



***CATALYTIC GASIFICATION OF OIL PALM FROND BIOMASS IN
SUPERCRITICAL WATER FOR HYDROGEN PRODUCTION USING
SUPPORTED AND DOPED MAGNESIUM OXIDE CATALYSTS***

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By

MOHD SUFRI BIN MASTULI

**Thesis Submitted to the School of Graduate Studies, Universiti Putra
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Doctor of Philosophy**

August 2019

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

CATALYTIC GASIFICATION OF OIL PALM FROND BIOMASS IN SUPERCRITICAL WATER FOR HYDROGEN PRODUCTION USING SUPPORTED AND DOPED MAGNESIUM OXIDE CATALYSTS

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Utilization of hydrogen as an energy carrier for transportation sector and other energy utilities could reduce the dependency on conventional fossil fuels and cater the increasing energy demands. The combustion of hydrogen gas (H_2) in a fuel cell engine produces only water as its by-product with zero greenhouse gases that did not promoting the global warming. Production of H_2 from biomass is one of the ultimate goals in renewable and sustainable energy development program. Various technologies have been developed for the conversion of biomass into combustible hydrogen. In this study, supercritical water gasification (SCWG) was used to convert the oil palm frond (OPF) biomass into H_2 -rich syngas. Two series of catalysts namely supported and doped magnesium oxide (MgO) catalysts were synthesized and characterized before catalyzing the SCWG reaction that enhanced the total H_2 yield. Non-noble metal supported catalysts such as 20NiO/MgO, 20CuO/MgO and 20ZnO/MgO were synthesized using an impregnation method. The 20ZnO/MgO catalyst found to be produced the highest H_2 yield even though it possessed the smallest specific surface area. Other factors such distribution, basicity and bond strength of the catalysts played important roles for higher catalytic performances. It is also believed that the catalyst stability can be further improved by doping the active metal into the crystal structure of the MgO catalyst. Therefore, the Ni doped MgO catalysts ($Mg_{1-x}Ni_xO$) and the Zn doped MgO catalysts ($Mg_{1-x}Zn_xO$) with $x = 0.05, 0.10, 0.15, 0.20$, were synthesized using a self-propagation combustion method. Interestingly, the Rietveld refinements showed contraction of crystal structure for the Ni doped MgO catalysts and expansion of crystal structure for the Zn doped MgO catalysts, upon increasing the metal contents. It means the crystallite size, surface area, porosity and basicity were affected. The correlation between catalytic performance and properties for selected supported and doped MgO catalysts were investigated. The doped catalysts have larger surface areas than

the supported catalysts, which can be arranged in the order of $\text{Mg}_{0.80}\text{Ni}_{0.20}\text{O}$ ($67.9 \text{ m}^2 \text{ g}^{-1}$) > $\text{Mg}_{0.80}\text{Zn}_{0.20}\text{O}$ ($36.3 \text{ m}^2 \text{ g}^{-1}$) > $20\text{NiO}/\text{MgO}$ ($30.1 \text{ m}^2 \text{ g}^{-1}$) > $20\text{ZnO}/\text{MgO}$ ($13.1 \text{ m}^2 \text{ g}^{-1}$). Whether supported or doped, the Ni-based catalysts always exhibited larger surface area than that of the Zn-based catalysts. Unexpectedly, the Zn-based catalysts produced higher H_2 yield from the SCWG of OPF biomass although these catalysts have smaller surface areas. When compared to the non-catalytic SCWG reaction, the H_2 yield increased by 187.2% for $20\text{NiO}/\text{MgO}$, 269.0% for $20\text{ZnO}/\text{MgO}$, 361.7% for $\text{Mg}_{0.80}\text{Ni}_{0.20}\text{O}$, and 438.1% for $\text{Mg}_{0.80}\text{Zn}_{0.20}\text{O}$. The $\text{Mg}_{0.80}\text{Ni}_{0.20}\text{O}$ catalyst gave the highest H_2 yield because it had the highest number of basic sites approximately twenty-fold higher than that of the $20\text{ZnO}/\text{MgO}$ catalyst. It also proved to be the most stable catalyst, as verified from the X-Ray photoelectron spectroscopy (XPS) outcomes. As such, this study concludes that the catalytic performances do not only depend on the specific surface area, but also influenced by the basicity properties and the catalyst stability. In addition, the doped catalysts may serve as a new catalyst system for the SCWG for hydrogen production.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**PENGEGASAN BERMANGKIN BIOJISIM PELEPAH KELAPA SAWIT
DALAM AIR SUPERGENTING BAGI PENGHASILAN HIDROGEN
MENGUNAKAN MANGKIN MAGNESIUM OKSIDA YANG TERSOKONG
DAN TERDOP**

