

STEAM REFORMING OF GASIFIED BIOMASS TAR FOR HYDROGEN
PRODUCTION OVER NICKEL–DOLOMITE BASED CATALYST

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DEDICATION

This thesis is wholeheartedly dedicated to my beloved parents for their unconditional love, endless support and encouragement during the challenges of my graduate school and life.

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ABSTRACT

Catalytic steam reforming is a promising approach to address tar formation and improve hydrogen (H₂) production from biomass gasification. In this research, multi-compound tar model (phenol, toluene, naphthalene, and pyrene) was steam reformed for H₂ production over various types of 10 wt.% dolomite promoted 10 wt.% nickel based catalysts supported on alumina, lanthana, ceria, and zirconia. The research aims to synthesize nickel-dolomite catalyst for steam reforming of gasified biomass tar for optimum H₂ production. The catalysts were characterized by thermogravimetric analysis, temperature programmed reduction, temperature programmed desorption, nitrogen physisorption, and X-ray diffraction. The results showed that the addition of dolomite promoter to the catalysts strengthened the metal-support interaction and basicity of the catalyst. Steam reforming for catalyst screening was carried out at 700 °C with steam to carbon (S/C) molar ratio of 1 and gas hourly space velocity (GHSV) of 20,453 mL/h g_{cat}. The Ni/dolomite/La₂O₃ (NiDLa) catalyst displayed mesoporous structure, high reducibility, and basicity, which lead to superior carbon conversion to gas (77.66 mol%) and H₂ yield (66.20 mol%). In addition, spent NiDLa exhibited the lowest amount of filamentous coke (110 mg/g_{cat}) formation after 5 hours of reaction compared to the other catalysts investigated. Findings on effect of reaction condition revealed that higher temperature (> 750 °C), S/C ratio that is close to the stoichiometric value (1), and moderate GHSV (12,000 – 18,000 h⁻¹) can improve carbon conversion to gas and H₂ yield. The optimum conditions were found to be 775 °C of temperature, 1.02 of S/C molar ratio, and 14,648 h⁻¹ of GHSV which resulted in 99.94 mol% of carbon conversion to gas and 82.84 mol% of H₂ yield. This finding is close to the predicted 98.96 mol% of carbon conversion to gas and 82.00 mol% of H₂ yield by response surface method.

ABSTRAK

Pembentukan semula stim bermangkin merupakan kaedah yang berpotensi untuk menangani pembentukan tar dan meningkatkan penghasilan hidrogen (H_2) daripada penggasan biojisim. Dalam kajian ini, model tar pelbagai sebatian (fenol, toluena, naftalena, dan pirena) telah digunakan untuk penghasilan H_2 melalui pembentukan semula stim dengan menggunakan pelbagai jenis 10 % berat nikel berasaskan mangkin yang digalakkan dengan 10 % berat dolomit di sokong alumina, lanthana, ceria, dan zirkonia. Kajian ini bertujuan untuk mensintesis mangkin nikel-dolomit untuk pembentukan semula stim biojisim tar dan bergas bagi penghasilan H_2 yang optimum. Mangkin-mangkin dicirikan menggunakan analisis termogravimetrik, pengurangan pengaturcaraan suhu, nyaherapan pengaturcaraan suhu, pejerapan fizikal nitrogen, dan pembelaun sinar-X. Keputusan menunjukkan bahawa penambahan penggalak dolomit kepada mangkin memperkuat interaksi logam-sokongan dan meningkatkan sifat beralkali mangkin. Penapisan mangkin dijalankan melalui pembentukan semula stim pada suhu $700\text{ }^\circ\text{C}$, nisbah molar stim kepada karbon (S/C) 1, dan halaju ruang gas setiap jam (GHSV) $20,453\text{ mL/h g}_{\text{cat}}$. Mangkin Ni/dolomit/ La_2O_3 (NiDLa) mempunyai struktur mesoporous, kebolehturunan tinggi dan sifat beralkali tinggi menyebabkan penukaran karbon ke gas (77.66 mol%) dan hasil H_2 (66.20 mol%) yang unggul. Tambahan pula, mangkin NiDLa menyebabkan pembentukan filamen karbon kok yang paling rendah (110 mg/ g_{cat}) selepas 5-jam tindakbalas berbanding dengan mangkin lain yang kaji. Dapatan kajian kesan keadaan tindakbalas menunjukkan bahawa suhu yang tinggi ($> 750\text{ }^\circ\text{C}$), nisbah S/C yang hampir dengan nilai stoikiometri (1), dan GHSV yang sederhana ($12,000 - 18,000\text{ h}^{-1}$) bermanfaat untuk penukaran karbon kepada gas dan hasil H_2 . Keadaan optimum didapati pada suhu $775\text{ }^\circ\text{C}$, nisbah molar S/C 1.02, dan GHSV $14,648\text{ h}^{-1}$ yang menghasilkan 99.94 mol% penukaran karbon ke gas dan 82.84 mol% hasil H_2 . Dapatan ini menghampiri keputusan yang diramalkan oleh kaedah permukaan sambutan iaitu 98.96 mol% penukaran karbon ke gas dan 82.00 mol% hasil H_2 .

