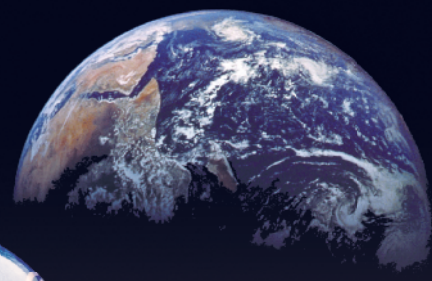


Green Energy and Technology

Hafiza Shukor
Muaz Mohd Zaini Makhtar
Abu Zahrim Yaser *Editors*



Renewable Energy from Bio-resources in Malaysia

 Springer

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Editors

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*We dedicate this book to our families
and friends....*

Foreword by Zaliman Sauli



Sustainable Development has become the main focus of recent national policies, strategies, and development plans of many countries. Malaysia, together with other 192 world leaders, has reaffirmed commitments to support and implement this United Nations (UN) 2030 Agenda for 17 Sustainable Development Goals (SDGs) and 169 targets. This will be our collective blueprint for Malaysia's sustainable future that is inclusive for everyone. Sustainable Development Goal (SDG) 7 on energy, has served to guide international cooperation and policy-making to achieve universal, sustainable energy access by 2030 by ensuring affordable, reliable, sustainable, and modern energy access for all by the accelerated deployment of renewable energy sources.

As one of the public universities in Malaysia, Universiti Malaysia Perlis (UniMAP) is actively involved in the research areas of engineering, engineering technology, technology, and sciences, including renewable energy. The Centre of Excellence for Biomass Utilization (CoEBU) established in 2015 has put great efforts in doing research and innovation involving the utilization of biomass for many valuable products such as renewable energy through green technologies. In line with Malaysia's direction in championing 20% power generation capacity for renewable

energy by 2025, feasible strategies and solutions for sustainable future energy production should be planned. The biofuel research group under CoEBU has done much research on renewable energy production from biomass using *modern bioenergy technology* like bioethanol, biobutanol, biodiesel, biogas production, and Microbial Fuel Cells (MFC).

Renewable Energy from Bio-resources in Malaysia is a book that gathers all the experts in renewable energy research from diverse biomass which would benefit all the readers who are eager to know more about Malaysia's potential bio-resources for renewable energy production. It is such a great accomplishment for the team to publish the book under the prestigious publisher of Springer Nature's Books. This book also presents the visibility of networking between UniMAP represented by Dr. Hafiza Shukor as the main editor together with Assoc. Prof. Dr. Abu Zahrim Yaser from **Universiti Malaysia Sabah (UMS)** and also Dr. Muaz Mohd Zaini Mokhtar from **Universiti Sains Malaysia (USM)** through the editing of the book. Publishing a research work or chapter in the book is also a great tool for making your research content more visible. This will increase the chances of your research being noticed, used, and having an impact that can increase your reputation and chances of success in your academic work. Congratulations to the CoEBU research team for the effort and I look forward to more book publications from UniMAP experts that should greatly benefit many, especially lecturers, researchers, policymakers, and matters relating to renewable energy in Malaysia.

Thank you and enjoy reading the book.



Prof. Ts. Dr. Zaliman Sauli
Vice Chancellor
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Foreword by Ku Syahidah Ku Ismail

Renewable energy is a fascinating topic especially when it involves the use of amazing microbes and utilizing agricultural wastes. To realize the conversion of biomass to renewable energy such as bioethanol, biobutanol, and biodiesel, it takes a multidisciplinary team consisting of microbiologists, chemical engineers, bioprocess engineers, and technologists. Thus, this book is the first publication to combine the expertise on renewable energy from the Centre of Excellence for Biomass Utilization (CoEBU), Universiti Malaysia Perlis (UniMAP). The contexts of discussion are related to scenarios and bio-resources available in Malaysia, the technologies to produce biofuels, and future projections to realize a successful biorefinery in Malaysia.

This book is suitable for those interested to grasp the knowledge on the feasible processes to pre-treat biomass and to produce biofuels. It may also be used as a reference book for undergraduates and postgraduates pursuing study in biofuel technologies. This book is one of our supports towards Sustainable Development Goals (SDG) number 7, to achieve affordable and clean energy.

I would like to express my sincerest gratitude to all authors who participated in every page of this book. I am grateful to all CoEBU researchers, Faculty of Chemical Engineering Technology, UniMAP, the Research Management Centre (RMC), UniMAP, and publisher for providing direct and indirect assistance towards the publication of this book. My heartfelt gratitude to Dr. Hafiza Shukor, Dr. Muaz Mohd Zaini Makhtar, and Assoc. Prof. Abu Zahrim Yaser for editing from scratch until fruition. Finally, it is hoped that this book will serve our readers well, and we would be grateful to receive comments and suggestions for improvement.

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Preface

This book focuses on the current activities and research in Malaysia related to the conversion of bio-resources to renewable energy and biofuel. Muhammad Anas Nagoor Gunny *et al.* reported that Malaysia has strengthened its commitment to increase carbon-neutral energy sources and recently upgraded its renewable energy target in the country (Chapter “[Current Status of Renewable Energy Development](#)”). Saleha Shamsudin *et al.* have provided the overview of solid biomass generated in Malaysia by various sectors in Chapter “[Characteristics and Potential of Renewable Bioresources](#)”. The agriculture sector, which includes oil palm, rice, sago, and other crops, is the largest provider of biomass. In terms of government aid, sustainability certification system, logistical and technological viability, this chapter analyses the possibilities and constraints of biomass as a feedstock for renewable energy use in Malaysia. Muhammad Najib Ikhmal Mohd Sabri *et al.* have extended the adoption of environmentally friendly technology for the pre-treatment of bio-resources (Chapter “[Different Types of Pre-Treatments for Renewable Bioresources](#)”). The biomass pre-treatment is crucial since the conversion processes contribute to the efficiency of Greenhouse Gas (GHG) generation. Then, the emerging of thermochemical processes technology for bioresource pre-treatment is further discussed by Khairudin Md Isa’s research team (Chapter “[Technologies for Biomass Thermochemical Conversion](#)”). Direct combustion, pyrolysis, gasification, and liquefaction are examples of thermochemical conversion processes that are viewed as potential for renewable energy sources. This opens the possibility of using the thermochemical conversion pathway to transform biomass into a lucrative liquid product.

The abundant of biomass in Malaysia is a fortune future for the country since the production of bioethanol could be an alternative to the declining of petroleum reserves, and when it is mixed with gasoline, it could behave as a clean fuel. Chapter “[Bioethanol as a Potential Renewable Energy](#)” authored by Ku Syahida Ku Ismail addresses the raw materials and procedures of how bioethanol could be a transportation fuel. It also goes over the various bioethanol production technologies as well as potential microorganisms in general. Furthermore, Malaysia’s bio-resources can be used to make a variety of biofuels, including biobutanol, a four-carbon alcohol with remarkable properties like gasoline. The research team led by Hafiza Shukor

described the issues and solutions linked to the development of biobutanol production (Chapter “[Bioconversion of Malaysia Renewable Energy Resources to Biobutanol](#)”). Overall, this chapter will provide a clearer picture of the present state of biobutanol production in Malaysia using renewable resources. Through the findings from Ahmad Hafidz Mohammad Fauzi *et al.*, Chapter “[Recent Progress of Biodiesel Production](#)” focuses on the Malaysian biodiesel situation, including the present biodiesel trend and biodiesel synthesis techniques in manufacturing facilities. The chapter also further discusses the biodiesel standards and specifications for use in Malaysia.

Muhammad Najib Ikhmal Mohd Sabri *et al.* explained the implementation of Anaerobic Digestion (AD) technology which involves the bioconversion of biore-source to a renewable energy catalysed by various microorganisms (Chapter “[Critical Appraisal of Anaerobic Digestion Processes for Biogas](#)”). The goal of this chapter is to give a comprehensive overview of the AD system, its technical constraints, and the possibilities of AD use in power generation. The book continues with the Microbial Fuel Cell (MFC) technology as one of the emerging technologies for biomass conversion which focuses on simultaneous wastewater treatment and power production. Huzairy Hassan *et al.* described the potential of the technology that seems to be the appropriate solution for these environmental challenges (Chapter “[Current Status on Microbial Fuel Cell \(MFC\) Technology](#)”). The chapter elaborates on the technology potential, current MFC situation, and the major issues that academics and scientists are grappling with when it comes to the scalability of MFC technology. Finally, the problems that are impeding the advancement of renewable energy in Malaysia, notably bioethanol and biodiesel, are discussed by Khadijah Hanim Abdul Rahman *et al.* in Chapter “[Renewable Energy: The Past and the Future](#)”. Following that, some contemporary breakthroughs and technology for the developments of second, third, and fourth generations were evaluated for their potential to boost bioenergy production feasibility. The author ended the chapter by highlighting the importance of Renewable Energy (RE) empowerment in accomplishing the goals listed in Malaysia’s Sustainable Development Goals.

Perlis, Malaysia
Penang, Malaysia
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Hafiza Shukor
Muaz Mohd Zaini Makhtar
Abu Zahrim Yaser

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Biomass Utilization (CoEBU), UniMAP has strengthened the academic exchange of expertise between UniMAP and WISE researchers mostly from Universiti Teknologi Malaysia (UTM) and Universiti Sains Malaysia (USM).

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Current Status of Renewable Energy Development



Ahmad Anas Nagoor Gunny, Mohd Faiz Mohamad Shahimin,
Alina Rahayu Mohamed, and Mohd Faizal Ab Jalil

Abstract Malaysia is blessed with rich natural resources that can be potential sources for the generation of sustainable clean energy. Natural resources such as hydro, solar, lignocellulosic biomass can be harnessed for the generation of renewable energy. In the effort to mitigate global climate change, Malaysia has strengthened its commitment to increase carbon-neutral energy sources and recently has upgraded its target of renewable energy in the country's energy mix from 20 to 31% by 2025. With Malaysia's unique geographical and socio-economic advantages, a variety of renewable energy technologies can be developed in Malaysia. To propel Malaysia's renewable energy agenda, aggressive actions were taken, via the establishment of various policies and enactments of several acts, to strengthen and boost the implementation of renewable energy in governmental agencies and private sectors and from individuals to corporates. Several initiatives and incentives were also launched, namely the Small Renewable Energy Power (SREP) Programme, Feed-in Tariff (FiT), and Net Energy Metering (NEM) schemes, by the government to achieve the target of renewable energy percentage in the total energy mix. Renewable energies, such as hydro and solar, have taken a tremendous leap in technological development and implementation in Malaysia, however, biomass-based renewable energy is still in its infancy stage. Being a country with high agricultural activities and products, biomass-based renewable energy has high potential in Malaysia. In this chapter, we will be giving an overview of Malaysia's renewable energy resources, the launched policies and schemes in promoting the development of renewable energies, and the potential of palm oil plantation and oil palm industries in advancing biomass-based renewable energy technologies.

Keywords Renewable energy resources · Renewable energy resources policies · Palm oil

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1 Renewable Energy Resources in Malaysia

The global economy is driven by fossil fuels, which are used in power generation, transportation, and chemical industries. Currently, fossil fuels account for ~85% of the global primary energy supply [1]. In tandem with population and economic growth, energy demand and consumption are also increasing. The increased human activities increase carbon emission to the atmosphere, which leads to the current alarming progression of global warming [2]. Hence, many initiatives have been launched to phase out fossil fuels and replace them with sustainable energy sources to become carbon neutral by the Seventh Sustainable Development Goal (SDG 7: Affordable and clean energy) established by the United Nations General Assembly.

Realizing the future importance of renewable energy, Malaysia has included renewable energy as part of its fifth fuel strategy in the energy mix under the National Energy Policy 2001. The potential renewable energies that were identified were biomass, hydro and solar. In 2010, the Malaysian government approved the National Renewable Energy Policy & Action Plan (NREPAP) and in the following year, the Renewable Energy Act 2011 and Sustainable Energy Development Authority (SEDA) Act 2011 were enacted. Two initiatives under SEDA were launched to propel the development of renewable energies in Malaysia: (1) The Feed-in Tariff (FiT), and (2) Net Energy Metering (NEM). The FiT was launched to promote renewable energy development via an incentives mechanism targeting energy sources from biomass, biogas, solar, (small-scale) hydro, and geothermal energy sources, whereas NEM was introduced to address business value proposition to commercialize solar energy capture using photovoltaics (PV) on rooftops. Other solar energy-related initiatives, namely Large-Scale Solar (LSS) and Self-consumption (SELCO), which were managed by Malaysia Energy Commission, were also introduced to realize Malaysia's decarbonization agenda.

Since the launch of NREPAP, Malaysia has seen a tremendous increment in primary energy supply from renewable resources (excluding large hydropower [>100 MW]) (Table 1) [3]. Owing to the rich renewable energy potential in Malaysia, a steady increase in renewable energy supply is attained. However, to achieve Malaysia's revised goal of 31 and 40% of renewable energy capacity mix by 2025 and 2035, respectively, continuous development in various renewable energy technologies is essential [4]. Currently, Strategic Framework has been formulated in the Renewable Energy Transition Roadmap (RETR), focussing on technology-specific pillars related to solar, bioenergy, hydro, and other new energy technologies.

1.1 Hydro

Hydropower has become the most important clean energy in Malaysia as it accounts for the majority of the electricity generation of Malaysia from renewable energy. In 2016, hydropower generation contributed ~13% (~20,280 GWh) of Malaysia's

Table 1 Summary of total primary energy supply (tonne of oil equivalent [ktoe]) by fuel type in Malaysia from 2011 to 2018

Year	Natural gas	Crude oil	Coal & coke	Hydropower	Renewable energy (Biodiesel, biomass, biogas, and solar)	Total
2011	69,849	28,325	1,838	1,850	176	102,038
2012	62,580	29,115	1,860	2,150	451	96,156
2013	64,406	28,576	1,824	2,688	821	98,315
2014	63,091	29,545	1,694	3,038	868	98,236
2015	67,209	32,440	1,614	3,582	966	105,811
2016	69,673	33,234	1,522	4,501	818	109,747
2017	71,140	32,807	1,884	6,240	795	112,867
2018	68,253	31,996	1,672	6,230	1,263	109,414

Table 2 List of large hydropower stations in Malaysia and their respective power generation

Plant	State	MW
Bakun Dam	Sarawak	2400
Murum Dam	Sarawak	944
Pergau Dam	Kelantan	600
Sultan Mahmud	Terengganu	400
Hulu Terengganu	Terengganu	265
Ulu Jelai Power Station (completed 2016)	Pahang	372
Temenggor Power Station	Perak	348
Sultan Idris Woh Power Station	Pahang	150
Sultan Azlan Shah Kenering Power Station	Perak	120
Sultan Yusof Jor Power Station	Pahang	100
Batang Ai Dam	Sarawak	100
Sultan Azlan Shah Bersia Power Station	Perak	72
Tenom Pangi Dam	Sabah	66
Sungai Piah Lower Power Station	Perak	54
Chenderoh Power Station	Perak	40.5

total power generation [5]. The power generations from hydropower are majorly generated by large hydropower stations (generate more than 30 MW) as listed in Table 2. Having 189 rivers, Malaysia has an extraordinary geographical advantage in the development of hydropower stations. Additionally, Malaysia experiences more than average rainfall per year, which makes a great contribution to the power generation capability. However, due to Malaysia being one of the world's mega biodiversity countries, the development of large hydropower is not desirable anymore as the development of large dams in the upstream area interrupts the natural biogeochemical cycles and destroys habitats of many unique aquatic and terrestrial lives.

To minimize the environmental impact and tackle the cost-related issues in the development of hydropower stations, small-scale hydropower (SSHP) is the most attractive option for electricity generations, especially for communities in remote areas. Not only can the SSHP replace the dependency on fossil fuels for power generations in the rural areas, if the SSHP is implemented responsibly, but the environmental and social impact can also be minimized [6]. For rural communities, decentralized generation of hydroelectricity can contribute significantly to improving the economic conditions. Hence, SSHP may provide cost-effective energy alternatives to grid extension or isolated diesel mini-grids in rural areas of Malaysia [6]. Malaysia's unique topography and geographical advantage that receives high average annual rainfall make SSHP a significantly potential technology that can be implemented widely.

To widely develop SSHP projects throughout Malaysia, however, improvements in various sectors are required including the development of training and service centres for SSHP, distribution of annual river water level status and rainfall data, simplification of complex regulatory and bureaucracies, financial incentives, and buildup of SSHP-related capacities and experts [7].

1.2 Solar

Renewable energy from solar has a high potential to be the best environment-friendly electricity generation. The rapid development of solar technologies makes it a promising source of clean and sustainable energy in the coming decades. The advancement in solar technology has also contributed to the decline of cost, which makes it more attractive to even the public. Solar energy is harvested via photovoltaics (PV), which can be customized to fit the needs of its commercial and residential end-users, in the form of large-scale solar (LSS) or stand-alone systems.

Power generation from solar, however, can be unpredictable as solar energy highly depends on climate and irradiation variation. Hence, the power generation and output are often inconsistent and require additional protection against overcurrent, under-current, and frequency stability [8]. This effect is more prominent in LSS PV as the fluctuation in power generation and output are bigger. Despite the challenges mentioned above, the potential of solar energy generation as one of the main contributors towards Malaysia's target of 31% renewable energy by 2025 has been recognized with the announcement of the latest Net Energy Metering (NEM) 3.0 in December 2020 [9]. Under the NEM scheme, consumers are to instal PV systems on rooftops of commercial and residential buildings for self-consumption first and exportation of excess energy to Tenaga Nasional Berhad (TNB). Although the Malaysia Energy Commission recommends crystalline silicon PV modules for the NEM, Malaysia's unique climate can affect the output power and efficiency. A recent study [10] examined the performance of amorphous silicon and crystalline silicon PV modules and their study shows that amorphous silicon PV modules would give higher energy yield and expedite the NEM payback period. Currently, investigations on PV are still

being performed to further improve its performance and optimize its solar energy harvesting efficiency.

1.3 Biomass

Globally, biomass accounts for 10% of the total energy supply [11], surpassing other renewable energy sources. However, renewable energy from biomass is yet to be fully manipulated in Malaysia despite having large biomass potential from agricultural activities [12, 13]. The recent focus on the development of solar PV has accelerated the renewable energy capacity installation but due to the nature of solar power generation, dependency on solar PV will lead to grid system instability [12]. Hence, having large biomass resources from palm oil waste, rice husks, coconut waste, sugar cane waste, municipal waste, and forestry waste [5], biomass plays a vital role in the renewable energy sector in Malaysia.

The main advantage of biomass over other renewable energies is its availability and storable capability. Besides the potential in gasification, co-firing and direct combustion in conventional power plants to generate electricity [14]; biomass has the potential to replace fossil fuels in terms of functionality and power output, in which, biomass can be converted into different forms of energy including bioethanol, biodiesel, biomethane, biohydrogen, and bio-crude oil [11]. Since fossil fuels are majorly used in Malaysia, particularly in the transportation sector, biomass offers highly flexible and greener alternatives.

To manage the escalating energy demand in both the industry and transportation sectors, modern forms of bio-based energy are essential. However, due to challenges involving policy, uncertain involvement of public and private sectors, lack of sufficient funding, research and development, data reliability issues, underdeveloped biomass industries, and lack of local skilled personnel, renewable energy from biomass cannot be fully utilized [14]. Hence, to fully utilize the biomass energy potential estimated at 29,000 MW, advancement in biomass utilization technologies needs to be improved. The advancement in biomass utilization may be attained through policy refinement, up-gradation of national technology standards, maintenance and training centres establishment, awareness of biomass technologies via integration in education syllabus, local and international cooperation/partnerships, and intellectual property transfer [14].