Oleh

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Penggunaan hidrogen sebagai pembawa tenaga untuk sektor pengangkutan dan kemudahan tenaga lain boleh mengurangkan kebergantungan kepada bahan bakar fosil konvensional dan memenuhi kehendak tenaga yang semakin meningkat. Pembakaran hidrogen dalam sel bahan api kenderaan hanya menghasilkan air sebagai produk sampingan dengan gas rumah hijau yang kosong yang mana tidak akan menyebabkan pemanasan global. Penghasilan hidrogen daripada biojisim merupakan satu daripada matlamat utama dalam program pembangunan tenaga boleh diperbaharui dan lestari. Pelbagai teknologi telah dibangunkan untuk menukarkan biojisim kepada hidrogen mudah bakar. Dalam kajian ini, pengegasan super genting (SCWG) telah digunakan untuk menukar biojisim pelepah kelapa sawit kepada *syngas kaya*-H₂. Dua siri mangkin yang dinamakan magnesium oksida (MgO) yang tersokong dan terdop telah disintesis dan dicirikan sebelum memangkinkan tindak balas SCWG bagi meningkatkan total H₂ yang dihasilkan. Mangkin logam bukan murni berpenyokong seperti 20NiO/MgO, 20CuO/MgO and 20ZnO/MgO telah disintesis menggunakan kaedah pengisitepuan. Didapati mangkin 20ZnO/MgO menghasilkan H₂ yang tertinggi walaupun ianya mempunyai luas permukaan yang terkecil. Faktor-faktor lain seperti serakan, sifat bes dan kekuatan memainkan peranan penting untuk prestasi pemangkinkan yang tinggi. Adalah dipercayai juga bahawa kestabilan mangkin boleh dipertingkatkan melalui pagedopan logam aktif ke dalam struktur kristal mangkin MgO tersebut. Oleh yang demikian mangkin Ni terdop MgO (Mg_{1-x}Ni_xO) dan mangkin Zn terdop MgO (Mg_{1-x}Zn_xO) telah disintesis menggunakan kaedah pembakaran penswarambatan. Menariknya, kaedah penapisan Rietveld menunjukkan pengecutan sel untuk mangkin Ni terdop MgO dan perkembangan sel untuk mangkin Zn terdop MgO, dengan penambahan kandungan logam. Ini

bermaksud saiz kristal, luas permukaan, kelianan dan sifat bes adalah terkesan. Hubung kait antara prestasi pemangkinan dan sifat-sifat mangkin untuk mangkin MgO yang tersolong dan terdop turut dikaji. Mangkin yang terdop mempunyai luas permukaan yang lebih besar yang boleh disusun mengikut urutan of $\text{Mg}_{0.80}\text{Ni}_{0.20}\text{O}$ ($67.9 \text{ m}^2 \text{ g}^{-1}$) > $\text{Mg}_{0.8}\text{OZn}_{0.20}\text{O}$ ($36.3 \text{ m}^2 \text{ g}^{-1}$) > 20NiO/MgO ($30.1 \text{ m}^2 \text{ g}^{-1}$) > 20ZnO/MgO ($13.1 \text{ m}^2 \text{ g}^{-1}$). Tidak kira tersokong atau terdop, mangkin berasaskan Ni biasanya mempunyai luas permukaan lebih besar berbanding mangkin berasaskan Zn. Adalah di luar jangkaan apabila mangkin berasaskan Zn dengan luas permukaan lebih kecil untuk SCWG menghasilkan H_2 lebih tinggi daripada biojisim OPF. Apabila dibandingkan dengan tindak balas tanpa mangkin, penghasilan H_2 meningkat sebanyak 187.2% untuk 20NiO/MgO , 269.0% untuk 20ZnO/MgO , 361.7% untuk $\text{Mg}_{0.80}\text{Ni}_{0.20}\text{O}$, dan 438.1% untuk $\text{Mg}_{0.8}\text{OZn}_{0.20}\text{O}$. Mangkin $\text{Mg}_{0.80}\text{Ni}_{0.20}\text{O}$ menghasilkan H_2 yang paling tinggi kerana ia mempunyai tapak bes yang lebih banyak; lebih kurang dua puluh kali ganda lebih tinggi daripada mangkin 20ZnO/MgO . $\text{Mg}_{0.80}\text{Ni}_{0.20}\text{O}$ juga telah terbukti sebagai mangkin paling stabil, seperti yang disahkan oleh keputusan spektroskopi fotoelektron sinar-X (XPS). Daripada kajian ini dapat disimpulkan bahawa prestasi pemangkinan oleh mangkin yang telah disintesis bukan sahaja bergantung kepada luas permukaan spesifik, tetapi juga dipengaruhi oleh bilangan tapak bes dan kestabilan mangkin.. Oleh yang demikian, mangkin terdop boleh menjadi sistem mangkin baharu untuk tindak balas SCWG.

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LIST OF ABBREVIATIONS

AC	Activated carbon
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
Btu	British thermal unit
CNT	Carbon nanotube
DSC	Differential scanning calorimetry
eV	Electron volt
EDX	Energy dispersive X-Ray
EFB	Empty fruit bunches
FCC	Face centered cubic
FESEM	Field emission scanning electron microscope
FWHM	Full width half maximum
FID	Flame ionization detector
GC	Gas chromatography
HRTEM	High resolution transmission electron microscope
ID	Inner diameter
IUPAC	International Union of Pure and Applied Chemistry
ICDD	International Centre for Diffraction Data
MESTECC	Ministry of Energy, Science, Technology, Environment and Climate Change
MOE	Ministry of Education
MPa	Megapascal
NIST	National Institute of Standards and Technology

OD	Outer diameter
OECD	Organization for economic co-operation and development
OPF	Oil palm frond
POME	Palm oil mill effluent
SS	Stainless Steel
SCW	Supercritical water
SCWG	Supercritical water gasification
STA	Simultaneous thermogravimetric analyzer
TCD	Thermal conductivity detector
TGA	Thermogravimetric analysis
TPD-CO ₂	Temperature programmed desorption-carbon dioxide
vol.%	Volume percent
wt.%	Weight percent
WGSR	Water-gas shift reaction
WGS	Water-gas shift
XPS	X-Ray photoelectron spectroscopy
XRD	X-Ray diffractometer