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LIST OF ABBREVIATIONS

Al_2O_3	-	Alumina
ANOVA	-	Analysis of variance
ATR	-	Autothermal reforming
Au	-	Gold
BBD	-	Box-Behnken design
BET	-	Brunauer Emmett Teller
BJH	-	Barret-Joyner-Halenda
CaO	-	Calcium oxide
$\text{CaMg}(\text{CO}_3)_2$	-	Dolomite
CaO/MgO	-	Calcined state of dolomite
Ce	-	Cerium
CeO_2	-	Ceria
CH_4	-	Methane
CO	-	Carbon monoxide
Co	-	Cobalt
CO_2	-	Carbon dioxide
CO_2 -TPD	-	Temperature programmed desorption of carbon dioxide
Cu	-	Copper
CuO	-	Copper oxide
$\text{C}_4\text{H}_6\text{NiO}_4$	-	Nickel acetate
$\text{C}_6\text{H}_6\text{O}$	-	Phenol
C_7H_8	-	Toluene
C_{10}H_8	-	Naphthalene
$\text{C}_{16}\text{H}_{10}$	-	Pyrene
DOE	-	Design of Experiment
Fe	-	Iron
FE-SEM	-	Field emission scanning electron microscopy
Fe_2O_3	-	Iron oxide
GC-TCD	-	Gas chromatography with thermal conductivity detector

GHSV	-	Gas hourly space velocity
HC	-	Hydrocarbon
He	-	Helium
H ₂	-	Hydrogen
H ₂ -TPR	-	Temperature programmed reduction of hydrogen
IEA	-	International Energy Agency
K ₂ O	-	Potassium oxide
La ₂ O ₃	-	Lanthana
Mg	-	Magnesium
MgO	-	Magnesium oxide
Mn	-	Manganese
Ni	-	Nickel
NiCl ₂	-	Nickel chloride
NiD	-	Ni/dolomite
NiDAI	-	Ni/dolomite/Al ₂ O ₃
NiDCe	-	Ni/dolomite/CeO ₂
NiDLa	-	Ni/dolomite/La ₂ O ₃
NiDZr	-	Ni/dolomite/ZrO ₂
NiO	-	Nickel oxide
Ni(NO ₃) ₂	-	Nickel nitrate
Ni(NO ₃) ₂ ·6H ₂ O	-	Nickel nitrate hexahydrate
NiS	-	Nickel sulfide
O ₂	-	Oxygen
Pd	-	Palladium
PLOT	-	Porous layer open tubular
POX	-	Partial oxidation
Pt	-	Platinum
Rh	-	Rhodium
RSM	-	Response surface methodology
Ru	-	Rutherfordium
SBA-15	-	Well-order hexagonal mesoporous silica
SEM	-	Scanning electron microscopy
SiC	-	Silicon carbide
SD	-	Standard deviation