2 Renewable Energy Policies in Malaysia

The Malaysian Government introduced a thrust for Renewable Energy (RE) and established RE as the 5th fuel strategy in the energy mix under the National Energy Policy in 2001 in response to quick depletion of energy resources and to attain energy security [15].

Following that, new energy policies and programmes were launched by the Malaysian Government to offer all stakeholders secured and sustainable energy, efficient resource utilization and allocation, environmental protection, and high-quality service delivery [16]. In the 9th Malaysia Plan (2006–2010), the target of achieving 5% of RE in the country's energy mix was set [17]. However, currently, RE only accounts for 8% of Malaysia's total energy generation mix [18] and its revised targets achieve 30% penetration by 2025 [4].

Since Malaysia is a country blessed with an abundance of fossil fuels, shifting Malaysia's reliance on conventional fuels will require immense efforts by the government, and various relevant parties and agencies to cement a more significant contribution of RE in the energy mix [16].

2.1 Small Renewable Energy Power (SREP)

The Small Renewable Energy Power (SREP) Programme was the premier policy mechanism implemented by the Malaysian government to support the development of small-scale renewable electricity in Malaysia from 2001 to 2010. As discussed earlier, RE is targeted to contribute 5% (equivalent to 500 MW) of energy generation capacities by 2005. To meet this goal, the programme was launched to intensify the development of renewable energy as the fifth fuel resource [19] under a Special Committee on RE (SCORE). This programme is aimed to support electricity supply to major utilities in Malaysia. Among the electric utilities are Tenaga Nasional Berhad (TNB) in Peninsular Malaysia and Sabah Electricity Sendirian Berhad (SESB) in Borneo [19]. However, the programme was unsuccessful, according to Sovacool & Drupady [20], due to technical issues such as power plant design, inadequate training issues, and expensive feasibility studies. In addition, they also found the economic worldview in Malaysia that prioritized low electricity tariffs, unattractive financing rates, and lack of a strongly implemented national policy framework also are major obstacles to the development and success of the programme [20]. Low electricity tariffs, unattractive financing rates, and weak implementation of the national policy framework were also identified as major causes of the program's stunted development [20].

Lessons learned from the limited achievement of the SREP Programme from 2001 to 2008, prompted the Ministry of Energy, Green Technology and Water (KeTTHA) to come up with a new RE Policy and Action Plan which emphasizes the need for a more comprehensive new RE policy and action plan. The policy and action plan are to accelerate the development of RE in the country. In the report produced by KeTTHA [19], the RE policy has layout five objectives that embody the elements of energy, industry, and environmental policies; (1) to elevate RE portioning the national power generation mix; (2) to support the development of RE industry; (3) to guarantee reasonable RE generation cost; (4) to preserve the environment for future generation; and (5) to improve awareness on the significant function of RE to the nation.

2.2 *Malaysia's Feed-In Tariff (Fit) Scheme*

Feed-in Tariff (FiT) scheme is being introduced as one of the initiatives under RE policy to accelerate the growth of RE to achieve a revised target of RE. Under the FiT scheme, the renewable resources utilized for the generation of electricity are required to be locally sourced [21]. The FiT scheme is regarded as one of the most impactful and prominent programmes. The Sustainable Energy Development Authority (SEDA) is a legislative body primarily responsible for managing and administering the FiT initiatives established under the RE Act of 2011 [22, 23]. The scheme enforced Distribution Licensees (DLs), such as TNB, to purchase RE-based electricity produced from Feed-in Approval Holder [21]. The DLs are required to pay for RE generated to the electricity grid based on time consumption.

Hence, the FiT programme would ensure the viability and sustainability of RE. In addition, the programme would benefit long-term investment in companies' industries and also for individuals. FiT encourages the general public to become power producers and it is regarded as a game-changer in the energy industry. Commercial entities and individuals are permitted to produce RE from four sources (solar PV, biogas, biomass, and mini-hydro) and sell it to Tenaga Nasional Berhad (TNB) through the utility grid, as required by the RE Act 2011. Individuals or homeowners, on the other hand, are limited to solar PV generation [22].

2.3 *Net Energy Metering (Nem) Scheme*

In addition to the FiT scheme, to strengthen RE utilization embarked upon in Malaysia, Net Energy Metering (NEM) scheme is introduced to promote RE in Malaysia. NEM Scheme was launched in November 2016 by the Malaysian Government with a quota allocation of 500 MW up to the year 2020 to facilitate Malaysia's RE utilization. The idea of NEM is to produce electricity from the solar PV system and any surplus will be supplied and sold to the distribution licensee such as TNB at the current average cost. As part of continuous support to promote the NEM uptake, the NEM 2.0 was introduced on 1st January 2019, and the true net energy metering concept was adopted, where surplus energy generated from solar PV is allowed to be supplied back to the grid on a "one-on-one" offset basis [24].

In short, the NEM scheme applies to all domestic, commercial, and industrial sectors as long as they are the customers of TNB for consumers from Peninsular Malaysia or SESB if the consumer is staying in Sabah and FT for Labuan residents. The PV systems are allowed to be installed at the appropriate location within their premises. Solar PV technology, under the NEM scheme, is the only green technology promoted to the public at a large scale to contribute to the production of clean energy from renewable resources, hence reducing the dependency on electricity originated from generators powered by fossil fuels [25].

2.4 Zero Energy Building (Zeb) Facilitation Programme

Apart from these schemes, as part of the continuous initiatives to boost the application of RE in Malaysia, the Sustainable Energy Development Authority (SEDA) also engaged in developing facilities that utilize the use of RE to reduce electricity usage. Many countries such as Japan, Singapore, and the European Union (EU) are actively promoting the programme known as Zero Energy Building (ZEB) which is to develop facilities that apply RE as its source of function. This programme is also introduced to reduce the carbon emissions from buildings to the atmosphere and is said to be one of the contributors to carbon dioxide (CO₂) generation.

In Malaysia, the implementation of ZEB began in 2002 with the integrated energy-efficient building design programme. The objective of this programme is to reduce dependency on non-RE sources, pollution, and energy consumption while preserving the health, safety, and comfort of the residents by promoting the application of RE in new and existing buildings [26].

Abdellah et al. [27] reported that some of the current green design practices for healthcare buildings in Malaysia are adopting ZEB design practices. Additionally, governmental buildings that were designed based on ZEB have managed to reduce 50% of energy consumption. Hence, the applications of RE in buildings should be considered in the design and planning phase such as adaptations of technology to harvest solar and wind energy for electricity; biomass and municipal waste for generation of biogas and electricity; and other natural resources e.g. rainwater harvesting [26].

3 The Abundance of Palm Oil Waste in Malaysia and Types of Biomass Waste Available

In Malaysia, crude palm oil production (CPO) has become a major industry that supports the Malaysian economy and it was reported that the export revenue from CPO was approximately RM 67.6 billion [28]. Processing of fresh fruit bunch in the industry for CPO production has co-generated a huge amount of biomass waste. The biomass waste from CPO processing is regarded as a potential source of renewable energy which is sustainable. This is elaborated in detail in the subsequent subchapter.

Malaysia is blessed with large oil palm (*Elaeis guineensis*) plantations since Malaysia's weather is suitable for its growth all year round [29]. Malaysia is the second-largest producer of palm oil worldwide [30]. Palm oil industries produce various biomass wastes including empty fruit bunches (EFB), palm kernel shell (PKS), mesocarp fibre (MF), and palm oil mill effluent (POME) [31] whereas biomass wastes, such as oil palm fronds (OPF) and oil palm trunks (OPT), are produced at the plantation [32]. Approximately from every tonne of fresh fruit bunch production, 230 kg of EFB is generated [33]. It was also reported that approximately 15.8–17.0 million tonnes of empty fruit bunch (EFB) were generated, and the number

of wastes being produced is on the rise as the plantation area increases over the years [29]. With the ever-increasing amount of biomass waste being produced by oil palm plantation and palm oil industries, management of these wastes are of concern. With the advancement of technologies related to the up-gradation of biomass waste, oil palm-related wastes of low values can be turned into high-value energies via biotechnological and thermochemical methods. The following are discussions on the thermochemical routes in converting biomass into high-value energies.

3.1 Pyrolysis

Pyrolysis is a thermochemical process on biomass whereby biomass undergoes decomposition reaction at moderate temperature in the absence of oxygen or under an inert environment. The products of biomass pyrolysis are bio-oil (or pyrolytic oil), bio-char, and biogas or gaseous products [35]. Bio-oil is composed of an aqueous phase and an organic phase [36]. The aqueous phase is composed of light and low molecular weight oxygenated compounds and the organic phase is composed of various insoluble organic compounds of high molecular weight [36].

The pyrolysis of raw oil palm biomass, such as EFB and PKS, to maximize the bio-oil yields using different types of reactors and conditions are shown in Table 3. The bio-oil yields are in the range of 40.81–55.1 wt% [37–44].

Recently, the OPF and OPT were analyzed by proximate analysis and thermogravimetric analyzer to investigate its suitability as a potential biomass feedstock in thermochemical processes like pyrolysis, gasification, and combustion [45]. A recent study reported that the volatile matter content for both is in the range of 62.28–66.10% with the main or active pyrolysis process occurring in the temperature range of 200–500 °C [45]. This study confirmed that OPF and OPT are also suitable for thermochemical processes.

Bio-oil from raw biomass has several disadvantages such as low pH, high corrosivity with high water content [46]. Therefore, the quality of bio-oil could be improved through several strategies. The catalyst addition into the biomass during the pyrolysis process is one of the strategies that could enhance the decomposition of biomass towards the formation of lighter and less viscous bio-oils. The integration of catalysts in biomass pyrolysis or catalytic pyrolysis is a promising strategy towards either improving the light organic fractions in bio-oil or improving the Physico-chemical properties of bio-oil as well as increasing the bio-oil yield [47–49]. The catalytic pyrolysis process is listed in Table 3 as well.

3.2 Liquefaction

Liquefaction is the conversion of biomass into value-added fuels and chemical feedstocks using solvent at the temperature range of 120–180 °C in the presence of acid or

Table 3 The reported studies on pyrolysis and catalytic pyrolysis of oil palm biomass

Feedstock	Temp (°C)	Instrument	Bio-oil yield (wt%)	Catalyst	References
EFB	450	Fluidized bed reactor	55.1	–	[39]
EFB	442.15	Fixed-bed reactor	46.02	–	[42]
EFB	442.15	Fixed-bed reactor	46.2	–	[43]
EFB	500	Fixed-bed	40.81	–	[43]
Palm shell	500	Fixed-bed	46.4	–	[41]
Palm shell	500	Fixed-bed	45.9	–	[40]
Mesocarp fibre	550	Fixed-bed	48–50	–	[44]
Palm Frond	550	Fixed-bed	45–47	–	
Empty Fruit Bunch Biomass Pellets	–	multimode microwave irradiation	5–21	–	[50]
Palm Pressed Fibre (PPF)	500	Fixed-bed	44.35	–	[51]
			41.07	CuO/ZrO ₂	
EFB	300	Semi-batch reactor	30	–	[46, 52]
			28	HZSM-5	
EFB	550	Fixed bed reactor	43.49	–	[53]
			Improved by 15 wt%	CaO	
EFB	575 °C	Fixed bed reactor	42.3 ± 1.5	–	[54]
			39.9 ± 0.6	5 wt% CaO	
			40.4 ± 0.4	10 wt% CaO	
			39.3 ± 1.5	5 wt% MgO	
			42.3 ± 1.8	10 wt% MgO	
			44.7 ± 1.6	5 wt% ZnO	
			42.2 ± 0.7	10 wt% ZnO	
EFB	500	Fixed bed reactor	39.95	–	[55]
			42.70	Al ₂ O ₃	

basic catalysts, or a higher temperature of 180–250 °C in the absence of catalysts [56, 57]. Meanwhile, hydrothermal liquefaction is an emerging technology that allows the conversion of biomass into bio-oil in water as the medium, in which the biomass does not undergo the initial drying process. It is usually conducted in the presence of organic solvent with or without a catalyst in the temperature range of 270–370 °C at elevated pressure [58]. The list of hydrothermal liquefaction and liquefaction is listed in Table 4.

Table 4 The reported studies of liquefaction and its emerging technique using oil palm waste biomass in Malaysia

Feedstock	Temp (°C)	Process	Instrument	Liquid yield (wt%)	Solvent	Pressure	Catalyst	Condition	References
Palm-pressed fibre modelling	210–330 °C	Liquefaction	High-pressure autoclave reactor	38	Methanol	10 bars	–	sub/supercritical	[59]
				36	Ethanol and Acetone				
				38.5	Dioxane				
EFB palm mesocarp fibre, PMF palm kernel shell PKS	290	Hydrothermal liquefaction	Batch reactor	50.90	Water	25–35 MPa	–	sub/supercritical	[57]
				37.39					
				34.32					
				38.53					
OPF	100–230	Liquefaction	Tubular reactor	Furfural yield ~38 wt% at 230 °C and 20 min	Water		–	Subcritical	[60]

3.3 Gasification

Gasification is a biomass thermochemical conversion process into gaseous mixtures in the presence of air/oxygen, steam and flue gases and the product gases can be directly burnt for energy [61]. The gasification process can be performed using catalysts such as MgO and CaO targeting to increase hydrogen production. Hydrogen is the biogas that is desired from the catalytic gasification of biomass [62]. Meanwhile, some other studies focussed on the derivation of fundamental information such as the chemical reaction kinetics. The list of gasification, catalytic gasification, and co-gasification that used oil palm waste are as shown in Table 5.

3.4 Combustion

Combustion is a thermochemical conversion process on biomass that is conducted under an oxidative environment (in the presence of oxygen or air) to extract energy from the biomass (Lee et al. 2014). Table 6 lists the research in the combustion process that utilized oil palm waste in the processing.

3.5 Conclusions

Biomass energy sources, solar energy, and hydropower are the three main forms of renewable energy generation in Malaysia. Both solar and hydropower renewable energy technologies have advanced tremendously in recent years. However, biomass energy is still in its infancy stage despite having been promoted for decades. Nevertheless, the usage of biomass energy, such as in the generation of electricity, still has enormous potential in Malaysia due to Malaysia's vast biomass resources, particularly from the oil palm industry. Hence, further investments and incentives in developing biomass energy technologies by private investors and the government, respectively, are crucial to advance the biomass energy agenda in Malaysia.

The existence of numerous policies, funding, and financing schemes indirectly boost diverse parties' interest and participation in the implementation of renewable energy sources. The government's efforts and resolve, as well as the full usage of all renewable energy resources available in Malaysia, whether developed or not, can indirectly reduce reliance on fossil fuels. As a result, the creation of renewable energy sources can significantly reduce greenhouse gas emissions, thereby reducing global warming and ensuring the sustainability of our environment in line with the United Nation's Sustainable Development Goals (SDG).

Table 5 The reported studies on gasification, co-gasification, and catalytic gasification of oil palm biomass

Feedstock	Temp (°C)	Instrument	H ₂ yield (wt%)	Kinetics model	Activation energy (kJ/mol)	Catalyst	Pretreatment	References
EFB	50–700	Gasification instrument	Increased by 74%	–	–	Nano Cao	–	[62]
			Increased by 227%					
Raw EFB	800–900	Simultaneous thermal analyzer	–	–	29.76	–	–	[63]
Raw MF					64.93			
Raw PKS					80.07			
EFB					68.65–68.67			
MF	83.71–86.90	Torrefaction at 280 °C	–	–	–	–	–	
PKS	15.29–35.25							
Oil palm shell (OPS) shell	800–1000	Thermogravimetric analyzer	–	Arrhenius	253.9	Fe(NO ₃) ₃	Carbonization	[64]
Lignin and char from EFB pyrolysis	Room temp-1000	Thermogravimetric analyzer	–	Least square estimation	298.5	–	–	[65]
	650–750	Gasifier Pure steam gasifying agent CaO as the CO ₂ adsorbent	Predicted 102 g H ₂ /kg of biomass	–	–	–	–	[66]

(continued)

Table 5 (continued)

Feedstock	Temp (°C)	Instrument	H ₂ yield (wt%)	Kinetics model	Activation energy (kJ/mol)	Catalyst	Pretreatment	References
Palm kernel shell (PKS)	581–819, Optimum is 692	Thermogravimetric analyzer Steam as gasifying agent Coal bottom ash and CaO as CO ₂ adsorber The optimum conversion is 0.779	–	–	–	–	–	[61]

Table 6 List of combustion processes using oil palm waste

Feedstock	Temp (°C)	Process	Instrument	CO ₂ yield (%)	Ea value (kJ/mol)	References
PKS	25–1100	Combustion	Thermogravimetric analyzer	–	139.49 ± 49	[67]
PMF					118 ± 49	
EFB					105 ± 56	
Bio coal from OPF pyrolysis mixed with sub-bituminous coal	600–900	Co-combustion	Lab-scale updraft fluidized bed reactor	16.53	–	[68]

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Characteristics and Potential of Renewable Bioresources



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Abstract This chapter presents an overview of solid biomass produced by different sectors in Malaysia. Malaysia is renowned as a tropical country that is rich with diverse biodiversity. The tropical climate is favourable for the production of various crops, fruits, and vegetables in the agricultural sector. The major contributor of biomass is the agricultural sector mainly oil palm, rice, sago, and others. Oil palm biomass is produced abundantly at plantations and mills in their daily operation. Therefore, biomass management at the source and exploitation of the biomass into biofuel and value-added products are essential for the sustainability of the national agricultural sector. Agricultural biomass is composed of lignocellulosic components comprising an interwoven mesh of three primary lignocellulosic components namely cellulose, hemicellulose and lignin possess a crucial determination of a physical and chemical characteristic of the biomass. Hence, the characteristic of the lignocellulosic biomass is a vital key in considering the pretreatment steps, utilization, and final products. Globally, the significant depletion of fossil fuels (oil, coal, and gas) drives many countries to generate clean renewable energy in order to provide for the increasing trend of national energy consumption. Malaysia is also committed to generating renewable energy from local bioresources using biomass from the agricultural sector. This chapter discusses the potential and challenges of biomass

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as feedstock for renewable energy utilization in Malaysia in terms of government assistance, sustainability certification scheme, logistics, and technology feasibility. A strategic plan of biomass utilization, as well as good cooperation between government and private sectors, will improve Malaysia in achieving the target for renewable energy generation in the future.

Keywords Biomass characteristics · Agricultural biomass · Biomass utilization

1 Categories and Types of Biomass Resources in Malaysia

Biomass is extremely valuable for the generation of new, structurally complex, bioactive compounds, and clean energy sources. Biomass-dendromass and phytomass of lignocellulose is a natural material consisting of complex heterogeneous cell-structured macromolecules (lignin, hemicellulose, and cellulose) and various organic and inorganic structures of low molecular weight [1]. Biomass can be considered into several main types; agricultural biomass (phytomass grown on agricultural land), forest biomass (firewood, residual from forestry and wood industry), and residual biomass (by-products of agriculture and manufacturing industry) [2]. Malaysia is a tropical country (warm and wet weather year-long) that has large areas of natural arable land for crop production. The annual production of important crops including the plantation in Malaysia is presented in Table 1. Major biomass resources in Malaysia can be categorized into different sectors: residues from agriculture (palm oil mill waste, paddy straw, rice husk, banana stems, sugarcane bagasse, etc.), forestry (wood from pulp, paper industries, and logging activities), and municipal waste (Fig. 1). In line with the major crop produced in Malaysia, oil palm biomass contributes the largest amount of biomass. Each year about 168 million tonnes of biomass is generated in Malaysia as a prospective bioenergy resource and long-term solution to the nation's energy demand [3].