CHAPTER 1

INTRODUCTION

1.1 Background of research

1.1.1 Current global energy outlook

According to International Energy Outlook 2018 that reported by the U.S. Energy Information Administration (www.eia.gov), the energy consumption by the non-OECD (Organization for Economic Co-operation and Development) countries began to exceed the OECD countries' consumption started in 2007 with the value of 241 quadrillion Btu (British thermal unit) and this trend is projected to increase up to 739 quadrillion Btu in 2040. In 2017, the energy consumption by the non-OECD countries was 353 quadrillion Btu as compared to 245 quadrillion Btu for the OECD countries. Figure 1.1 (a) shows the energy consumption and energy projection for the non-OECD countries from 1990 until 2040, in which Asia is projected to have the largest energy consumption. The reasons for this significant increment are due to the population and economic growths, as well as the fast progress in the service and manufacturing sectors, particularly for the developing countries to achieve sophisticated living styles. Therefore, all the energy sources either non-renewable or renewable, except the coal, are projected to increase in term of consumption as shown in Figure 1.1 (b).

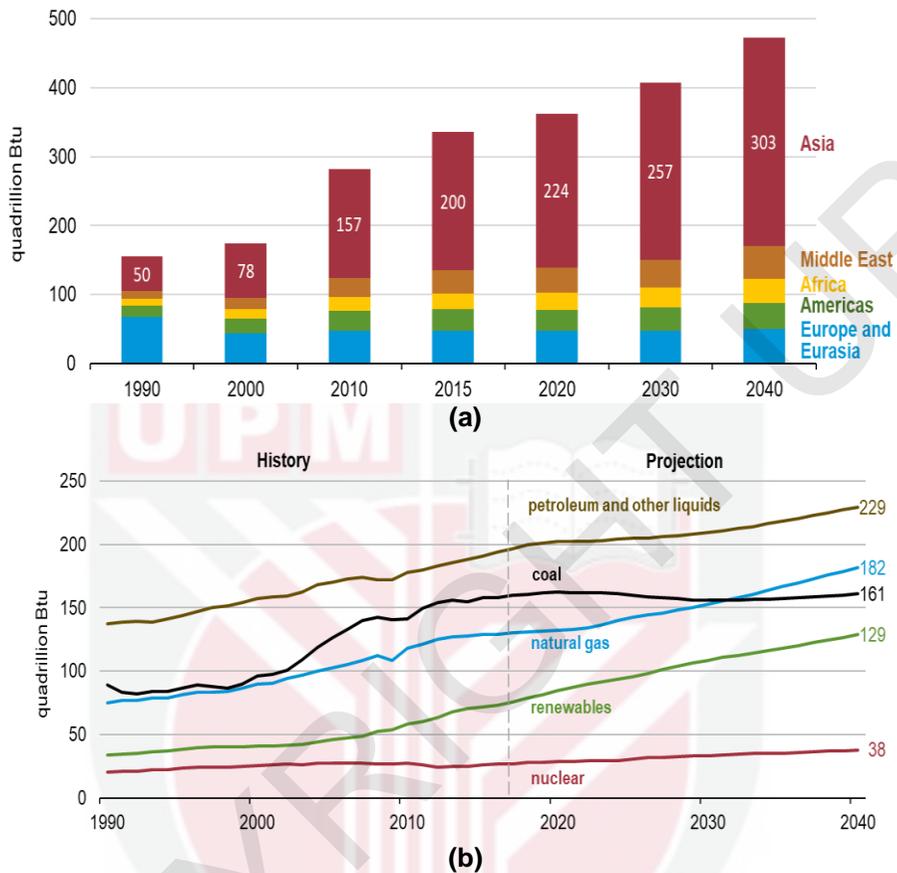
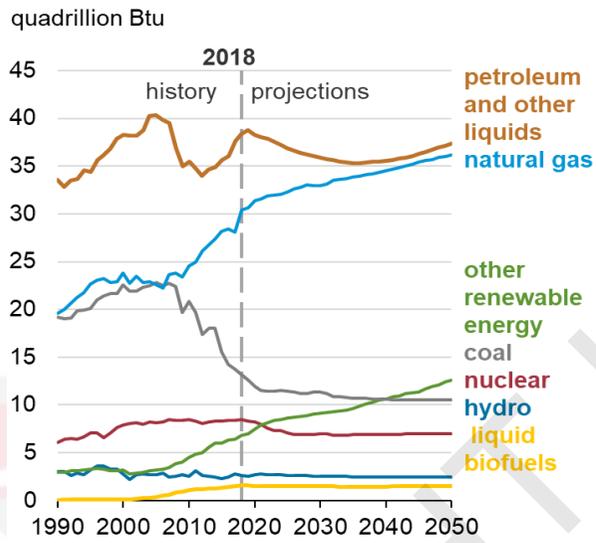
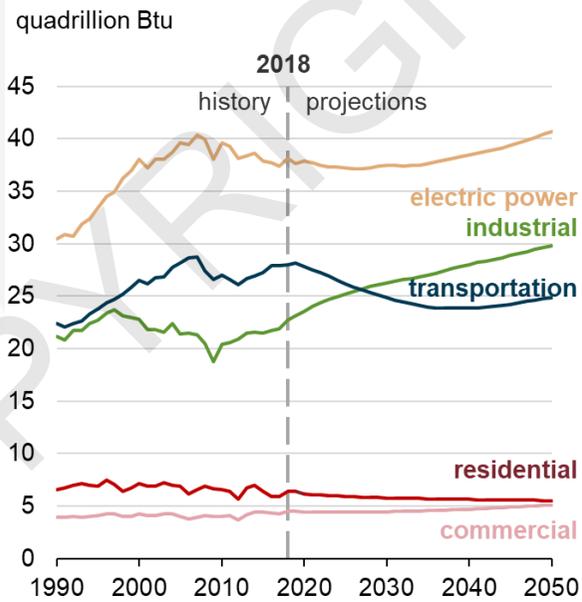


Figure 1.1 : Energy consumption and projection for (a) the non-OECD countries and (b) the energy sources
 (Source: International Energy Outlook 2018)

For the renewable energy, it can be harvested from various types of natural resources such as solar, wind, tidal, geothermal, hydrothermal and biomass. These renewable resources can be produced both clean and green fuels that environmentally tolerable to sustain the world energy demands. Based on the Annual Energy Outlook 2019 (www.eia.gov), the relationship between energy consumption and energy projection in term of energy sources, application sectors and CO₂ emission can be summarized as in Figure 1.2.



