GLYCEROL DRY REFORMING FOR HYDROGEN-RICH PRODUCTION OVER Ni/CaO, Ni/ZrO_2 and 5%Re-Ni/CaO

NUR NABILLAH BT MOHD ARIF

MASTER OF SCIENCE

UNIVERSITI MALAYSIA PAHANG

SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Master of Science in Chemical Engineering

_____

(Supervisor's Signature)

Full Name :Dr Sumaiya bt Zainal Abidin @ Murad

Position :Senior lecturer

Date :

_____

(Co-supervisor's Signature)

Full Name : Dr Vo Nguyen Dai Viet

Position : Senior lecturer

Date :

STUDENT'S DECLARATION

I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

_____

(Student's Signature)

Full Name : NUR NABILLAH BT MOHD ARIF

ID Number : MKC14013

Date :

GLYCEROL DRY REFORMING FOR HYDROGEN-RICH PRODUCTION OVER Ni/CaO, Ni/ZrO_2 and 5%Re-Ni/CaO

NUR NABILLAH BT MOHD ARIF

Thesis submitted in fulfillment of the requirements
for the award of the degree of
Master of Science

Faculty of Chemical Engineering and Natural Resources

UNIVERSITI MALAYSIA PAHANG

July 2017

ACKNOWLEDGEMENTS

In the name of Allah S.W.T the Most Beneficent and the Most Merciful. The deepest sense of gratitude to the Almighty for the strength and ability to complete this undergraduate research project. Infinite thanks we brace upon Him.

A special gratitude I give to my supervisor, Dr Sumaiya bt Zainal Abidin @ Murad, for her tireless efforts, patience, advice, and on-going support, as well as her excellent guidance for this project. My heartiest gratitude also extends to my co-supervisor Dr. Vo Nguyen Dai Viet who has in all way guided and corrected my mistakes in the completion of this study.

Furthermore I would also like to acknowledge with much appreciation to the entire staff and instructors of Faculty of Chemical and Natural Resources Engineering laboratory for giving permission and cooperation throughout the experimental work conducted. Specials thanks goes to my friends, Norazimah, Asmawati, Ahada, Shabirah, and Munirah who always give support and help me to finish this study.

My special gratidue goes to my beloved parents, Mohd Arif b Mohd Ayob and Siti Haslina bt Rahmat, and my brothers and sisters, Mohd Akhmal Hakim, Mohd Amirul, Nur Intan Nadia, and Nur Nadia Najwa, who always support and encourage me with their best wishes.

TABLE OF CONTENT

DECLARATION

TITLE PAGE

ACKNOWLEDGEMENTS **ii**

ABSTRAK **iii**

ABSTRACT **iv**

TABLE OF CONTENT **v**

LIST OF TABLES **x**

LIST OF FIGURES **xi**

LIST OF SYMBOLS **xv**

LIST OF ABBREVIATIONS **xvi**

CHAPTER 1 INTRODUCTION **1**

1.1 Background of studies 1

1.2 Problem statement 2

1.3 Objective 3

1.4 Scope of studies 4

1.5 Significance of study 4

1.6 Organisation of thesis 5

CHAPTER 2 LITERATURE REVIEW **7**

2.1 Overview 7

2.2 Energy crisis 7

2.3 Non-renewable sources as global source of energy 9

2.4 Renewable material as alternative source for non-renewable energy 14

2.5 Potential application of waste glycerol 18

2.6 Hydrogen gas as a source of energy 20

2.7 Thermochemical process for hydrogen production with glycerol as feedstock 24

2.7.1 Steam reforming 25

2.7.2 Pyrolysis 25

2.7.3 Partial oxidation 26

2.7.4 Autothermal reforming 27

2.7.5 Dry reforming 27

2.8 Selection of catalysts for glycerol dry reforming 29

2.8.1 Catalyst 30

2.8.2 Catalyst support 31

2.8.3 Catalyst promoter 35

2.9 Summary 38

CHAPTER 3 MATERIALS AND METHOD 39

3.1 Introduction 39

3.2 Materials and chemicals 39

3.3 Flowchart for overall experiment 41

3.4 Preparation of catalysts 42

3.4.1 Preparation of non-promoted catalysts (Ni/CaO and Ni/ZrO_2) 42

3.4.2 Preparation of 5% of Re promoted on 15%Ni/CaO 42

3.5 Catalyst Characterisation 43

3.5.1 Scanning electron microscopy (SEM) 43

3.5.2 Nitrogen physisorption 44

3.5.3 X-Ray Diffraction (XRD) 44

3.5.4 Temperature Programmed Calcination (TPC) 45

3.5.5 Temperature Programmed Oxidation (TPO) 45

3.5.6 Temperature programmed reduction (H_2-TPR) 45

3.5.7 Temperature programmed desorption (TPD) 45

3.5.8 Field emission scanning electron microscope – Energy dispersive X-ray (FESEM-EDX) 46

3.6 Blank test 47

3.7 Experimental setup for glycerol dry reforming 47

3.8 Glycerol dry reforming reaction metrics 49

3.9 Gas product analysis 50

3.10 Summary 51

CHAPTER 4 SCREENING OF CATALYST FOR NI SUPPORTED ON DIFFERENT OXIDES (CAO AND ZRO_2) 52

4.1 Introduction 52

4.2 Transient profile for blank test 52

4.3 Glycerol dry reforming for hydrogen production over Ni based catalysts: CaO and ZrO_2 54

4.3.1 Physicochemical Characterisation of Ni/CaO and Ni/ZrO_2 catalysts 54

4.3.2 Glycerol Dry Reforming for Hydrogen Production over the Non-Promoted Catalysts (Ni/CaO & Ni/ZrO_2) 68

4.4 Glycerol dry reforming for hydrogen production over Ni based catalysts: effect of promoter 72

4.4.1 Physicochemical Characterisation of Re-Ni/CaO catalyst 72

4.4.2 Glycerol Dry Reforming for Hydrogen Production over 5%Re-Ni/CaO catalysts 79

4.5 Summary 81

CHAPTER 5 EFFECT OF REACTION PARAMETERS TOWARDS GLYCEROL DRY REFORMING 83

5.1 Introduction 83

5.2 Effects of CO_2 to $C_3H_8O_3$ Feed (CGR) 83

5.2.1 Effect of CO_2 to $C_3H_8O_3$ Feed (CGR) on Glycerol Conversion 84

5.2.2 Effect of CO_2 to Glycerol Feed (CGR) on Hydrogen Yield 87

5.2.3 Effect of CO_2 to Glycerol Feed (CGR) on Formation Rate of the Product. 92

5.3 Effect of Temperature: Glycerol Conversion, Hydrogen Yield, and Formation Rate of Gaseous Products 95

5.4 Effect of Gas Hourly Specific Velocity (GHSV) 100

5.5 Summary 101

CHAPTER 6 CONCLUSION 103

6.1 Introduction 103

6.2 Conclusion 103

6.3 Recommendations 104

REFERENCES 106

APPENDIX A CALCULATION ON PARTIAL PRESSURE RELATED WITH CGR 120

APPENDIX B CALCULATION ON PARTIAL PRESSURE RELATED WITH CGR 122

APPENDIX C RELATION OF RESULT FROM GC WITH GLYCEROL CONVERSION AND HYDROGEN YIELD 123

APPENDIX D CRYSTALLITE SIZE 125

APPENDIX E GAS HOURLY SPECIFIC VELOCITY (GHSV) 127

LIST OF TABLES

Table 2.1	CO_2 emissions from fossil fuels sources (million metric tons)	12
Table 2.2	Chemical and physical properties of glycerol	19
Table 2.3	General properties of H_2	21
Table 2.4	Advantages and challenges for three basic technologies in hydrogen production	23
Table 2.5	Catalysts and operating condition used in glycerol dry reforming	29
Table 2.6	List of various support that used in reforming reaction	34
Table 2.7	List of catalyst and operating condition from previous research works	37
Table 3.1	List of chemicals and gases used	40
Table 3.2	GC chromatography retention time for gases and standard gas concentration	51
Table 4.1	Crystallite diameter from XRD analysis	55
Table 4.2	Crystallite size for Ni/ZrO_2 catalyst from XRD analysis	56
Table 4.3	Specific surface area for non-promoted catalyst	59
Table 4.4	Acidic properties of 15%Ni/CaO and 15%Ni/ZrO_2 with their pure support	68
Table 4.5	Crystallite size from XRD analysis for 15%Ni/CaO and 5%Re-Ni/CaO	73
Table 4.6	Specific surface area for non-promoted and promoted catalysts	74
Table 4.7	Summary of acid property for 5%Re-Ni/CaO	79
Table 5.1	EDX analysis on spent catalysts of 15%Ni/CaO and 5%Re-Ni/CaO	92
Table 5.2	Glycerol conversion and gas product yield at different values of GHSV (manipulated by mass of catalyst from 0.1 to 0.5 g).	100