Table 1 Production and planted area of important crops in Malaysia 2019

Crops	Production (Tonnes)	Area planted (Hectares)	References
Palm oil	19,858,367	5,900,157	[4]
Paddy	2,348,931	671,870	[5]
Rubber	639,830	1,083,992	[4]
Coconut	536,605	86,466	[4]
Sago	199,370	41,082	[4]
Pepper	34,294	7,375	[4]
Sugarcane	20,761	1,403	[6]
Herb	9,018	2,315	[7]
Cocoa	1,004	15,008	[4]

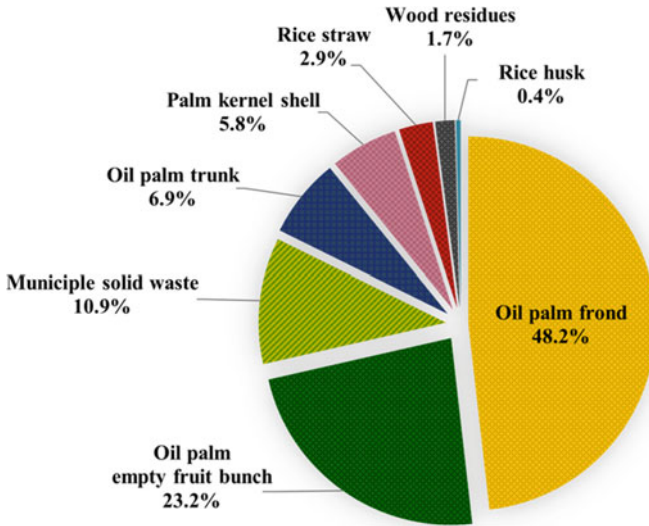


Fig. 1 Biomass availability in Malaysia [9]

Palm oil is majorly produced in Malaysia and served as a long-term agriculture investment in Malaysia [8]. Substantial total agricultural wastes in Malaysia are derived from oil palm plantations [9]. The lignocellulose of oil palm wastes can be converted into value-added products, for example, glucose which could be further fermented into biofuel. Presently, feedstocks of cellulose-based biomass for conversion into biofuels are larger in volume than any other carbohydrate source. Lignocellulose biomass refers to plant materials that are mainly composed of cellulose and hemicellulose that are bound together by lignin (Fig. 2). Each year, the production of rice in Malaysia (Kedah, Penang, Perak, Kelantan, Selangor, and Terengganu) is approximately up to 75% to supply local demand with the remaining sourced out from Southeast Asia countries such as Thailand, Vietnam, and Indonesia [11]. Rice cultivation activities are expected to grow due to increased demand and population. Rice producing industry generates three main by-products: rice straw, rice husk, and rice bran. When the grain had been harvested, the rice straw became the vegetative residue. Rice husk is the hard-protecting coating of grains that is broken up from the brown rice grain. Rice bran is the residues from the milling process that has been the profitable vegetative waste as a protein supplement in livestock farms. In contrast with rice straw and rice husk wastes remain unutilized. On the other hand, sago is also deemed to be one of the most potential feedstocks for the production of value-added products. In brief, sago hampas is a solid by-product resulting from the sago starch extraction process. It is made up of 58% of starch, 32% of cellulosic materials as well as 4% of lignin [12, 13]. It is interesting to mention that the considerably low amount of lignin content in sago hampas suggests no pretreatment process is required before fermentation. Several studies identified sago hampas as a substrate

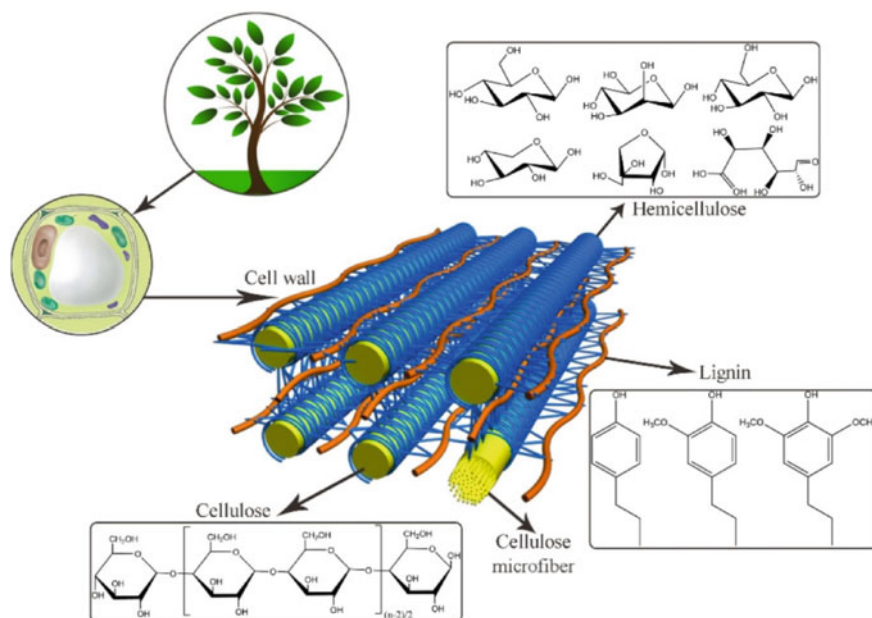


Fig. 2 The simplified general plant cell wall structure [10]

for the production of sugars [14, 15], bioenergy, and biofuels, including biohydrogen [12], bioethanol [16], biobutanol [17], and bioelectricity [18, 19].

1.1 Palm Oil Industry

The commercial oil palm (*Elaeis guineensis*) cultivated in Malaysia originated from Africa. It was introduced into Malaya (later named Malaysia) in 1875 as an ornamental plant and only in 1917; it was first cultivated for commercial purposes in Tennamaran Estate, Kuala Selangor [20]. Since the 1960s, oil palm plantings in many parts of the world including Malaysia have seen significant expansion (Fig. 3). Over the past 50 years (1970–2018), the production of palm oil on the world market has been 35 times higher and the consumption in producing countries themselves has also increased dramatically [21]. Malaysia is the world's second-largest palm oil producer and the largest exporter in the international market [22]. Malaysia's palm oil production is almost 50% of the world's total production (crude palm oil and palm kernels oil) and the industry also produces millions of tonnes of residues or by-products which contain valuable resources yet to be fully utilized. Currently with about 5.9 million hectares of oil palm are cultivated in Malaysia, these plantations produce over 11.9 million tonnes of oil and more than 100 million tonnes of biomass residues per year [23]. This huge quantity of biomass includes the empty fruit bunch

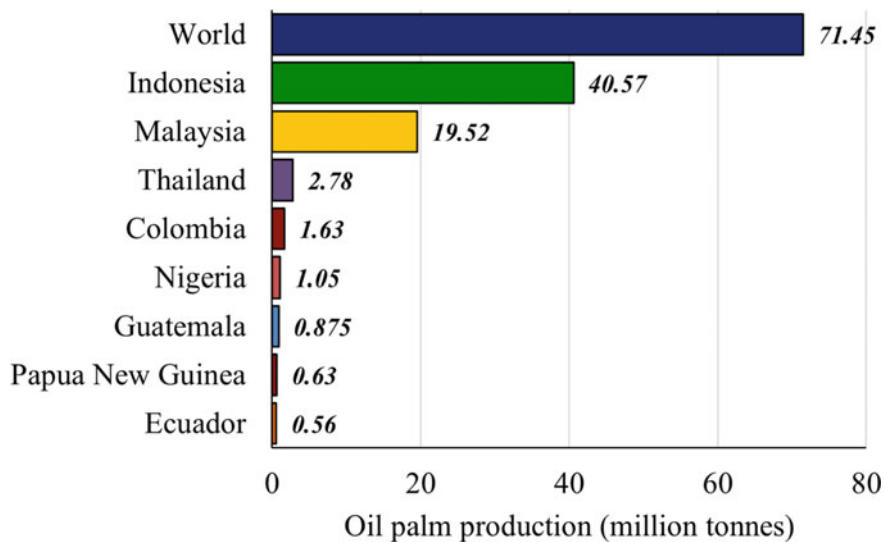


Fig. 3 World major producers of oil palm (1960–2018)

(EFB), pressed fruit fibre (PFF) or mesocarp fibre (MF), palm kernel shell (PKS), palm oil mill effluent (POME), oil palm trunks (OPT), and fronds (OPF). Until now the major portion of resources used is mesocarp fibre and kernel shells as main thermal energy sources in generating process steam and electricity in the palm oil mill. However, only 60% of these resources are used as fuel in boilers [24].

More than 10 million tonnes of EFB are generated from more than 30 million tonnes per annum of fresh fruit bunches (FFB) [23]. Only 10% of the EFB is used as mulching material to protect the soil surface, conserve soil water and nutrients and the rest are burnt in incinerators in the palm oil mills to produce bunch ash or dumped in areas adjacent to the mill which generate environmental problems such as air and odour pollution in the nearby localities [25]. Another barrier that hindered the use of EFB as mulching material is their bulkiness with high moisture content resulting in transportation difficulties [26]. OPF and OPT are other biomass generated in oil palm plantations. OPF is available daily during harvesting of ripe fruit bunches by pruning of fronds and is traditionally used as mulching materials in plantations. OPT becomes available during the felling of old trees and replanting of the oil palm trees every 25 years. Previously, the burning of the OPT was carried out for fast disposal until stringent open burning regulations prevented this method of trunk disposal. The OPT is shredded and left in the field to decompose naturally. Overall, much of palm biomass remains as waste and awaits commercial exploitation. The total production and possible uses of the palm biomass are presented in Table 2. Oil palm biomass enriched with holocellulose can be converted into fermentable sugars and subsequently used for various bioproducts (bioethanol, biomethanol, biohydrogen, polyhydroxyalkanoates, polylactic acid, and others).

Table 2 Production and potential uses of palm biomass for biofuels

Oil Palm biomass	Production	Current uses	Potential uses
Empty Fruit Bunch (EFB)	15.8 million tonnes per annum [30]	<ul style="list-style-type: none"> • Mulching materials [31] • Ash (Organic fertilizer) and soil conditioner in the plantation [25, 32–34] 	<ul style="list-style-type: none"> • Kraft pulping and bioethanol [35] • Polyhydroxyalkanoates (PHAs) or Polylactic acid (PLA) [36] • Glucose [37, 38] • Bioethanol [39–42] • Biogas [43] • Cellulase enzyme [44]
Pressed Fruit Fibre (PFF)	9.66 million tonnes per annum [45]	<ul style="list-style-type: none"> • Fuel boilers [24, 46] 	<ul style="list-style-type: none"> • Fillers in thermoplastics and thermoset composites [36] • Oil palm ash (OPA) is produced after the combustion of oil palm fibre and shell as an adsorbent for toxic gas and heavy metal removal [47]
			<ul style="list-style-type: none"> • As a support carrier for ethanol production by <i>Candida shehatae</i> TISTR5843 in immobilization system [48] • Briquettes [46]
Palm Kernel Shell (PKS)	5.20 million tonnes per annum [45]	<ul style="list-style-type: none"> • Fuel boilers [24] • Road surfacing on estates [25, 49] 	<ul style="list-style-type: none"> • Activated carbon [50] • Charcoal derived from oil palm shells can be coated with chitosan [51] • Briquettes [46]
Oil Palm Trunk (OPT)	2.515 tonnes of oil palm trunks per hectare after 25 years growth before replanting [32]	<ul style="list-style-type: none"> • Mulch 	<ul style="list-style-type: none"> • Sugars for bioethanol production [52]
Oil Palm Frond (OPF)	10.88 tonnes of oil palm fronds per hectare [32]	<ul style="list-style-type: none"> • Mulch 	<ul style="list-style-type: none"> • Oil palm frond based ruminant pellet [36]

(continued)

Table 2 (continued)

Oil Palm biomass	Production	Current uses	Potential uses
Palm Oil Mill Effluent (POME)	40 million tonnes of POME per annum [53]	<ul style="list-style-type: none"> Organic fertilizer in oil palm areas [25] 	<ul style="list-style-type: none"> Methane [49, 54] Biohydrogen [54] Polyhydroxyalkanoates (PHAs) [55]

1.2 Rice Biomass

Malaysia has contributed 3.1 million tonnes of rice straw and 0.48 million tonnes of rice husk annually [27]. Rice straw is separated from the grains after being threshed either manually, using stationary threshers, or combined harvesters. The rice husk or rice hull is the coating on a seed or grain of rice. It is formed by hard materials comprising silica and lignin to protect the seed during the growing season. Each kilogramme of milled white rice resulted in approximately 0.2 kg of rice husk during milling and 1–1.5 kg rice straw depending on varieties, cutting height of the stubbles, and moisture content during harvest [28, 29]. Common products from rice husks are solid fuel (loose form, briquettes, and pellets), carbonized rice husk produced after burning, and the remaining rice husk ash after combustion.

1.3 Sago

Sarawak, Malaysia is known to be one of the largest sago starch exporters in the world which accounted for 55,000–65,000 tonnes/year [56]. With that matter, it has generated approximately 50–100 tonnes per day of sago hampas, especially in Sibuh and Mukah division [57] and it is expected to exponentially increase over the year due to the demand. It is fascinating to note that due to the presence of lignocellulosic fibrous components in the sago hampas, it has been used as animal feed [58], mushroom culture's medium [59, 60] as well as particleboard manufacture [61].

2 Biomass Characteristics and Compositions

In general, about 30–60% cellulose, 20–40% of hemicellulose, and 10–30% of lignin are available in different kinds of lignocellulosic biomass sources [62]. These differences within this range either for the same species or between different biomass would depend on the growing location, season, harvesting methods as well as analytical procedures used [63]. Cellulose and hemicellulose are carbohydrate polymers that are built up by long chains of sugar monomers. Therefore, they are potential sources

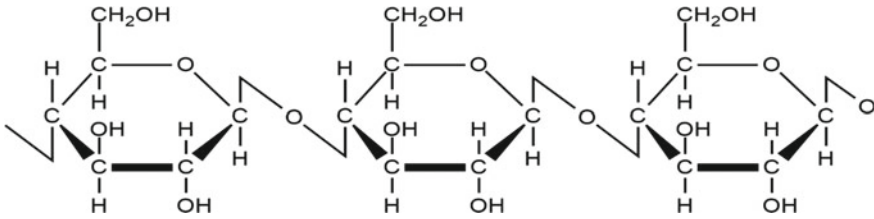


Fig. 4 Partial structure of cellulose molecules showing the β -linkage of glucose units [70]

of fermentable sugars but are not readily available for hydrolysis without pretreatment [64]. Lignin is a phenolic polymer in the plant cell walls. This compound binds cellulose and hemicellulose, imparts further strength, offers rigidity, and provides resistance against pests and diseases [65]. Besides these major constituents, the plant cell wall also contains pectic substances, proteins, waxes, cutin, suberin, and sporopollenin in smaller portions [66].

2.1 Cellulose

Cellulose is a linear polymer of homopolysaccharide (an unbranched polymer) composed of repeating glucose monomers that are linked together by β -1-4-glycosidic bonds or in short it is a highly crystalline polymer of glucose. The basic structure of cellulose is $(C_6H_{10}O_5)_n$. Based on structural characteristics, cellobiose is the repeating subunit in cellulose, in which each glucose unit is rotated 180° relative to its neighbour [67]. The individual cellulose chains are packed together and weakly bound through hydrogen bonding into ‘elementary fibrils’ [68, 69]. These ‘elementary fibrils’ about 3–4 nm wide (about 36 chains) are bundled together into organized parallel cellulose-fibrils called crystalline microfibrils which make up the core of a cellulose microfibril and are difficult to degrade [69]. Within the microfibrils, cellulose in plants is also found in the form of an amorphous structure, where the elementary fibrils are attached or cross-linked together by hemicelluloses, with the amorphous polymers of different sugars as well as other polymers such as pectin and covered by lignin [67, 69]. Generally, hydrolysis can reduce the cellulose to a cellobiose repeating unit ($C_{12}H_{22}O_{11}$) and ultimately to a glucose ($C_6H_{10}O_5$) unit by cellulase. The partial structure of a cellulose molecule is illustrated in Fig. 4.

2.2 Hemicellulose

Hemicellulose, non-cellulosic structural polysaccharides, or sometimes also called polyose are branched heteropolysaccharides that exist in association with cellulose and lignin in the plant cell wall [62, 67]. Hemicellulose is composed of shorter chain

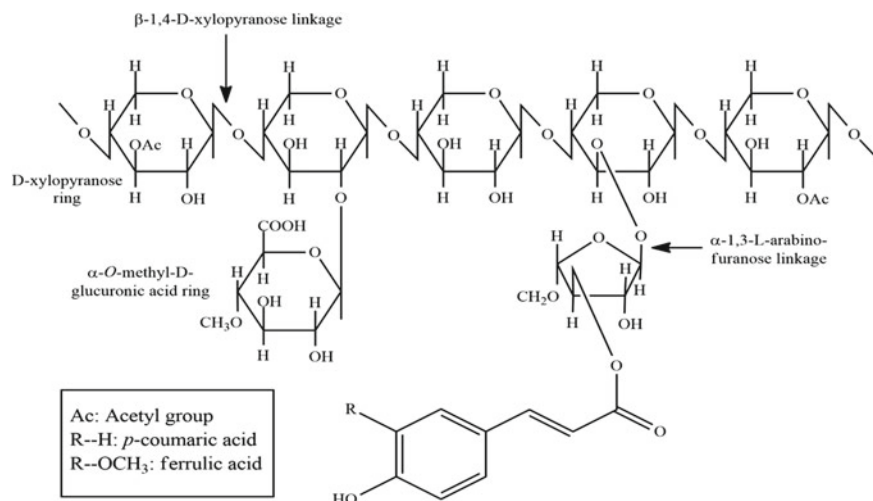


Fig. 5 Schematic illustration of sugar units of hemicelluloses [75]

polysaccharides which act as a linkage between lignin and cellulose. In general, hemicellulose may contain pentoses (β -D-xylose, α -L-arabinose), hexoses (β -D-mannose, β -D-glucose, α -D-galactose) and/or uronic acids (α -D-glucuronic, α -D-4-O-methylgalacturonic and α -D-galacturonic acids) [65, 69, 71, 72]. It is a low molecular weight compound that is much easier to hydrolyze than cellulose [62]. According to Miller et al. [67], hemicelluloses are typically composed of main-chain backbones of xylan which consists of β -1,4-linked-D-glucopyranose and β -D-mannopyranose units with α -1,6 galactose residues. Other non-cellulosic structural polysaccharides like arabinogalactan are also commonly found in the plant cell wall. Many side-chain constituents namely arabinofuranosyl, acetyl, feruloyl, and methylglucuronyl groups branch off the main backbone. The most important hemicelluloses are xylans and glucomannans, with xylans being the most abundant component of hardwoods and herbaceous plants [71]. Xylose is one of the major building blocks of hemicellulose or fermentable sugars present in lignocellulosic biomass and the second most abundant carbohydrate polymer in nature after glucose [73, 74]. Within the plant cell wall structure, the hemicelluloses are thought to coat the cellulose-fibrils resulting in reduced accessibility of the cellulose-fibrils. Therefore, pretreatment and enzymatic hydrolysis of the hemicellulose component is essential to facilitate complete cellulose degradation [65]. The sugar units of hemicelluloses are illustrated in Fig. 5.