(a)



(b)

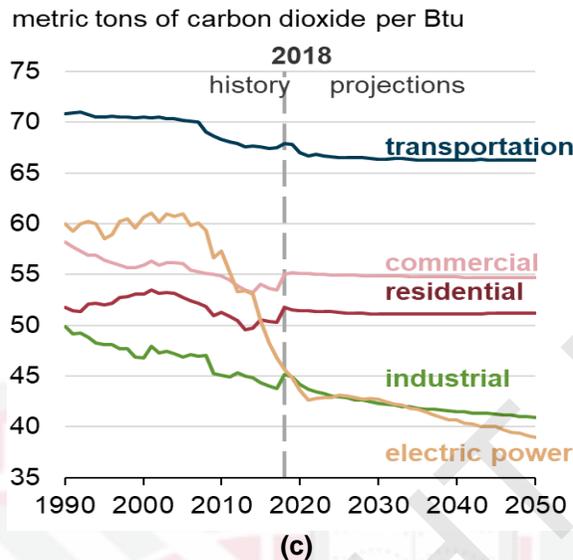


Figure 1.2 : Energy consumption and energy projection by (a) energy sources, (b) application sectors and (c) CO₂ emission by the sectors
(Source: Annual Energy Outlook 2019)

The utilization of non-renewable energy sources is responsible for the global warming and climate change, which associated with the oscillating of fuel prices and uncertainties of fuel reserves, the energy paradigm is shifted from the non-renewable to the renewable. Interestingly, the combination between non-renewable and renewable energies can reduce the CO₂ emission from all the sectors with the transportation is expected to be consistent as the major contributor of CO₂ as a greenhouse gas that promoting the global warming. Therefore, hydrogen gas (H₂) that derived from the renewable resource has gained a great attention as energy carrier for the transportation sector due to the success of fuel cell technology (Dodds *et al.*, 2015).

1.1.2 Hydrogen as energy carrier

Hydrogen is the simplest, lightest and most abundant element on earth. It consists only one proton and one electron. The atomic number and atomic weight of hydrogen are 1 and 1.008. Its monoatomic form (H) is constituted approximately 75% the mass of the universe. At standard temperature and pressure, it appears as diatomic gas molecule (H₂), which is non-metallic, colorless, tasteless, odorless and also non-toxic, but highly combustible. The H₂ can be used as energy storage and energy carrier. However, it does not exist in nature because it can easily escape from the earth's gravity than other heavier gases. The H₂ can be produced from covalent compounds such as water and hydrocarbons. The first artificial hydrogen gas was discovered by Robert Boyle

in 1671 after reacted the iron filings with diluted acid. In 1766, Henry Cavendish recognized that gas as a discrete substance and called it as an inflammable air because it burned when ignited and also produced water after the ignition as reported by him in 1781. Later in 1783, Antoine Lavoisier named the constituent element as hydrogen (from the Greek: *hydro* is water and *genes* is creator, thus; hydrogen is water creator) after he successfully reproduced the Cavendish's experiment that water is produced when hydrogen is burned. Hydrogen gas (H_2) can be used in a broad range of applications such as for ammonia and fertilizer production, petroleum refining, shielding gas for welding, hydrogenation agent for chemical reaction, rotor coolant in electrical generator, co-reactant for chemical, petrochemical and pharmaceutical industries, electronic manufacturing, energy storage and power generation, and many others. Besides that, the H_2 can be combusted in a fuel cell to generate electricity, power and heat. Figure 1.3 illustrate the production of electricity from the fuel cell technology.

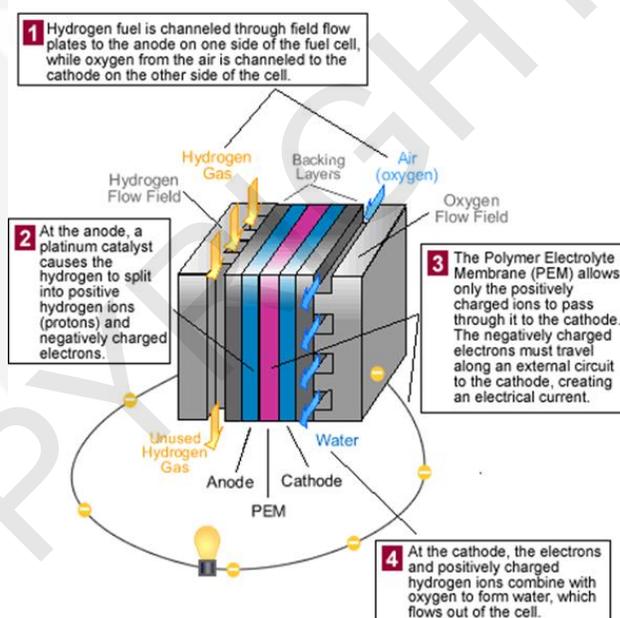


Figure 1.3 : Electricity production from fuel cell technology using hydrogen gas (Dodds *et al.*, 2015)

The H_2 can be produced from various domestic resources, from non-renewable such as fossil fuel, natural gas, nuclear and coal, until renewable likes solar, wind, hydrothermal and geothermal. The technology and energy density related the hydrogen gas is given in Figure 1.4. Presently, worldwide research is focusing on the production of hydrogen from the biomass because it is expected to become a major source of energy and to play an important role in economic development.