LIST OF FIGURES

Figure 2.1	Global energy consumption from 1980 to 2030	8
Figure 2.2	Energy demand by sector in Malaysia from 1980 to 2011	9
Figure 2.3	The sources of energy in 2007	10
Figure 2.4	The world production of coal from year 2013 to 2015	11
Figure 2.5	Natural gas production from 1980 until 2010	13
Figure 2.6	CO_2 emissions from fossil fuels and other sources of energy in 2013	14
Figure 2.7	Global consumption of primary energy projected from 1990 to 2030	15
Figure 2.8	Conversion routes of biomass to energy	16
Figure 2.9	Crude glycerol prices from 2004 until 2011 in US	18
Figure 2.10	Utilisation of crude glycerol via its processing routes	19
Figure 2.11	Industrial uses of glycerol	20
Figure 2.12	Different methods in the production of hydrogen from different sources	21
Figure 2.13	Process flow for hydrogen production via gasification of biomass	24
Figure 3.1	Overall flowchart for experimental work	41
Figure 3.2	Catalyst preparation of non-promoted catalyst via the wet impregnation method	42
Figure 3.3	Catalyst preparation of promoted catalyst by wet impregnation method	43
Figure 3.4	Experimental setup for dry reforming reaction	48
Figure 3.5	Schematic diagram of reactor used in experimental work	49
Figure 4.1	Effect of catalyst over glycerol conversion as a function of time (Reaction conditions: T = 700 °C, P_{gly} = 8.41 kPa, and GHSV = 3.6×10^4 mL g_{cat}^{-1} h^{-1})	53
Figure 4.2	Effect of CO_2 over glycerol conversion as a function of time (Reaction conditions: T = 700 °C, P_{gly} = 8.41 kPa, and GHSV = 3.6×10^4 mL g_{cat}^{-1} h^{-1})	54
Figure 4.3	XRD pattern of synthesised catalysts with various CaO loadings (a)100% CaO, (b) 5%Ni/CaO, (c) 10%Ni/CaO, and (d) 15%Ni/CaO. CaO (□), NiO (○), and $Ca(OH)_2$ (●).	56
Figure 4.4	XRD pattern of synthesized catalysts with various ZrO_2 loadings (a)100% ZrO_2 (b)5%Ni/ZrO_2 (c)10%Ni/ ZrO_2 and (d)15%Ni/ ZrO_2. ZrO_2 (◊), NiO (○)	57

Figure 4.5	Morphology structure of (a) 5%Ni/CaO, (b)10%Ni/CaO, and (c) 15%Ni/CaO catalysts calcined at 500 °C for 5 h, at a magnification of 5k×	60
Figure 4.6	Morphology structure of (a) 5%Ni/ZrO_2, (b) 10%Ni/ZrO_2, and (c) 15%Ni/ZrO_2 catalysts calcined at 500 °C for 5 h, at a magnifiction of 5k×	61
Figure 4.7	TPC analysis for a series of loading of Ni/CaO catalyst at 10 °C min^{-1} from 25 °C to 900 °C	63
Figure 4.8	TPC analysis for a series of loading of Ni/ZrO_2 catalyst at 10 °C min^{-1} from 25 °C to 900 °C	63
Figure 4.9	Temperature-programmed reduction for (a) 100% CaO and (b) 15%Ni/CaO	65
Figure 4.10	Temperature-programmed reduction for (a) 100% ZrO_2 and (b) 15%Ni/ZrO_2	65
Figure 4.11	NH_3-TPD profiles of (a) 100% CaO and (b) 15%Ni/CaO [Analysis was run from room temperature to 900 °C at a ramping rate of 10 °C min^{-1}]	67
Figure 4.12	NH_3-TPD profiles of (a) 100% ZrO_2 and (b) 15%Ni/ZrO_2 [Analysis was run from room temperature to 900 °C at a ramping rate of 10 °C min^{-1}]	67
Figure 4.13	Glycerol conversion for Ni/CaO and Ni/ZrO_2 catalysts as a function of time (Reaction conditions: T = 700 °C, P_{gly} = 8.41 kPa, and GHSV = 3.6×10^4 mL g_{cat}^{-1} h^{-1})	70
Figure 4.14	Hydrogen yield of Ni/CaO and Ni/ZrO_2 catalysts as a function of time (Reaction conditions: T = 700 °C, P_{gly} = 8.41 kPa, and GHSV = 3.6×10^4 mL g_{cat}^{-1} h^{-1}]	71
Figure 4.15	XRD pattern of non-promoted and promoted catalysts (a) 15%Ni/CaO and (b) 5%Re-Ni/CaO. CaO (□), ReO_3 (▲), NiO (○), and $Ca(OH)_2$ (●).	73
Figure 4.16	Morphology structure of the calcined (a) 15%Ni/CaO and (b) 5%Re-Ni/CaO	75
Figure 4.17	Thermogravimetric analysis of 15%Ni/CaO and 5%Re-Ni/CaO at 10 °C min^{-1} from 25 to 900 °C	76
Figure 4.18	Temperature-programmed reduction profile of (a) 15%Ni/CaO and (b) 5%Re-Ni/CaO at 10 °C min^{-1} from 300 to 900 °C	77
Figure 4.19	NH_3-TPD profile of (a) 15%Ni/CaO and (b) 5%Re-Ni/CaO at 20 °C min^{-1} from 100 to 700 °C	78
Figure 4.20	CO_2-TPD profiles of 5%Re-Ni/CaO from 100 to 900 °C at a ramping rate of 20 °C min^{-1}]	78
Figure 4.21	Glycerol conversion of 15%Ni/CaO and 5%Re-Ni/CaO at 700 °C (Reaction conditions: P_{gly} = 8.41 kPa, GHSV = 3.6×10^4 mL g_{cat}^{-1} h^{-1}, time = 180 min)	80

Figure 4.22 Hydrogen yield of 15%Ni/CaO and 5%Re-Ni/CaO at 700 °C (Reaction conditions: P_{gly} = 8.41 kPa, GHSV = 3.6 × 10^4 mL g_{cat}^{-1} h^{-1}, time = 180 min) 81

Figure 5.1 Glycerol conversion profile of 15%Ni/CaO at different CGR values (Reaction conditions: T = 700 °C, P_{gly} = 8.41 kPa and GHSV = 3.6 × 10^4 mL g_{cat}^{-1} h^{-1}, time = 180 min). 85

Figure 5.2 Glycerol conversion profile of 5%Re-Ni/CaO at different CGR values.(Reaction conditions: T = 700 °C, P_{gly} = 8.41 kPa and GHSV = 3.6 × 10^4 mL g_{cat}^{-1} h^{-1}, time = 180 min) 85

Figure 5.3 Glycerol conversion profile of 15Ni/CaO at different reaction conditions of CO_2 but fixed condition of reaction temperaure of 700 °C and GHSV of 3.6 × 10^4 mL g_{cat}^{-1} h^{-1}, time: 180 min. 86

Figure 5.4 Glycerol conversion for 15%Ni/CaO and 5%Re-Ni/CaO at different CGR (Reaction conditions: T = 700 °C, P_{gly} = 8.41 kPa, and GHSV = 3.6 × 10^4 mL g_{cat}^{-1} h^{-1}, time = 120 min). 87

