



UNIVERSITI PUTRA MALAYSIA

***CALCIUM OXIDE-BASED CATALYSTS FOR CONVENTIONAL AND
SUPERCRITICAL WATER GASIFICATION OF PALM FRUIT BUNCHES
IN HYDROGEN PRODUCTION***

SIVASANGAR SEENIVASAGAM

FS 2015 87



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By

SIVASANGAR SEENIVASAGAM

**Thesis Submitted to School of Graduate Studies, Universiti Putra Malaysia, in
Fulfillment of the Requirements for the Degree of Doctor of Philosophy**

May 2015

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Dedicated

*To my parents Mr & Mrs
Seenivasagam and Mageswarie*

and

*To my Siblings
Subramaniam, Vijayan,
Selvam and Kayathiri*

*This humble work is a sign of my love to
you!*

Abstract of thesis presented to the senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Doctor of Philosophy

CALCIUM OXIDE-BASED CATALYSTS FOR CONVENTIONAL AND SUPERCRITICAL WATER GASIFICATION OF PALM FRUIT BUNCHES IN HYDROGEN PRODUCTION

By

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May 2015

Chairman: Professor. Dr. Taufiq-Yap Yun Hin, PhD, CChem, FRSC (UK)
Faculty : Science

Hydrogen shows great potential as a clean and alternative energy resource that could reduce the dependency of fossil fuel consumption. Commercially, hydrogen is produced from natural gas reforming and coal gasification. Apart from this, biomass conversion via gasification method is regarded as a promising technique for hydrogen production. Empty palm fruit bunches (EFB) are considered as an abundant biomass waste which is a potential feedstock for gasification process.

In this investigation, catalytic EFB conversion into hydrogen were studied in two different prominent gasification methods that include conventional (900°C in partial O₂ environment) and supercritical water gasification reaction (380 °C). Hence, a series of CaO based catalysts were synthesized via wet impregnation method using bulk CaO as a base added with primary (Ni) and secondary (La, Mg, Ba, Nd, Na, K, Zn, Co and Fe) dopants. The prepared catalysts were characterized by x-ray diffraction (XRD), N₂ adsorption-desorption (BET), thermal gravimetric analysis (TGA), temperature programmed reduction (TPR-H₂) and temperature programmed desorption (TPD-CO₂). Furthermore, the effects of catalyst in EFB conversion to hydrogen were tested in both gasification techniques.

Preliminary catalytic studies show that BaO doped NiO-CaO catalyst was found to be very active in conventional gasification while ZnO doped NiO-CaO catalysts in supercritical water gasification reaction (SCWG). Both catalysts exhibit high selectivity towards hydrogen production. This is due to improvements in catalytic activity of NiO-CaO with additions of BaO or ZnO dopants that enhances gasification of EFB and promote hydrogen favored reactions. In comparison with both techniques SCWG reaction shows several advantages over conventional gasification such as lower reaction temperature, higher hydrogen yield, tolerate high moisture content feedstock (EFB), reduce tar production and shorter reaction time. Therefore, SCWG reaction was selected for EFB conversion using ZnO doped NiO-CaO catalysts with both unreduced and reduced catalysts. The catalytic results of reduced ZnO/Ni-CaO catalyst shows significant improvement in terms of hydrogen selectivity. Formation of Ni_{0.8}Zn_{0.2}O

solid solution phase on the CaO surface was found to be the active in catalyzing water gas shift reaction while the presence of metallic Ni promotes carbon gasification and reforming reactions.

The highest hydrogen concentration ($105.7 \text{ mmol mL}^{-1}$) was observed with 5 wt.% ZnO doped 5 wt.% Ni-CaO catalyst and found to be increased with increasing reaction time. Further, Ni and ZnO loading were increased in catalyst formulation even though concentration of hydrogen didn't display any significant difference. This is due to the possible particle agglomerations on the CaO surface. However, only slight improvement in carbon gasification is observed with 8 wt.% of Ni loading. Therefore, based on the information obtained Ni loading in the range of 5-8 wt.% with 5 wt.% of ZnO on CaO was predicted as an optimum catalyst formulation that provides high catalytic activity and selectivity towards hydrogen production.