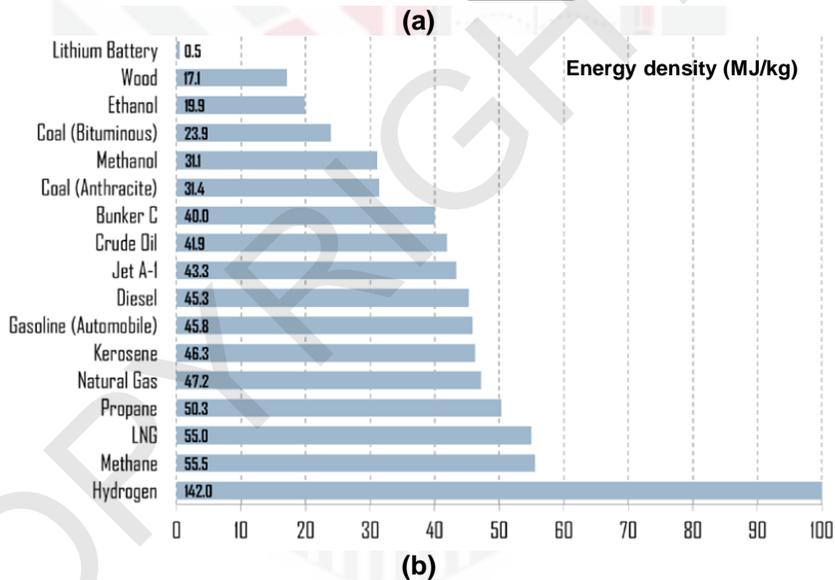
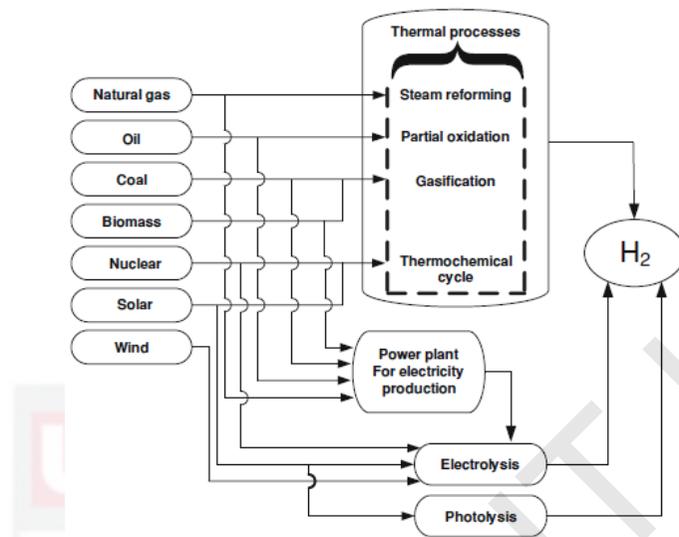


Figure 1.4 : (a) Technologies for hydrogen production and (b) comparison of energy densities (Corbo, 2011)

1.1.3 Potential of oil palm biomass for hydrogen production

Oil palm (*Elaeis guineensis*) is originated from the South Africa and it grows at all tropical areas of the world. The oil palm has become as an important agricultural crop to many Southeast Asian countries including Malaysia. In 1870, it was first introduced to Malaysia as an ornamental plant. Currently, Malaysia is ranked second after Indonesia as the world's producer and exporter of palm oil.

The Malaysian palm oil industry has grown significantly over many years in which the palm oil production has increased from 2.5 million tonnes in 1980 to 21.0 million tonnes in 2017 (Onoja *et al.*, 2018). Every year Malaysia alone produced more than 30% of the total world palm oil production. Figure 1.5 shows the Malaysian palm oil production for three consecutive years. It shows the sustainability of palm oil production in Malaysia. The statistics related to Malaysian palm oil industry can be obtained from the website of Malaysian Palm Oil Council (www.mpoc.org.my).



Figure 1.5 : Malaysia palm oil production from 2015 to 2017 (source: www.mpoc.org.my)

Besides producing the palm oil, Malaysia also produces a large quantity of oil palm biomass every year. The palm oil only forms about 10% of the whole oil palm tree, while the other 90% remains as the biomass (Basiron, 2007). Basically, the oil palm tree is a single-stemmed and it can grow up to 20 m tall. The oil palm fruits are reddish in colored and grow in large bunches, each weighing at about 10 – 40 kg with up to 200 individual fruits. The fruit comprises a single seed (kernel) and surrounded by the soft pulp (mesocarp). Oil palm fruits are usually harvested after 3 years from planting. Maximum yield is achieved in the 12 – 14th years and then continuously declining until the end of the 25th year. As mentioned, the Malaysian palm oil industry produces a large quantity of oil palm biomass including trunk, frond, empty fruit bunches (EFB), mesocarp fiber, kernel shell and palm oil mill effluent (POME) from the fruit harvesting and oil extraction processing. The oil palm biomasses are shown in Figure 1.6 and their chemical composition are given in Table 1.1.