2.3 Lignin

Lignin is a phenolic aromatic macromolecule that is primarily formed by free-radical polymerization of ρ -hydroxy cinnamyl alcohol units with varying methoxyl contents

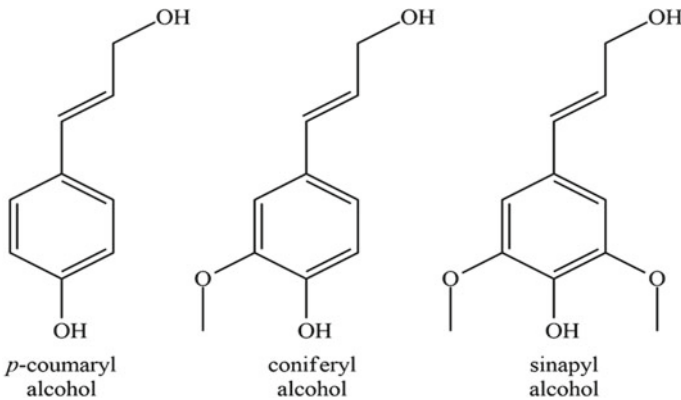


Fig. 6 Schematic illustration of building units of lignin [79]

commonly known as phenylpropane units [65]. The three monomeric unit precursors of lignin are based on: coniferyl alcohol, sinapyl alcohol, and *p*-coumaryl alcohol, and they vary among species [76] (Fig. 6). Lignin, in general, is an important structural component serving as a supporting agent and gives strength to the cell biomass. It glues together the other fractions in the complex phenolic polymers and assists in the resistance of biomass against microbial attack and decay [77, 78]. Therefore, lignin is considered an important barrier to polysaccharide utilization such as hydrolysis by cellulases. It is believed that the existence of strong carbon–carbon ($C - C$) and ether ($C - O - C$) linkages in lignin affect its susceptibility to chemical disruption.

2.4 Empty Fruit Bunch: Production, Structural Characteristics and Uses

The EFB is abundant solid biomass or residue from the palm oil industry which are produced in large amounts from the FFB of oil palm. According to Tan et al. [39], FFB comprises 21% palm oil, 7% palm kernel, 14% PPF, 7% PKS, and 23% EFB. It has been estimated that for every kilogramme of palm oil produced roughly 4 kg of dry biomass is generated [80]. Hence, every year approximately 15 million tonnes of EFB are produced in Malaysia and about 37.7 million tonnes are produced globally [34]. In short, EFB is the largest residual product of the palm oil milling process. EFB is the residual bunch remaining after the reddish palm oil is removed from the FFB by the thresher during oil extraction [39]. The process flow of the palm oil mill demonstrates the types of oil palm biomass available and the EFB generated (Fig. 7) [54, 55, 80, 81]. The typical palm oil milling process in Malaysia is the wet process which uses a lot of water in the sterilization and extraction process.

The milling process generates vast amounts of wastewater effluent (POME) which are from three main sources, namely sterilizer condensate, sludge separator, and the

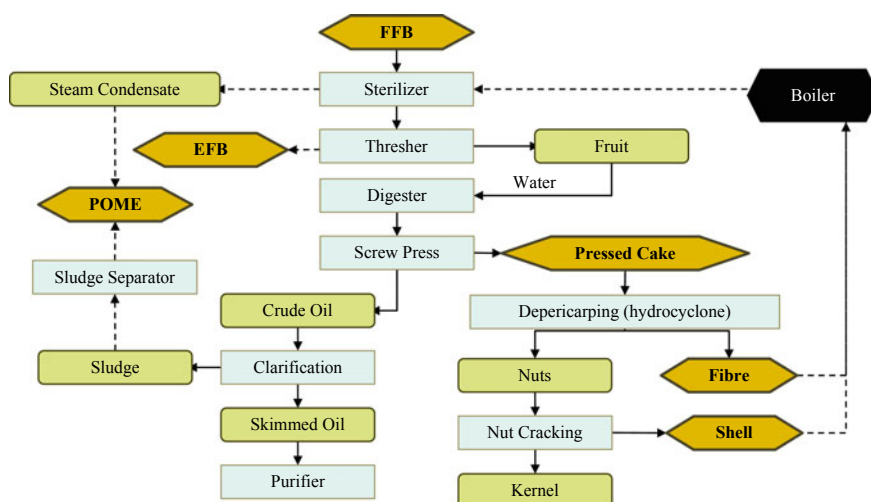


Fig. 7 Process flow diagram of fresh fruit bunch processing and biomass generation in palm oil mills

hydro-cyclone [53]. Sterilization of FFB at high temperature (140 °C) under pressurized steam (0.28 MPa) for 75–90 min is the beginning stage of the milling process. The sterilization process introduces moisture into the nuts, causes the detachment of the kernel from the shell wall, and loosens kernels within their shells. The sterilized FFB is then fed into a rotary drum thresher for stripping the fruits and conveying the empty wet bunches called EFB to the dumping ground. EFB is categorized as fibrous crop residue or known as the lignocellulosic residue. EFB consists of almost 70% of water and 30% solids which comprise lignocellulosic materials [82]. Based on composition EFB is comparable to those of hardwoods (Table 3). The main components of EFB are cellulose, hemicellulose, and lignin. It is estimated that EFB is composed of 43–60% cellulose, 19–34% hemicellulose, and 12–24% lignin. Cellulose is a polymer of the hexose sugar glucose, while hemicellulose is a pentose sugar-containing mainly xylose.

These sugars can be used as substrates for the production of a wide variety of compounds by chemical and biochemical processes. Since the solid EFB bunches are rich in cellulose and hemicellulose that are cross-linked with lignin which is not easily

Table 3 Chemical composition of empty fruit bunch, hardwood, and softwood

Biomass residues	Chemical composition (%)			
	Cellulose	Hemicellulose	Lignin	References
Empty fruit bunch	43–60	19–34	12–24	[38, 83–86]
Hardwood	40–55	24–40	18–25	[87]
Softwood	45–50	25–35	25–35	[87]

decomposed, degraded, or hydrolyzed into their monomers, these bunches must be subjected to pretreatment involving physical, chemical, or biological processes to cleave the chains or dissolve the lignin before production of useful chemicals and biofuels.

2.5 Rice Husk and Rice Straw: Production, Structural Characteristics and Uses

A low bulk density rice husk is produced off-site during grain processing and is normally 20–25% of the overall weight of milled paddy [29]. A rice husk is yellowish in colour, convex shape, and consists of rigid materials such as opaline silica and lignin acting as seed protection. Rice husk has become a source for many silicon compounds, including silica (SiO_2), silica carbide (SiC), silicon (Si), silica nitride (Si_3N_4) meanwhile for the chemical composition contains 74% organic and 26% of inorganic [88]. When rice husk is burned or carbonized rice husk is formed, it generates 17–26% of rice husk ash which is another important product that can be obtained from rice husk [89]. Table 4 shows the chemical composition of rice husk and Table 5 shows the composition of organic compounds in rice husk. Rice husk has a global potential as a renewable feedstock for the generation of biofuels. Moreover, the estimated additional revenue can also be improved by high calorific value lignin after the production of biofuels. Thus, rice husk is an excellent potential raw material, economical, and abundant source for future biofuels production and has the potential to provide a high yield of biofuels [90].

Rice straw is a waste from the collection of rice grains. A substantial large quantity of waste and the fact that it is non-food, this lignocellulosic waste was promoted as a possible source of material for global ethanol production [96]. The quantity of straw

Table 4 Lignocellulosic composition of rice husk

Constituents	Composition (%)			
Cellulose	35.6	34.4	40.0	35.23
Hemicellulose	29.3	29.3	15.0	24.39
Lignin	20.0	19.2	20.0	12.92
References	[91]	[92]	[93]	[94]

Table 5 The composition of the rice husk organic compound [95]

Content	Percentage (%)
Carbon	39.8–41.1
Hydrogen	5.7–6.1
Oxygen	0.5–0.6
Nitrogen	36.6–37.4

Table 6 Chemical composition of rice straw [100]

Biomass	Rice straw (%)
Cellulose	32.0
Hemicellulose	35.7
Lignin	22.3
Extractive matter	10.0

Table 7 Characterize monomers of each component in rice straw [101]

Cellulose	Hemicellulose	Lignin
D-glucose	Pentose Xylose Arabinose	Phenolic monomers Coniferyl alcohol Coumaryl alcohol Sinapyl alcohol
	Hexose Mannose Galactose Glucose	
	Uronic acids 4-o-methyl glucuronic acid D-glucuronic acid D-galacturonic acid	

that can be collected from year to year, such as the annual variability in straw production, the yield of straw varies greatly between regions and countries, the modern grain harvesting method, and also the cereal breeding directly towards the development of short stem varieties [97]. The processing of rice straw sugars by enzymatic reaction attracts manufacturing attention due to the light reaction conditions used and the fairly pure formulation of products [98]. The important components of the rice straw are cellulose, lignin, hemicellulose, phenol fraction, and silica [99]. Table 6 shows the composition of rice biomass and Table 7 is the characterization of monomers of each component. Components of lignocellulosic biomass are the polysaccharides that are built up by different types of monomers. To alter the structure of the polysaccharides, a pretreatment method is required to improve the accessibility of hemicellulose and cellulose in enzymatic hydrolysis or fermentation.

2.6 *Sago Hampas: Production, Structural Characteristics and Uses*

Generally, based on Table 8, sago hampas is made up of 58% of starch, 32% of cellulosic materials as well as 4% of lignin [12, 13]. The considerably low amount of lignin content in sago hampas and valued as energy feedstock since no pretreatment is needed before the fermentation process.

Table 8 Chemical composition of sago hampas

References	[19]	[18]	[16]
Composition (%) (Dry basis)			
Starch	58.0 ± 0.02	54.6	55.4
Cellulose	21.0 ± 0.71	21.4	23.6
Hemicellulose	13.4 ± 0.94	10.3	9.1
Lignin	5.4 ± 0.55	3.3	4.0
Ash	3.13 ± 0.13	ND	2.2

ND: Not detected

3 Potential of Biomass Utilization as a Feedstock for Renewable Energy in Malaysia

Renewable energy alternatives in Malaysia are primarily solar, biogas, biomass, and mini-hydro. In the recent decades, the utilization of biomass as renewable feedstock increased as the Malaysian government implemented national policies and strategies such as the National Green Technology Policy (2009), National Renewable Energy Policy and Action Plan (2010), New Energy Policy (2010), Renewable Energy Act (2011) and National Biomass Strategy 2020 (2011) [102]. The objectives of these policies are to reduce the national dependency on fossil fuel and promote renewable energy initiatives to meet the national energy requirement that increases yearly which is projected will be 103 million tonnes of oil equivalent (Mtoe) by 2035 [103].

3.1 Government Assistance

Malaysia also pledged and assured to reduce its greenhouse gas emissions of Gross Domestic Product by 45% by 2030 under the Paris Agreement as compared to intensity in 2005 at the 2015 United Nations Climate Change Conference (COP 21) [104]. The recent report from IPCC [105] indicates that the global mean surface temperature which ranged from 1.8 to 4.0 °C would rise sharply in the next century and beyond if existing patterns of human activity are left unchecked. To achieve this voluntary target, an agency in Malaysia such as the Sustainable Energy Development Authority (SEDA) is responsible to execute the action plan to enhance the activity and project related to renewable energy by managing the implementation of the Feed-in Tariff (FiT) mechanism. Figure 8 exhibits that renewable energy generation from biomass is the second-highest contributor after solar photovoltaic from 2012 until 2018. This remarkable potential of biomass utilization in Malaysia should be increased in the coming years as Malaysia has abundant biomass resources that can be utilized to generate electricity.

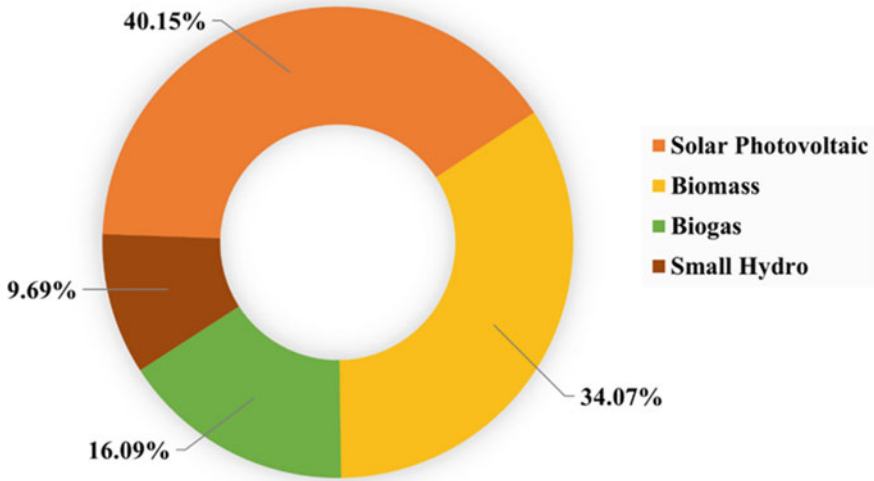


Fig. 8 Renewable energy generation projects that have achieved commercial operations since 2012 in Malaysia [106]

3.2 Environmental Sustainability

In the eco-awakening era, the dramatic rise of concern towards the environment drives the Malaysian government to reduce its greenhouse gas (GHG) emissions from the palm oil industry through the Malaysian Sustainable Palm Oil (MSPO) certification scheme. Figure 9 shows the annual carbon dioxide emission reduction from the commercial operation of solar photovoltaic energy, biomass, biogas, and small hydro in Malaysia. A promising option for renewable energy from biomass is vividly seen as it records the second-highest carbon dioxide reduction after solar photovoltaic energy. The entire oil palm industry (plantation and mill operators) is mandatory to apply the MSPO scheme starting from 31 December 2019 [107]. Currently, 437 out of 455 palm oil mills (96.04%) in the country have been certified as MSPO compliant [108]. MSPO-certified palm oil mills are required to generate renewable energy sources to reduce national GHG emissions. With the vital principle of protecting the environment, the MSPO certification helps to promote and encourage all palm oil millers to generate electricity by their own produced solid biomass. This sustainable certification scheme should be extended to other agricultural sectors in Malaysia to initiate renewable energy from other crops such as rice straw, rice husk, landscape waste, and others.

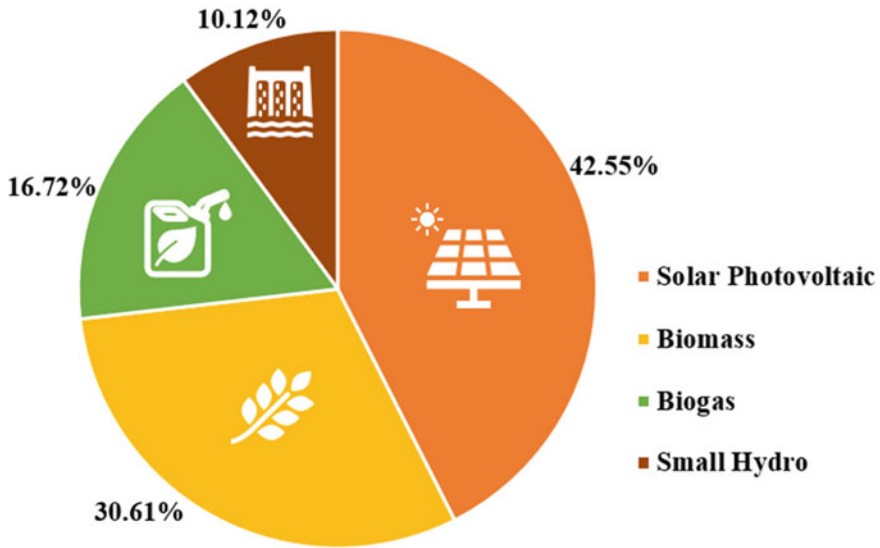


Fig. 9 Annual CO₂ emissions reduction from renewable energy projects that have achieved commercial operations (2012–2018) in Malaysia [106]

3.3 Biomass Availability and Logistic Facilities

The agricultural sector contributed 7.1% to the national Gross Domestic Product (GDP) in 2019 with oil palm being the largest contributor at 37.7% [109]. Hence, biomass from the agricultural sector is abundantly produced at the mill and available all year round. The main challenges to utilizing Malaysian biomass as a feedstock for biofuel are collection, transportation, and storage issues. For instance, OPF is the largest biomass produced during pruning in the oil palm plantation area. However, the OPF is not collected and transported out of the oil palm plantation [110]. Eventually, the OPF biomass is left for the plantation nutrient recycling purpose. Another case example is EFB which has a high moisture content of around 50–60%. The biomass undergoes a sterilization step in a digester at the beginning of the FFB processing in the palm oil mill. The water molecule from the steam is locked by oil residue and this contributes to the high moisture content of EFB. Consequently, this condition is very favourable for fungal degradation which caused a serious issue in further exploration of EFB utilization. The EFB is produced abundantly at the palm oil mill and needs to be transported rapidly to the operator or buyer. Some of the palm oil millers have shredded the EFB and increased their opportunity to sell the EFB to other parties. By referring to the module of other developed countries on this issue, for example in the United States, the facility of biomass drying, grinding and briquetting is centralized for a certain number of mills [111]. Therefore, the facility can be shared by the mills

and it is considered a cost-effective strategy. This collective effort is essential to achieve the ideal cost of feedstock, quantity, and quality for the future of renewable energy from biomass.

3.4 Technology Feasibility

Lignocellulosic biomass is directly incinerated from the source as solid biofuel for electricity. The biomass power plant at Prolific Yield Palm Oil Mill in Sandakan, Sabah uses EFB as primary fuel with oil palm shells and mesocarp fibres as secondary fuels. The biomass power plant is capable of generating 12 Megawatt of electricity [112]. Meanwhile, liquid biofuel production requires a pretreatment step, saccharification, and fermentation. An efficient pretreatment method is required to release all monomers from lignocellulosic biomass for conversion into biofuels. The inefficiency of pretreatment conversion facility, core technology, and equipment shortage may hinder the production of biofuel. The pretreatment step and hydrolytic enzyme possess a domino effect on the subsequent steps in biofuel production, technically and economically [113]. Moreover, high energy consumption and high capital cost in the pretreatment process lead to the high risk of investment. In the Malaysian scenario, most of the small and medium enterprises (SMEs) in the oil palm industry are operating at a small financial budget and hardly venture into value-added bioproduct from the biomass [114]. Nevertheless, OPF juice exhibited a promising potential as a feedstock for bioethanol production as the OPF only required a pressing machine to obtain the juice and directly can be fermented into bioethanol [115].

4 Conclusion

The utilization of renewable bioresources has become a more promising technology due to the main concern of high dependency on non-sustainable resources. Biomass is one of the best potential candidates to be an alternative source for renewable energy. Hence, Malaysia is blessed with abundant biomass resulting from agricultural sectors, including oil palm, rice, and sago. The biomass generated from each sector has it is before fermentation which is further used in different applications. In this chapter, we have critically summarized each biomass produced from the oil palm, rice, and sago industry in Malaysia. Furthermore, we have details about individual biomass from respective agricultural industries, related to their production, structural characteristics as well as uses. In addition, we also have critically discussed other potential factors contributing to the utilization of biomass in renewable energy production in Malaysia. All in all, Malaysia is deemed to have a strong platform in implementing the biomass utilization strategy and further developing the next new era in renewable energy development.