SiO	-	Silica oxide
SR	-	Steam reforming
S/C	-	Steam/carbon
TGA	-	Thermogravimetric analysis
TiO ₂	-	Titanium dioxide
TPO	-	Temperature programmed oxidation
VP-SEM	-	Variable-pressure scanning electron microscopy
WGS	-	Water gas shift
WHSV	-	Weight hourly space velocity
XRD	-	X-ray diffraction
ZrO ₂	-	Zirconia
Zn	-	Zinc

LIST OF SYMBOLS

D	-	Dispersion
d_{Ni}	-	Crystallite size e
d_p	-	Pore size
p/p_o	-	Relative pressure
R^2	-	Correlation coefficients value
S_{BET}	-	Brunauer Emmett Teller surface area
V_{total}	-	Total pore volume
X	-	Gaseous product (H ₂ , CO, CO ₂ , CH ₄)
x	-	Coded values of variable, temperature (x_1), S/C ratio (x_2), space time (x_3)
x	-	Conversion fraction of, tar (x_{tar}), phenol (x_{phenol}), toluene ($x_{toluene}$), naphthalene ($x_{naphthalene}$), pyrene (x_{pyrene})
y	-	Predicted response, conversion (y_1), H ₂ yield (y_2)
θ	-	Diffraction peak angle
λ	-	Wavelength of incident x-ray
β	-	Coefficient, constant (β_0), linear (β_i), quadratic (β_{ii}), interaction (β_{ij})
β	-	Half width of diffraction peak
ε	-	Statistical error term

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CHAPTER 1

INTRODUCTION

1.1 Background Study

The rapid depletion of fossil fuels and associated environmental issues such as global warming and climate change are becoming global concerns. However, the worldwide energy demand is continuously increasing at an alarming rate year after year. According to the finding of International Energy Agency (IEA), global energy demand increased by 2.1 % in 2017 which is more than twice the rate of previous year [1]. With regard to electricity generation in 2017, fossil fuel was responsible for 81 % of the total world energy as compared to other energy sources including renewables and nuclear [1]. Globally, fossil fuel-related carbon dioxide (CO₂) emissions showed an increment of 1.4 % in 2017 [1]. Consequently, the upsurge in fossil fuel demand infers higher socio-economic and environmental cost. Therefore, the exploitation of alternative energy sources to replace conventional fossil fuels is indispensable.

Currently, hydrogen (H₂) gas is considered as crucial commodity to sustainably generate electricity in 21st century. Among the existing fuels and energy carriers, H₂ has the highest energy density and its energy yield is up to 122 kJ/kg [2]. Its energy yield is approximately 2.75 times higher than most hydrocarbon (HC) fuels [2]. By employing H₂ gas, the crises of supply disruption and the impact of greenhouse gas emissions associated with conventional fossil fuel-based energy systems can be avoided. Basically, H₂ utilization generates only water vapor as a by-product with zero greenhouse gas emissions, during H₂ gas combustion with oxygen (O₂) in internal engine or electrochemically converting H₂ gas in fuel cell [3].

However, H₂ does not occur naturally on earth but commonly exists as part of other substances in nature such as water, alcohol, natural gas, biomass, coal, and HC. Consequently, it can only be obtained from H₂-containing resources through chemical reaction processes. In recent years, numerous technologies including thermochemical conversion [4-6], electrolysis [7], and photolysis [8] are under investigation for H₂ production. Among these possible options, biomass gasification is considered a promising and economical technology [9, 10]. Biomass gasification technology encompasses thermochemical process that converts organic substances from agriculture and forestry into syngas rich in H₂ and carbon monoxide (CO) along with a small amount of CO₂ and methane (CH₄).