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

**MANGKIN BERASASKAN KALSIUM OKSIDA UNTUK KONVENSIONAL
DAN SUPERKRITIKAL AIR PENGEKASAN TANDAN KOSONG BUAH
KELAPA SAWIT DALAM PENGELUARAN HIDROGEN**

Oleh

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Hidrogen menunjukkan potensi yang besar sebagai sumber tenaga bersih dan alternatif yang boleh mengurangkan kebergantungan penggunaan bahan api fosil. Secara komersial, hidrogen yang dihasilkan daripada pembentukan semula gas asli dan pengegasan arang batu. Selain itu, penukaran biojisim melalui kaedah pengegasan dianggap sebagai teknik yang berpotensi untuk pengeluaran hidrogen. Tandan kosong buah sawit (EFB) dianggap sebagai sisa biomas yang banyak dan merupakan bahan mentah yang berpotensi untuk proses pengegasan.

Dalam penyiasatan ini, penukaran EFB bermangkin kepada hidrogen telah dikaji dalam dua kaedah pengegasan utama yang berbeza iaitu konvensional (900 °C dalam persekitaran separa O₂) dan tindak balas pengegasan airlampau genting (380 °C). Oleh itu, satu siri pemangkin berasaskan CaO telah disintesis melalui kaedah pengisitepuan basah menggunakan CaO pukal sebagai asas yang ditambah dengan primer (Ni) dan sekunder (La , Mg , Ba , Nd , Na , K, Zn, Co dan Fe) sebagai bahan dop. Mangkin yang disediakan telah dicirikan oleh x-ray pembelauan (XRD), N₂ penyerapan -penyerapan (BET), analisis gravimetrik haba (TGA), suhu diprogramkan penurunan hidrogen (TPR-H₂) dan suhu diprogramkan penyerapan karbon dioksida (TPD - CO₂). Tambahan pula, kesan mangkin dalam penukaran EFB untuk penghasilan hidrogen telah diuji dalam kedua-dua teknik pengegasan .

Kajian awal mangkin menunjukkan bahawa BaO yang didopkan dalam mangkin NiO-CaO didapati sangat aktif dalam pengegasan konvensional manakala ZnO yang didopkan dalam mangkin NiO-CaO pada teknik tindak balas pengegasan airlampau genting (SCWG). Kedua-dua mangkin menunjukkan pemilihan yang tinggi ke arah pengeluaran hidrogen. Ini adalah disebabkan penambahbaikan dalam aktiviti mangkin NiO-CaO dengan kehadiran BaO atau ZnO sebagai bahan dop yang meningkatkan pengegasan EFB serta menggalakkan tindak balas penghasilan hidrogen. Sebagai perbandingan antara tindak balas kedua-dua teknik, SCWG menunjukkan beberapa kelebihan berbanding pengegasan konvensional seperti suhu tindak balas yang lebih rendah, hasil hidrogen yang lebih tinggi, sesuai dengan bahan mentah yang mempunyai kandungan kelembapan yang tinggi (EFB), mengurangkan pengeluaran tar dan masa tindak balas yang lebih pendek. Oleh itu, tindak balas SCWG telah dipilih untuk penukaran EFB menggunakan ZnO yang didopkan dalam mangkin NiO-CaO yang

mengalami penurunan dan tanpa penurunan. Keputusan mangkin ZnO/Ni-CaO yang diturunkan menunjukkan peningkatan yang ketara dari segi pemilihan hidrogen. Pembentukan $\text{Ni}_3\text{Zn}_2\text{O}$ fasa larutan pepejal di permukaan CaO yang didapati aktif dalam memangkinkan tindak balas peralihan air-gas manakala kehadiran logam Ni menggalakkan pengegasan karbon dan tindakbalas pembentukan semula.

Kepekatan hidrogen tertinggi ($105.7 \text{ mmol mL}^{-1}$) telah diperolehi dengan mangkin 5wt.% ZnO didopkan dengan 5wt% Ni-CaO dan didapati meningkat dengan peningkatan masa tindak balas. Tambahan pula, peningkatan Ni and ZnO dalam formulasi mangkin, tidak meningkatkan penghasilan hidrogen kerana berlakunya penggumpalan zarah-zarah di atas permukaan CaO. Walau bagaimanapun, sedikit peningkatan dalam pengegasan karbon diperhatikan dengan pemuatan 8 wt.% Ni dalam mangkin. Oleh itu, berdasarkan maklumat yang diperolehi pemuatan Ni dalam lingkungan 5-8 wt.% serta 5 wt.% ZnO pada CaO telah diramalkan sebagai formula mangkin yang optimum yang memberikan aktiviti pemangkinan yang tinggi di samping pemilihan penghasilan hidrogen yang lebih tinggi.