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Different Types of Pre-Treatments for Renewable Bioresources



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Abstract Bioresource also namely as biomass is considered as a type of functional non-fossilized natural waste and organic materials that can be renewed makes it sustainable for the environment and economy. These natural bioresources require treatments and conversion stages to improve the characteristics and functionality of biomass, transforming it into useful forms of energy. Many biomass conversion technologies have evolved for the past decades, which primarily focused on three main routes; biochemical, thermochemical, and physicochemical methods. The high demand for biomass escalated due to the rapid globalization, industrialization, and human activities overloading our atmosphere with the excessive emission of carbon dioxide and global warming. The average global temperature has risen at approximately 0.07 ± 0.07 °C from 1999 through 2008. Roughly in 2020, the earth is about 0.1 °C warmer than before. The carbon dioxide emission to the atmosphere can be suppressed by substituting fossil fuels with biomass, as biomass is considered a carbon-neutral energy source. The equilibrium between carbon released and absorbed from the combustion of biomass is balanced from the biogenic process where the carbon sequestered during the biomass growth, is released back to the atmosphere during the combustion process. The pre-treatment and conversion methods of the biomass contribute to the effectiveness of the production of greenhouse gas (GHG), which is primarily caused by carbon dioxide emission. Thus, this chapter discusses the various aspects of these different pre-treatment approaches for renewable biomass.

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1 Introduction

The search for a less expensive alternative supply of petrol with minimum environmental impact has become the focus of interest. Biomass, for example, is regarded as a long-term resource that can be used to produce biofuel on a big scale, which can be used as a substitute fuel and may provide a solution to environmental issues. Bioenergy products such as bioethanol, biohydrogen, and biodiesel can be made from lignocellulose biomass, a huge renewable bioresource derived from plants. Lignin, cellulose, and hemicellulose, which make up the plant cell wall, are referred to as ‘lignocellulosic biomass’. There are strong cross-linking interactions between these components, which impede the breakdown of the plant cell wall. Ester and ether connections cross-link polysaccharides and lignin. Plant cell wall structure is stabilized by microfibrils generated by cellulose, hemicellulose, and lignin. Lignocellulose wastes (LCW) are the world’s greatest renewable bioresource reservoir, yet they are squandered as pre- and post-harvest agricultural wastes. As a result, several pre-treatments must be taken to make use of these renewable resources in the manufacture of bioenergy products (Fig. 1). This chapter only focuses on the thermochemical, physicochemical, and biochemical treatments.

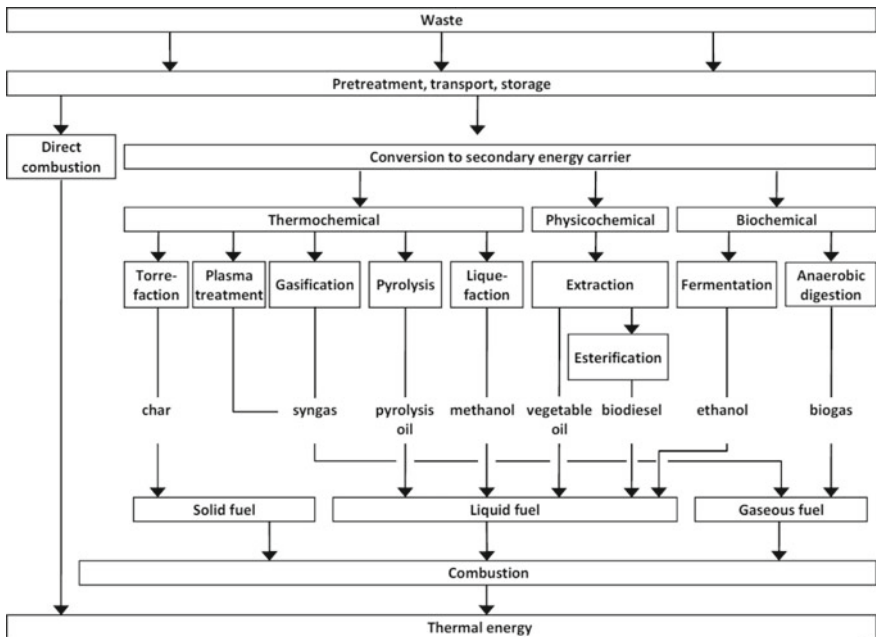


Fig. 1 Different pre-treatment for bioresource wastes

2 Thermochemical

The decomposition of organic matter in biomass for the creation of biofuels such as liquid, gaseous, and solid fuels is referred to as thermochemical conversion. When compared to chemical and biochemical processes, thermochemical conversion is the simplest method for converting biomass into biofuel. Unlike biological processes, which can only convert a portion of the biomass, thermochemical processes can transform all the carbon in the feedstock in most cases. Due to its higher oxygen concentration than coal, biomass is a reactive and desirable fuel for thermochemical reactions. Table 1 shows the many types of thermochemical treatments for biomass and where they fit into which treatment category. This section describes an advanced thermal conversion system that uses high-temperature gasification of biomass, syngas, or hydrogen-rich gas.

2.1 Torrefaction

Torrefaction is a viable approach for increasing biomass's fuel characteristics. Torrefaction, as defined in most research, is a low-temperature (200–300 °C) thermal conversion technique for biomass that operates in the absence of oxygen under atmospheric circumstances. This procedure improves the biomass's physical, chemical, and biological makeup, making it more suitable for co-firing and gasification [1–3]. Roasting, slow- and mild pyrolysis, wood cooking, and high-temperature drying are all terms for torrefaction [1].

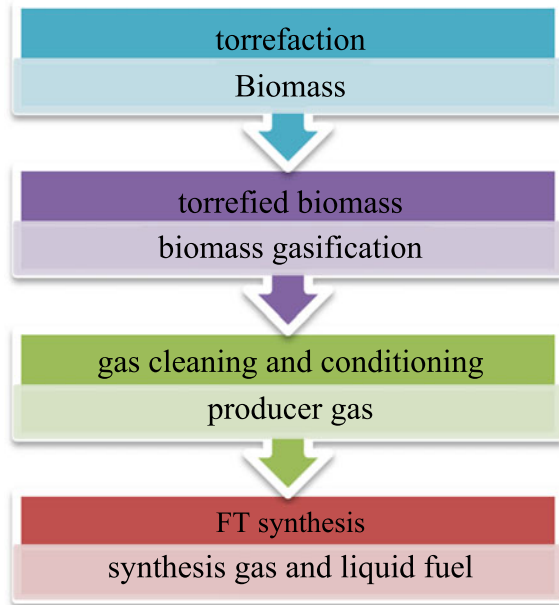
Torrefaction is currently a trendy topic among businesses all around the world. The companies want to use the technology to pre-treat biomass and use the result as a replacement for traditional pellets used in co-firing boilers as well as a raw material for biofuel production. There are numerous advantages to using torrefaction in biomass to liquid chain (Fig. 2).

Understanding the composition of plant components will aid in comprehending the biomass degradation reaction during thermal pre-treatment. When biomass is heated, it undergoes thermal degradation, which is generally accompanied by mass

Table 1 Types of thermochemical pre-treatment for bioresource

Type of thermochemical	Description
Pyrolysis	Thermal degradation of organic material in the absence of oxygen,
Gasification	Partial oxidation
Incineration	Full oxidative combustion
Plasma-based technologies	Combination of (plasma-assisted) pyrolysis/gasification of the organic fraction and plasma vitrification of the inorganic fraction of waste feed
Combination processes	Combination of different thermochemical processes

Fig. 2 Simplified biomass to a liquid chain with torrefaction as one step



loss. The degree of thermal degradation is determined by the residence time and temperature, and Brodeur et al. [24] have extensively documented this process. At drying temperatures of 50–150 °C, biomass loses moisture and shrinks, and most of the chemical contents of the biomass are not yet volatilized. The lignin softens around 120–150 °C, making the material more appropriate for densification since the lignin functions as a binder. Due to thermal degradation of biomass solids, the temperature range of 150–200 °C, also known as the reactive drying range, commences the rupture of hydrogen and carbon bonds, resulting in the emission of lipophilic extractives and compounds. This temperature also causes structural deformation, which means that if the biomass is rewetted, it will lose its capacity to restore its previous structure.

Depolymerization of hemicelluloses also produces shorter, condensed polymers with solid structures, according to Brodeur et al. [4, 24]. Carbonization and devolatilization occur when the temperature is raised even higher, also known as destructive drying (200–300 °C). These temperatures represent the torrefaction process limits, which cause the breakdown of most inter- and intramolecular hydrogen bonds, as well as C–C and C–O bonds, resulting in the formation of hydrophilic extractives, carboxylic acids, alcohols, aldehydes, ether, and gases such as CO, CO₂, and CH₄. Cell structure is entirely broken at these temperatures, and the biomass loses its fibrous nature and becomes brittle. The mass loss is minimal at temperatures below 250 °C, as the predominant biomass degradation occurs due to limited devolatilization and carbonization of the hemicellulose. Hemicellulose decomposes rapidly at temperatures above 250 °C, yielding volatiles and a char-like solid residue.

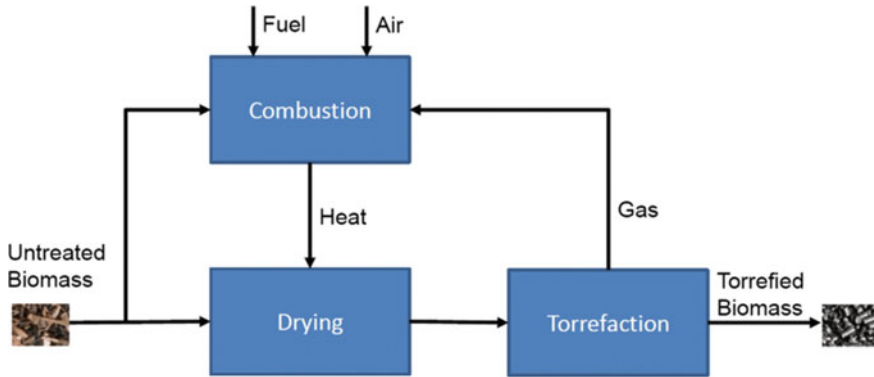


Fig. 3 Typical torrefaction flow diagram [24]

Devolatilization and carbonization of lignin and cellulose are limited [5]. Mass loss during torrefaction at 200–300 °C is primarily due to moisture loss and decomposition (devolatilization), especially of hemicellulose and some lignin. Around 200–280 °C, xylan-based hemicellulose decomposes [4]. Lignin breakdown occurs more slowly, but at a faster rate, beginning at around 200 °C [6]. Figure 3 depicts a typical torrefaction flow diagram.

2.2 Plasma Treatment

Plasma is a type of substance made up of ions and electrons. It's essentially an electrified gas with freely moving electrons in both the negative and positive states. The scenario arises as a result of adding more energy to a gas, which causes negatively charged electrons to break out from the nucleus. Plasma can be thought of as a partially ionized gas on a deeper level. It is made up of neutral atoms, atomic ions, electrons, molecular ions, and molecules that exist in both excited and ground states. As a result, the positive and negative charges balance each other, and many of these charges are electrically neutral. Plasma's great electrical conductivity is due to the presence of charged particles. Plasma carries a lot of internal energy since it is made up of electrons, molecules or neutral gas atoms, positive ions, UV light, and excited gas molecules and atoms. Plasma treatment begins when all of these molecules, ions, and atoms come together and engage with a specific surface.

Thermal plasmas have several benefits, including a high temperature, high intensity, non-ionizing radiation, and a high energy density. The heat source is also directed, with abrupt interfaces and severe thermal gradients that are independent of chemistry. While burning fossil fuels can reach temperatures of up to 2000 °C, electrically generated thermal plasmas can reach temperatures of up to 20,000 °C. Thermal

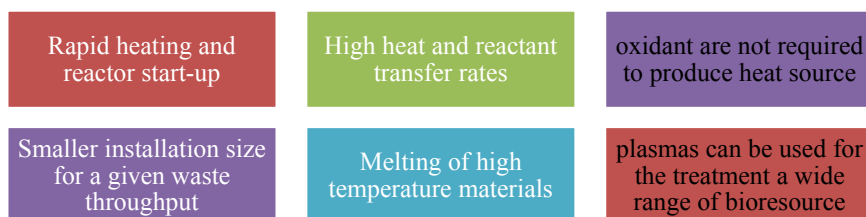


Fig. 4 Plasma advantages

plasma reactors have several additional benefits for the treatment of bioresource waste, including (Fig. 4).

The usage of electrical power as an energy source has the potential to be a disadvantage, particularly from an economic standpoint [7]. A comprehensive cost comparison, on the other hand, frequently indicates the economic viability of plasma-based technologies.

2.3 Gasification

The next method is gasification, a thermal decomposition technique used to convert biomass into combustible synthesis gas (syngas) such as carbon dioxide (CO_2), hydrogen, and nitrogen, and methane through a controlled process involving high temperature and low levels of oxygen. This process usually happens in a gasifier to ensure proper reactions between biomass and gasifying agents. Among the common gasifiers are fixed-bed gasifiers, fluidized bed gasifiers, entrained flow gasifiers, and rotary drum gasifiers, all of which are known to have distinguished designs and characteristics. In the gasifier, there are five distinct thermal processes occurred which are drying, pyrolysis, combustion, cracking, and reduction (Fig. 5).

Gasification started with a drying process at 100–150 °C to remove any moisture contents in the biomass. Usually, biomass contains 5–35% water content, and this can be removed through heating at >100 °C [9]. This initial step is crucial as insufficient water removal may affect the gasification process and the produced gas composition. The next process is pyrolysis, a heating process without air at 200–500 °C. At this stage, there will be large quantities of solid residues, char, and various tar gasses and liquids produced. These side products, especially tar could condense in the gasifier and interrupt the operation by clogging the equipment. Thus, it is important to properly remove or crack the large complex tar molecule either through catalyst cracking or thermal cracking. In catalyst cracking, a catalyst such as alkali metal salts does not only increase the gas yield and gasifier performance but is also effective for tar elimination. As for thermal tracking, it utilizes the heating process, wherein 99% tar was shown to reduce at 900 °C. Additionally, the cracking process also requires a proper mixture between combustible gases and oxygen, wherein the heat produced

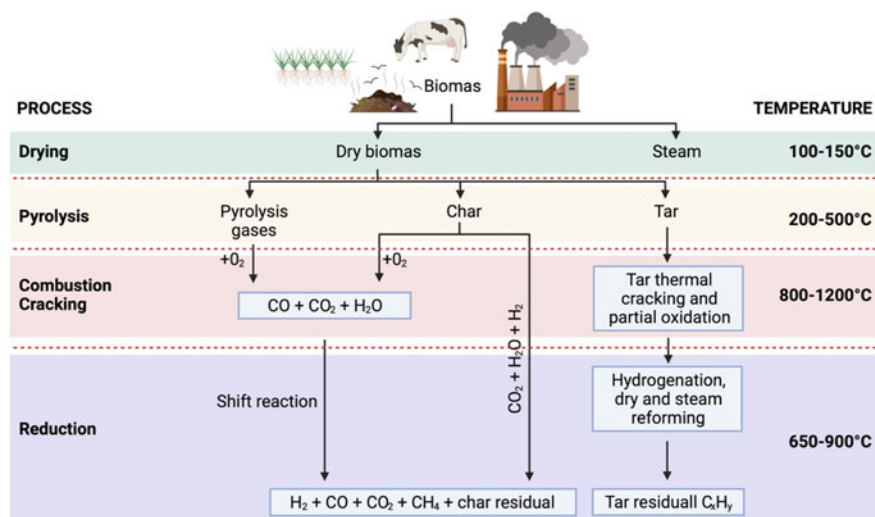


Fig. 5 Gasification process. During gasification, 5 different processes, including drying, pyrolysis, combustion, cracking, and reduction occurred at various temperatures starting from 100 to 1200 °C (Adapted from [8]). Created with [BioRender.com](https://www.biorender.com)

through this mixing process is crucial for later gasification reactions. Compared to direct combustion, the combustion process that occurred during gasification is partial and can extract only 60–90% of the energy stored in biomass. However, it is much safer for the environment, compared to the direct combustion method that promotes the emission of pollutants such as fumes and smoke into the atmosphere.

The last stage is reduction, a process in which the oxygen atoms are removed from hydrocarbon molecules, leading to the formation of carbon monoxide, hydrogen, and methane that can be applied to boilers and gas turbines, or used as precursors for synthesizing other chemicals such as synthetic lubrication oil and fuel through a Fischer–Tropsch (FT) synthesis. FT synthesis is a technology utilizing polymerization reaction to produce liquid hydrocarbons fuel. Besides, the methane produced can also be purified and upgraded via methanation to fuel up a car.

2.4 Pyrolysis

As mentioned previously, pyrolysis is a heating process in the absence of oxygen to generate bio-oil. Since there is no oxygen, the combustion process did not occur, making the chemical compounds such as cellulose, hemicellulose, and lignin decomposed into combustible gases and char, and subsequently, some of the gases condensed into a combustible liquid known as bio-oil. This process can be categorized into fast, and slow pyrolysis (Table 2), depending on its heating rate and yield.

Table 2 Comparison between pyrolysis and gasification [10]

Method	Mode	Condition	Yield percentage		
			Bio-oil (%)	Char (%)	Gas (%)
Pyrolysis	Fast	<ul style="list-style-type: none"> • 500 °C • very short HVRT (~1 s) • short solids RT 	75	12	13
	Slow	<ul style="list-style-type: none"> • 400 °C • long HVRT (days) • long solids RT 	35	35	30
Gasification		<ul style="list-style-type: none"> • 800–900 °C • short HVRT • short solids RT 	1–5	<1	95–99

HVRT: hot vapour residence time; RT: Residence time

Fast pyrolysis is more preferred due to its rapid reaction and high bio-oil production. Compared to gasification that is known to produce 95–99% syngas with low or medium heating value, pyrolysis was shown to generate up to 30% high-quality syngas, suitable for boilers, engines, and turbines.

There are several reactions occurred during pyrolysis, including dehydration, depolymerization, fragmentation, and charring (Table 3). The process usually started with dehydration, wherein it is necessary to maintain the moisture content of the feedstock at ~10% [10] as it might affect the production of bio-oil. Next is depolymerization of bond linkages between the monomers which result in the production of combustible gases such as CO and CO₂.

Fragmentation of the covalent bond of the unit monomers and polymer also happened, leading to the formation of a short-chain and some incondensable gases. However, the compound produced during these initial reactions is usually unstable, and they need to undergo several cracking or recombination reactions. The last

Table 3 The list of common pyrolysis reactions at different temperatures [11]

Temperature	Type of reactions	End products
<350 °C	Dehydration, depolymerization, charring, free radical generation	Carbonyl and carboxyl group production
350–450 °C	Substitution for breaking of glucoside chain of polysaccharide	Tar production containing levoglucosan, anhydrides, and oligosaccharides
>450 °C	Dehydration, rearrangement of fission of sugar units	Acetaldehyde, glyoxalin, and acrolein production
>500 °C	A mixture of all the above process	A mixture of all the above products
Condensation	Unsaturated products condensed and cleaved to the char or combustible gas condensed	A highly reactive char residue containing trapped free radicals Bio-oil

process is the condensation of combustible gases, leading to bio-oil production. The bio-oil produced usually will be upgraded through emulsions process before can be applied as biofuel for transportation or heat and power generation.

Additionally, to enhance the efficacy of the pyrolysis process, several pre-treatments can be done which include physical, chemical, biological, and thermal. Physical pre-treatments refer to the modulation of biomass particles to the appropriate size, while chemical and biological pre-treatments utilize the use of ammonia or rot fungi, respectively. As for thermal pre-treatments, the biomass is commonly dried before the pyrolysis process to conserve energy as water vapourization requires some energy consumption. Thus, drying the biomass will decrease the energy needed to increase the feedstock temperature to the process temperature with a higher ramping rate.