The presence of impurities in the syngas such as tar, ash, nitrogen-, and sulfur-containing compounds is highly unacceptable especially tar. This is because tar is a complex mixture of condensable aromatic and oxygenated HCs that condenses at low temperature and subsequently lead to process-related problems. For instance, filter clogging, plugging of downstream equipment, and coke deposition on the downstream catalyst [11, 12]. More importantly, the formation of tar represents a decrease in conversion efficiency since biomass is converted to tar instead of syngas. Hence, the physical removal and further reduction/oxidation of tar is essential in order to improve the production of syngas.

Generally, reforming techniques are categorized into 3 types: steam reforming (SR), partial oxidation (POX), and autothermal reforming (ATR). However, SR is reported to have the superior H₂ yield [13]. It is the most developed and attractive technique providing a conversion mechanism for liquid HCs. This is because SR offers higher concentration of H₂ in the reformat, which is about 70 to 80 vol.% on a dry basis compared to other reforming technologies (40-50 vol.%) [14]. In addition, it produces about 100,000 Nm³/hr of H₂ gas on an industrial scale [15]. For comparison the resulting cost of H₂ by conventional steam methane reforming is less than \$ 2.00/kg at comparable natural gas in year 2017 [16]. Furthermore, based on the higher heating value, SR of CH₄ had achieved up to 85% of thermal efficiency. Whereas, only 60 to 75% of thermal efficiency was achieved by both ATR and POX [17].

In the present study, tar which is the major undesired by-product derived from biomass gasification was converted into H₂ gas by SR over dolomite promoted Ni-based catalysts. The components of tar model selected are the major chemical composition contained in the gasified biomass tar as reported by Singh et al. [18]. The representatives selected are phenol for phenolic and heterocyclic HCs, toluene for one-ring aromatic HCs, naphthalene for two-ring aromatic HCs and pyrene for four-ring and higher HCs.

Among the various existing catalysts, Ni-based catalysts have been extensively employed for SR because of their low price and pronounced performance in O-H, C-H, and C-C bonds rupture [19, 20] along with the additional activity for water gas shift (WGS) reaction [19, 21]. However, Ni-based catalysts are prone to active sites deactivation as a result of coke formation [22]. Dolomite which serves as the promoter was added to catalyst to suppress the deposition of coke and improve the catalytic activity per unit surface area. Furthermore, dolomite plays an essential role in CO₂ sorption to promote the water-gas shift (WGS) reaction, which results in the production of H₂ rich fuel gas [23]. The oxide supports that were used in this study include alumina (Al₂O₃), lanthana (La₂O₃), ceria (CeO₂), and zirconia (ZrO₂).

1.2 Problem Statement

The presence of unacceptable levels of tar in the syngas is the primary challenge of biomass gasification. This implies that less biomass is converted into syngas and consequently reduce the total H₂ production. Furthermore, the production of tar in biomass gasification also contributed to syngas end-use problems. These problems typically include blockages and corrosion in downstream filters, fuel line, engine nozzles, and turbines [11]. Typically, tar content in syngas produced from biomass gasification ranges from 0.5 to 100 g/Nm³, depending on the biomass feedstock, operating condition, and gasifier [18, 24]. However, the tolerance limit of

tar in syngas for various applications is 1, 5, and 100 mg/Nm³ in fuel cells, gas turbines, and internal combustion engines, respectively [24]. Although physical separation considerably removes tar from product gas, it has great potential to create secondary pollution. Thus, SR is a promising technique to convert the separated tar into valuable H₂ rich gas.

To date, most research studies deal with the SR based on an individual tar model compound, typically phenol, benzene, toluene or naphthalene over a variety of supported metal catalysts. Nevertheless, the composition of real biomass tar is complex and each component possesses a mutual influence on SR performance. Josuinkas et al., [25] investigate the effect of feedstock composition on catalytic performance during SR. They reported that the mixture of toluene and naphthalene altered the catalytic activity and reduce the feed conversion as compared to individual feed compound. Therefore, a research that can reflect the real condition of biomass tar SR is necessary. In the present research, the tar model was made up of phenol, toluene, naphthalene, and pyrene.

