

**DILUTE SULFURIC ACID HYDROLYSIS
OF RED MACROALGA *EUCHEUMA*
DENTICULATUM WITH MICROWAVE-
ASSISTED HEATING FOR BIOCHAR AND
BIOETHANOL PRODUCTION**

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EUCHEUMA DENTICULATUM WITH MICROWAVE-ASSISTED HEATING
FOR BIOCHAR AND BIOETHANOL PRODUCTION**

by

TEH YONG YI

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Requirements for the Degree of
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TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT	ii
TABLE OF CONTENTS	iv
LIST OF TABLES	viii
LIST OF FIGURES	ix
LIST OF ABBREVIATIONS	xi
LIST OF SYMBOLS	xiv
ABSTRAK	xv
ABSTRACT	xvii
CHAPTER ONE: INTRODUCTION	
1.1 Energy sector landscape	1
1.2 Overall renewable energy	4
1.3 Development of bioenergy in Southeast Asia	5
1.4 Potential of bioenergy as alternative renewable energy	8
1.5 Problem Statement	11
1.6 Objectives	13
1.7 Scope of study	13
1.8 Thesis organization	14

CHAPTER TWO: LITERATURE REVIEW

2.1	Macroalgae as biofuel feedstock	16
2.2	Thermochemical conversion	20
2.3	Hydrolysis	22
2.3.1	Enzymatic hydrolysis	22
2.3.2	Chemical hydrolysis	24
2.3.2 (a)	Alkaline hydrolysis	24
2.3.2 (b)	Acid hydrolysis	25
2.4	Microwave-assisted heating	29
2.5	Acid hydrolysis with microwave-assisted heating	34
2.5.1	Lignocellulosic biomass	35
2.5.2	Microalgae and macroalgae	38
2.6	Fermentation	40
2.7	Summary	43

CHAPTER THREE: MATERIALS AND METHODS

3.1	Raw materials and chemicals	45
3.1.1	Feedstock preparation	45
3.1.2	Chemicals and standards	45
3.1.3	Experimental flow chart	47
3.2	Experimental setup	49
3.3	Chemical composition analysis of raw feedstock	52
3.4	Chemical properties of raw feedstock and biochar	53
3.4.1	Proximate analysis	53
3.4.1 (a)	Determination of moisture content	53

3.4.1 (b)	Determination of ash content	53
3.4.1 (c)	Determination of volatile matter content	54
3.4.1 (d)	Determination of fixed carbon content	54
3.4.2	Elemental analysis	54
3.4.3	Fiber analysis	55
3.4.4	Determination of crystallinity	58
3.4.5	Determination of functional groups	59
3.5	Physical properties of raw feedstock and biochar	59
3.5.1	Calorific value	59
3.5.2	Solid yield, energy density and energy yield	59
3.5.3	Surface morphology	60
3.6	Thermal analysis	60
3.7	Determination of reducing sugars and by-product concentrations	60
3.8	Fermentation process	61
3.8.1	Cell cultivation	61
3.8.2	Yeast dry cell mass (DCM) concentration	62
3.8.3	Fermentation of hydrolysate	62
3.8.4	Determination of bioethanol concentration	63

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1	Chemical composition of raw feedstock	64
4.2	Acid hydrolysis with microwave-assisted heating	66
4.2.1	Proximate analysis	67
4.2.1 (a)	Determination of moisture content	67
4.2.1 (b)	Determination of ash content	70

4.2.1 (c)	Determination of volatile matter content	71
4.2.1 (d)	Determination of fixed carbon content	73
4.2.2	Elemental analysis	74
4.2.3	Fiber analysis	79
4.2.4	Determination of crystallinity	80
4.2.5	Determination of functional groups	82
4.2.6	Calorific value	85
4.2.7	Solid yield, energy density and energy yield	88
4.2.8	Surface morphology	91
4.2.9	Thermal analysis	93
4.2.10	Determination of reducing sugars and by-product concentrations	96
4.3	Fermentation	103
4.3.1	Determination concentration of sugars, by-product and ethanol	105