ACKNOWLEDGEMENTS

It is great privilege to express my sincere thanks to my supervisor Professor. Dr. Taufiq Yap Yun Hin, Department of chemistry, Universiti Putra Malaysia, I whole-heartedly express my gratitude for his precious guiding spirit, highest humanitarian values, tireless help, sustained encouragement, valuable suggestion and keen interest evinced throughout the research period without which, this thesis would not have seen the beacon light in my path of research. His visionary thoughts and energetic working style have influenced me greatly as a researcher.

I am so grateful to Professor. Dr. Zulkarnain Zainal and Assoc. Professor. Dr. Salmiaton Ali for their guidance, encouragement, confident and simplicity motivated me in various aspects during the course study.

I am deeply indebted to Professor. Dr. Ambar Yarmo (Universiti Kebangsaan Malaysia) and Professor. Dr. Kuniyuki Kitagawa (Nagoya University), for their dexterous help, unrelaxing support and for providing me adequate laboratory facilities in the laboratories.

I extend my sincere thanks to all the staff, in Department of chemistry, for their constant support throughout this study. Their prompt assistance in technical issues has helped me to complete my research work on time. I express my special thanks to all the members of PutraCAT laboratory for their support and willingness to share expertise during the time of research.

I feel ecstatic to express my heartfelt thanks to my beloved family and treasured friends especially to Kumar Arumugam, Prathipraj Punasegaran and Tachaini Kandasamy for their priceless support and tireless encouragement. This success is made possible through their constant love during my ups and downs and words of wisdom which kept me going till the end. Thank you for always being there for me, by means of their love, care, sacrifice and prayers which allowed me to be as ambitious as I wanted.

I certify that a Thesis Examination Committee has met on 25 June 2015 to conduct the final examination of Sivasangar Seenivasagam on his thesis entitled “Calcium Oxide-Based Catalysts for Conventional and Supercritical Water Gasification of Palm Fruit Bunches in Hydrogen Production” in accordance with the Universities and University College Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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LIST OF ABBREVIATIONS

AC	Activated Carbon
BET	Brunauer Emmett Teller
BJH	Barrett-Joyner-Halenda
BTU	British-Thermal Unit
BTX	Benzene, Toluene and Xylene
CGR	Carbon Gasification Ratio
CHNS/O	Carbon, Hydrogen, Nitrogen, Sulphur/ Oxygen
DTG	Derivative Thermogravimetry
EFB	Empty Palm Fruit Bunches
ER	Equivalence Ratio
FCC	Fluid Catalytic Cracking
FTIR	Fourier transform infrared spectroscopy
FWHM	Full width at half maxima
GC	Gas Chromatography
HGR	Hydrogen Gasification Ratio
JCPDS	Joint Committee on Powder Diffraction Standards
LPG	Liquefied Petroleum Gas
MPOB	Malaysian Palm Oil Board
MS	Mass Spectrometer
OD	Outside Diameter
PAH	Poly Aromatic Hydrocarbon
PG	Palygorskite
POME	Palm Oil Mill Effluent
QMA	Quadruple Mass Analyzer
RE	Renewable energy
SCWG	Supercritical water gasification
TCD	Thermal Conductivity Detector
TGA	Thermal Gravimetric Analysis
TPD	Temperature Programmed Desorption
TPG	Temperature Programmed Gasification
WGS	Water Gas Shift
XPS	X-ray photoelectron spectroscopy
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Background.

According to the United Nation's report, current global population is around 7.2 billion and it is projected to increase up to 8.1 billion in the next 12 years and estimated of 9.6 billion by 2050 (United Nation, 2014). Energy is the key element of human survival and obtaining the source becomes fundamental in order to sustain the population growth. Currently, non-renewable fuel resources includes hydrocarbon fuel from petroleum, coal and natural gas are the primary source of energy. Based on International energy outlook 2013 by the US Energy Administration, global energy consumptions were 524 quadrillion British thermal units (btu) in 2010 and expected to rise 56% (820 quadrillion btu) by 2040 (Energy Information Administration, 2013). The steady economic growth of developing countries, sophisticated living, and exponential increment in human population boost the demand for energy resource. Exploiting non-renewable resources for energy causes serious environment deterioration such as diminishing ozone layer, global warming, and drastic climate change and so on. Besides, the uncertainties of fossil fuel reserves also threaten the energy security of the rising demand and for future utilization. At the brink of global energy crisis, renewable energy (RE) utilization initiated a new era on energy harvesting methods which are considered to be clean and sustainable.

