GLYCEROL STEAM REFORMING WITH CERIA PROMOTED NICKEL-ALUMINA CATALYSTS FOR HYDROGEN PRODUCTION

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by

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DEDICATION

I dedicate this work to my wife Bontu Adugna Mulisa whose love gives meaning to my life and to my mom and dad who taught me the value of the Three P’s – persistence, perseverance and patience in life.

CERTIFICATE

This is to certify that the thesis entitled **“GLYCEROL STEAM REFORMING WITH CERIA PROMOTED NICKEL-ALUMINA CATALYSTS FOR HYDROGEN PRODUCTION”**, being submitted by **Mr. Hundessa Dessalegn Demsash** to the **Indian Institute of Technology Delhi**, for the fulfillment of the degree of **Doctor of Philosophy**, is a record of bonafide research work carried out by him under my guidance and supervision.

The results contained in this thesis have not been previously submitted, in part or whole, to any university or institution for any degree, diploma, or other qualification.

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ABSTRACT

The excessive emissions of anthropogenic greenhouse gases associated with utilization of fossil fuel and its subsequent global warming have become vital issues nowadays. We have reached limits of considerable seriousness than ever in the recent years. Hence, in lieu of fossil fuels, there should be a shift to low-carbon energy supply for this century and beyond. Among the alternatives, biodiesel has been found to be a promising renewable fuel and globally its production has increased significantly in recent years. This has resulted in a surfeit of crude glycerol as a by-product. Consequently, the valorization of bio-glycerol has been targeted worldwide to make biodiesel production cost competitive.

Steam reforming of glycerol to produce clean fuel such as hydrogen is a potential method of recuperating glycerol from biodiesel. Since the effectiveness of this process depends on efficient catalysts with good selectivity and stability as well as milder process conditions, the current work aims to develop improved catalysts. Moreover, there is a scarcity of kinetic data in the literature for glycerol steam reforming which can be used for designing reactors. Hence, kinetic modeling was also carried out.

In the current work, six catalysts (three nickel-alumina, two ceria promoted nickel-alumina and one ruthenium doped ceria promoted nickel-alumina) were prepared with wet impregnation method and tested for 30 wt. % glycerol aqueous solution in a packed bed reactor. Characterization of fresh and spent catalysts was carried out with BET surface area, X-ray diffraction, scanning electron microscopy, temperature programmed reduction, temperature programmed oxidation and pulse hydrogen chemisorption techniques to relate catalyst properties and catalytic performance.

The range of parameters that favor high hydrogen yield was first examined with Aspen Plus thermodynamic analysis. The reaction was then conducted at temperatures from 550 °C to 800 °C, atmospheric pressure and weight hourly space velocity (WHSV) of 6.8 to 17 h^{-1}.

Among tested monometallic catalysts, $10Ni/Al_2O_3/5CeO_2$ was found to be stable for 16 total hours on stream while $10Ni\text{-}1Ru/Al_2O_3/5CeO_2$ showed the superior catalytic performance and stability for 24 hours on stream. With this catalyst, best hydrogen selectivity of 88.6 % was obtained versus thermodynamic selectivity of 95.9 % at 650^{o}C. Furthermore, the catalyst showed minimal coking tendency.

Then, by using both power law and heterogeneous kinetic models (Langmuir-Hinshelwood and Eley-Rideal), kinetic models were developed and tested. The models have been subjected to statistical investigation and Langmuirian model discrimination guidelines. The Langmuir-Hinshelwood associative single site adsorption kinetic model was found to fulfill both criteria. With the activation energy of 69.74 kJ/mol, it was found in good agreement with the power law type kinetic model. Hence, it can adequately describe glycerol steam reforming under the reaction conditions.

Finally, with developed kinetics, modeling and simulation of combustion coupled reformer was carried out. In the reformer simulation, the counter-current flow configuration was found to operate better than the co-current coupled process in terms of supplying required heat input for the reformer and product yield. Product yields of 5.2 and 5.8 moles of H_2 per mole glycerol reacted were obtained in co-flow and counter-flow respectively.