Figure 1.6 : Oil palm biomasses (Onoja *et al.*, 2018)

Table 1.1 : Chemical composition of oil palm biomass

Biomass	Cellulose (wt.%)	Hemicellulose (wt.%)	Lignin (wt.%)	Reference
EFB	23.7	21.6	29.2	(Samiran <i>et al.</i> , 2015)
OPF	40.0	30.8	29.5	(Kristiani <i>et al.</i> , 2013)
Trunk	34.4	23.9	35.9	(Abnisa <i>et al.</i> , 2013)
Shell	27.7	21.6	44.0	(Abnisa <i>et al.</i> , 2011)
Fiber	34.5	31.8	25.7	(Koba & Ishizaki, 1990)

Therefore, there is a greater potential to convert the oil palm biomass into value-added products and renewable energy sources. The biomass-derived energy is one of the goals for global renewable and sustainable energy development program (Hosseini & Wahid, 2016). Although the biomass is categorized as a renewable resource, the direct use of the biomass for energy applications is not convenient due its low energy density (Lu *et al.*, 2014). The biomass should be converted into liquid or gaseous fuels, such as hydrogen gas (H₂). Currently, the main interest is the production of H₂ from the oil palm biomass. In a particular, the oil palm frond (OPF) is the largest amount of palm solid residue as compared to other oil palm biomasses, that is abundantly available at oil palm plantation (Hosseini *et al.*, 2015). Moreover, the OPF biomass contained the highest amount of cellulose and hemicellulose, and the lowest amount of lignin, which presents a great potential to be employed as a feedstock for hydrogen production (Kelly-Yong *et al.*, 2007; Mohammed *et al.*, 2011).

The H₂ derived from the biomass can be considered as a clean fuel because the combustion of hydrogen in a fuel cell produces only water as its by-product, unlike the fossil fuels that emit greenhouse gases and promoting global warming (Guo *et al.*, 2010). It is expected to take a significant role in future energy demand due to the raw material availability. The Malaysian Government has identified the oil palm biomass as the biggest resource that can be easily developed, thus having the greatest potential for bringing renewable energy into the mainstream energy supply. Figure 1.7 illustrates the Malaysian roadmap for production of hydrogen from the biomass until 2030 (Mohammed *et al.*, 2011). This could make Malaysia to be one of the major contributors of renewable energy in the world. As such, various advanced technologies have been developed for the conversion of biomass into combustible hydrogen (Pereira *et al.*, 2012; Puig-Arnavat *et al.*, 2010; Sansaniwal *et al.*, 2017).

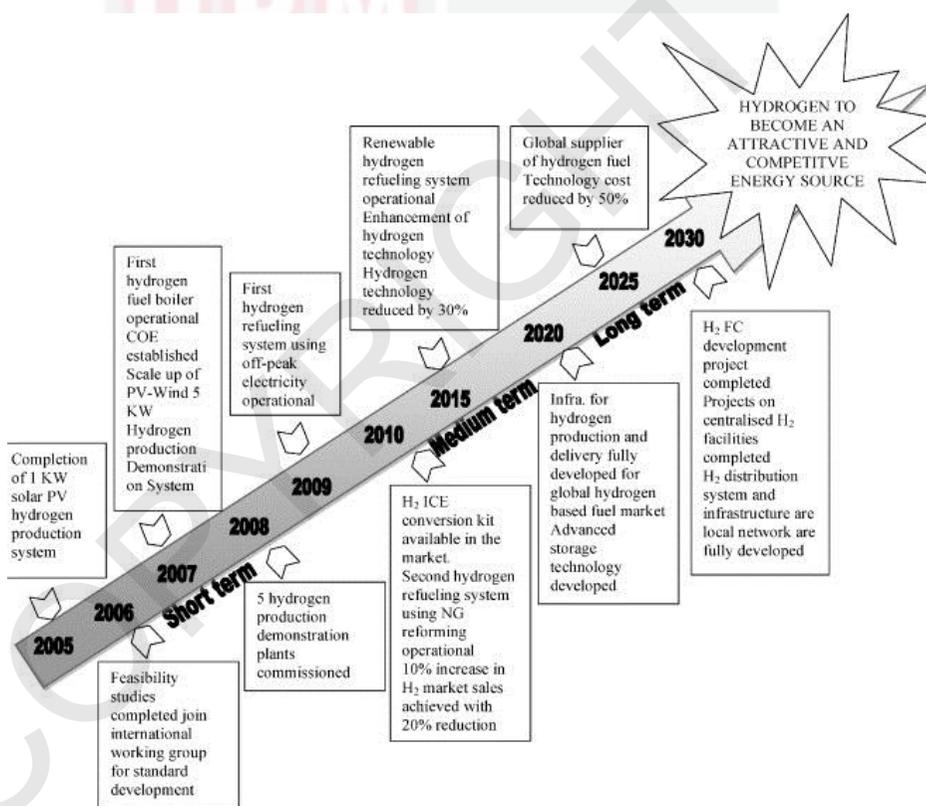


Figure 1.7 : Hydrogen roadmap for Malaysia (Mohammed *et al.*, 2011)

1.2 Problem statements

Oil palm is one of the major economic crops in many Southeast Asian countries including Malaysia (Kelly-Yong *et al.*, 2007). The Malaysian palm oil industry has grown tremendously for many years to become a major producer and exporter for the world palm oil production. Besides producing palm oil, Malaysia also generates a large amount of oil palm biomass such as frond, trunk, empty fruit bunches (EFB), mesocarp fiber, kernel shell and palm oil mill effluent (POME), that can be obtained from the plantation, fruit harvesting and oil extraction activities (Mohammed *et al.*, 2011). The commercial applications of the oil palm biomass are very limited. The kernel shell and mesocarp fiber are usually combusted in the boiler to produce steam, heat and electricity for the mill operations. The empty fruit bunches, which not suitable to be combusted due to its high moisture content, are burned in incinerators and releases harmful gases. Meanwhile, the oil palm trunk and frond are still under-utilized and abundantly available at oil palm plantation. It is worthy to mention that the oil palm frond (OPF) biomass is not only the largest quantity among the oil palm biomass (Hosseini *et al.*, 2015), but also contained the highest amount of cellulose and hemicellulose with the lowest amount of lignin (Hosseini & Wahid, 2016), which presents a great potential to be used as a feedstock for production of renewable hydrogen gas.