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

5.1	Conclusions	108
5.2	Recommendations	109

REFERENCES	110
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APPENDICES

LIST OF PUBLICATION

LIST OF TABLES

		Page
Table 2.1	Carbohydrate composition in macroalgae, microalgae and lignocellulosic biomass (Jung et al., 2013; Lobban and Wynne, 1981)	17
Table 2.2	Process parameters of thermochemical conversion (Chen et al., 2015a)	21
Table 2.3	Comparison of acid hydrolysis from various algae biomass	27
Table 2.4	Loss factor of material at frequency of 3 GHz (Osada and Yoshioka, 2015)	32
Table 2.5	Comparison of acid hydrolysis with microwave-assisted heating from different feedstocks	37
Table 3.1	List of chemicals used in the experimental work	46
Table 4.1	Chemical composition of raw <i>E. denticulatum</i>	65
Table 4.2	Proximate analysis of raw bagasse, microalga and macroalga as well as their derived biochar	68
Table 4.3	Elemental analysis of raw bagasse, microalga and macroalga as well as their derived biochar	75
Table 4.4	Cellulose contents in the raw macroalga and its derived biochar	79
Table 4.5	Spectral band assignments of raw macroalga and biochar	82
Table 4.6	Higher heating value (HHV) of raw bagasse, microalga and macroalgae as well as their derived biochar	87
Table 4.7	Solid yield, energy density and energy yield of raw bagasse, microalga and macroalgae as well as their derived biochar	89
Table 4.8	Concentrations and yield of reducing sugars and by-product	97
Table 4.9	Comparison of hydrolysis from various macroalgae and operating conditions	102
Table 4.10	The performance of separate hydrolysis and fermentation of macroalgae	107

LIST OF FIGURES

		Page
Figure 1.1	Total final energy consumption by sector for the year 1995, 2015 and 2035 (BP, 2017)	2
Figure 1.2	Renewable energy capacity by source in Southeast Asia, 2006-2015 (ACE, 2018)	6
Figure 1.3	Potential bioenergy pathways: From feedstock to final energy use (Chen et al., 2015a; IEA, 2017b; Rowbotham et al., 2012)	9
Figure 2.1	(a) Brown macroalgae (b) Green macroalgae (c) Red macroalgae (Photo by DOF, 2016)	17
Figure 2.2	Structure of polysaccharides in red macroalgae (Wei et al., 2013)	18
Figure 2.3	The electromagnetic spectrum (Leadbeater and McGowan, 2013)	30
Figure 2.4	The Embden-Meyerhof pathway and Leloir pathway for ethanol synthesis (Caputto et al., 1967; van Maris et al., 2006)	42
Figure 3.1	Picture of <i>E. denticulatum</i> a) dried samples b) ground samples	45
Figure 3.2	Flow diagram of the research methodology	48
Figure 3.3	Experimental setup for microwave-assisted sulfuric acid hydrolysis	49
Figure 3.4	Cover shot of microwave heating experimental setup	51
Figure 3.5	Flow diagram of biochar and bioethanol production from <i>E. denticulatum</i>	52
Figure 3.6	Diagram outlining the principal steps of the procedure for fiber analysis	55
Figure 4.1	The van Krevelen diagram of raw macroalga and its derived biochar (DW designates the condition of hydrolysis with distilled water)	77
Figure 4.2	XRD patterns of raw macroalga and its derived biochar at heating temperatures of (a) 150 °C, (b) 160 °C and (c) 170 °C	81

Figure 4.3	FTIR spectra of raw macroalga and its derived biochar at heating temperatures of (a) 150 °C, (b) 160 °C and (c) 170 °C	83
Figure 4.4	SEM images of raw macroalga and its derived biochar (×3000)	92
Figure 4.5	(a) TGA and (b) DTG thermograms of raw macroalga and its derived biochar	94
Figure 4.6	Sugar decomposition pathway (Almeida et al., 2009; Jeong et al., 2012)	98
Figure 4.7	Fermentation profile of hydrolysate	105

LIST OF ABBREVIATIONS

ACE	ASEAN Centre for Energy
ADF	Acid detergent fiber
ADL	Acid detergent lignin
AIA	Acid insoluble ash
AOAC	Association of Official Agricultural Chemists
ASEAN	Association of Southeast Asian Nations
ASTM	American Society for Testing and Materials
CS	Combined severity
DCM	Dry cell mass
DOF	Department of Fisheries Malaysia
DSC	Differential scanning calorimetry
DTG	Derivative thermogravimetry
EA	Elemental analyzer
EGA	Evolved gas analysis
EEF	Energy enhancement factor
ELSD	Evaporating light scattering detector
GHz	Gigahertz
FAO	Food and Agriculture Organization of the United Nations
FC	Fixed carbon
FID	Flame ionization detector
FT-IR	Fourier transform infrared
GC	Gas chromatography
GHG	Greenhouse gas
GW	Gigawatt