Figure 5.5 Hydrogen yield profile of 15%Ni/CaO at different CGR values (Reaction conditions: T = 700 °C, P_{gly} = 8.41 kPa, and GHSV = 3.6 × 10^4 mL g_{cat}^{-1} h^{-1}, time = 180 min). 88

Figure 5.6 Hydrogen yield profile of 5%Re-Ni/CaO at different CGR values (Reaction conditions: T = 700 °C, P_{gly} = 8.41 kPa, and GHSV = 3.6 × 10^4 mL g_{cat}^{-1} h^{-1}, time = 180 min). 89

Figure 5.7 Hydrogen yield profile of 15%Ni/CaO and 5%Re-Ni/CaO at different CGR values (Reaction conditions: T = 700 °C, P_{gly} = 8.41 kPa, and GHSV = 3.6 × 10^4 mL g_{cat}^{-1} h^{-1}, time = 120 min). 89

Figure 5.8 FESEM images of spent catalysts of (a)15%Ni/CaO and (b)5%Re-Ni/CaO at 15k× of magnification. 91

Figure 5.9 TGA curves for the spent catalysts of 15%Ni/CaO and 5%Re-Ni/CaO. 92

Figure 5.10 Formation rates of gaseous products for 15% Ni/CaO at different CGR values (Reaction conditions: T = 700 °C, GHSV = 3.6 × 10^4 mL g_{cat}^{-1} h^{-1}). 93

Figure 5.11 Formation rates of gaseous products for 5%Re-Ni/CaO at different CGR values (Reaction conditions: T = 700 °C, GHSV = 3.6 × 10^4 mL g_{cat}^{-1} h^{-1}). 94

Figure 5.12 Comparison of H:CO for 15%Ni/CaO and 5%Re-Ni/CaO at different CGR values (Reaction conditions: T = 700 °C, GHSV = 3.6 × 10^4 mL g_{cat}^{-1} h^{-1}, and time = 120min). 95

Figure 5.13 Effect of temperature on glycerol conversion for 15%Ni/CaO (Reaction conditions: P_{gly} = 8.41 kPa, CGR=1:1, and GHSV = 3.6 × 10^4 mL g_{cat}^{-1} h^{-1}). 97

Figure 5.14 Effect of temperature on glycerol conversion for 5%Re-Ni/CaO (Reaction conditions: P_{gly} = 8.41 kPa, CGR=3:1, and GHSV = 3.6 × 10^4 mL g_{cat}^{-1} h^{-1}). 97

Figure 5.15 Glycerol conversion for 15%Ni/CaO and 5%Re-Ni/CaO at different reaction temperatures (Reaction conditions: P_{gly} = 8.41 kPa, CGR=1:1 for Ni/CaO and CGR=3:1 for Re-Ni/CaO, GHSV = 3.6×10^4 mL g_{cat}^{-1} h^{-1}, and time = 120 min). 98

Figure 5.16 Hydrogen yield for 15%Ni/CaO and 5%Re-Ni/CaO at different reaction temperatures (Reaction conditions: P_{gly} = 8.41 kPa, CGR=1:1 for Ni/CaO and CGR=3:1 for Re-Ni/CaO, GHSV = 3.6×10^4 mL g_{cat}^{-1} h^{-1}, and time = 120 min). 98

Figure 5.17 Effect of temperature towards the products formation rate at CGR of 1:1 for the 15%Ni/CaO (Reaction conditions: P_{gly} = 8.41 kPa, GHSV = 3.6×10^4 mL g_{cat}^{-1} h^{-1}, and time = 120 min). 99

Figure 5.18 Effect of temperature towards the rate of formation of products at CGR of 3:1 for the 5%Re-Ni/CaO (Reaction conditions: P_{gly} = 8.41 kPa, GHSV = 3.6×10^4mL g_{cat}^{-1} h^{-1}, and time = 120 min). 99

LIST OF SYMBOLS

°C	Degree Celsius
α	Weak sites
β	Intermediate sites
γ	Strong sites
Al_2O_3	Aluminium oxide
$BiOH_2$	Biological hydrogen
CaO	Calcium oxide
CeO	Cerium oxide
CH_3OK	Potassium methoxide
CH_3ONa	Sodium methoxide
Co	Cobalt
Cu	Copper
H_2SO_4	Sulphuric acid
KOH	Potassium hydroxide
La_2O_3	Lanthanum oxide
Na	Sodium
NaOH	Sodium hydroxide
Ni	Nickel
Pd	Palladium
Pt	Platinum
Re	Rhenium
Rh	Rhodium
SiO_2	Silicon dioxide
SBA 15	Mesoporous silica
T	Temperature
TiO_2	Titanium dioxide
Y_2O_3	Yttrium oxide
ZrO_2	Zirconium oxide

LIST OF ABBREVIATIONS

CGR	Carbon to glycerol feed ratio
CO	Carbon monoxide
CO_2	Carbon dioxide
EEA	European Environment Agency
EIA	Energy Information Administration
FESEM-EDX	Field emission scanning microscopy/energy dispersive
FFA	Free fatty acid
H/CO	Hydrogen to carbon monoxide ratio
H_2	Hydrogen
H_2O	Water
IEA	International Energy Agency
LH	Langmuir-Hinshelwood
SEM	Scanning electron microscopy
Syngas	Synthesis gas
TGA	Thermogravimetric analysis
TPO	Temperature programmed oxidation
WGFR	Water to glycerol feed ratio
WGS	Water gas shift reaction
GHSV	Gas hourly specific velocity
XRD	X-ray diffraction

GLYCEROL DRY REFORMING FOR HYDROGEN-RICH PRODUCTION OVER Ni/CaO, Ni/ZrO_2 and 5%Re-Ni/CaO

NUR NABILLAH BT MOHD ARIF

Thesis submitted in fulfillment of the requirements
for the award of the degree of
Master of Science