Renewable energy (RE) is an alternative and nonpolluting energy resource that could be obtained from nature through various sources such as solar, wind, biomass, geothermal, tidal waves and hydropower. It is estimated that renewable energy supply is around 14% of current global energy demand from various sources (World Energy Assessment, 2000) and expected to increase in near future. Table 1.1 summarizes the trend of global renewable energy usage and its predicted projection in upcoming decades.

Table 1.1 Global energy usage projection (Kralova and Sjoblom, 2010).

Year	2001	2010	2020	2030	2040
Total consumption (Million tons oil Equivalent)	10038	10549	11425	12352	13310
Biomass	1080	1313	1791	2483	3271
Large hydropower	22.7	266	309	341	358
Geothermal	43.2	86	186	333	493
Small Hydropower	9.5	19	49	106	189
Wind	4.7	44	266	542	688
Solar thermal	4.1	15	66	244	480
Photovoltaic	0.1	2	24	221	784
Solar thermal electricity	0.1	0.4	3	16	68
Marine	0.05	0.1	0.4	3	20
Total RE	1365.5	1745.5	2964.4	4289	6351
RE contribution (%)	13.6	16.6	23.6	34.7	47.7

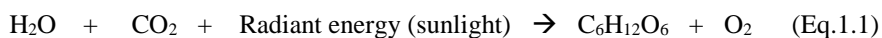
However, renewable energy harnessing methods are suffering from several barriers such as cost-effectiveness, technical drawbacks, market price fluctuation, institutional, political and regulatory disputes and also from social and environmental constraint (Painuly, 2001). Despite the various obstacles, renewable energy utilization flourished globally with emerging sophisticated technologies that enhance the efficiency of the process. Malaysia is blessed with both renewable and non-renewable resources that are sufficient enough to meet the current energy demand. However, the country policy to reduce the dependence of fuel as a primary energy resource and CO₂ release to the environment promotes the indigenous renewable resources. Various renewable energy resources available in Malaysia and its estimated energy values (Ministry of Energy, Green Technology and Water, 2013) were presented in Table 1.2. Among the resources, biomass (forest residue, oil palm wastes, mill residue, municipal wastes and rice husk) possess high potential as an alternative energy resource. Malaysia's geographical location supports a huge amount of vegetation including growth of dense tropical rain forest and vast agricultural activities (palm oil, rubber, ext.) throughout the year. Primarily, biomass is combusted to generate heat for many processes including cooking in rural areas. Thus, the biomass plays an important role in global energy crisis dilemma to fulfill the everlasting demand with minimal environmental impact.

Table 1.2 Renewable energy resources in Malaysia.
(Ministry of Energy, Green Technology and Water, 2013)

Renewable energy resources	Energy value (annual) in RM (million)
Forest residue	11984
Oil palm residue	6379
Solar thermal	3023
Mill Residue	836
Hydro power	506
Solar Pv	378
Municipal wastes	190
Rice husk	77
Land fill gas	4

1.1 Biomass

Biomass is a generalized term for all types of organic wastes that are divided into pythomass (plants biomass) and zoomass (animal biomass) when plants are consumed as a food source by animals. The basic building units of biomass, carbohydrates were produced via photosynthesis reactions (Eq.1.1) where the energy from the sun light is stored into chemical bonds. In detail CO₂ from the air and water are converted into basic sugars in the presence of sun lights which is made up the structural components of biomass (Saidur, *et al.*, 2011). Figure 1.1 elucidates the classifications of biomass wastes generated from various sectors:



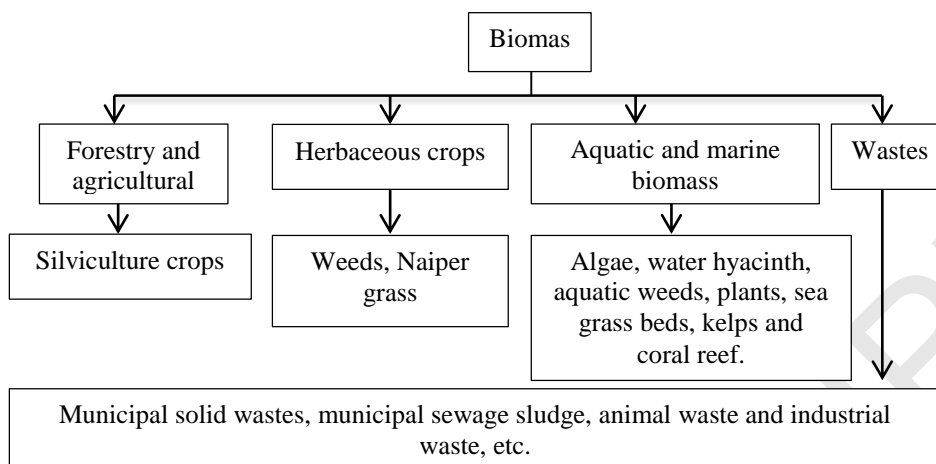


Figure 1.1 Biomass classifications (Panwar *et al.*, 2012).

There are several important stimuli behind the leading driving force of biomass utilization as a potential renewable resource. Direct combustion of biomass or its conversion into various fuels sources are considered clean and zero carbon emission compared to fossil fuel. Theoretically, there is no net addition of CO₂ to the environment from biomass derived energy, whereby it is consumed by growing plants and fixed back into carbonaceous compounds via photosynthesis reactions (Saidur *et al.*, 2011). Furthermore, there are several factors that have been identified for the growing interest on biomass exploitation for energy. According to Mckendry (2002), the key elements of biomass conversion are:

- a) Technological advancement in terms of conversion methods with higher efficiency and low cost biomass residues application that had suppressed the overall cost of power generation compared to commercial process using fossil fuels.
- b) Energy crops cultivation on the spare land due to surpluses in food production in Western Europe and US that provide a profitable market for non-food crops farming to meet energy demand.
- c) Global warming and climate change caused by excessive greenhouse gases emission mainly CO₂ from fossil fuel burning demand a dramatic shift to renewable energy to mitigate the harmful gas release to the atmosphere.

Agricultural wastes are promising biomass resources that consist of byproducts from cultivated crops. Commercial scale plantations such as oil palm, sugarcane, rice and wheat generate large volume of wastes that lead to waste management problems. Even though some of the biomasses were combusted onsite to produce steam and electricity, their abundance create serious environmental problems.

1.2 Problem statement

Oil palm or scientifically known as *Elaeis guineensis*, is a plant which yield fruits that are rich in edible oil. Originated from West Africa, it is cultivated largely in tropical areas such as Malaysia which has wet and humid climate throughout the year (Kelly-Yong *et al.*, 2007). Palm Oil is the second largest traded vegetable oil in the world with core consumptions in the food based sectors and recently into biofuel (Sumathi *et al.*, 2008). Due to vast application and growing demand for the oil, palm plantation areas has expanded tremendously for the past few decades. According to Malaysia Palm Oil Board, over 5.08 million hectares of land being used for palm oil harvesting with its crude oil production around 18.8 million tonnes annually (MPOB, 2014). Exponential growth in palm oil sector emanates large amount of byproducts both from the field (trunks, fronds) and from oil extraction mills (empty palm fruit bunches, fibers, shells and mill effluents). Currently, palm fronds and trunks are underutilized and the abundance of mill wastes caused major waste disposal problem. It is reported that 90% of palm tree become biomass wastes and only 10% yield palm oil (Basiron, 2007). Palm oil industry in has Malaysia generates 80 million tonnes of dry biomass in the year 2010 and is expected to increase 85-110 million tonnes by 2020 as well as POME from 60 million to 70-110 million tone (Agensi Inovasi Malaysia, 2011). However, only a small fraction of the biomasses were utilized with poor efficiency and open burning is practiced widely and contributes to serious air pollutions (Sulaiman *et al.*, 2010).