HHV	Higher heating value
HTL	Hydrothermal liquefaction
HPLC	High performance liquid chromatography
IBI	International Biochar Initiative
IEA	International Energy Agency
IRENA	International Renewable Energy Agency
mb	Million barrels
mHz	Megahertz
MSW	Municipal solid waste
mtoe	Million tonnes oil equivalent
MW	Megawatt
NDF	Neutral detergent fiber
NREL	National Renewable Energy Laboratory
PV	Photovoltaic
RFA	Renewable Fuels Association
RO	Reverse osmosis
SEDA	Sustainable Energy Development Authority of Malaysia
SEM	Scanning electron microscope
SIEW	Singapore International Energy Week
TG	Thermogravimetry
TGA	Thermogravimetric analyzer
tmoe	Thousand million oil equivalent
TMA	Thermomechanical analysis
USDA	United States Department of Agriculture
UV	Ultraviolet

VM	Volatile matter
VRE	Variable renewable energy
XRD	X-ray diffractometer
YEPG	Yeast extract peptone galactose
5-HMF	5-(hydroxymethyl)furfural

LIST OF SYMBOLS

Symbol	Description	Unit
ADF_F	Final weight of sample for ADF	g
ADF_I	Initial weight of sample for ADF	g
ADL_F	Final weight of sample for ADL	g
D_E	Energy density of biochar	Dimensionless
$[EtOH]_{max}$	Highest ethanol concentration achieved during fermentation	g/L
$HHV_{biochar}$	HHV of biochar	MJ/kg
HHV_{raw}	HHV of raw biomass	MJ/kg
$m_{biochar}$	Mass of biochar	g
m_{raw}	Mass of raw biomass	g
NDF_F	Final weight of sample for NDF	g
NDF_I	Initial weight of sample for NDF	g
$[Sugar]_{ini}$	Total initial sugar concentration at onset of fermentation	g/L
W_C	Weight of crucible	g
W_{CC}	Weight of crucible and cover	g
W_I	Initial weight	g
W_F	Final weight	g
W_1	Weight of sample and crucible	g
W_2	Weight of ash and crucible	g
$Y_{biochar}$	Solid yield of biochar	%
Y_E	Energy yield of biochar	%
$Y_{P/S}$	Ethanol yield	g/g
$Y_{\%T}$	Percent theoretical yield	%

**HIDROLISIS MAKROALGA MERAH *EUCHEUMA DENTICULATUM*
DENGAN LARUTAN ACID SULFURIK DENGAN MENGGUNAKAN
SISTEM PEMANASAN GELOMBANG MIKRO BAGI PENGHASILAN
BIOARANG DAN BIOETANOL**

ABSTRAK

Eucheuma denticulatum ialah sejenis makroalga merah yang berpotensi sebagai stok suapan untuk penghasilan biotena kerana makroalga ini mengandungi kandungan karbohidrat yang tinggi, mudah diperolehi serta proses penghasilan hanya menggunakan tanah yang sedikit. Oleh sebab kandungan karbohidrat yang tinggi, makroalga boleh dihidrolisis menjadi gula mudah ditapai dan ditukar kepada bioetanol oleh mikroorganisma semulajadi. Walau bagaimanapun, pemanasan haba konvensional yang memindahkan haba dari permukaan ke pusat bahan menjadikan proses pemanasan agak lambat dan tidak cekap. Oleh itu, masa pemanasan yang berpanjangan telah mengurangkan kuantiti gula dan meningkatkan pula penghasilan produk sampingan yang boleh menjejaskan proses penapaian seterusnya. Dalam kajian ini, hidrolisis asid dengan pemanasan gelombang mikro dijalankan dalam ketuhar gelombang mikro pada frekuensi 2.45 GHz dan kuasa 800W. Dengan pemanasan dielektrik gelombang mikro, ia bukan sahaja dapat menangani masalah yang dibangkitkan di atas, malahan ia dapat meningkatkan prestasi proses hidrolisis dan menghasilkan bioarang, gula dan bahan kimia yang bernilai tinggi daripada makroalga. Tujuan utama kajian ini adalah untuk mengkaji sifat-sifat bioarang yang dihasilkan sebagai sumber biotena selepas makroalga melalui proses hidrolisis gelombang mikro. Proses hidrolisis dijalankan pada kepekatan asid sulfurik 0.1M dan 0.2M, suhu pemanasan antara 150-170 °C dan masa pemanasan selama 10 minit.