Faculty of Chemical Engineering and Natural Resources

UNIVERSITI MALAYSIA PAHANG

July 2017

ABSTRAK

Peningkatan jumlah pengeluaran biodiesel akan menyebabkan penghasilan gliserol berlebihan, dan dijangkakan sebanyak 3 mega ton gliserol mentah akan terhasil pada tahun 2020. Ini akan menyebabkan krisis lebihan bekalan yang seterusnya mempengaruhi harga pasaran bahan tersebut. Penukaran gliserol kepada gas sintetik melalui proses reformasi kering adalah salah satu alternatif potensi kepada krisis di samping dapat membantu mengatasi masalah alam sekitar yang berkait dengan pemebebasan gas rumah hijau. Kajian ini melaporkan tentang kemungkinan penggunaan gliserol pembaharuan kering dengan menggunakan beberapa jenis mangkin yang berbeza. Di dalam kajian ini, nikel disokong di atas dua jenis oksida iaitu kalsium dan zirkonium oksida dan seterusnya renium (Re) akan ditambah ke atas pemangkin yang terbaik melalui kaedah penjenjalan secara basah. Tindak balas ini dijalankan di dalam reaktor keluli tahan karat pada pelbagai suhu (600 °C$\leq$T$\leq$900 °C), nisbah karbon dioksida kepada gliserol (1, 3, 5) dan juga kadar berat kecepatan ruang (7.22×10^4<GHSV(mL $g_{cat}^{-1}s^{-1}$)<1.44×10^4). Pencirian dan analisis terhadap pemangkin baru dan pemangkin yang telah digunakan telah dilakukan melalui teknik *X-ray diffraction (XRD), Scanning electron microscopy (SEM), Nitrogen physisorption and Temperature programmed calcination (TPC), Temperature programmed oxidation (TPO)* dan *Field emission scanning microscopy/Energy dispersive X-ray (FESEM-EDX)*. Di dalam proses penyaringan pemangkin, komposisi oksida dan Re telah dimanipulasi dan tindak balas telah dijalankan pada kondisi yang sama iaitu pada suhu (700 °C), CGR (1) dan GHSV (3.6×10^4 mL g_{cat}^{-1} h^{-1}). Berdasarkan proses penyaringan pemangkin yang mempunyai oksida sahaja, 15%Ni/CaO telah menghasilkan saiz kristalit yang kecil yang membawa kepada penyebaran NiO secara serata dan seterusnya meninggikan luas permukaan pemangkin. 15%Ni/CaO juga memiliki kepekatan tapak beralkali tinggi yang membantu untuk menyekat pengendapan karbon. Di dalam kajian tindak balas, 15%Ni/CaO memperolehi penukaran gliserol dan penghasilan hydrogen tertinggi iaitu pada 32.33% dan 28.83%. Kemudian, pemangkin ini dipertingkatkan lagi dengan pertambahan 5%Re yang bertindak sebagai penggalak kepada pemangkin. Untuk pemangkin 5%Re-Ni/CaO, saiz kristalit yang dihasilkan adalah kecil dan berada dalam julat di antara 0.49 sehingga 0.90 nm. Ia merupakan faktor yang menyebabkan pengurangan permukaan pemangkin kerana halangan di dalam penyokong pemangkin. Pertambahan Re juga mempercepatkan pengurangan NiO kepada Ni disamping meningkatkan kepekatan tapak asid. Keadaan ini membantu meningkatkan aktiviti pemangkin untuk mencapai penukaran gliserol sehingga 44%. Daripada kajian tindak balas, penukaran gliserol tertinggi berlaku pada suhu 800 °C dengan CGR pada 1 untuk pemangkin tanpa Re dan CGR pada 3 untuk pemangkin dengan Re pada GHSV yang sama iaitu 3.6×10^4 mL g_{cat}^{-1} h^{-1}. Kajian tindak balas juga menunjukkan kebanyakan gas hidrogen dihasilkan melalui peguraian gliserol dan reaksi perpindahan air-gas. Pertambahan suhu dan GHSV melebihi titik optimum adalah tidak bermanfaat kerana menyebabkan pengendapan karbon yang banyak di atas permukaan pemangkin melalui proses hidrogenasi karbon dioksida (CO_2) dan metanasi. Kewujudan karbon berserabut pada telah dibuktikan pada analisis FESEM-EDX dan TPO.

ABSTRACT

Increase in biodiesel production has lead towards a glut production of glycerol where it is estimated that 3 megatons of crude glycerol will be produced by 2020. This leads towards oversupply crisis of glycerol and simultaneously influences its market price. Conversion of glycerol into hydrogen via dry reforming is a potential alternative to overcome this crisis which helps to overcome the environmental problems related with the greenhouse gases production. This work focused on the feasibility of glycerol dry reforming over a series of synthesised catalysts. In this work, nickel was supported with different oxides namely calcium oxide and zirconium oxide. The best oxide support was then promoted with rhenium via wet impregnation technique. The reaction was conducted in a stainless-steel fixed bed reactor at various temperatures of 600–900 °C, carbon dioxide to glycerol ratios of 1, 3, and 5, and gas-hourly space velocity (GHSV) of 7.20×10^4 to 1.44×10^4 mL g_{cat}^{-1} h^{-1}. The physichochemical characterisations of the catalysts were analysed using X-ray diffraction (XRD), scanning electron microscopy (SEM), nitrogen physisorption, temperature programmed calcination (TPC), temperature-programmed oxidation (TPO), and field emission scanning microscopy/energy dispersive X-ray analysis (FESEM-EDX). In the screening stage, the Ni/oxide support loadings were varied and carried out at a fixed reaction condition of T (700 °C), CGR (1), and GHSV (3.6×10^4 mL g_{cat}^{-1} h^{-1}). Based on the screening study, 15%Ni/CaO exhibited smaller crystallite size that leads to well dispersion of NiO and high catalysts specific surface area. In TPD-NH_3 analysis, 15%Ni/CaO possessed greater basic site concentration that helped in suppressing the carbon deposition. In the reaction study, this catalyst achieved 32.33% of glycerol conversion and 28.83% of hydrogen yield. After selecting the best catalyst support, the properties of the catalyst was enhanced with the addition of 5%Re as the catalyst promoter. For 5%Re-Ni/CaO catalyst, the crystallite size was found to be small within the range of 0.49 to 0.90 nm. This condition has significantly reduced the specific surface area of the catalyst due to the partial blockage of catalyst support. Besides that, Re promotion also helped to speed up the reduction of NiO to Ni and increased the acid site of catalyst. This condition has improved the catalytic activity of the promoted catalyst up to 44% of glycerol conversion. From the reaction study, the highest glycerol conversion and hydrogen yield were successfully achieved at the temperature of 800 °C and GHSV of 1.44×10^4 mL g_{cat}^{-1} h^{-1} with CGR of 1 for non-promoted catalyst and CGR of 3 for promoted catalyst. It is determined that hydrogen gas was majorly produced from glycerol decomposition and indirectly from water gas shift reaction. Increment of temperature and GHSV beyond the optimum point is not beneficial due to the CO_2 hydrogenation and methanation processes that built up of carbon deposition on the surface of catalyst. The formation of whisker carbon for both catalysts is proven in FESEM-EDX and TPO analysis.

REFERENCES

Adhikari, S., Fernando, S. D., & Haryanto, A. (2009). Hydrogen production from glycerol : An update. *Energy Conversion and Management*, *50*(10), 2600–2604.

Adhikari, S., Fernando, S., Gwaltney, S. R., Filip To, S. D., Mark Bricka, R., Steele, P. H., & Haryanto, A. (2007). A thermodynamic analysis of hydrogen production by steam reforming of glycerol. *International Journal of Hydrogen Energy*.

Afsharzade, N., Papzan, A., Ashjaee, M., Delangizan, S., Passel, S. Van, & Azadi, H. (2016). Renewable energy development in rural areas of Iran. *Renewable and Sustainable Energy Reviews*, *65*, 743–755.

Ahmad, a. L., Yasin, N. H. M., Derek, C. J. C., & Lim, J. K. (2011). Microalgae as a sustainable energy source for biodiesel production: A review. *Renewable and Sustainable Energy Reviews*, *15*(1), 584–593.

Ajanovic, A. (2008). On the economics of hydrogen from renewable energy sources as an alternative fuel in transport sector in Austria. *International Journal of Hydrogen Energy*, *33*(16), 4223–4234.

Akorede, M. F., Hizam, H., Ab Kadir, M. Z. A., Aris, I., & Buba, S. D. (2012). Mitigating the anthropogenic global warming in the electric power industry. *Renewable and Sustainable Energy Reviews*, *16*(5), 2747–2761.

Alipour, Z., Rezaei, M., & Meshkani, F. (2014). Effect of alkaline earth promoters (MgO, CaO, and BaO) on the activity and coke formation of Ni catalysts supported on nanocrystalline Al2O3 in dry reforming of methane. *Journal of Industrial and Engineering Chemistry*, *20*(5), 2858–2863.

Allan, D., & Davis, P. E. (2007). Refining Review- A Look behind the fence. *Oilfield Review*, 14–21.

Alvarez, J., Kumagai, S., Wu, C., Yoshioka, T., Bilbao, J., Olazar, M., & Williams, P. T. (2014). Hydrogen production from biomass and plastic mixtures by pyrolysis-gasification. *International Journal of Hydrogen Energy*, *39*(21), 10883–10891.

Anand, P., & Saxena, R. K. (2012). A comparative study of solvent-assisted pretreatment of biodiesel derived crude glycerol on growth and 1,3-propanediol production from Citrobacter freundii. *New Biotechnology*, *29*(2), 199–205.

Apak, S., Atay, E., & Tuncer, G. (2016). Renewable hydrogen energy and energy

efficiency in Turkey in the 21st century. *International Journal of Hydrogen Energy, Article in*, 1–7.

Asokan, P., Saxena, M., & Asolekar, S. R. (2005). Coal combustion residues - Environmental implications and recycling potentials. *Resources, Conservation and Recycling*, *43*(3), 239–262.