Thermochemical process such as gasification is widely used to produce gas from the biomass (Schiefelbein, 1989; Vick, 1981). The biomass gasification will produce a mixture of combustible gas, mainly composed of hydrogen (H₂), carbon monoxide (CO), carbon dioxide (CO₂) and methane (CH₄) with different ratios depending on the gasification operating parameters. The gas mixture also known as a syngas (synthesis gas). Small quantities of liquid oil, tar and char also can be formed as the gasification products. Conventionally, the gasification is carried out at reaction temperature of above 700 °C with O₂, CO₂, air and steam or their mixtures added into the gasifier as the gasifying medium to allow the partial oxidation and reforming the biomass (Sutton *et al.*, 2001). The biomass that contained higher amount of moisture needs to be dried before the gasification processes in order to obtain higher conversion efficiencies, which is not economical for industries. Besides, the problems associated with the quality of gas product due to tar and char impurities are the main challenges for the gasification technology. The present of these impurities in the syngas can cause blockage and corrosion of the reactor as well as reduce the overall efficiency of the gas yield. Several attempts have been carried out to reduce the tar and char contents in the gas products (Rapagna *et al.*, 1998; Tomishige *et al.*, 2004; Wei *et al.*, 2007). Catalysts are widely used to improve the quality of the syngas and to enhance the production of H₂-rich gas from biomass with a tar-free and a char-free of products. For examples, naturally occurring catalysts (dolomite and olivine), alkali metals (KOH, K₂CO₃, Na₂CO₃, CaCO₃, CsCO₃, KCl, ZnCl₂ and NaCl) and nickel-based catalysts.

As an alternative, the wet biomass can be gasified in water at supercritical condition ($T \geq 374$ °C and $P \geq 22.1$ MPa) without any costly drying pre-treatment due to the supercritical water is used as the reaction medium to produce the hydrogen gas (Guo *et al.*, 2010). This technology is called “supercritical water gasification” (SCWG). Most of organic compounds can be dissolved in supercritical water leading to high conversion of biomass into gas product (Elliott, 2008). Additionally, the H_2 is produced at high pressure, thus, requiring less energy to pressurize the gas product in a storage tank (Abdoulmoumine *et al.*, 2015). Tar and char problems also can be suppressed during the SCWG of biomass (Shen & Yoshikawa, 2013). Nonetheless, the gas product from the SCWG of biomass is not limited to H_2 alone as it generates other carbon gases with varied ratios (Matsumura *et al.*, 1997; Xiaodong *et al.*, 1996). Therefore, the addition of catalyst during the SCWG process is vital to alleviate the H_2 yield and to suppress the formation of other gases. Various types of biomass have been used in SCWG for production of hydrogen (Albarelli *et al.*, 2015; Cengiz *et al.*, 2016; Nanda *et al.*, 2017; Rana *et al.*, 2018). However, the mechanism of the SCWG of biomass is complicated due to its complex chemical structure that heavily cross-linked between the cellulose, hemicellulose and lignin. Therefore, many researchers are investigating the SCWG of model compound of the biomass such as cellulose, glucose, hemicellulose, xylan and lignin (Kang *et al.*, 2016a; Tülay *et al.*, 2016; Yoshida & Matsumura, 2001). Regardless of model compounds and real biomass, the yield and composition of the gas products are depending on the reactor design, choice of catalyst and various SCWG operating parameters such as temperature, pressure, feedstock concentration and reaction time (Furimsky, 1998; Guo *et al.*, 2010; Leung *et al.*, 2004; Sutton *et al.*, 2001). For the non-catalytic SCWG, high gas yield can be obtained at higher temperature and pressure with longer reaction time from the diluted feedstock. However, the composition of the produced gas can be varied and the production of H_2 -rich syngas is only possible at harsh conditions. Therefore, the addition of catalysts during the SCWG process is highly required, not only to reduce the severity of the non-catalytic SCWG operating conditions, but also to shift the distribution of the gas composition to H_2 -rich syngas by the aid of water-gas shift reaction (Ahmad *et al.*, 2016; Correa & Kruse, 2018; Prabhansu *et al.*, 2015; Sansaniwal *et al.*, 2017).

