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 एंडोथेमिक 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 रिफैक्टर 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 डिज़ाइन 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 'वोलूमेट्रिक 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 फ़ीड) और रीसायकल स्कीम का भी पता लगाया गया।

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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}]
Ea	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 [$m^2\ s^{-1}$]
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 [$m^2\ s^{-1}$]
D_M	Molecular diffusivity [$m^2\ s^{-1}$]
C_C	dimensionless coke concentration [-]
R_C	reaction rate of coke [mol $m^{-3}\ s^{-1}$]
T	temperature [K]
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}]
ε	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