Auroux, A., Monaci, R., Rombi, E., Solinas, V., Sorrentino, A., & Santacesaria, E. (2001). Acid sites investigation of simple and mixed oxides by TPD and microcalorimetric techniques. *Thermochimica Acta*, *379*(1-2), 227–231.

Authayanun, S., Arpornwichanop, A., Paengjuntuek, W., & Assabumrungrat, S. (2010). Thermodynamic study of hydrogen production from crude glycerol autothermal reforming for fuel cell applications. *International Journal of Hydrogen Energy*, *35*(13), 6617–6623.

Ayodele, B. V, Safdar, S., Shiung, S., Osazuwa, O. U., Khan, M. R., & Kui, C. (2016). Journal of Natural Gas Science and Engineering Syngas production from CO 2 reforming of methane over neodymium sesquioxide supported cobalt catalyst. *Journal of Natural Gas Science and Engineering*, *34*, 873–885.

Bahari, M. B., Chin, B., Ji, T., Danh, H. T., Pham, T. L. M., Ainirazali, N., & Vo, D. N. (2016). Hydrogen-rich Syngas Production from Ethanol Dry Reforming on La-doped Ni / Al $_2O_3$ Catalysts : Effect of promoter loading. *Procedia Engineering*, *00*, 654–661.

Bahari, M. B., Phuc, N. H. H., Abdullah, B., Alenazey, F., & Vo, D. V. N. (2015). Ethanol dry reforming for syngas production over Ce-promoted Ni/Al_2O_3 catalyst. *Journal of Environmental Chemical Engineering*, (2015), 1–9.

Balat, M. (2009). Global Status of Biomass Energy Use. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, *31*(13), 1160–1173.

Bartholomew, C. H. (2001). Mechanisms of catalyst deactivation. *Applied Catalysis A: General*, *212*(1-2), 17–60.

Basri, N. A., Ramli, A. T., & Aliyu, A. S. (2015). Malaysia energy strategy towards sustainability: A panoramic overview of the benefits and challenges. *Renewable and Sustainable Energy Reviews*, *42*, 1094–1105.

Boerrigter, H., & Rauch, R. (2006). Review of applications of gases from biomass gasification. *ECN Biomass, Coal and Environmental …*, (June), 33.

Brutschin, E., & Fleig, A. (2016). Innovation in the energy sector -The role of fossil fuels and developing economies. *Energy Policy*, *97*, 27–38.

Buffoni, I. N., Pompeo, F., Santori, G. F., & Nichio, N. N. (2009). Nickel catalysts applied in steam reforming of glycerol for hydrogen production. *Catalysis Communications*, *10*(13), 1656–1660.

Bujang, a. S., Bern, C. J., & Brumm, T. J. (2016). Summary of energy demand and renewable energy policies in Malaysia. *Renewable and Sustainable Energy Reviews*, *53*, 1459–1467.

Chemia I Inżynieria Ekologiczna S. (2011). Ecological Chemistry and Engineering. *Society of Ecological Chemistry and Engineering*, *18*(6), 1–132.

Chen, Y., Yu, J., & Kelly, P. (2014). Does the China factor matter: What drives the surge of world crude oil prices? *The Social Science Journal*, *53*(1), 1–12.

Chong, C., Ni, W., Ma, L., Liu, P., & Li, Z. (2015). The use of energy in Malaysia: Tracing energy flows from primary source to end use. *Energies*, *8*(4), 2828–2866.

Ciftci, A., Ligthart, D. a J. M., Sen, a. O., Van Hoof, A. J. F., Friedrich, H., & Hensen, E. J. M. (2014). Pt-Re synergy in aqueous-phase reforming of glycerol and the water-gas shift reaction. *Journal of Catalysis*, *311*, 88–101.

Clomburg, J. M., & Gonzalez, R. (2013). Anaerobic fermentation of glycerol: A platform for renewable fuels and chemicals. *Trends in Biotechnology*, *31*(1), 20–28.

Cook, K. M., Perez, H. D., Bartholomew, C. H., & Hecker, W. C. (2014). Effect of promoter deposition order on platinum-, ruthenium-, or rhenium-promoted cobalt Fischer-Tropsch catalysts. *Applied Catalysis A: General*, *482*, 275–286.

da Silva Veras, T., Mozer, T. S., Da Costa, D., Messeder, R., Santos, D., Da, A., & Esar, S. C. (2016). Hydrogen: Trends, production and characterization of the main process worldwide, 1–16.

da Silveira, V. R., Melo, D. M. A., Barros, B. S., Ruiz, J. A. C., & Rojas, L. O. A. (2016). Nickel-based catalyst derived from NiO–$Ce_{0.75}Zr_{0.25}O_2$ nanocrystalline composite: Effect of the synthetic route on the partial oxidation of methane. *Ceramics International*, *42*(14), 16084–16089.

Das, T. K., Jacobs, G., Patterson, P. M., Conner, W. A., Li, J., & Davis, B. H. (2003).

Fischer-Tropsch synthesis: Characterization and catalytic properties of rhenium promoted cobalt alumina catalysts. *Fuel*, *82*(7), 805–815.

Dave, C. D., & Pant, K. K. (2011). Renewable hydrogen generation by steam reforming of glycerol over zirconia promoted ceria supported catalyst. *Renewable Energy*, *36*(11), 3195–3202.

Demirbas. (2008). Comparison of transesterification methods for production of biodiesel from vegetable oils and fats. *Energy Conversion and Management*, *49*(1), 125–130.

Demirbas, A. (2009). Progress and recent trends in biodiesel fuels. *Energy Conversion and Management*, *50*(1), 14–34.

Demirbas, T., & Demirbas, a. H. (2010). Bioenergy, Green Energy. Biomass and Biofuels. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, *32*(12), 1067–1075.

Dias, J. A. C., & Assaf, J. M. (2003). Influence of calcium content in Ni/CaO/γ-Al_2O_3 catalysts for CO2-reforming of methane. *Catalysis Today*, *85*(1), 59–68.

dos Santos, K. G., Eckert, C. T., De Rossi, E., Bariccatti, R. A., Frigo, E. P., Lindino, C. A., & Alves, H. J. (2017). Hydrogen production in the electrolysis of water in Brazil, a review. *Renewable and Sustainable Energy Reviews*, *68*(October 2016), 563–571.

Ebshish, A., Yaakob, Z., Narayanan, B., & Bshish, A. (2011). The Activity of Ni-Based Catalysts on Steam Reforming of Glycerol for Hydrogen Production. *Internation Journal of Integrated Engineering*, *3*(1), 5–8.

Ebshish, A., Yaakob, Z., Narayanan, B., Bshish, A., & Wan Daud, W. R. (2012). Steam reforming of glycerol over Ni supported alumina xerogel for hydrogen production. *Energy Procedia*, *18*, 552–559.

Estellé, J. (2003). Comparative study of the morphology and surface properties of nickel oxide prepared from different precursors. *Solid State Ionics*, *156*(1-2), 233–243.

Estellé, J., Salagre, P., Cesteros, Y., Serra, M., Medina, F., & Sueiras, J. E. (2003). Comparative study of the morphology and surface properties of nickel oxide prepared from different precursors. *Solid State Ionics*, *156*(1-2), 233–243.

Fan, X., Burton, R., & Zhou, Y. (2010). Glycerol (Byproduct of Biodiesel Production) as a Source for Fuels and Chemicals - Mini Review. *The Open Fuels & Energy Science Journal*, *3*, 17–22.

Fernandez, Y., Arenillas, A., Bermudez, J. M., & Menendez, J. a. (2010). Comparative study of conventional and microwave-assisted pyrolysis, steam and dry reforming of glycerol for syngas production, using a carbonaceous catalyst. *Journal of Analytical and Applied Pyrolysis*, *88*(2), 155–159.

Fernández, Y., Arenillas, A., Díez, M. A., Pis, J. J., & Menéndez, J. A. (2009). Pyrolysis of glycerol over activated carbons for syngas production. *Journal of Analytical and Applied Pyrolysis*, *84*(2), 145–150.