2.5 Liquefaction

Another way to produce bio-oil from biomass is through liquefaction, wherein the biomass is fragmented into small molecules with the help of various factors such as heat, pressure, catalyst, and solvents. This process can be categorized into indirect or direct liquefaction, depending on the involvement of the gasification process (Fig. 6). In the indirect liquefaction, biomass is first gasified in the presence of

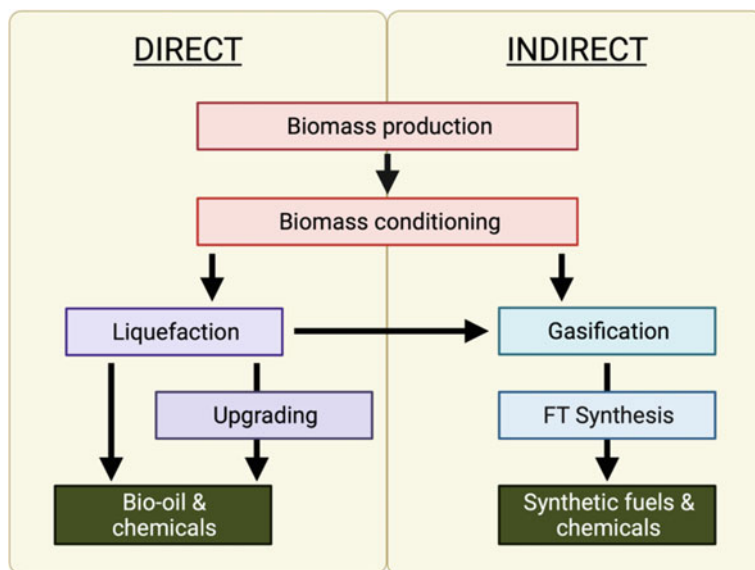


Fig. 6 Comparison between direct and indirect liquefaction. Direct liquefaction does not require gasification and Fischer–Tropsch synthesis while indirect liquefaction includes both of the processes to produce synthetic fuels and chemicals [12]. Created with [BioRender.com](https://www.biorender.com)

oxygen to produce syngas and subsequently undergoes an FT synthesis or methanol synthesis to produce various chemicals, including methyl alcohol, dimethyl ether, and ethyl alcohol. As for direct liquefaction, it involves pyrolysis, solvolysis liquefaction, or hydrothermal liquefaction to generate liquid tars, bio-oil, and condensable organic vapours. Accordingly, the product may also require substantial upgrading or also known as hydrodeoxygenation (HDO), wherein the oxygen is removed from the oxygen-containing compound in the bio-oil to increase the share of aromatics, alkenes, alkanes, and energy density.

Solvolysis liquefaction involved the use of organic solvents such as ethylene glycol, dioxane, and acetone to liquify biomass at 120–250 °C. Compared to pyrolysis, solvolysis liquefaction is better as it can help to prevent cross-linked and reverse reactions occurring between products by diluting the product concentration.

As for hydrothermal liquefaction (HTL), it is a process of biomass conversion to liquid fuels at a low temperature (280–370 °C) in a pressurized environment (10–25 MPa) [13, 14]. These conditions are enough to break the biopolymeric structure into liquid components and also help to maintain the product in either a liquid or supercritical state [15]. During HTL, water is an important reactant and catalyst, wherein it is necessary to degrade the large molecule into a smaller fragment (Fig. 7) [16]. This is contrary to pyrolysis that requires a drying or dehydration process as the presence of water might affect the production of bio-oil. The main product obtained through HTL is liquid bio-crude oil that has high economic potential and is suitable for transportation grade fuel after being upgraded such as via catalytic hydrotreating [13, 17].

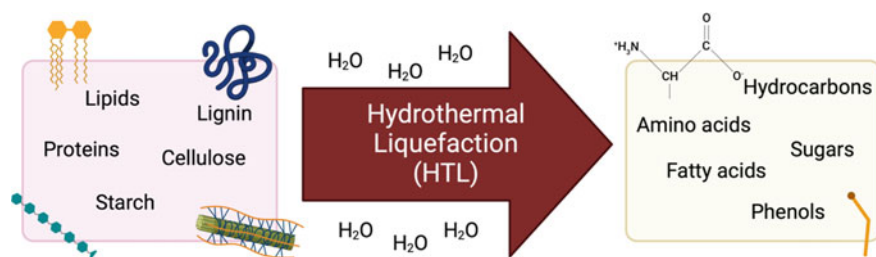


Fig. 7 Degradation of the large molecule into smaller fragments during hydrothermal liquefaction. Water is a crucial reactant during the hydrothermal liquefaction process, where it facilitates the breakdown process of large molecules such as lipids and proteins into smaller molecules, including fatty acids and amino acids [16]. Created with [BioRender.com](https://www.biorender.com)

3 Physico-Chemical Pre-Treatment Method of Biomass

3.1 Introduction

Lignocellulose is the main type of plant biomass that is composed of cellulose, hemicellulose, and lignin. Having high carbon to nitrogen ratio, lignocellulosic is rich in carbohydrates and protein-deficient materials, where the complex structure of cellulose is wrapped by a dense structure of [18]. The chemical composition of lignocellulosic biomass is presented in Fig. 8. Cellulose structure is responsible for the rigid cell wall protecting the plant cell, which is made of glucose molecules, linked via beta 1,4-glycosidic bonds. Cellulose is also composed of random amorphous and ordered crystalline arrangements, and these orientations are crucial for the functionality of cellulose. Meanwhile, lignin is composed of cross-linked components of three monolignols; coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol [19]. The main functions of the irregular amorphous three-dimensional structure include protection against pathogens, supporting the structure of the biomass counter to physical and metabolism damages, and transporting water and nutrients in plant stems [20–22].

The enhancement of bioconversion of lignocellulosic and other types of biomasses can be optimized from the pre-treatment process. This process modifies the structure of the biomass to boost high yields and overcome recalcitrance. The pre-treatment

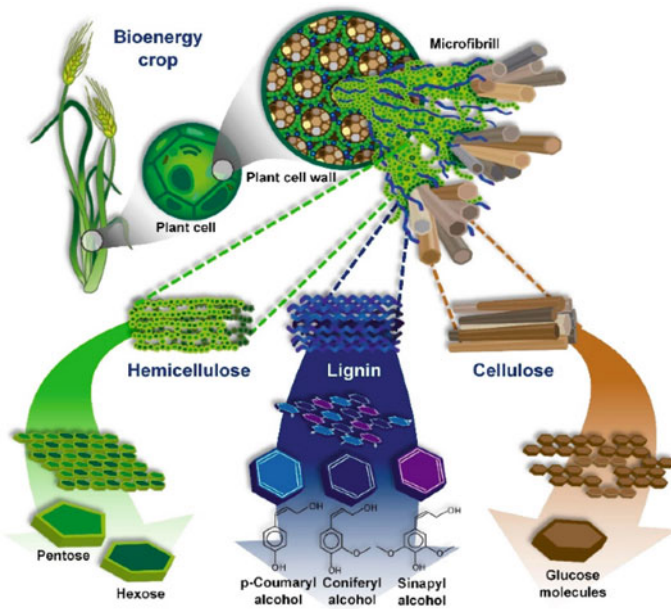


Fig. 8 Composition of lignocellulosic biomass [20]. No permission required CCBY

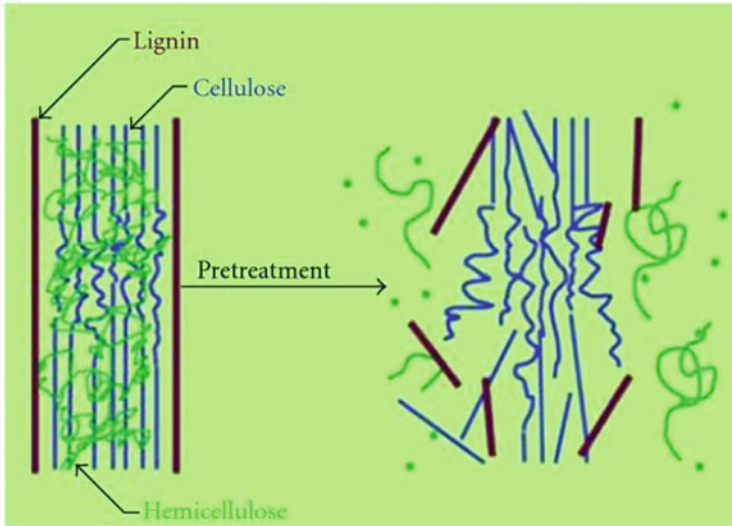


Fig. 9 Effect of pre-treated lignocellulosic biomass [24]. No permission required CCBY

of the biomass enhances the accessibility of enzyme hydrolysis and digestibility to depolymerize the biomass into fermentable sugars [23]. Four main pre-treatment methods namely, chemical, mechanical, physicochemical, and biological. In this subchapter, the elaboration of the physicochemical pre-treatment method of biomass will be discussed and explored. The generic aim of the pre-treatment process of biomass is to eliminate the hemicellulose and lignin, and regulate the level of crystallinity of the cellulose, and also enhance the porosity of the biomass.

Physicochemical is a combination of physical and chemical pre-treatment processes to elevate the digestibility of the biomass. The main purposes of physicochemical biomass pre-treatment are similar to other pre-treatment approaches that include high yield of digestible solids during enzyme hydrolysis; the avoidance of sugars degradation; minimization of inhibitors formation for succeeding fermentation steps; lignin recovery for conversion; and economical friendly for operation through heat and power optimization [24]. However, there are some added values of the physicochemical method over other processes, which will be discussed in a later section (Fig. 9).

3.2 Steam Explosion

The most commonly used and efficient physicochemical method for biomass pre-treatment is the steam explosion. Initially, the biomass is subjected to saturated steam at temperature and pressure ranges of 160–260 °C and 0.7–4.8 MPa for a defined

amount of time. This allows thorough access of steam into the inner structures of the biomass through its cell wall due to high vapor-phase diffusion, which results in hydrolysis and the release of hemicellulose [25–27]. The pH of the biomass is lowered to 3–4 due to the release of acids from the hemicellulose fraction, which results in an autohydrolysis process of hemicellulose. This causes the cleavage of glycosidic bonds and reduces the degree of polymerization of hemicellulose which enhances enzyme digestibility [27–29]. Upon opening the reactor valve to discharge the biomass slurry into a blow tank, the pressure build-up inside the reactor drops abruptly to 1 bar, enlarging the volume of the biomass rapidly, and flash evaporation of superheated water occurs, causing defibration, defibrillation, and rupture of fibres [27, 30]. This is what is referred to as a ‘steam explosion’. Residence time t_{res} , applied pressure P , steam temperature T , and moisture content are the critical factors in the steam explosion method, where low temperature and long residence time are preferred [31].

Table 4 tabulates the typical parameter for the steam explosion pre-treatment method, and the effect measured from varying the parameter. Variation of the parameter has significant impacts on the size and pore size of the broken fibres [32], amount of derived glucose [6], saccharide and ethanol yield values [4, 33], and correlation between the amount of cellulose and glucose yield after enzymatic hydrolysis [34]. Steam explosion is a universal pre-treatment process of biomass as the efficiency of the process can be enhanced by using catalysts such as H_2SO_4 , CO_2 , or SO_2 [26]. Apart from the high yield of biomass extraction, this method also requires low usage

Table 4 Parameters of steam explosion pre-treatment method of some types of biomass

Biomass	Steam explosion parameter	Effect measured from varying-parameter	Reference
Rice straw	$T = 225\text{--}251\text{ }^\circ\text{C}$ $t_{res} = 0.5\text{--}10\text{ min}$ $P = 2.55\text{--}4.02\text{ MPa}$	<ul style="list-style-type: none"> • Increase t_{res} resulted in more shattered and broken fibres, and eventually formed very fined fibres, similarly to fibre size/length • Pore size was maximum at $t_{res} = 2\text{ min}$, and the pore size increased with applied pressure but declined at $P = 4.02\text{ Mpa}$ • The number of soluble sugars formed was maximum at $2.55\text{ Mpa} < P < 3.53\text{ Mpa}$, and $t_{res} = 1\text{--}3\text{ min}$ 	[32]
Branches pruned from pear trees	$T = \text{up to } 248\text{ }^\circ\text{C}$ $t_{res} = \text{up to } 5\text{ min}$ $P = \text{up to } 45\text{ atm}$	To produce biofuel of ethanol <ul style="list-style-type: none"> • Maximum reduction of lignin was observed at $P = 25\text{ atm}$, $T = 224$ • Sugars derived from cellulose decreased with increasing steam pressure • Glucose concentration for all pressure samples increased after saccharification, where the enzymatic saccharification rate was the highest at $P = 35\text{ atm}$ 	[6]

(continued)

Table 4 (continued)

Biomass	Steam explosion parameter	Effect measured from varying-parameter	Reference
Wheat straw	$T = 180\text{--}200\text{ }^{\circ}\text{C}$ $t_{\text{res}} = 5\text{--}20\text{ min}$	<ul style="list-style-type: none"> • Saccharide yield increased to 41.2 g/L for glucose at $t_{\text{res}} = 15\text{ min}$, $T = 200\text{ }^{\circ}\text{C}$, and for xylose (18.9 g/L) at $t_{\text{res}} = 10\text{ min}$, $T = 190\text{ }^{\circ}\text{C}$ • The combination of the steam explosion of wheat straw in dH₂O (1:1) yields high levels of glucose at $22.6 \pm 0.4\text{ g/L}$ and xylose at $16.4 \pm 1\text{ g/L}$ • Hydrolysates prepared are suitable growth substrate for yeast <i>Y.lipolytica</i> 	[33]
Softwood	$T_1 = 180\text{ }^{\circ}\text{C}$ $T_2 = 210\text{ }^{\circ}\text{C}$	<ul style="list-style-type: none"> • Two-step pre-treatment enables enhanced hydrolysis process • At T_1, hemicellulose was solubilized • At T_2 with pressurized environment broke down carbohydrate linkages • Ethanol yield increased and operation costs decreased due to the lesser enzyme dosage needed to access the cellulose structure 	[4]
Reed straw	$T = 200\text{--}240\text{ }^{\circ}\text{C}$ $t_{\text{res}} = 2\text{--}8\text{ min}$	<ul style="list-style-type: none"> • High sugar and glucose yields after 60 h of enzymatic hydrolysis, steam-exploded at 220 °C for 5 min. The amount of cellulose increased by 38% after pre-treatment • Reorganization of biomass structure and morphology after pre-treatment assisted in enzymatic hydrolysis for sugar production 	[34]

of chemicals and minimal energy consumption, which in turn establishes an environmentally and economically friendly process. Moreover, the equipment corrosion associated with acid handling is minimal due to a mild pH of reaction media [35]. One common issue encountered during this process is high fermentation inhibitors can be possibly produced at high temperatures that can limit the digestibility of the biomass [26, 36]. Steam explosion pre-treatment process has been a preferred and effective method for microbial bioethanol for biogas production [37]; wood pellets industry to obtain dimensionally stable and durable pellets [38]. Lam et al. (2011) also mentioned that steam-exploded wood also favours materials with good fuel properties such as high heating value and low moisture absorption [30]. This sulphur-free method also favours an integration possibility with the presence of bioethanol manufacturers, biorefineries, pulp, and paper industries [39].

3.3 Liquid Hot Water (LHW)

Liquid hot water (LHW) pre-treatment works similarly to the steam explosion method and received interest in the production of hydrogen, methane, and ethanol from lignocellulosic biomass [40]. Instead of steam, this process uses hot water and high pressure to enhance the disintegration and breakdown of the biomass [24]. The water temperature is normally set at the range 170–230 °C, and pressure at up to 5 MPa. Similarly, fibre with steam-exploded pre-treated biomass fibre results in hydrolysis of hemicellulose and removal of lignin, and the suppression of fermented initiators formation [26, 41]. The pre-treatment process is an essential step to elevate the enzymatic saccharification to facilitate lignocellulosic bioconversion. Autohydrolysis also is the main working principle of LHW to enable the lignocellulosic substrate accessible to enzymes, and eventually release fermentable sugars for energy-consuming applications [42]. They also reported that the percentages of enzymatic hydrolysis of green peppers increased with water temperature and pre-treatment time, and the value increased over 100% when the biomass was pre-treated at 180 °C for 40 min, compared with untreated samples [42].

In another study on LHW-pre-treated biomass, the conversion of treated straw (175 °C for 35 min) yielded over 60% methane compared to untreated straw [43]. Increasing temperature and pre-treatment time also reduces acetyl group and xylan in water-insoluble solids, enabling digestible substrate of wheat straw [44]. They also reported that at high temperature and residence time (200 °C for 40 min), the high output (96%) of the hydrolysed enzyme was achieved. This suggests that high temperature and optimum residence time enable the disintegration of the lignocellulosic substrate. Shang and co-workers also reported that LHW treatment at $T = 225$ °C resulted in adverse effects in methanol conversion, thus the pre-treatment temperature is not practical for straw [43].

LHW is another economical option for the physicochemical pre-treatment method of biomass, which process does not require the usage of hazardous chemicals or acids. However, the catalytic reaction of LHW enables the conversion of biomass, enhancing the yield. Adding about 0.45% v/v of sulfuric acid, the maximum glucose yield at over 90% from enzymatic hydrolysis of corn stover biomass, compared to only 52% when sulfuric acid was not incorporated [45]. They also reported formic and phosphoric acids enabled the enhanced glucose yield but not as much as sulfuric acid. However, using acid as a catalyst in the LHW pre-treatment process generates inhibitory by-products and toxic compounds such as furans and acids, which opposed the acid-catalysed steam explosion pre-treatment [40, 46]. Figure 10 compares the surface morphology of untreated, LHW-pre-treated, and acid-catalysed LHW-pre-treated lignocellulosic biomass samples. Raw samples portray a compact, connected, and rigid structure, and pre-treated sample surfaces are more separated and exposed [40].