Generally, fibers and shells were combusted in the boiler to generate steam and electricity for the mill operations. Difficulties arise with EFB disposal where burning in the incinerator is banned in Malaysia due to release of harmful gaseous. However, EFB is rich in inorganic contents and only small portion of the material is used for mulch to return the nutrients to the soil. Besides, higher moisture content of materials makes it a poor fuel source for combustion and remained piled up in the mill sites to be decomposed in open air (Abdullah and Sulaiman, 2013). Therefore, waste management problem arise to dispose the abundant EFB waste without serious environmental consequences. Proper utilization of palm waste is essential especially targeted on EFB that lack in particular usage. Therefore, alternative ways have been carried out to convert the abundance of EFB into useful form of energy. Hydrogen is considered a prolific source of clean energy and has important role in the socioeconomic growth near future. Biomass derived hydrogen is a promising approach besides the general production routes from fossil fuels such natural gas and coal reforming.

Biomass conversion methods have been classified into three categories: i) Thermochemical conversion ii) Biological conversion (Biochemical conversion) iii) Mechanical conversion and the selection of the methods are depended on the type and quantity of the desired feedstock (Saxena *et al.*, 2008). Among the techniques, thermochemical method has additional advantages such as lower reaction time, flexibility in the feedstock selection (various type of feedstock can be used), diverse application of the derived product gas (H₂, Fisher Tropsch-Diesel, Synthetic gasoline and Chemicals synthesis) and also the products are more compatible with existing petroleum refining operation (Kumar *et al.*, 2009). There are three main thermal routes available for biomass conversion into various form of energy (heat, fuel gas and bio-oil) via combustion, gasification, and pyrolysis (Bridgwater, 2003). Gasification route has received wide interest due to its higher conversion efficiency (Lahijani and Zainal,

2011). It is referred to as a unique form of pyrolysis reaction at higher reaction temperature that converts carbonaceous biomass materials into valuable gases (H_2 , CO, CO_2 and CH_4) in a partial oxygen environment or using oxidant such as steam and CO_2 (Zhang *et al.*, 2010a).

Apart from this, supercritical water gasification (SCWG) is another unique gasification technique that uses water as a gasifying medium. The drastic changes in the nature of water such as low dielectric constant, number of hydrogen bonds and its weaker strength enables water to behave like an organic solvent at supercritical condition (Temperature > 373 °C and pressure 22 Mpa). This phenomenon provides an effective homogenous environment that increases the reaction rate and reduces the mass transfer limitation problem (Savage, 1999). Besides, the ability of SCWG that could tolerate the high moisture content feedstock in the reaction is an additional advantage that reduces the operational cost by surpassing the feedstock drying step.

Syngas (H_2 and CO) is the main product of gasification reaction that fall into various applications assort from combustible fuel gas for steam/heat generation, a source of hydrogen that substitute the natural gas reforming, feed the fuel cell and used in chemical synthesis (Rezaiyan and Cheremisinoff, 2005). However, gasification technique suffers from severe tar formation during the biomass conversion which is considered as a major obstacle in the process. Tar is a complex mixture of poly-aromatic compounds derived from biomass that failed to degrade into lighter gases completely. It is part of the product gas stream, which condensed in the downstream equipment's and clogged the reactors systems and its pipelines.

There are many ways that have been tried to reduce tar in the products gas stream either being discarded totally or by reformed into lighter gases. Various methods are developed to crack the produced tar such as thermal cracking which increase the operational cost. Therefore, it has been concluded that catalysts application for tar cracking possess several advantages that includes, lower reaction temperature and increase the hydrogen yield via reforming and water gas shift reactions. However, severe catalyst deactivation is occurred due to inefficiency of the employed catalysts. Generally, noble metal catalysts exhibit remarkable catalytic activity and resist to early catalyst deactivation. However, higher cost of noble metals restricts its application in tar cracking. Therefore, urgency in the development of an inexpensive catalyst that shows high catalytic activity and selectivity in tar cracking and reforming reactions are prioritized.

1.3 Scope of study

In this investigation, tri-metal oxide catalysts were prepared via wet impregnation method. Bulk CaO is used as a base catalyst and added with primary dopant (nickel) and series of secondary dopants (lanthanum, magnesium, barium, neodymium, sodium, potassium, zinc, cobalt and iron). The prepared catalysts (CaO-NiO-x, x = secondary dopants) were studied in EFB gasification reaction in two different methods (conventional gasification (900 °C) and supercritical water gasification (380 °C) that varied with reaction temperatures and environment. The effects of dopants on the synthesized catalysts preliminarily were compared in terms of tar cracking abilities and hydrogen yield. Based on the preliminary catalytic results, the best performing catalyst were selected to a further study on its dopant compositions to attain the maximum hydrogen yield.