Fernández, Y., & Menéndez, J. A. (2011). Influence of feed characteristics on the microwave-assisted pyrolysis used to produce syngas from biomass wastes. *Journal of Analytical and Applied Pyrolysis*, *91*(2), 316–322.

Foo, K. Y. (2015). A vision on the opportunities, policies and coping strategies for the energy security and green energy development in Malaysia. *Renewable and Sustainable Energy Reviews*, *51*, 1477–1498.

Fukuda, H., Kondo, A., & Noda, H. (2001). Biodiesel fuel production by transesterification of oils. *Journal of Bioscience and Bioengineering*, *92*(5), 405–416.

Gallo, A., Pirovano, C., Ferrini, P., Marelli, M., Psaro, R., Santangelo, S., Faggio, G., & Dal Santo, V. (2012). Influence of reaction parameters on the activity of ruthenium based catalysts for glycerol steam reforming. *Applied Catalysis B: Environmental*, *121-122*, 40–49.

Göransson, K., Söderlind, U., He, J., & Zhang, W. (2011). Review of syngas production via biomass DFBGs. *Renewable and Sustainable Energy Reviews*, *15*(1), 482–492.

Goula, M. A., Lemonidou, A. A., & Efstathiou, A. M. (1996). Characterization of Carbonaceous Species Formed during Reforming of CH_4 with CO_2 over Ni/CaO–Al_2O_3 Catalysts Studied by Various Transient Techniques. *Journal of Catalysis*, *161*(2), 626–640.

Guo, P., Wang, T., Li, D., & Zhou, X. (2016). How energy technology innovation affects transition of coal resource-based economy in China. *Energy Policy*, *92*, 1–6.

He, Q. (Sophia), McNutt, J., & Yang, J. (2017). Utilization of the residual glycerol from biodiesel production for renewable energy generation. *Renewable and Sustainable Energy Reviews*, *71*, 63–76.

Hirai, T., Ikenaga, N. O., Miyake, T., & Suzuki, T. (2005). Production of hydrogen by steam reforming of glycerin on ruthenium catalyst. *Energy and Fuels*, *19*(4), 1761–1762.

Holladay, J. D., Hu, J., King, D. L., & Wang, Y. (2009). An overview of hydrogen production technologies. *Catalysis Today*, *139*(4), 244–260.

Hu, D., Gao, J., Ping, Y., Jia, L., Gunawan, P., Zhong, Z., Xu, G., Gu, F., & Su, F. (2012). Enhanced Investigation of CO Methanation over Ni/Al_2O_3 Catalysts for Synthetic Natural Gas Production. *Industrial & Engineering Chemistry Research*, *51*(13), 4875–4886.

Huang, Z. Y., Xu, C. H., Meng, J., Zheng, C. F., Xiao, H. W., Chen, J., & Zhang, Y. X. (2014). Glycerol steam reforming to syngas over Ni-based catalysts on commercial Linde-type 5A zeolite modified by metal oxides. *Journal of Environmental Chemical Engineering*, *2*(1), 598–604.

International Energy Agency (IEA). (2015). CO_2 Emissions From Fuel Combustion-Highlights. Retrieved from https://www.iea.org/publications/freepublications/publication/CO2EmissionsFromFuelCombustionHighlights2015.pdf *Iea*, *S/V*(IEA - STATISTICS), 1–139.

International Energy Agency (IEA). (2016). *Key Coal Trends*. Retrieved from https://www.iea.org/publications/freepublications/publication/coal-information---2016-edition---excerpt---key-coal-trends.html.

International Energy Agency. (2006). Hydrogen Production and Storage. R&D Priorities and Gaps. *Hydrogen Implementing Agreement*, *13*, 392–392.

Iriondo, A., Barrio, V. L., Cambra, J. F., Arias, P. L., Güemez, M. B., Navarro, R. M., Sánchez- Sánchez, M. C., & Fierro, J. L. G. (2008). Hydrogen production from glycerol over nickel catalysts supported on Al_2O_3 modified by Mg, Zr, Ce or La. *Topics in Catalysis*, *49*(1-2), 46–58.

Jacobs, G., Das, T. K., Zhang, Y., Li, J., Racoillet, G., & Davis, B. H. (2002). Fischer-Tropsch synthesis: Support, loading, and promoter effects on the reducibility of cobalt catalysts. *Applied Catalysis A: General*, *233*(1-2), 263–281.

Kalamaras, C. M., & Efstathiou, a. M. (2013). Hydrogen Production Technologies: Current State and Future Developments. *Conference Papers in Energy*, *2013*, 9.

Karemore, A. L., Vaidya, P. D., & Sinha, R. (2016). On the dry and mixed reforming of methane over Ni / Al_2O_3- Influence of reaction variables on syngas production. *International Journal of Hydrogen Energy*, 1–13.

Kunkes, E. L., Simonetti, D. A., Dumesic, J. A., Pyrz, W. D., Murillo, L. E., Chen, J. G., & Buttrey, D. J. (2008). The role of rhenium in the conversion of glycerol to synthesis gas over carbon supported platinum – rhenium catalysts. *Journal of Catalysis*, *260*(1), 164–177.

Larimi, A. S., Kazemeini, M., & Khorasheh, F. (2016). Highly selective doped PtMgO nano-sheets for renewable hydrogen production from APR of glycerol. *International Journal of Hydrogen Energy*, *41*(39), 17390–17398.

Lean, H. H., & Smyth, R. (2014). Disaggregated energy demand by fuel type and economic growth in Malaysia. *Applied Energy*, *132*, 168–177.

Lee, H. C., Siew, K. W., Gimbun, J., & Cheng, C. K. (2013). Application of cement clinker as Ni-catalyst support for glycerol dry reforming. *Bulletin of Chemical Reaction Engineering and Catalysis*, *8*(2), 137–144.

Lee, H. C., Siew, K. W., Gimbun, J., & Cheng, C. K. (2014). Synthesis and characterisation of cement clinker-supported nickel catalyst for glycerol dry reforming. *Chemical Engineering Journal*, *255*, 245–256.

Lee, O. K., & Lee, E. Y. (2016). Sustainable production of bioethanol from renewable brown algae biomass. *Biomass and Bioenergy*, *92*, 70–75.

Leung, D. Y. C., Wu, X., & Leung, M. K. H. (2010). A review on biodiesel production using catalyzed transesterification. *Applied Energy*, *87*(4), 1083–1095.

Li, J., Jacobs, G., Zhang, Y., Das, T., & Davis, B. H. (2002). Fischer-Tropsch synthesis: Effect of small amounts of boron, ruthenium and rhenium on Co/TiO2 catalysts. *Applied Catalysis A: General*, *223*(1-2), 195–203.

Lin, Y. C. (2013). Catalytic valorization of glycerol to hydrogen and syngas. *International Journal of Hydrogen Energy*, *38*(6), 2678–2700.

Lisboa, S., Santos, D. C. R. M., Passos, F. B., & Noronha, F. B. (2005). Influence of the addition of promoters to steam reforming catalysts, *101*, 15–21.

Liu, S. K., & Lin, Y. C. (2014). Generation of syngas through autothermal partial oxidation of glycerol over $LaMnO_3$- and $LaNiO_3$-coated monoliths. *Catalysis Today*, *237*, 62–70.

Liu, S., Xu, L., Xie, S., Wang, Q., & Xiong, G. (2001). Partial oxidation of propane to syngas over nickel supported catalysts modified by alkali metal oxides and rare-earth metal oxides, *211*, 145–152.

Luo, N., Fu, X., Cao, F., Xiao, T., & Edwards, P. P. (2008). Glycerol aqueous phase reforming for hydrogen generation over Pt catalyst - Effect of catalyst composition and reaction conditions. *Fuel*, *87*(17-18), 3483–3489.

Mackaluso, J. D., & Mackaluso, J. D. (2007). The use of syngas derived from biomass and waste products to produce ethanol and hydrogen. *MMG 445 Basic Biotechnology eJournal*, *3*, 98–103.

Majewski, A. J., Wood, J., & Bujalski, W. (2013). Nickel-silica core@shell catalyst for methane reforming. *International Journal of Hydrogen Energy*, *38*(34), 14531–14541.