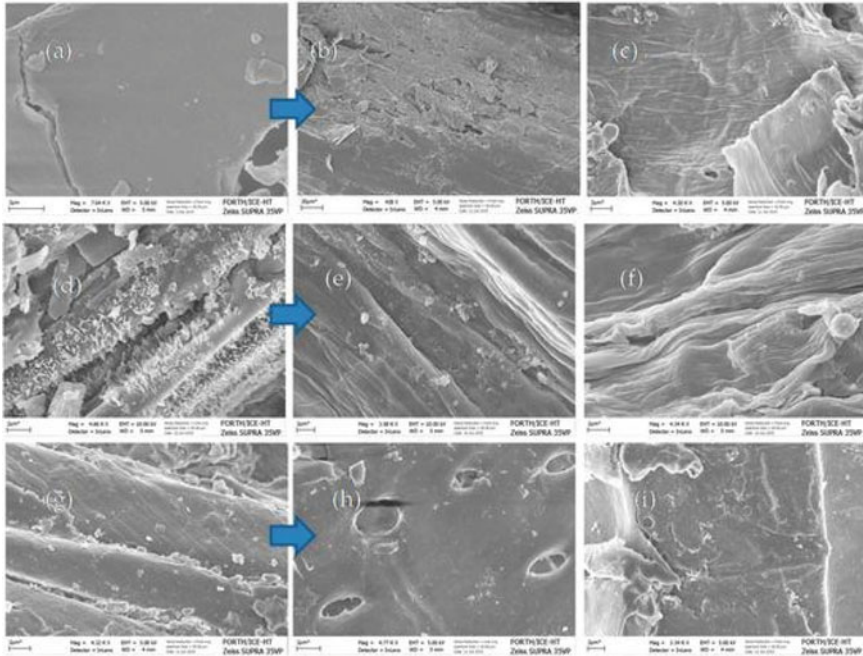


Fig. 10 Surface micrographs of (a) untreated sunflower straw, (d) untreated grass lawn, (g) untreated poplar sawdust, (b) LHW-treated sunflower straw, (e) LHW-treated grass lawn, (h) LHW-treated poplar sawdust, (c) Acid-catalysed LHW-treated sunflower straw, (f) Acid-catalysed LHW-treated grass lawn, (i) Acid-catalysed LHW-treated poplar sawdust [40]. No permission required CC BY

3.4 Ammonia Fibre Explosion (AFEX) and Recycle Percolation (ARP)

Ammonia fibre explosion (AFEX) is another important method of physicochemical pre-treatment of biomass. Classified in the same biomass pre-treatment category, AFEX works similarly to the steam explosion, where the biomass sample is exposed to high pressure (above 3 MPa) for 30–60 min, then depressurized [26, 47]. One main difference between AFEX, LHW, and steam explosion is the usage of liquid ammonia at moderate temperature (60–100 °C) for AFEX-treated samples. The swelling of the biomass enables the biomass sample to be accessed and eventually depolymerized, and reduces the cellulose crystallinity and resulting in an increase of carbohydrates reactivity [23, 26]. The structure of the biomass disintegration depends on the process temperature, eventually affecting the abruptness of ammonia vapourization during depressurization [24]. Ammonia loading is the main key parameter of this process in determining the sugars yield [48]. AFEX has many advantages against other pre-treatment methods, including the absence of inhibitors as side products, and the need for further post-process of the pre-treatment such as washing and recovery of the

produced inhibitors [46]. Furthermore, the usage of lower temperatures than steam explosion and LHW methods boosts the contribution of AFEX on the environmental and economic factors [48]. However, the AFEX pre-treatment method is often associated with a controversial excessive usage of ammonia, which can be harmful to the environment after its usage due to its hygroscopic and cryogenic properties [49]. AFEX is proven to be an effective method in much agricultural waste such as corn stover, switchgrass, and sugarcane bagasse, even though sometimes higher temperature than optimum is required to enhance chain cleavages to produce high sugar yields [49, 50]. On the other hand, biomass with high lignin content such as softwood is challenging to be digested via AFEX pre-treatment and requires an oxidative agent such as hydrogen peroxide and peracetic acid to enhance lignin cleavage [51]. The presence of high lignin in biomass limits the enzymatic hydrolysis of cellulose as lignin is considered a recalcitrant [52].

Another physicochemical pre-treatment process that utilizes ammonia is the ammonia recycle percolation (ARP). Biomass is pre-treated with an aqueous ammonia solution (10–15%) through a slightly pressurized packed bed percolation reactor at high temperature, where the ammonia causes swelling of the biomass, increasing the accessibility of the biomass surfaces, and eventually delignify the cellulosic structure [23]. Ammonia will be fed into a recovery system after the treatment process using a steam-heated evaporator [53]. The pre-treatment temperature is around 140–210 °C, while the reaction time is longer (up to 120 min) compared to AFEX [24]. Similarly to AFEX, high temperatures of the process could cause some loss of hemicellulose sugars [54], and ARP may not be an effective pre-treatment process for highly loaded lignin in biomass, while the benefits were reported in herbaceous biomass [47, 55].

Lignin content in AFP-pre-treated corn stover was reduced by up to 85%, and hemicellulose was solubilized down to 40%, meanwhile, the crystalline structure of the cellulose was unchanged [54]. In another work on corn stover pre-treatment via AFP, half of the xylan was solubilized, with enzymatic digestibility over 90% at FPU/g-glucan enzyme loading [56]. Figure 11 summarizes the schematic flowchart and mass balance for the conversion of 100 g of corn stover to fermentable sugars, and the recovery of ammonia after evaporation, and its reuse for ARP pre-treatment [57]. In their work, the low liquid ammonia (ELLA) system was used, where ammonia mist (0.16 g—NH₃/g-biomass) was incorporated at a solid/liquid (S/L) ratio of 0.45, at a pre-treatment temperature of 90 °C for 24 h. Truang and Kim (2018) also reported that the ELLA method is a low-energy technology and more economical and feasible for scaling up due to reduced usage of ammonia and water, compared to other pre-treatment methods [57].

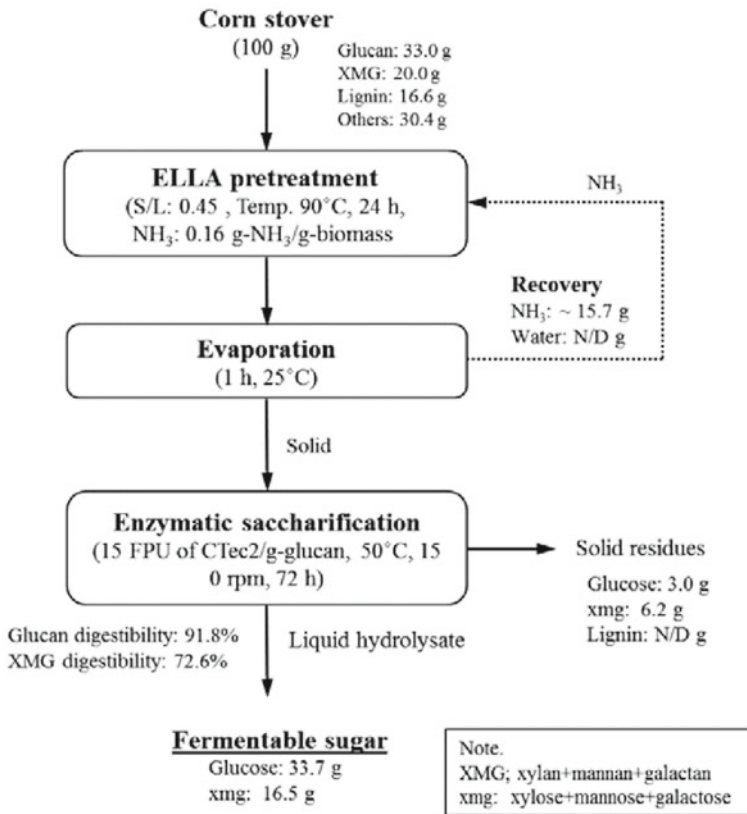


Fig. 11 Schematic flowchart of corn stover to sugars [57]—No permission required CCBY

3.5 CO₂ Explosion

The carbon dioxide (CO₂) explosion method is a pre-treatment process of biomass that utilizes supercritical CO₂ at a pressure of 275 bar, and low-pressure CO₂ at a pressure around 30 bar. The pre-treatment temperature is marginally lower than the steam explosion method, at around 35–175 °C. The decompression of explosion induced by CO₂ enables the disruption of the crystallinity of lignocellulose and removal of lignin, and also the exploration of porous networks of the biomass, increasing its surface area [48, 58]. The expansion of the biomass surface area allows the enzymatic hydrolysis process [24, 26]. Avicel is a commercial highly crystalline material, was pre-treated via CO₂ explosion to increase the reactivity of cellulose, enhancing the hydrolysis rate [59]. This method was proven to produce more glucose from Avicel compared to untreated samples. The Avicel structural changes were observed via X-ray diffraction (XRD) peaks, where the peak at $2\theta = 35^\circ$ was removed and

the crystallinity of Avicel was reduced by 50% after the treatment in a supercritical environment [59]. Santos et al., 2011 [60] reported that when the pre-treatment temperature is low, the disruption of Avicel crystalline structure was insignificant, where there were no changes in XRD peaks [60]. The 50% improvement in glucose yield was also reported in CO₂ exploded biomass samples, and results from simultaneous fermentation and saccharification tests also revealed the increment of carbon source from the cellulosic materials for ethanol production [61].

Table 5 tabulates the effect of variation of pre-treatment parameters on the yield produced from different types of biomass. The balance between residence time, pre-treatment temperature and pressure is essential in determining the end yield of the

Table 5 Different parameters of CO₂ explosion pre-treatment method of some types of biomass on the yield produced

Biomass	CO ₂ explosion parameter	Conversion yield	Reference
Bagasse and Recycled Paper	$T = \text{up to } 80\text{ }^{\circ}\text{C}$ $P = \text{up to } 3000\text{ atm}$	<ul style="list-style-type: none"> Glucose yield increases with temperature and pressure of pre-treatment 	[61]
Rice straw	$T = 110\text{ }^{\circ}\text{C}$ $t_{\text{res}} = 30\text{ min}$ $P = 300\text{ bar}$ CO ₂ -biomass ratio = 5:1	<ul style="list-style-type: none"> Glucan conversion yield at about $32.4 \pm 0.5\%$ for treated sample compared to only $27.7 \pm 0.5\%$ for the untreated sample 	[62, 63]
Sugarcane bagasse	$T = 220\text{ }^{\circ}\text{C}$ $t_{\text{res}} = 5\text{ min}$ Moisture content = 11% CO ₂ = 3% by weight from the water content of material	<ul style="list-style-type: none"> Glucan yield increases up to 800% when the samples were treated 	[63, 64]
Sugarcane bagasse	$t_{\text{res}} = 5\text{ and } 60\text{ min}$ $P = 12\text{ and } 14\text{ MPa}$	<ul style="list-style-type: none"> At high pressure (14 MPa), glucose yield increases with temperature At $P = 12\text{ MPa}$ for $t = 5\text{ min}$, the glucose yield is about 30% more than in 60 min 	[60]
Wheat straw	Combination of acetic acid + Steam + Supercritical CO ₂ at $T = 220\text{ }^{\circ}\text{C}$ for $t = 30\text{ min}$	<ul style="list-style-type: none"> The amount of produced reducing sugars were 20% more than the combination of water + steam + Supercritical CO₂ 	[65]
Southern yellow pine and aspen	$T = 165\text{ }^{\circ}\text{C}$ $P = 3100\text{ psi}$ Moisture content = up to 73%	<ul style="list-style-type: none"> Reducing sugar yields boosted from 14.5 to 84.7% after pre-treatment for aspen, and from 12.8 to 27.3% for southern yellow pine 	[66]

biomass conversion, and this is a mutual criterion for most physicochemical biomass pre-treatment methods. One important characteristic that boosts up the conversion yield of the biomass pre-treated via the CO₂ method is moisture content. The moisture available in the biomass, along with the presence of CO₂ generates carbonic acid, which facilitates hemicellulose hydrolysis [67, 68]. This is also reported by Zhao et al. (2017), for the yield of reduced sugars from CO₂/liquid hot water pre-treated Sorghum stalk [69]. They also revealed that a high yield is achievable at lower temperatures and reaction times. Taylor et al. (2019) [58] added that the efficiency of the acid-induced hydrolysis and the explosion-derived shear forces, the biomass feedstock must retain some amount of water or moisture to gain acidity of CO₂ [26, 58]. However, CO₂ explosion is not one of the most economical ways available as the usage of high pressure is the pivot key factor of achieving high yield [24]. On the contrary, depending on the aim of the pre-treatment process, the supercritical CO₂ method is easily available and does not require the usage of hazardous chemicals and solvents, therefore the utilization of this method can be techno-economically viable [70]. Furthermore, recycled CO₂ can be used to utilize the CO₂ life cycle without burning natural gas, as recycled CO₂ is functional and also used as a feedstock to make new plastic materials [71].

The biomass pre-treatment process via physicochemical procedure is proven to be efficient and effective to elevate the yield of the bioconversion process. This section discussed the assortment of commonly used physicochemical pre-treatment procedures, steam explosion, liquid hot water, ammonia, and supercritical carbon dioxide.

4 Biochemical

Apart from being great resources to produce biofuels and platform chemicals, biomass and waste materials have the potential to be used in place of fossil-derived resources [72]. Sugars and starch-containing compounds, for example, have been the subject of much research and commercialization because these compounds can be categorized as quickly degradable biomaterials, which makes them attractive candidates. However, as the exploitation of such non-poisonous substances for the manufacture of non-food products competes with human nourishment and the use of arable lands, ethical concerns have been raised. Additionally, the readiness of edible materials restricts their use as feedstock for non-food commercial bioprocesses due to the scarcity of available resources.

Renewable biofuels and chemicals made from biomass are increasingly being recognized as a more environmentally acceptable alternative to petroleum-based products. Governments have embraced the concept of using plant material as a source for fuels and commodity chemicals to reduce their reliance on the unpredictable petroleum market, which has become increasingly precarious. It is not only economic factors that are driving this trend; it is also related to social and political factors as well. It has been established that global warming is caused by CO₂ emissions,

Table 6 Nutrient sources for industrial fermentation

Nutrient	Raw material
<i>Carbon sources</i>	
Glucose	Corn, sugar, starch, cellulose
Sucrose	Sugarcane, sugar beet molasses
Lactose	Milk whey
Fats	Vegetable oils
Hydrocarbons	Petroleum fractions
<i>Nitrogen sources</i>	
Protein	Soybean meal, corn steep liquor, distiller's solubles
Ammonia	Pure ammonia or ammonia salts
Nitrate	Nitrate salts
<i>Phosphate sources</i>	
	Phosphate salts

which are primarily derived from the combustion of fossil fuels. This has led to a shift towards biofuels and biomaterials coupled with degrading and finite carbon fossil energy resources and uncertainty in petroleum supply. Lignin was historically considered to be one of the key components of lignocellulosic biomass. Its excellent chemical features nonetheless make it a suitable option for the manufacture of bio-based products. One of the challenges is that lignin is highly resistant to chemical and biological reactions. In addition, the best lignin used for bio-refining should preferably be low in hemicellulose and sulphur, soluble in organic solvents, and consistent overall.

The biochemical sector now lacks an abundant source of sugar to produce goods with greater value. An ideal source of sugar must be affordable, easily accessible, and somewhat pure throughout the year. These can be fermented into useful compounds such as ethanol, xylitol, arabitol, succinic acid, and lactic acid by biological conversions. Although lignocellulosic biomass is a plentiful source of sugar, it requires costly and energy-intensive processing and is rarely uniform in composition. Hence, incorporating biochemical production into an existing market, like sulphite pulping, opens the door to the possibility of utilizing sugar streams that are already generated during the pulping process while also eliminating the need for pre-treatment because the subsequent streams are mostly delignified. Because of this, organism-specific chemical compounds are required as the growth (nutrient) medium to increase the rate of microorganism growth and, consequently, the rate of synthesis of diverse chemical compounds in artificial culture. It is the types and relative concentrations of the ingredients in the medium, the pH, temperature, purity of the cultivated microbe, and other factors that influence microbial growth and, consequently, the production of biomass (which is the total mass of cells or the organism being cultured) and the synthesis of various compounds in the cultured organism. The nutrient sources for industrial fermentation are given in Table 6.

Pre-treatment of lignocellulosic biomass is believed to improve the permeability of holocellulose (cellulose and hemicellulose) to its fermenting sugars, and the lignocellulose can be produced without pre-treatment by only 20% of the theoretical sugar yield [73, 74]. Currently, the most expensive component of the process after the raw material is the biomass pre-treatment stage. Thermal and mechanical processes are energy-intensive and thus carbon-intensive, as they produce CO₂ indirectly. Chemical methods degrade the biomass, resulting in the formation of biochemical inhibitors as by-products [75, 76] and entail expensive neutralization processes [77].

When compared to alternative pre-treatment procedures, the use of microorganisms for the removal of the lignin fraction provides several advantages. First and foremost, microorganisms act in their natural environment, removing the need for thermal and electrical energy inputs. In comparison to chemical pre-treatment, biochemical pre-treatment produces no chemical metabolites, which frequently hinder cellulose breakdown. Normally, lignocellulosic biomass is a structural component of plants that is high in lignin, hemicellulose, cellulose, and pectin. These components are integrated into a molecular medium using relatively little amounts of monosaccharides, carbohydrates, proteins, and fatty acids.

Microorganisms and enzymes are used in hydrolysis to degrade biomass, which results in the production of biofuels as well as the synthesis of specific platform chemicals in biochemical refineries. Moreover, through fermentation reactions, biohydrogen (H₂) and bioethanol (CH₃CH₂OH) can be produced from lignocellulosic biomass, which is both environmentally beneficial and cost-effective in terms of biofuel generation. Lignocellulosic biomass resources are processed using a biochemical technique to yield three unique useful products: cellulose (C₆-sugars), hemicellulose (C₅/C₆-sugars), and lignin. Separate pre-treatment of the acquired precursors is followed by conversion into useful biofuel products during the subsequent bio-refining procedures. Lignocellulosic cellular components account for approximately 75% of all fermentable materials used in the production of liquid biofuels, making them a significant future supply for fermentable materials. To produce liquid fuels (alcohols) and chemicals, the lignocellulosic biomass is first converted into low carbon soluble and fermentable sugar intermediates via microbial enzyme hydrolysis of higher C₅ and C₆ sugar moieties, followed by fermentation using specific biocatalysts such as *S. cerevisiae*, *Z. mobilis*, *T. reesei*, *C. thermocellum*, and *C. phytofermentans*. Hence, the following subtopics will be discussed in-depth about the fermentation and anaerobic digestion process as part of the biochemical treatment for the biomass.

4.1 Fermentation

Fermentation is the process of transforming carbohydrates to alcohols and carbon dioxide under anaerobic circumstances utilizing yeast enzymes. Fermentation has been around for thousands of years, with its earliest use in the production of beer, wine, and a variety of other alcoholic beverages. Despite its simplicity, this reaction

has undergone significant development over the years to aid in the commercialization of the production of ethanol from lignocellulosic material. Fermentation is a metabolic process in which organic chemicals, notably CHO, are broken down to release energy without the presence of a terminal electron receptor such as oxygen. As with the hydrolysis process, this final step in the conversion of biomass to ethanol has undergone major changes to accommodate the addition of pentose or C₅ sugars. For example, when corn was used as the feedstock for bioprocessing, the only accessible reducing sugar was glucose. Given the extensive research and operation of glucose-fermenting methods over the years, this phase was the quickest and most economical.

By using biocatalysts to catalyse the fermentation of pre-treated biomass containing five-carbon and six-carbon sugars, desirable products can be produced. Fermentation is a term used to describe the chemical changes that appear during the breakdown of complex organic substrates in the presence of microbes that are catalysed by enzymes and produce energy. Yeast and bacteria are examples of microorganisms. The bacterium *Zymomonas mobilis* and the yeast *Saccharomyces cerevisiae* are responsible for the production of ethanol. In high concentrations, succinic acid is produced by *Actinobacillus succinogens*, which are taken from the rumen ecosystem. All the sugars present in the biomass should be digestible by the fermentation microorganisms to ensure that the ethanol generation from biomass is cost-effective. The possibility of a bacterium capable of fermenting all cellulosic sugars, including glucose and xylose, has been raised in several scientific publications. The experimental data from their results were utilized to create a mathematical model that represented the fermentation process in detail. The overall reaction of hexose fermentation to ethanol is:



A typical method of fermentation lignocellulosic hydrolysate is to employ yeast, namely *S. cerevisiae* (baker's yeast), which is generally available and can thrive on simple sugars such as sucrose and disaccharide sucrose as well as lignocellulose. It is also employed in the production of alcoholic beverages as well as in the leavening of bread, and it is usually considered to be safe for consumption. Assimilation of furfural by *Saccharomyces cerevisiae* has been shown to impede the growth of other microbes. It is among the most stress-tolerant bacteria, making it a significant trait for industrial application. *S. cerevisiae*, on the other hand, is unable to utilize pentoses to produce ethanol. Additionally, pentoses can be used to maximize ethanol yield and prevent complications during wastewater treatment. Numerous species of microorganisms classified as follows are employed in fermentation processes:

1. PROKARYOTIC
 - i. Unicellular: bacteria, cyanobacteria
 - ii. Multicellular: cyanobacteria
2. EUKARYOTIC

- i. Unicellular: yeasts, algae
- ii. Multicellular: fungi, algae

Organisms grow through a series of sophisticated energy-based processes. Microorganisms develop at a different rate depending on multiple culture conditions, which should produce enough energy for various chemical reactions. To produce a specific chemical, particularly exact cultural conditions at a specified growth rate are required. Numerous systems are now computer-controlled. Microorganisms require organism-specific chemical compounds as a growth (nutrient) medium to develop rapidly and hence synthesize a variety of chemical compounds under artificial culture. Variety and relative concentrations of the medium's components, pH, temperature, purity of cultured organism, and other factors all regulate microbial growth and, therefore, the generation of biomass (the total mass of cells or the organism being cultivated) as well as the synthesis of various chemicals.