Many types of catalysts either homogeneous or heterogeneous have been reported in literatures for the catalytic SCWG of both model compounds and real biomass (Adamu *et al.*, 2017; Ge *et al.*, 2014; Li *et al.*, 2018; Sheikhdavoodi *et al.*, 2015; Weijin *et al.*, 2017). Recently, the nickel based heterogeneous catalysts that supported on various types of activated carbons and metal oxides and also promoted by a wide range of transition metals are used in the SCWG reactions to maximize the H_2 yield in the gas product (Barati *et al.*, 2014; Norouzi *et al.*, 2017; Rashidi & Tavasoli, 2015; Tavasoli *et al.*, 2016). The added catalysts should be enhancing the H_2 yield and suppressing the carbon-based gases. It means that the catalysts are not only active for H_2 formation, but also selective to H_2 , hence, the H_2 -rich gas can be produced from the biomass *via* SCWG reaction. From the literature survey, most of the researchers are focused on the activity and selectivity of the commercialized and synthesized of supported and

promoted nickel-based catalysts for the SCWG (Pooya *et al.*, 2011; Chan & Tanksale, 2014a; Correa & Kruse, 2018; Hosseini & Wahid, 2016; Reddy *et al.*, 2014). Only a few of them are reported the stability (Furusawa *et al.*, 2007; Li *et al.*, 2018; Zhang *et al.*, 2012) of the catalysts and none research groups are studied the potential of doped nickel-based catalysts, which are expectedly highly stable because more interaction between the nickel and the support, also reduce the sintering and dissolution of the nickel in supercritical water, that beneficial for the catalytic performances.

1.3 Scope of research

In this research, the MgO supported Ni, Cu and Zn oxides catalysts were synthesized using an impregnation method. Meanwhile, both Ni doped MgO catalysts ($Mg_{1-x}Ni_xO$: $x = 0.05, 0.10, 0.15, 0.20$) and Zn doped MgO catalysts ($Mg_{1-x}Zn_xO$: $x = 0.05, 0.10, 0.15, 0.20$) were synthesized using the self-propagating combustion method. The thermal profiles of the obtained precursors of all the catalysts were studied using simultaneous thermogravimetric analyzer (STA). From the STA findings, all the precursors were calcined in a furnace under air at 600 °C for 6 h. The phase of all the calcined catalysts was confirmed using X-Ray diffractometer (XRD) and the XRD data for the doped catalysts were further analyzed using Rietveld refinement method to study their crystal structures. The morphologies of all the catalysts were observed *via* a field emission scanning electron microscope (FESEM) and a high-resolution transmission electron microscope (HRTEM). Energy X-Ray dispersive (EDX) that integrated with the FESEM also used to measure the elemental compositions for each catalyst. The isotherm, surface area and porosity distribution for all the catalysts were measured using a BELSORP-mini II instrument from BEL Japan Inc. The isotherms were analyzed using Brunauer-Emmett-Teller (BET) and the Barrett-Joyner-Halenda (BJH) methods. The strength and density of basicity properties of each catalyst were analyzed using a temperature programmed desorption of carbon dioxide (TPD- CO_2) analyzer. Last but not least, the chemical environments in all the synthesized catalysts were carried out using X-Ray Photoelectron Spectroscopy (XPS) measurement. All the synthesized catalysts were characterized for the SCWG using OPF biomass. The gas products that produced from the non-catalytic and catalytic SCWG were analyzed using gas chromatography (GC). The yield and composition of the gas products were calculated and compared. The relationship between catalyst properties and catalytic performances during the SCWG reactions were discussed in detail.

1.4 Significance of research

In Malaysia, the production of renewable energy from the biomass is still low even though a huge amount of biomass is generated especially from the oil palm industry. The is due to a lot of challenges including the availability of

economically viable technology, sophisticated and sustainable natural resources management, and proper market strategies under competitive energy markets. Amidst these challenges, the development and implementation of suitable policies by the local-policy makers are still the single and most important factor that can determine a successful utilization of renewable energy in a particular country. Therefore, further efforts, researches and strategic plans must be developed and implemented correctly. Ultimately, the race to the end line must begin with the proof of biomass ability to sustain in a long run as a sustainable and reliable source of renewable energy.

The successful completion of this research will enhance the understanding on the catalytic SCWG of biomass. Tailoring the catalysts for the SCWG with larger surface area and higher catalytic sites is necessary for improving the activity, selectivity and stability of the catalysts and making the SCWG as an economically viable gasification process. In addition, the successful of converting the oil palm frond biomass to syngas with high H₂ content through the SCWG assisted by supported and doped of MgO catalysts will make the abundant of oil palm biomass in Malaysia turns to some value-added products. As the Malaysian palm oil industry produces a huge quantity of oil palm biomass every year, there is a greater interest in the utilization of the oil palm biomass for production of hydrogen gas.

This research is aligned with inspiration of the Ministry of Energy, Science, Technology, Environment and Climate Change (MESTECC) and the Ministry of Education (MOE) of Malaysia as the targeted national research area for the nation's advancement in knowledge based economy. It also will contribute to the nation's aspiration to increase the ratio of Research Scientists and Engineers (RSE population) according to the 11th Malaysia Plan for the nation's development (2015 – 2020). The Malaysian Government is started to promote the utilization of renewable energy since year 1999 and recognized it as the 5th fuel for the country. Hydrogen energy is identified as most viable long term of renewable energy and alternative to the fossil fuel.

1.5 Objectives of research

The main aim of this research is to synthesize new catalysts for supercritical water gasification of biomass for hydrogen production. The catalytic performances between new catalysts (called doped catalysts) and conventional catalysts (called supported catalysts) are compared in catalyzing the SCWG of OPF biomass to produce H₂-rich syngas. In order to achieve this aim, the following objectives are listed.

- a) To synthesize and characterize the NiO, CuO and ZnO supported MgO catalysts.
- b) To synthesize and characterize the Ni doped MgO catalysts and Zn doped MgO catalysts.
- c) To study the catalytic performance of the synthesized catalysts for the SCWG of OPF biomass.
- d) To investigate the correlation between the catalytic performance and properties of both supported and doped MgO catalysts in SCWG reactions.



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