Marchetti, J. M., Miguel, V. U., & Errazu, a. F. (2007). Possible methods for biodiesel production. *Renewable and Sustainable Energy Reviews*, *11*(6), 1300–1311.

Martín, M., & Grossmann, I. E. (2014). Optimal simultaneous production of hydrogen and liquid fuels from glycerol: Integrating the use of biodiesel byproducts. *Industrial and Engineering Chemistry Research*, *53*(18), 7730–7745.

Marx, S. (2016). Glycerol-free biodiesel production through transesterification: A review. *Fuel Processing Technology*, *151*, 139–147.

Meshkani, F., & Rezaei, M. (2011). Ni catalysts supported on nanocrystalline magnesium oxide for syngas production by CO_2 reforming of CH4. *Journal of Natural Gas Chemistry*, *20*(2), 198–203.

Mohammadi, M., Najafpour, G. D., Younesi, H., Lahijani, P., Uzir, M. H., & Mohamed, A. R. (2011). Bioconversion of synthesis gas to second generation biofuels: A review. *Renewable and Sustainable Energy Reviews*, *15*(9), 4255–4273.

Montzka, S. A., Dlugokencky, E. J., & Butler, J. H. (2011). Non-CO_2 greenhouse gases and climate change. *Nature*, *476*(7358), 43–50.

Moralesa, T. C., Olivab, V. R., & Velázquezc, L. F. (2014). Hydrogen from renewable energy in Cuba. *Energy Procedia*, *57*, 867–876.

Nagarajan, D., Lee, D.-J., Kondo, A., & Chang, J.-S. (2017). Recent insights into biohydrogen production by microalgae – From biophotolysis to dark fermentation. *Bioresource Technology*, *227*(1), 373–387.

Nasir, M., Shahirah, N., Ayodele, B. V, Gimbun, J., Lam, S. S., & Cheng, K. (2016). Renewable Syngas Production from Thermal Cracking of Glycerol over Praseodymium-Promoted Ni/Al_2O_3 Catalyst. *Applied Thermal Engineering*.

Nor Shahirah, M. N., Abdullah, S., Gimbun, J., Ng, Y. H., & Cheng, C. K. (2016). A study on the kinetics of syngas production from glycerol over alumina-supported samarium-nickel catalyst. *International Journal of Hydrogen Energy*, *41*(25), 10568–10577.

Ong, C. H., Chan, H. J., & Cheng, C. K. (2015). Synthesis and characterisation of La-Co/MgO catalyst for methane dry reforming. *Journal of Engineering Science and Technology*, *10*(Spec.issue3), 79–89.

Ordin, P. M. (1997). Safety standard for hydgogen and hydrogen systems. Guidelines for Hydrogen System Design, Materials Selection, Operations, Storage, and Transportation. *National Aeronautics and Space Administration*, 1–389.

Pairojpiriyakul, T., Croiset, E., Kiatkittipong, K., Kiatkittipong, W., Arpornwichanop, A., & Assabumrungrat, S. (2014). Catalytic reforming of glycerol in supercritical water with nickel-based catalysts. *International Journal of Hydrogen Energy*, *39*(27), 14739–14750.

Peres, A. P. G., Silva, N. de L. da, Maciel, M. R. W., & Filho, R. M. (2011). Syngas Production from Crude Glycerol Using Pyrolysis. *Journal. of Chemistry. & Chemical. Engineering.*, *5*, 141–145.

Phromprasit, J., Powell, J., Wongsakulphasatch, S., Kiatkittipong, W., Bumroongsakulsawat, P., & Assabumrungrat, S. (2016). Activity and stability performance of multifunctional catalyst (Ni/CaO and Ni/$Ca_{12}Al_{14}O_{33}$-CaO) for bio-hydrogen production from sorption enhanced biogas steam reforming. *International Journal of Hydrogen Energy*, *41*(18), 7318–7331.

Pompeo, F., Nichio, N. N., Souza, M. M. V. M., Cesar, D. V., Ferretti, O. A., & Schmal, M. (2007). Study of Ni and Pt catalysts supported on α-Al_2O_3 and ZrO_2 applied in methane reforming with CO_2. *Applied Catalysis A: General*, *316*(2), 175–183.

Profeti, L. P. R., Dias, J. A. C., Assaf, J. M., & Assaf, E. M. (2009). Hydrogen production by steam reforming of ethanol over Ni-based catalysts promoted with noble metals. *Journal of Power Sources*, *190*(2), 525–533.

Quincoces, C. E., Dicundo, S., Alvarez, A. M., & González, M. G. (2001). Effect of addition of CaO on Ni/Al_2O_3 catalysts over CO_2 reforming of methane. *Materials Letters*, *50*(1), 21–27.

Ramachandran & Menon. (1998). An overview of industrial uses of hydrogen. *International Journal of Hydrogen Energy*, *23*(7), 593–598.

Rezaei, M., Alavi, S. M., Sahebdelfar, S., Xinmei, L., & Qian, L. (2007). CO 2 -CH 4 Reforming over Nickel Catalysts Supported on Mesoporous Nanocrystalline Zirconia with High Surface Area. *Energy*, *81*(14), 581–589.

Ritter, J. a, & Ebner, a D. (2006). Overview of hydrogen production technologies. *2006 AIChE Spring Annual Meeting*, *49*, 481–482. Retrieved from http://www.scopus.com/inward/record.url?eid=2-s2.0-56549095649&partnerID=40&md5=760328e978795963e958f1681391d7a3

Robinson, a. B., Robinson, N. E., & Soon, W. (2007). Environmental effects of increased atmospheric carbon dioxide. *Journal of American Physicians and Surgeons*, *12*(7), 79–90.

Rosen, B. a., Gileadi, E., & Eliaz, N. (2016). Electrodeposited Re-promoted Ni foams as a catalyst for the dry reforming of methane. *Catalysis Communications*, *76*, 23–28.

Saad, J. M., Nahil, M. A., & Williams, P. T. (2014). Influence of process conditions on syngas production from the thermal processing of waste high density polyethylene. *Journal of Analytical and Applied Pyrolysis*, *138*, 156–163.

Sadanandam, G., Sreelatha, N., Sharma, M. V. P., Reddy, S. K., Srinivas, B., Venkateswarlu, K., Krishnudu, T., Subrahmanyam, M., & Kumari, V. D. (2012). Steam Reforming of Glycerol for Hydrogen Production over Ni/SiO_2 Catalyst. *ISRN Chemical Engineering*, *2012*, 1–10.

Samiran, N. A., Jaafar, M. N. M., Ng, J. H., Lam, S. S., & Chong, C. T. (2016). Progress in biomass gasification technique - With focus on Malaysian palm biomass for syngas production. *Renewable and Sustainable Energy Reviews*, *62*, 1047–1062.

Sanchez, E. A., & Comelli, R. A. (2014). Hydrogen production by glycerol steam-reforming over nickel and nickel-cobalt impregnated on alumina. *International Journal of Hydrogen Energy*, *39*(16), 8650–8655.

Saraswat, S. K., & Pant, K. K. (2012). Thermo Catalytic Decomposition of Methane – A Novel Approach to Cox Free Hydrogen and Carbon Nanotubes Production over Ni / SiO_2 Catalyst, *1*(2), 2–6.

Seung-Hoon, K., Jae Sun, J., Eun Hyeok, Y., Kwan Young, L., & Dong Ju, M. (2014). Hydrogen production by steam reforming of biomass-derived glycerol over Ni-based catalysts. *Catalysis Today*, *228*, 145–151.

Shakeri, J., Hadadzadeh, H., & Tavakol, H. (2014). Photocatalytic reduction of CO_2 to CO by a dinuclear carbonyl polypyridyl rhenium(I) complex. *Polyhedron*, *78*, 112–122.

Shamsuddin, A. H. (2012). Development of Renewable Energy in Malaysia-Strategic Initiatives for Carbon Reduction in the Power Generation Sector. *Procedia Engineering*, *49*(0), 384–391.