1.4 Objectives

Objectives of this study are:

- i. To synthesize effective modified CaO based catalysts and characterized with x-ray diffraction (XRD), Brunner Emmet Teller (BET), thermal gravimetric analysis (TGA), temperature programmed reduction (TPR-H₂) and temperature programmed desorption (TPD-CO₂).
- ii. To investigate the thermal degradation of EFB and lignocellulosic model compounds in both conventional gasification and supercritical water gasification.
- iii. To evaluate the catalytic activity and hydrogen selectivity of the developed catalysts on EFB conversion into hydrogen rich product gas.
- iv. To compare the potential of both biomass conversion techniques respect to biomass conversion efficiency and product yield selectivity.
- v. To optimize the catalytic reaction condition and catalyst formulation to attained maximum hydrogen yield and EFB conversion.

1.6 Organization of the thesis

Based on the research objectives, this thesis is divided into 9 chapters as follows:

Chapter 1 presents the general information about global energy crisis issues and potential of renewable energy utilization that is readily available in Malaysia. An overlook of existing biomass conversion technologies with its advantages and disadvantages were discussed in problem statement section.

Chapter 2 in the literature review section, the role of different types of catalysts used in the gasification techniques (conventional gasification and supercritical water gasification) were elaborated in detail. Furthermore, the effect of catalysts on particular reactions such as tar cracking and reforming, hydrogen yield and reaction temperature was discussed.

Chapter 3 describes the methodology of our experimental works that includes catalysts preparation method, characterizations techniques, catalytic studies and also product analysis.

In Chapter 4, conventional gasification (900 °C) of EFB and lignocellulosic model compounds in the absence of catalyst was reported. Fundamental behavior of the feedstock in terms of thermal stability and degradation patterns with reaction temperature was evaluated.

Chapter 5 describes the non-catalytic supercritical water gasification (380 °C) reaction using EFB, POME and lignocellulosic model compounds.

Chapter 6 reports on the catalyst application in conventional gasification (900 °C) in terms of the effect of added dopant on tar cracking, biomass degradations and hydrogen yield.

Chapter 7 elucidates the catalytic activity of synthesized catalysts in supercritical water gasification (380 °C) of EFB to hydrogen rich product gas.

Chapter 8 optimized the selected catalyst synthesis with different amount of dopants loading and evaluation of its catalytic activity in EFB supercritical water gasification.

Lastly, Chapter 9 presents the general discussions and conclusions with suggestions for future works based on our understanding and outcomes from this study.

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LIST OF PUBLICATIONS

A-Publications in referred journals

Taufiq-Yap, Y. H., **Sivasangar, S** and 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, 158-165. (Impact factor : 3.651)

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Taufiq-Yap, Y. H and **Sivasangar, S.** A Catalyst Applicable For Gasification of Biomass And A Method Using The Same. 2013. File for patent (**P12013701336**).

V.G. Kumar Das, W. Pei Meng, Irene Ling, M.Z Noor Idayu, **S. Sivasangar**, S. Nitia, K and R. Nur Dayana. Captivating Lindau-Dedicated to Chemistry. Kuala Lumpur: Akademik Sains Malaysia, 2013. ISBN 978-983-2915-06-5

B- Papers presented at Seminars/ Conferences

Taufiq-Yap, Y. H., **Sivasangar, S** and Salmiaton, A. (2011). Hydrogen Production From Catalytic Gasification Of Empty Palm Fruit Bunch (EPFB) Over Modified Cao Sorbent Based Catalysts 5th International Congress Of Chemistry And Environment, Glory Beach Resort, Port Dickson, Malaysia. (Oral Presentation).

Taufiq-Yap, Y. H. and **Sivasangar, S.** (2011). Nanosized Nickel Alumina Based Catalysts Synthesized Via Double Stage Wet Impregnation For Methane Dry Reforming. International Conference For Nano-Material Synthesis And Characterization, Malaysia. (Poster Presentation).

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C- Status of Submitted Papers to the ISI Journals

Sivasangar, S and Taufiq-Yap, Y. H. Catalytic supercritical water gasification of Empty palm fruits bunches using Zn doped Ni-CaO catalysts to promote the hydrogen yield. *Applied Catalysis A : General*. (Submitted).

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D- Awards

Research and Innovation Exhibition ” (PRPI). (2012). Universiti Putra Malaysia. **(Gold)**

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