Kualiti bioarang yang dihasilkan didapati lebih baik dengan peningkatan kandungan karbon unsur dan kandungan abu dan lembapan yang lebih rendah. Nilai kalori bioarang dapat ditingkatkan sehingga 45%, dan 39% hasil tenaga dapat dipulih kembali. Selain daripada bioarang, kepekatan gula dan produk sampingan juga ditentukan dan seterusnya ditukarkan kepada bioetanol. Hasil gula sebanyak 74.84% (51.47 g/L) dan produk 5-HMF yang berjumlah 0.20 g/L telah dicapai apabila biomassa dihidrolisiskan pada suhu 160 °C dengan kepekatan asid sulfurik 0.1M. Hasil bioetanol yang diperolehi adalah sebanyak 0.33 g/g (64.21%). Sebagai kesimpulan, hidrolisis dengan larutan acid sulfurik dalam sistem pemanasan gelombang mikro berpotensi untuk menghasilkan biotenaga, bioarang yang kaya dengan nutrien sebagai penambahbaik tanah dan bahan kimia yang bernilai tinggi.

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FOR BIOCHAR AND BIOETHANOL PRODUCTION**

ABSTRACT

Eucheuma denticulatum is a type of red macroalgae which are considered as potential feedstock for biofuel production due to high carbohydrate content, ease of availability and low arable land usage. Being such abundant in carbohydrates, macroalgae can be hydrolysed into fermentable sugars and converted to bioethanol by natural microorganisms. However, the conventional thermal heating that delivers heat from the surface to center of a material is comparatively slow and inefficient. As a result, the longer heating time gives rise to a dramatic reduction of reducing sugars but higher content of by-products, consequently inhibiting the subsequent fermentation. In this study, acid hydrolysis with microwave-assisted heating of macroalga was conducted in a 2.45 GHz microwave oven with 800W of power. The rapid and efficient of dielectric heating effect of microwave-assisted heating could address aforementioned problem, enhance the hydrolysis process and co-produce biochar, reducing sugars and valuable chemicals. This study was set out to study the properties of biochar as a source of biofuel after macroalga was subjected to microwave-assisted hydrolysis. The hydrolysis reactions were operated at sulfuric acid concentrations of 0.1M and 0.2M, reaction temperatures of 150–170 °C and a heating time of 10 min. The produced biochars were characterized and it was found that biochar qualities were improved with increased elemental carbon content and lower ash and moisture contents. The calorific value of the biochar was intensified up to 45%, and 39% of energy yield was recovered. Apart from biochar, the

concentrations of reducing sugars and by-product of hydrolysate were also determined and subsequently converted to bioethanol. The highest total reducing sugars were 51.47 g/L (74.84% yield) along with a low by-product 5-HMF of 0.20 g/L, when the biomass was treated under the conditions at 160 °C with 0.1M H₂SO₄. The ethanol yield obtained was 0.33 g/g, which corresponded to a 64.21% of yield. As a conclusion, acid hydrolysis with microwave-assisted acid hydrolysis has its great potential applications for the production of bioenergy, nutrient-rich biochar for soil amelioration and value-added chemicals.

CHAPTER ONE

INTRODUCTION

1.1 Energy sector landscape

Energy is an important sector which interplays between power generation, transportation, heating and cooling. The dynamics of energy consumption in the industry, transport, power and buildings sectors are depicted in Figure 1.1. Global energy consumption rose 53% from 8589 million tonnes oil equivalent (mtoe) in 1995 to 13147 mtoe in 2015 and it is expected to increase, reaching 17158 mtoe in 2035 (BP, 2017). Remarkably, energy consumption in Asia Pacific nearly increased 2.5 times over the two decades, contributing 5499 mtoe in 2015. This is due to Asia Pacific's economy shifted from an agricultural to an energy-intensive manufacturing industrial base (IRENA, 2018). Coal is mainly used in industry sector, contributing 44% of the total global consumption by energy source (BP, 2017).