Shao, S., Shi, A. W., Liu, C. L., Yang, R. Z., & Dong, W. S. (2014). Hydrogen production from steam reforming of glycerol over Ni/CeZrO catalysts. *Fuel Processing Technology*, *125*, 1–7.

Sharma, Y. C., & Singh, B. (2009). Development of biodiesel: Current scenario. *Renewable and Sustainable Energy Reviews*, *13*(6-7), 1646–1651.

Siew, K. W., Lee, H. C., Gimbun, J., & Cheng, C. K. (2013). Hydrogen production via glycerol dry reforming over La-Ni/Al_2O_3 catalyst. *Bulletin of Chemical Reaction Engineering and Catalysis*, *8*(2), 160–166.

Siew, K. W., Lee, H. C., Gimbun, J., & Cheng, C. K. (2014). Production of CO-rich hydrogen gas from glycerol dry reforming over La-promoted Ni/Al_2O_3 catalyst. *International Journal of Hydrogen Energy*, *39*(13), 6927–6936.

Singh, S. P., & Singh, D. (2010). Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review. *Renewable and Sustainable Energy Reviews*, *14*(1), 200–216.

Slinn, M., Kendall, K., Mallon, C., & Andrews, J. (2008). Steam reforming of biodiesel by-product to make renewable hydrogen. *Bioresource Technology*, *99*(13), 5851–5858.

Solarin, S. A., & Shahbaz, M. (2015). Natural gas consumption and economic growth: The role of foreign direct investment, capital formation and trade openness in Malaysia. *Renewable and Sustainable Energy Reviews*, *42*, 835–845.

Souza, G. de, Marcilio, N. R., & Perez-Lopez, O. W. (2014). Dry reforming of methane at moderate temperatures over modified Co-Al Co-precipitated catalysts. *Materials Research*, *17*(4), 1047–1055.

Sriram, N., & Shahidehpour, M. (2005). Renewable biomass energy. *IEEE Power Engineering Society General Meeting, 2005*, 1–6.

Srivastava, N., Rawat, R., Singh Oberoi, H., & Ramteke, P. W. (2014). A Review on Fuel Ethanol Production From Lignocellulosic Biomass. *International Journal of Green Energy*, *12*(9), 949–960.

Suffredini, D. F. P., Thyssen, V. V., de Almeida, P. M. M., Gomes, R. S., Borges, M. C., Duarte de Farias, A. M., Assaf E. M., Fraga, A. M., & =Brandão, S. T. (2016). Renewable hydrogen from glycerol reforming over nickel aluminate-based catalysts. *Catalysis Today*.

Takeda, H., Koike, K., Inoue, H., & Ishitani, O. (2008). Development of an Efficient Photocatalytic System for CO_2 Reduction Using Rhenium(I) Complexes Based on Mechanistic Studies. *Journal of the American Chemical Society*, *130*(6), 2023–2031.

Tang, S. B., Qiu, F. L., & Lu, S. J. (1995). Effect of supports on the carbon deposition of nickel catalysts for methane reforming with CO_2. *Catalysis Today*, *24*(3), 253–255.

Tang, S., Lin, J., & Tan, K. L. (1998). Partial oxidation of methane to syngas over Ni/MgO, Ni/CaO and Ni/CeO_2. *Catalysis Let*, *51*, 169–175.

Taufiq-Yap, Y. H., Sivasangar, S., & Salmiaton, A. (2012). Enhancement of hydrogen production by secondary metal oxide dopants on NiO/CaO material for catalytic gasification of empty palm fruit bunches. *Energy*, *47*(1), 158–165.

Therdthianwong, S., Therdthianwong, A., Siangchin, C., & Yongprapat, S. (2008). Synthesis gas production from dry reforming of methane over Ni/Al_2O_3 stabilized by ZrO_2. *International Journal of Hydrogen Energy*, *33*, 991–999.

Viswanadham, N., Kamble, R., Sharma, A., Kumar, M., & Saxena, a. K. (2008). Effect of Re on product yields and deactivation patterns of naphtha reforming catalyst. *Journal of Molecular Catalysis A: Chemical*, *282*(1-2), 74–79.

Wang, D., Czernik, S., & Chornet, E. (1998). Production of hydrogen from biomass by catalytic steam reforming of fast pyrolysis oils. *Fuel and Energy Abstracts*, *39*(3), 188.

Wang, H., Wang, X., Li, M., Li, S., Wang, S., & Ma, X. (2009). Thermodynamic analysis of hydrogen production from glycerol autothermal reforming. *International Journal of Hydrogen Energy*, *34*(14), 5683–5690.

Wang, W. (2010). Thermodynamic analysis of glycerol partial oxidation for hydrogen production. *Fuel Processing Technology*, *91*(11), 1401–1408.

Wei, J.-M., Xu, B., Li, J.-L., Cheng, Z.-X., & Zhu, Q. (2000). Highly Active and Stable Ni/ZrO_2 Catalyst for Syngas Production by CO_2 Reforming of Methane. *Applied Catalysis A: General*, *196*(2), L167–L172.

Wurzler, G. T., Rabelo-Neto, R. C., Mattos, L. V., Fraga, M. A., & Noronha, F. B. (2016). Steam reforming of ethanol for hydrogen production over MgO - Supported Ni-based catalysts. *Applied Catalysis A: General*, *518*, 115–128.

Yang, F., Hanna, M. a, & Sun, R. (2012). Value-added uses for crude glycerol-a byproduct of biodiesel production. *Biotechnology for Biofuels*, *5*(1), 13.

Yang, X., Wang, X., Gao, G., Wendurima, Liu, E., Shi, Q., Zhang, J., Han, C., Wang, J., Lu, H., Liu, J., & Tong, M. (2013). Nickel on a macro-mesoporous $Al_2O_3@ZrO_2$ core/ shell nanocomposite as a novel catalyst for CO methanation. *International Journal of Hydrogen Energy*, *38*(32), 13926–13937.

Yang, Y., Solgaard, H. S., & Haider, W. (2016). Wind, hydro or mixed renewable energy source: Preference for electricity products when the share of renewable energy increases. *Energy Policy*, *97*, 521–531.

Yu, S., Zhang, J., & Cheng, J. (2016). Carbon reduction cost estimating of Chinese coal-fired power generation units: A perspective from national energy consumption standard. *Journal of Cleaner Production*, *139*, 612–621.

Zabed, H., Sahu, J. N., Boyce, A. N., & Faruq, G. (2016). Fuel ethanol production from lignocellulosic biomass: An overview on feedstocks and technological approaches. *Renewable and Sustainable Energy Reviews*, *66*, 751–774.

Zain-Ahmed, A. (2008). Renewable energy, buildings and the fuel crisis. *International Conference on Construction and Building Technology*, (02), 13–24. Retrieved from http://www.uniten.edu.my/newhome/uploaded/coe/iccbt/iccbt 2008/conference f extract/UNITEN ICCBT 08 Renewable Energy, Buildings and the Fuel Crisis.pdf

Zangouei, M., Moghaddam, A. Z., & Arasteh, M. (2010). The influence of nickel loading on reducibility of NiO/Al2O3 catalysts synthesized by sol-gel method. *Chemical Engineering Research Bulletin*, *14*(2), 97–102.

Zhang, B., Tang, X., Li, Y., Xu, Y., & Shen, W. (2007). Hydrogen production from steam reforming of ethanol and glycerol over ceria-supported metal catalysts. *International Journal of Hydrogen Energy*, *32*(13), 2367–2373.

Zhang, Y., Xiong, G., Sheng, S., & Yang, W. (2000). Deactivation studies over NiO/γ-Al_2O_3 catalysts for partial oxidation of methane to syngas. *Catalysis Today*, *63*(2-4), 517–522.

Zhu, J., Peng, X., Yao, L., Shen, J., Tong, D., & Hu, C. (2011). The promoting effect of La , Mg , Co and Zn on the activity and stability of Ni / SiO_2 catalyst for CO_2 reforming of methane. *International Journal of Hydrogen Energy*, *36*(12), 7094–7104.