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NOTATIONS

Symbol	Definition	Unit
A_i	Area for in the mixture for chromatograph	m^2
A_n	Normalized area	
A_{std}	Area for standard mixture	m^2
C_E^{oc}	Dimensionless initial concentration of ethanol in combustor	
C_O^{oc}	Dimensionless initial concentration of oxygen in combustor	
$C_{glycerol}$	Molar concentrations of adsorbed glycerol	kmol/kg cat
C_{steam}	Molar concentrations of adsorbed steam	kmol/kg cat
C_{Pmix}	Heat capacity of mixture	J/kg/K
C_E	Ethanol concentration	mol/m^3
C_i	Species concentration	mol/m^3
c_i	Dimensionless concentration for species 'i'	
C_O	Oxygen concentration	mol/m^3
D	Metallic dispersion	%
$D_{glycerol,j}$	Molecular diffusivity of glycerol in 'j' species	m^2/s
Da_i	Damkohler number for species in the reformer	
Da_E	Damkohler number for ethanol in the combustor	
Da_O	Damkohler number for oxygen in the combustor	
d_c	Combustor diameter	m
d_r	Reformer diameter	m
d_p	Pellet diameter	m

E_A	Activation energy	kJ/mol
$F_{CH_4,out}$	Molar outflow of methane	mol/h
$F_{C_3H_8O_3,feed}$	Glycerol molar feed rate	mol/h
$F_{CO,out}$	Molar outflow rate of CO	mol/h
$F_{CO_2,out}$	Molar outflow of CO_2	mol/h
F_{feed}	Molar feed rate to the reactor	mol/h
$F_{H_2,out}$	Molar outflow of hydrogen	mol/h
$-\Delta H$	Heat of reaction	kJ/mol
$-\Delta H_{ads}$	Heat of adsorption	kJ/mol
h	Convective heat transfer	$kJ/m^2\ s\ K$
j_D	j-factor for mass transfer	
k	Reaction constant for power law type for $10Ni/Al_2O_3/5CeO_2$	$\left(\frac{kmol}{kg\ cat.}\right)^{1-n} h^{-1}$
k^c	Reaction constant for ethanol combustion	$\left(\frac{kmol}{m^3}\right)^{0.75} h^{-1}$
$K_{glycerol}$	Equilibrium constant for glycerol	$m^3/kmol$
K_{steam}	Equilibrium constant for steam	$m^3/kmol$
$k_{reaction}$	Reaction constant for heterogeneous kinetic models	$\frac{1}{h}\left(\frac{kmol}{kg\ cat.}\right)^{1-(m+n)}$
l	Bed length	m
L	Reactor length	m
m	Order of reaction with respect to glycerol	
m_i	Mass of species during GC calibration	kg
m_n	Dimensionless mass during GC calibration	
$m_{std.}$	Mass of standard mixture	kg
m_u	Mass of unknown species	kg
M_{wt}	Molecular weight	g/mol
n	Order of reaction with respect to steam	

n_{CH_4}	Molar percent of methane	%
$n_{C_3H_8O_3}$	Molar percent of glycerol	%
n_{CO}	Molar percent of CO	%
n_{CO_2}	Molar percent of CO_2	%
R	Universal gas constant	kJ/kmol K
r	Reaction rate	kmol/kg cat.s
RF	Response factor	
ΔS	Change in entropy	kg/J /K
T	Temperature	K
T^o	Inlet temperature	K
U	Over all heat transfer coefficient	kg/m^2 s K
u	Superficial velocity	m/s
U^*	Dimensionless overall heat transfer coefficient	
U^{*c}	Dimensionless overall heat transfer coefficient in reformer	
V_{ads}	Adsorbed volume	cm^3/g
V_g	Ideal gas volume at STP	cm^3
W_{cat}	Weight of catalyst	kg
X_{gly}	Conversion of glycerol	%

Greek letters	Definition	Unit
β_i	Dimensionless heat of reaction	
γ_i	Dimensions activation energy	
ε	Bed porosity	
η_i	Effectiveness factor	
Θ	Dimensionless temperature	
Θ_w	Dimensionless wall temperature	
$\theta_{glycerol}$	Glycerol surface coverage	
θ_{steam}	Steam surface coverage	
θ_v	Vacant sites	
μ_i	viscosity of species	kg/m·s
ξ	Dimensionless length	
ρ_{mix}	mixture density	kg/m^3

ACRONYMS

BET	Brunauer–Emmett–Teller
GHSV	Gas hourly space velocity
GSR	Glycerol steam reforming
ER	Eley-Rideal Mechanism
LH	Langmuir-Hinshelwood
NASA	National Aeronautics and Space Administration
NOAA	National Oceanic and Atmospheric Administration
TGA	Thermogravimetric analysis
TPO	Temperature programmed oxidation
TPR	Temperature programmed reduction
Vol. %	Volume percent
Wt. %	Weight percent
WCMR	Water to carbon molar ratio
WGMR	Water to glycerol molar ratio
WHSV	Weight hourly space velocity
XRD	X-ray diffraction