Driven by road infrastructure development and rising vehicle ownership, the energy use in transport sector grew modestly from 1995 to 2015. Oil is used primarily for road transport (95% of the total global consumption by energy source) (BP, 2017). The global car fleet will be doubled up and reached 2 billion by 2040. The energy use in the transport sector remains dominated by oil next decades, which fuel demand has grown rapidly amid growing economic, greater freight activities and rising consumption for trucks, cars, aviation and shipping (IEA, 2017c).

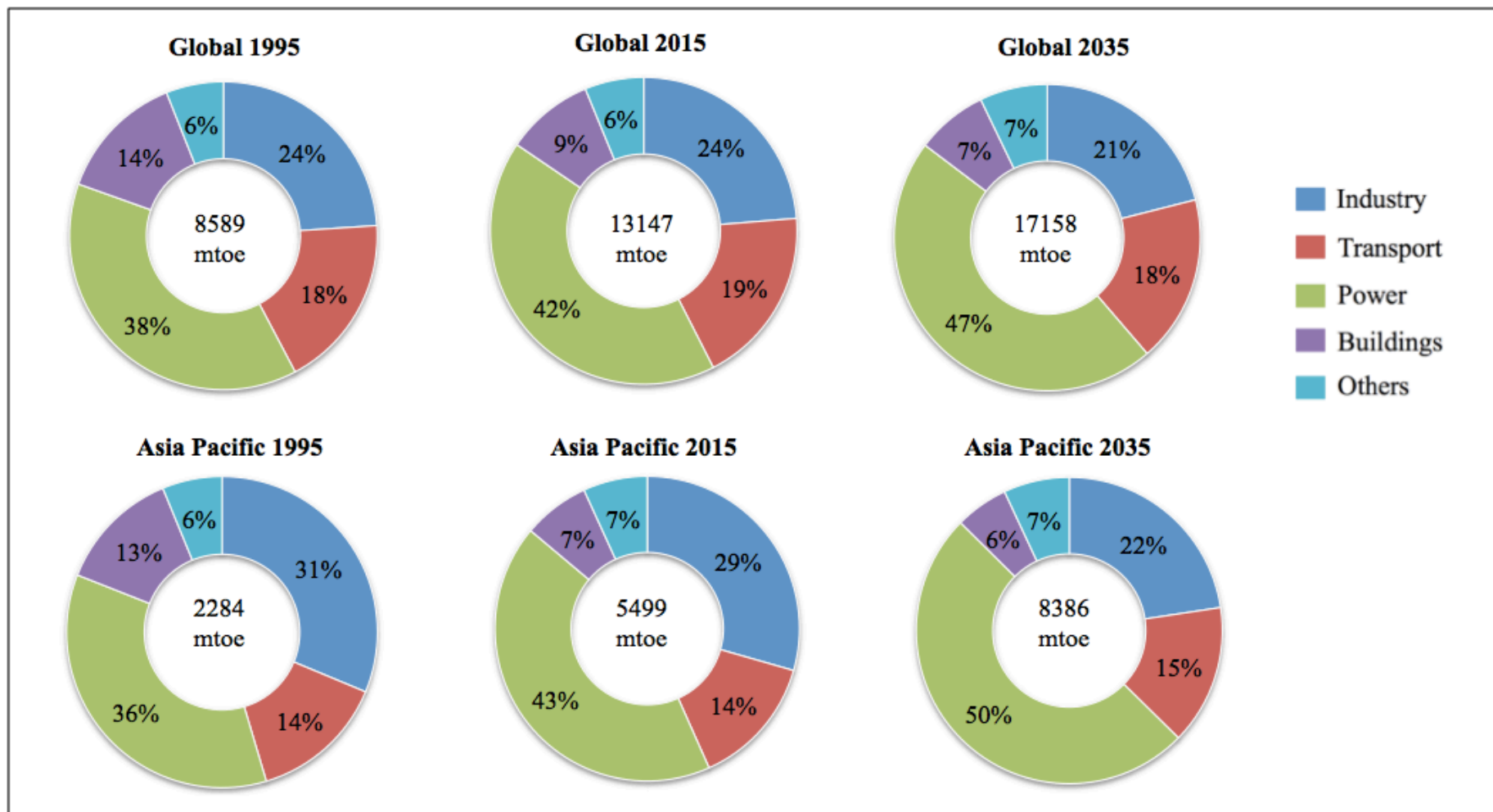


Figure 1.1 Total final energy consumption by sector for the year 1995, 2015 and 2035 (BP, 2017)

