity normalized by maximum as a function of hydraulic diameter and wall thickness (a) $k'_v = 33 \text{ s}^{-1}$ (b) $k'_v = 650 \text{ s}^{-1}$.	121
	(b) Normalized activity vs. monolith wall thickness as a function of k_l for the hydraulic diameter of 2 mm.	122
5.17	Comparison of normalized volumetric activity at various inlet velocities as a function of hydraulic diameter and wall thickness.	123
5.18	Temperature variation inside distant monolith channels for two reforming inlet velocities for (a) co-flow and (b) counter-flow configuration.	124
5.19	Temperature variation inside distant monolith channels for two reforming feed temperatures for (a) co-flow and (b) counter-flow configuration.	126
5.20	(a) Volumetric reactor activity and (b) Effectiveness factor for various values of effective diffusivity (D_{eff}).	127
5.21	(a) Volumetric reactor activity and (b) Effectiveness factor for various values of intrinsic reaction rate constant (k'_v).	128
5.22	Temperature profiles for co-flow and counter-flow configurations for various feed inlet velocities.	130
5.23	Temperature profiles for co-flow and counter-flow configurations for various feed inlet temperatures.	131
6.1	Evolution of (a) Ethanol conversion and (b) Coke concentration profiles under the adiabatic condition for $\lambda = 0$.	144
	Evolution of (c) Effectiveness factor and (d) Reforming zone temperature profiles under the adiabatic condition for $\lambda = 0$.	145
6.2	Evolution of (a) Ethanol conversion and (b) Temperature profiles under the adiabatic condition for $\lambda = 0.11$.	147
	(c) Evolution of coke concentration profiles under the adiabatic condition for $\lambda = 0.11$.	147

	Evolution of (d) Effectiveness factor and (e) Normalized pore radius profiles under the adiabatic condition for $\lambda = 0.11$.	149
6.3	Evolution of (a) Ethanol conversion and (b) Coke concentration profiles under the adiabatic condition for $\lambda = 0.16$.	150
	Evolution of (c) Effectiveness factor and (d) Pore radius profiles under the adiabatic condition for $\lambda = 0.16$.	151
6.4	Evolution of temperature in (a) Reforming section and (b) Combustion section for co-flow configuration.	152
	Evolution of temperature in (c) Reforming and (d) Combustion section for counter-flow configuration.	153
6.5	Evolution of (a) Coke concentration and (b) Catalyst activity.	154
	(c) Evolution of effectiveness factor.	155
6.6	(a) Variation of reactor efficiency with coke concentration.	157
	(b) Expanded view of Zone I (variation of reactor efficiency with coke concentration).	158
	(c) Variation of reactor efficiency with process time (Zone II) for various λ s under the adiabatic reactor condition.	158
	(d) Effect of heat integration on reactor efficiency for $\lambda = 0.11$.	159
7.1	Schematic representation of the recycle system.	166
7.2	Schematic illustration of discrete and continuous feed distribution.	167
7.3	(a) Temperature profiles in reforming section for various recycle ratios (counter-flow configuration).	170
	(b) Temperature profiles in combustion section and (c) Ethanol conversion in the reforming section for various recycle ratios (counter-flow configuration).	171
7.4	Temperature profiles in (a) reforming and (b) combustion section for various recycle ratios (co-flow configuration).	172
	(c) Ethanol conversion in the reforming section for various recycle ratios (co-flow configuration).	173
7.5	Pictorial representation of Case A presented in Table 7.2.	175
7.6	Temperature profiles in the reforming section for various distributed feed scenarios for Case A in Table 7.2.	175
	(c) Temperature profiles in the combustion section for various distributed feed scenarios for Case A in Table 7.2.	176

	(d) Ethanol conversion in reforming section for the subcases in Fig. 7.6(b).	177
7.7	Pictorial representation of cases presented in Table 7.2.	178
7.8	Temperature profiles in the reforming section for various distributed feed scenarios given in Table 7.2.	179
7.9	Effect of inlet flow rate on reforming section temperature for (a) subcase (c) of Case C and (b) subcase (b) of Case D.	180
	(c) Ethanol conversion in the reforming section for the cases in Fig. 7.9(b).	181
7.10	Temperature profiles in the reforming section for various distributed feed scenarios (Case A and B) in Table 7.3.	183
7.11	Schematic illustration of continuous feed distribution in both the sections.	183
7.12	Temperature profiles in the reforming section for various distributed feed scenarios (Case C ₁ and C ₂) in Table 7.3.	184
7.13	Reforming section temperature along the axial distance for subcase (a) of Case C ₁ .	185