Owing to the presence of catalyst provides a more efficient SR, several kinds of catalytic reforming have been developed. However, the extraordinary difficulty is to obtaining a high stability of catalyst which is selective for H₂ and also resistance to coke deposition [22, 26]. Ni-based catalysts have been extensively used in steam reforming but it is prone to deactivation of its active sites by coke formation [22, 27]. Recently, it has been reported that addition of alkaline earth metal oxides such as MgO and CaO as a promoter could neutralise the acidity of the catalyst and improve steam-carbon reaction, which in turn increases the coke suppression rate and catalytic stability [28-30]. Low cost and abundance naturally occurring minerals such as dolomite that contains both CaO and MgO. In addition, dolomite also give a positive impact on H₂ production by adsorbing CO₂ to shift the thermodynamic equilibrium of WGS reaction towards H₂ production [23]. Therefore, this study is conducted to develop oxide supported Ni-based catalysts using dolomite as promoter for SR of multi-compound tar model. To the best of my knowledge, there is no study has been reported utilizing a dolomite as promoter.

The SR parameters such as temperature, steam to carbon (S/C) ratio, and space velocity have been reported as major factors that influence the tar conversion and H₂ yield [22, 31, 32]. Besides, previous study also mentioned that the effect of operating parameters on tar conversion and H₂ yield is associated with catalyst used. For instance, Furusawa et al., [33] found that SR over Ni/MgO operated at high S/C ratio produced low amount of H₂ as compared to Ni/Al₂O₃. Therefore, one of the aim of this research is to study the effect of the operating parameters on carbon conversion to gas and H₂ yield over the studied catalyst. In order to ensure the optimum carbon conversion to gas and H₂ yielded from the tar SR over the studied catalyst, the optimization of operating parameters using response surface methodology (RSM) should be taken into account.

1.3 Objectives of Study

The aim of this research is to develop Ni-based catalyst for high carbon conversion to gas with maximum H₂ yield via SR of multi-component gasified biomass tar model. To achieve this aim, the following objectives have been planned:

- (a) To synthesize and characterize the Ni-based catalysts on several catalyst supports (Al₂O₃, La₂O₃, CeO₂, and ZrO₂) and dolomite as a catalyst promoter for hydrogen production via steam reforming of gasified biomass tar.
- (b) To determine the effect of steam reforming parameters on hydrogen production in terms of temperature, steam to carbon ratio, and gas hourly space velocity.

- (c) To optimize the operating parameters for hydrogen production via steam reforming of gasified biomass tar.

1.4 Scope of Study

In order to achieve the research objectives, the scope of this research was designed and listed as follows:

- (a) Catalytic SR was adopted to convert gasified biomass tar into H₂ rich gas over dolomite promoted Ni-based catalyst. The tar model was made up of 15 wt.% phenol, 50 wt.% toluene, 30 wt.% naphthalene, and 5 wt.% pyrene. The selected components are the major chemicals contained in the gasified biomass tar as reported by Singh et al., [18] and their composition are represents to their chemical family.
- (b) 5 types of 10 wt.% dolomite promoted 10 wt.% Ni-based catalysts were prepared using co-impregnation method. The oxide supports include Al₂O₃, La₂O₃, CeO₂, and ZrO₂. The catalysts were designated as Ni/dolomite (NiD), Ni/dolomite/Al₂O₃ (NiDAI), Ni/dolomite/La₂O₃ (NiDLa), Ni/dolomite/CeO₂ (NiDCe), and Ni/dolomite/ZrO₂ (NiDZr). The selection of 10 wt% Ni loading is due the best performance reported by previous literature as discussed in Section 2.7.1. Generally, the promoter loading is not more than 5 wt.% [34-36]. Since dolomite used contains 57.3 wt.% CaCO₃ and 41.8 wt.% MgCO₃, 10 wt.% of dolomite loading was selected in this research.