On the contrary, the buildings sector accounted for 9% of total final energy consumption in 2015, down from 14% in 1995 (BP, 2017). This trend was accompanied by rapid urbanization coupled with the improved energy access. Electric cooking, heating and cooling system have gained increasing popularity. Subsequently, electricity has replaced less efficient oil and coal for lighting and heating and thus electricity become a common alternative for a variety of energy demands (IRENA, 2018; SIEW, 2017). With the rising electricity demand, this trend is expected to continue over the next two decades. The growth in energy demand will be highest in power sector (45%), followed by transport (23%), industry (16%) and buildings (6%) (BP, 2017).

Interconnectedness, the hallmark of the information age, is spurring the development of information technology and artificial intelligence. This will greatly improve productivity of system and reinforce a more consumer-centric approach in the Industrial Revolution 4.0. Undoubtedly, growing automation and digitalization could boost electricity consumption exponentially (SIEW, 2017).

Moreover, transportation is a key area for electricity replacement. Beyond personal cars, transportation electrification is taking hold in public transit, commercial delivery vehicles and ride-sharing applications. Additionally, the electric vehicle market is now kicking off, with electric and plug-in vehicles amounting to 280 million by 2040 (IEA, 2017c; SIEW, 2017).

However, strong growth in fossil-fuel consumption increased roughly 75% in energy-related carbon dioxide (CO₂) emissions (IEA, 2017a). This alarming rise of carbon emissions has increased ambient temperature and heat wave events, consequently aggravating climate change (SEDA, 2017c). About 80% of natural disasters are “hydro-meteorological” events and these are expected to grow in

number and severity with the effects of climate change. With extreme weather events, high temperatures and extreme precipitation patterns, the climatic impacts can cause extensive damage to infrastructure and disrupt energy supply (IEA, 2017a).

Therefore, rising domestic energy demand and environmental impacts exacerbate energy security concerns. Against this backdrop, there is a need for energy players to stay nimble and forge a progressive energy landscape.

1.2 Overall renewable energy

Energy resources that are naturally replenishing such as biomass, geothermal, hydro, solar and wind could be harnessed as renewable energy. Renewable energy could address climate agenda by reducing harmful greenhouse gas (GHG) emissions during power generation, while offering as alternative energy which is available domestically and never-ending in supply.

Over the two decades, renewable energy increased dramatically from 599 mtoe in 1995 to 1258 mtoe in 2015, accounting 10% of total final energy generation (BP, 2017). The hydropower, bioenergy and geothermal are the main renewable energy resources. Despite the cost competition from onshore wind and solar photovoltaic (PV) technologies, bioenergy remains an important contributor to renewable energy. This is because bioenergy plants generally have higher capacity factor than variable renewable energy (VRE). Capacity factor is the ratio of electricity generation over an extended period (e.g. a year) compared to maximum theoretical generation possible given by the rated capacity of the technology. The capacity factors of renewable energy vary greatly depending on the availability of

energy source. In 2015, the average capacity factor of bioenergy was relatively higher (50%) when compared with 13% for solar PV and 26% for onshore wind (IEA, 2017b).

Moreover, countries with the hot and humid climate encountered certain limitations with their traditional solar power plants such as difficulties in installation and maintenance as well as frequent failures of consumables like external fans and fuses (SEDA, 2017a). As solar and wind are variable in nature, thus some intelligence in the network is required to balance the grid in terms of the dynamic electricity supply and demand (SEDA, 2017c). During January 2017, there was very prolonged cold weather throughout Europe, which coincided with very little wind and low hydro-electric reserves (Agora Energiewende and Sandbag, 2018). Hence, bioenergy is an excellent complement to renewables as a sustainable alternative fuel, providing grid stability and supply security.

1.3 Development of bioenergy in Southeast Asia

According to IEA (2017a), the energy demand in the Southeast Asia region has grown by 60% over the past 16 years, largely due to robust economic and demographic growth. Being a new heavyweight in global energy, a wide range of policy developments has been made in this region. As depicted in Figure 1.2, the share of renewable energy increased from 21.05 gigawatt (GW) (19% of the region's total electricity generation) in 2006 to 51.42 GW (27% of the region's total electricity generation) in 2015 (ACE, 2018).