LIST OF TABLES

Table	Page
2.1 Experimental studies on steam reforming of ethanol.	30
2.2 A brief review on the modeling of steam reforming of ethanol.	32
3.1 Kinetic parameters regressed for ethanol reforming section.	52
3.2 Reactor dimensions predicted for various scenarios (45% ethanol conversion).	54
3.3 Reactor dimensions predicted for various scenarios (80% ethanol conversion).	54
5.1 Optimal geometries for various (d_{hB} , t_{wB}) combinations.	106
5.2 Parameters used in simulations.	113
5.3 Average ethanol conversions in reforming section.	125
5.4 Optimal geometries for the various effective diffusivities (D_{eff}).	128
5.5 Optimal geometries for the various intrinsic rate constant (k'_v).	129
6.1 Kinetic parameters regressed for Wang et al. (2008).	136
6.2 Typical data used for deactivation model in steam reforming.	140
6.3 Simulation parameters used in the model.	143
7.1 Boundary conditions for the two sections in co-flow configuration.	168
7.2 Different scenarios discussed for distributed feed at discrete locations.	174
7.3 Different scenarios discussed for distributed feed fed continuously.	181

NOMENCLATURE

L_b	length of reactor [m]
D_p	catalyst particle diameter [m]
D	reactor diameter [m]
F	molar flow rate [mol s ⁻¹]
A_c	cross-sectional area [m ²]
n	reactor order [-]
c	specie concentration [mol m ⁻³]
E_a	activation energy [kJ mol ⁻¹]
R_G	gas constant [kJ mol ⁻¹ K ⁻¹]
ΔH	heat of reaction [kJ mol ⁻¹]
C_p	specific heat [kJ kg ⁻¹ K ⁻¹]
$\hat{C}_p$	molar heat capacity [kJ mol ⁻¹ K ⁻¹]
$\tilde{C}_p$	volumetric heat capacity [kJ m ⁻³ K ⁻¹]
V	volume of reactor [m ³]
W	weight of catalyst [kg]
C	dimensionless concentration [-]
R	radius [m]
r	reaction rate [mol m ⁻³ s ⁻¹]
k_{rxtr}	catalyst activity on reactor volumetric basis [s ⁻¹]
v	volumetric flow rate [m ³ s ⁻¹]
r_{app}	apparent reaction rate [mol m ⁻³ s ⁻¹]
$r_{cat,V}$	reaction rate [mol m ⁻³ _{cat} s ⁻¹]
U, h	heat transfer coefficient [W m ⁻² K ⁻¹]
u	velocity [m s ⁻¹]
X	conversion [-]
q	heat flux [W m ⁻³]
$\mathbf{u}$	velocity vector [m s ⁻¹]
p	pressure [Pa]
$\mathbf{I}$	identity matrix [-]
N_j	molar flux [mol m ⁻² s ⁻¹]
k	thermal conductivity [W m ⁻¹ K ⁻¹]
l_d	characteristic diffusion length [m]
k_v	intrinsic rate constant [(mol ⁻¹ m ³) ⁽ⁿ⁻¹⁾ s ⁻¹]

D_{eff}	effective diffusivity [$\text{m}^2 \text{s}^{-1}$]
r_m	effective molecular radius [m]
r_p	pore radius [m]
t	time [s]
c_C^0	maximum surface coke concentration [kg m^{-2}]
c_C	surface coke concentration at any instant [kg m^{-2}]
D_K	Knudsen diffusion at any instant [$\text{m}^2 \text{s}^{-1}$]
D_M	Molecular diffusivity [$\text{m}^2 \text{s}^{-1}$]
C_C	dimensionless coke concentration [-]
R_C	reaction rate of coke [$\text{mol m}^{-3} \text{s}^{-1}$]
T	temperature [K]
$\mathbf{n}$	normal vector [-]
r, z	space coordinates [m]
d_h	hydraulic diameter [m]
t_w	wall thickness [m]
t_c	washcoat thickness [m]
Da	Damkohler number [-]
d_t	tube diameter [m]
R_R	recycle ratio [-]
P	perimeter of reactor tube [m]
J	dimensionless source [-]
N_T	total number of distributed feed locations [-]
N	distributed feed location (1, 2, ..., N_T) [-]
H	Hydrogen
CD	Carbon dioxide
CO	Carbon monoxide
M	Methane
E	Ethanol
S	Steam

Greek letters

$\rho_{cat,b}$	bulk density of catalyst [kg m^{-3}]
$\mathcal{E}$	particle voidage [-]

ε_s	solid fraction [-]
ε_b	bed voidage [-]
η_{int}	internal effectiveness factor [-]
ϕ	thiele modulus [-]
τ	dimensionless time [-]
τ_m	Particle tortuosity [-]
ξ	dimensionless length [-]
β	dimensionless heat of reaction [-]
μ	dynamic viscosity [Pa s]
θ	dimensionless temperature [-]
ρ_c	bulk density of coke [kg m ⁻³]
γ	dimensionless activation energy [-]

Superscripts

0	initial
c	combustion
r	reforming
$*$	dimensionless
$'$	backward

Subscripts

i	reaction
j	component
cat	catalyst
s	solid
g	gas
in	inlet
B	backbone
S	steam
ss	side stream