- (c) All of the catalysts were characterized by thermogravimetric analysis (TGA) for thermal stability, temperature programmed reduction of hydrogen (H_2 -TPR) for reducibility of active metal, temperature programmed desorption of carbon dioxide (CO_2 -TPD) for basicity properties, nitrogen physisorption for textural properties, and X-ray diffraction (XRD) for crystalline properties.
- (d) For catalyst screening, 0.8 g of catalyst was reformed in a fixed bed reactor at 700 °C, S/C molar ratio of 1, and gas hourly space velocity (GHSV) of 20,453 mL/h g_{cat} under atmospheric pressure.
- (e) The most promising catalyst was selected based on the catalyst screening, and was used to study the effect of SR parameters on carbon conversion to gas and hydrogen yield. The operating parameters that influence the SR of gasified biomass tar were considered in this study. The chosen parameters were temperature (500-900 °C), S/C molar ratio (0.5-2.5), and GHSV (8,000-22,000 h^{-1}).
- (f) The parameters were further optimized by RSM in order to obtain maximum carbon conversion to gas with highest H_2 yield. A second-order factorial design called Box-Behnken design (BBD) was adopted to design the experiment by varying the SR parameters. The variables studied were temperature (600-800 °C), S/C molar ratio (1-2), and GHSV (12,000-22,000 h^{-1}), while the response were carbon conversion to gas and H_2 yield. The range of these three variables was determined based on the parametric study.
- (g) The coke formation of spent catalysts was evaluated by TGA, XRD, variable-pressure scanning electron microscopy (VP-SEM) or field emission scanning microscopy (FE-SEM).

1.5 Significance of Research

Following a great development and deployment in biomass gasification for H₂ production, there is a need to explore the SR of tar over a reliable catalyst. To date, there are not many studies focused on SR of multi-compounds tar model. Therefore, through this research, the real conditions of biomass tar SR can be reflected by employing a tar model made up of main representative of gasified biomass tar. This is importance in prediction and understanding the catalytic performance in real biomass tar SR process.

Catalyst with high activity, high thermal stability, high coking resistance and high mechanical strength are key elements in the reaction. To the best of my knowledge, no study is reported in the open literature using dolomite promoted Ni-based catalysts on catalyst support of Al₂O₃, La₂O₃, CeO₂, and ZrO₂ in SR of gasified biomass tar. In this research, dolomite was selected as an attractive catalyst promoter because of its numerous advantages such as environmental friendly, readily available, economic feasibility of material, high thermal stability, relatively mechanically resistant and higher resilience to catalyst poison [37]. Therefore, the catalyst in this research has a lower cost compared to noble metal based or promoted catalysts, which paves way for its application in large scale SR process.

Generally, reaction conditions also play crucial role in H₂ production in SR of gasified biomass tar. From this research, an optimal reaction conditions in terms of temperature, S/C ratio, and GHSV over the most promising catalyst was provided. This result can be applied in industrial SR of gasified biomass tar. By doing so, the new developed catalyst of this research has a great potential as an alternative catalyst for commercial SR of gasified biomass tar. Besides, this work would benefit in a number of particular areas such as reduction of energy consumption, catalyst usage, and also minimise expenses of feedstock. Thus, the result from the present research is expected to expand the frontier of knowledge in the field of SR catalyst.

1.6 Thesis Outline

This thesis is divided into five chapters. Chapter 1 introduces and addresses the current issues about the H₂ production and catalytic SR of tar. The problem statement, objectives, scope, and significance of this study are discussed in this chapter as well. Chapter 2 is a theoretical framework chapter which provides a literature review for the entire study which includes H₂, gasification, tar, SR, catalyst, and RSM. Apart from the theoretical literature review, previous researches on catalytic SR of tar also be reviewed. A detailed description of the catalyst synthesis, catalyst characterization, RSM design, and SR experimental method are mentioned in Chapter 3. Chapter 4 is being presented with various probable interpretations and discussions on the characteristic of catalyst, catalytic activity for catalyst screening, parametric effect on H₂ production and results of RSM. The last chapter, Chapter 5, concludes the research work and suggests several recommendation for future research.

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