Batch fermentation procedures, fed-batch fermentation processes, continuous operation fermentation processes, and immobilized cell systems are all types of industrial fermentation processes. When deciding which fermentation method to utilize, it is important to evaluate the qualities of the raw materials, the technological difficulty, and the yield of the process. Fed-batch ethanol production is currently the most widely utilized process in large-scale ethanol production. The phrase 'industrial fermentation' refers to any industrial process that produces a material that is beneficial to humans and that is dependent on the action of one or more microbes to manufacture the material. Generally, these operations are conducted out on a big scale. While some are fermentations in the traditional biochemical sense, the majority are aerobic processes in which the bacterium utilizes oxygen and entirely metabolizes CHO.

A fermenter is an apparatus used to carry out the fermentation process. Fermenters range in size from laboratory experimental versions with a capacity of one or two litres to industrial machines with a capacity of several hundred litres. Unlike a fermenter, which is used for the bulk culture of microorganisms, a bioreactor is used for the mass culture of plant or animal cells. Cell biomass can be used to easily remove the chemical substances created by these cultivated cells, such as medicinal medicines, from their environment. There are no differences in the engineering of fermenters and bioreactors, nor are there any differences in their operational parameters. It is becoming increasingly difficult to distinguish between the two notions, especially given the increasing participation of microorganisms as elicitors in various scenarios.

When doing batch-type fermentation, a tank of fermenters is filled with the raw materials to be fermented that have been prepared in advance. The temperature and pH for microbial fermentation are correctly controlled, and nutritive supplements are occasionally added to the produced mash to provide additional nutrients. In a pure culture technique, the mash is steam sterilized to kill any pathogens. The inoculum of a pure culture is added to the fermenter, from a separate pure culture vessel. Fermentation proceeds, and after the proper time the contents of the fermenter are taken out for further processing. The fermenter is cleaned, and the process is repeated. Thus, each fermentation is a discontinuous process divided into batches.

Meanwhile, in a continuous fermentation method, the substrate is continually fed to the fermenter at a fixed pace. This keeps the organisms in the logarithmic phase of growth. Continuous fermentation is a relatively complicated process in terms of design and arrangement. Microorganisms develop according to the characteristic growth curve, with a lag phase followed by a logarithmic phase, during batch fermentation. This is followed by a progressive slowing of growth until the stationary phase is reached. This is due to a deficiency of one or more important nutrients.

Numerous industrial processes, dubbed 'fermentations', are conducted under aerobic circumstances by microorganisms. It was important to provide a large surface area in older aerobic procedures by exposing fermenting material to air. Modern fermentation procedures maintain aerobic conditions in a closed fermenter containing submerged organisms. The fermenter's contents are stirred with an impeller and aerated by pumping sterilized air into the fermenter. Essentially, a fermenter capable of operating under microaerophilic or anaerobic circumstances will be identical to one designed to work under aerobic conditions, with the exception that the preparations for vigorous stirring and aeration will be omitted. However, many anaerobic fermentations require mild aeration during the initial development phase, as well as adequate N circulation for stirring and temperature maintenance.

Each process of a fermentation operation in an industrial setting can be divided into three primary stages: (1) upstream processing, (2) the fermentation process, and (3) downstream processing. Upstream processing is the first stage of any industrial fermentation operation. It is necessary to perform upstream processing such as formulating the fermentation medium, sterilizing air, fermentation medium, and the fermenter, preparing an inoculum for use, and inoculation of the fermentation media. With the addition of water and oxygen, a fermentation medium should have at least one of the following components: an energy source, a carbon source, a nitrogen source, and any micronutrients required for the growth of the microorganism. The following properties should be present in a medium that is used for large-scale fermentation to assure the long-term viability of the operation:

1. It should be cheap and easily available.
2. It should maximize the growth of the microorganism, productivity, and the rate of formation of the desired product.
3. It should minimize the formation of undesired products.

As a substrate for industrial fermentations, many waste products from other industrial processes are commonly used. These include molasses and lignocellulosic wastes as well as cheese whey and corn steep liquor. These waste products are modified by the addition of additional nutrients and then used as the substratum for various industrial fermentations. To avoid infection with any undesirable bacteria, it is necessary to sterilize the fermenter. Membrane filtration is used to sterilize the air, whereas heat sterilization is used to sterilize the medium. During the filter sterilization process, any nutritional component that is heat-labile is removed and then added to the sterilized medium. Sterilization of the fermenter can be done in conjunction with the medium or separately.

The fermentation process entails the proliferation of the microorganism as well as the generation of the desired product. Aspects of downstream processing that are important to consider include the recovery of products in their pure state and effluent treatment. If the product is produced intracellularly, product recovery is accomplished through a series of operations that include cell separation by centrifugation or filtration; product recovery by disruption of cells (if the product is produced intracellularly); and extraction and purification of the product. The effluents are then treated using a variety of processes that include chemical, physical, and biological treatment. Commercially important products of fermentation can be described in five major groups as follows:

1. Biomass (Baker's yeast, SCP, Starter cultures, animal feed, etc.)
2. Primary metabolites (amino acids, organic acids, vitamins, polysaccharides, ethanol, etc.) and secondary metabolites (antibiotics, etc.)
3. Bioconversion or biotransformation products (steroid biotransformation, L-sorbitol, etc.).
4. Enzymes (amylase, lipase, cellulase, etc.).
5. Recombinant products (some vaccines, hormones such as insulin and growth hormones, etc.).

It has been proven that fermentation can be used to produce ethyl alcohol, which can then be used in the creation of gasoline. Approximately 90% gasoline and 10% ethanol are used to make gasohol. The fermentation of agricultural and municipal wastes can provide the alcohol required to produce this product. The utilization of gasohol is a viable approach of utilizing renewable resources (plant material) to extend the availability of a non-renewable resource (gasoline). The fermentation process is also used in wastewater treatment. When wastewater is treated with activated sludge, aerobic microorganisms are used to break down the organic material present. During the recycling process, solid waste is turned into carbon dioxide, water, and mineral salts.

As a final point of reference, fermentation technology is a very active and rapidly expanding sector of biotechnology, consuming an ever-increasing number of processes and products. Having a longer history than any other area of biological sciences, fermentation technology will have a longer and brighter future in the service of humanity, encompassing such essential areas as food and medicine, among other things.

4.2 Anaerobic Digestion

Lignocellulosic biomass is abundantly available as raw material from agricultural solid waste. Anaerobic digestion (AD) is one of the most attractive technologies for turning solid organic waste into energy because of its economical and energy recovery benefits. Anaerobic digestion is a biological process involving the degradation of organic materials such as carbohydrates, lipids, and fats by microbes in the absence

of oxygen. Hydrolysis, acidogenesis, acetogenesis, and methanogenesis are among the metabolic events involved. It is characterized by a complicated breakdown of organic matter by a variety of anaerobic microbes. Biogas, a renewable source of energy, and digestate, an organic residue (digested material) that can be utilized as an organic fertilizer in agriculture, are two of AD's end products. Because of the reduced amount of water to be added to the raw material, high-solid AD, which is operated at a total solid (TS) content $>20\%$, is a good alternative to wet systems (TS $<10\%$) for the treatment of organic solid waste. The key advantages of this method are the lower energy requirements and smaller digesters required for the same organic loading rate, the simpler phase separation step for the digestate, and the fewer steps required for pre-treating feed materials.

Because of the presence of solids, the properties of water in high-solid anaerobic digesters are different from those of free water: a significant amount of water is bound to the solids, as opposed to free water. High-solid digestates are currently recognized as viscous-elastic materials with a high yield stress, which is characterized by high yield stress. The yield stress is the amount of force necessary to cause the medium to flow. In digestion medium, it grows in proportion to the total solids content (TS content) according to an exponential rule, and the size of the increase is also dependent on the physicochemical features of the solid matter (granulometry, waste origin, etc.). The rheological properties of waste are influenced by the makeup of the waste stream. Throughout digestion, anaerobic digestion changes the qualities of the food. There has also been limited research into the distribution of water in waste. Increased TS levels result in increased digester capacity and a reduction in the amount of water required to be added to the feed substrate. However, HSAD results in the accumulation of inhibitory metabolites such as H_2S , free ammonia nitrogen, and long-chain fatty matter, which can disrupt or slow down methanogenic activity in the presence of hydrogen sulphide (H_2S). Low methane yields and longer lag times before methane generation begin are two of the challenges associated with high-solids anaerobic digestion [78]. Many experiments have been conducted to improve the pre-treatment process of biomass material before its usage in the HSAD. However, the primary issue with HSAD is a lack of mass transfer and liquid transfer, which has resulted in a delay in the synthesis of biomethane as a result. The amount of water present and its mobility are crucial in enabling mass transfer.

Solid-state (SS) can be defined as a non-Newtonian, temperature-dependent suspension of organic and inorganic particles in an aqueous medium. The rheology of non-Newtonian fluids cannot be described by a single value of its viscosity (defined as the ratio between shear stress τ and shear rate γ), being τ not linearly proportional to γ . As a result, an apparent viscosity η (corresponding to a single point of the viscosity function) must be specified. The viscosity of non-Newtonian fluids also depends on their deformation history as a hysteresis loop is generated after removing the shear force. Sludge viscosity decreases as the shear rate increases (shear-thinning behaviour) due to modification of the sludge structure. This modification is time-dependent and, if the imposed shearing does not exceed the deformation limit of sludge flocs, disappears once the applied force is removed (thixotropic behaviour).

Meanwhile, dry solid-state (DSS) is a pseudoplastic fluid that exhibits yield stress. Yield stress fluid flows only if submitted to stress above a critical value ($\tau\gamma$) and can move from a solid to a liquid state in a reversible way due to the soft interactions existing among the elements composing their structure. The flow characteristics of these fluids are hard to predict as they feature solid and liquid regions difficult to locate. Reducing the yield stress of dry solid-state facilitates management operations such as storage and transportation and prevents the formation of a sludge crust in the digester [79]. The digestion time also plays an important role in determining the rheological behaviour. Füreder et al. (2018) [80] observed that digested DSS (6–8% TSS) with an SRT of 20 days had higher shear stress and friction loss compared to sludge with a 25-day Sludge Retention Time (SRT). Dai et al. (2014) [81] observed that ADS from HSAD (16% TS) with SRT of 30 days resulted in lower shear stress, viscosity, and yield stress compared to 20-day SRT sludge under both mesophilic and thermophilic conditions. The positive effects of SRT on sludge rheology can be attributed to the lower TS content of DSS digested with longer SRT.

Optimal physicochemical conditions for the growth of the appropriate microbial activity are required for the successful and efficient breakdown of organic matter in anaerobic digestion. The presence of moisture in the media was determined to be the most significant determining factor in solid anaerobic digestion experiments. Sprinklers or perforated pipes are commonly used in batch solid digesters to disperse the liquid layer, or leachate, over the top surface of the substrate to achieve the required moisture content in the solid medium. Sprinklers or perforated pipes are also used in continuous solid digesters to disperse the liquid layer, or leachate, over the top surface of the substrate. The objective of recirculation is to maintain an adequate amount of moisture in the bed while also encouraging inoculation and mass diffusion between the solid and the flowing liquids [82]. Although there has been some research into the hydrodynamics of leachate recirculation on the lignocellulosic biomass of EFB residues in High-Solid Anaerobic Digester (HSAD), there has only been a limited amount of information available. Figure 12 depicts the advantages and disadvantages of using the HSAD system, particularly for agricultural applications. To design



Fig. 12 Opportunities and challenges of HSAD system [84]

a liquid injection system that achieves uniform total solid (TS) in the solid medium, it is necessary to understand the flow characteristics and time required for leachate to pass through the solid medium. This knowledge is essential for determining the optimal liquid injection system, which includes the number of perforated pipes, the size and number of perforations, and other factors.

Several studies have demonstrated that the chemical composition and lignin content of different kinds of aquatic plants have an impact on the amount of methane produced by the plants. Under anaerobic digestion, lignin is only minimally reduced in plant materials, hence inhibiting microbial enzymatic assaults on the biomass. To break the lignin barrier in cellulose and hemicellulose and facilitate subsequent reactions, some tactics have been employed, such as co-digestion with other biomasses as well as physical, chemical, and biological pre-treatments of the cellulose and hemicellulose. Although the process may be constrained by a variety of factors, the properties of the raw materials, such as the composition and degradability of their chemical components, have a significant impact on the process. To avoid acidification, the co-digestion of materials with other materials, the preparation of substrates, and/or the regulation of the reactor parameters are all proposed methods of prevention [83].

The adoption of AD for biomass is limited by the features of the biomass, particularly the low C/N ratio. However, biomass is still a waste that may be valorized by AD, and it also has the potential to be a source of micronutrients for the process. Although positive results have been reported from the Co-AD process, there is still room for improvement in terms of understanding the synergism or antagonism impacts that the variety of feedstocks has on the process.

5 Conclusion

In this chapter, the versatility of the aforementioned processes can easily be adapted to the type and composition of the biomass, and the target ends usage of the conversion procedure. Combination with other pre-treatment processes such as the usage of acid, heated water, and catalyst can be modified with physicochemical processes to enhance the overall bioconversion procedure. Process parameters are crucial to determine the efficiency of the pre-treatment process, balancing the economy-environment spectrum. The advancement of pre-treatment methods suiting the demand in industries enables the discoveries of the multifunctionality of renewable biomass. The criteria for selection of pre-treatment method is heavily dependent on the energy usage and liberation, amount of feedstock and yield, the complexity of the setup, overall cost, and most vitally, the contribution towards the environment, which includes energy, toxicity, pollution, and contamination.

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Technologies for Biomass Thermochemical Conversion



Khairuddin Md Isa and Saiful Azhar Saad

Abstract In the past few decades, increasing environmental pollution and rapid depletion of conventional fossil fuels has fueled the requirement of alternative renewable sources of fuels. In this context, biomass-based bio-oil has received much interest as a renewable and sustainable alternative to crude petroleum. Thermochemical conversion processes including direct combustion, pyrolysis, gasification, and liquefaction are seen as promising to renewable energy sources. Pyrolysis is a promising route with suitable reactors and a quick process to produce liquid yield. In contrast to the first three options, which require dry biomass, hydrothermal liquefaction (HTL) is suitable for handling wet biomass with varying moisture contents, thus avoiding drying-related throughput. Thermochemical conversion to produce liquid yield using biomass as a feedstock still facing constraints to directly use the produced bio-oil. High oxygenated compounds of bio-oil seek an upgrading process to enhance the quality. However, a number of upgrading processes can be considered to enhance the oil's quality. Solvolysis using hydrogen donor solvents, alcohols and water is also the best option to explore to produce a good quality of bio-oil under thermochemical conversion. Malaysia is blessed with an abundant source of biomass due to agriculture activities, producing a massive amount of waste every year. This gives the advantage of utilizing the thermochemical conversion route as a promising process to convert biomass into a valuable liquid product.

Keywords Pyrolysis · Liquefaction · Biomass

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1 Introduction

Malaysia is blessed with a massively cheap supply of fossil energy resources such as gas, coal, and oil, and so far, its energy supply is still able to cater to the demand. However, like most industrial countries, Malaysia is facing the challenges of environmental issues such as greenhouse gases emission and requiring new sources of energy. Malaysia is benefiting from the massive amount of agricultural wastes generated from agriculture activities. Biomass is an important renewable source of energy and has been used to provide important global renewable energy sources. It is widely accepted that utilizing biomass as an energy source would bring social and economic benefits in the less developed regions of the world [1]. Malaysia could very soon experience an energy crisis and the additional effects of fossil fuels combustion and the issue of global warming have resulted in the idea of utilizing biomass as a feedstock for the production of renewable energy. The global warming issue has catalysed the requirement to utilize biomass, as its energy utilization gives less impact on environmental pollution than fossil fuel combustion [2].

Though having plenty of information and in-depth knowledge, thermochemical technologies are not developing as forecasted [3]. Lack of knowledge and ignorance are the main factors contributing to biomass underutilized. Institutions in Malaysia are actively conducting several research activities using biomass as feedstock, exploring the best way for biomass conversion into valuable chemical products. For example, conducting experiments on thermochemical conversion and investigating the suitable processes on various biomass feedstocks at different operating conditions such as temperature, reaction time, gas flow rate, and pressure [3, 4]. Biomass can be converted into alternative fuels via biochemical and thermochemical conversion and has been investigated worldwide [1, 5–10].

The pyrolysis of various biomass to produce a liquid yield and chemicals has gained attention by researchers worldwide [11–18]. For example, an empty fruit bunch has been converted using the pyrolysis process to produce chemical and bio-oil [19–21]. Pyrolysis techniques have shown a promising way to yield liquid fuels (approximately 70–80%), however, the product was found unstable and required post-treatment such as hydrotreating to enhance the quality [22]. Pyrolysis oil encompasses a high oxygen content and also high-water yield and this will give a low heating value and affect the quality of bio-oil. The upgrading methods can be employed to enhance the quality of bio-oil, such as emulsification, steam reforming, hydrodeoxygenation, and catalytic cracking.

The application of bio-oils from the thermochemical conversion is one possible response to substitute existing petroleum feedstocks to overcome issues such as climate change and fluctuated oil prices. However, the bio-oils generated from commercial pyrolysis processes such as fast pyrolysis and flash pyrolysis are facing low-quality issues which render them incompatible with conventional fuels, requiring post-treatment and upgrading processes.

2 Thermochemical Conversions

Biofuels and chemicals are the products of interest that can be produced via thermochemical conversions such as gasification, pyrolysis, and liquefaction [23]. However direct thermochemical conversion processes (liquefaction and pyrolysis), which are easier to operate and can be conducted in a short time conversion utilized, have recently been found to be suitable to operate. Figure 1 summarizes the potential products from thermal conversion.

2.1 Pyrolysis of Biomass

Pyrolysis is the thermal degradation of materials under an inert environment, or the condition when there is limited oxygen present to avoid complete combustion, to convert biomass into solid charcoal, liquid (bio-oil), and gases at higher temperatures [23, 25]. Typical product yields from various processes are given in Table 1 and Fig. 2. Nitrogen gas is usually utilized to give an inert environment. In the pyrolysis process, the biomass is heated at a rapid rate in an inert environment and the vapours generated are then condensed quickly. Pyrolysis of biomass is a promising pathway for the production of desired products. The main pyrolysis reaction is:



Proximate analysis is important to be investigated to understand the information of volatile matter of the biomass before the pyrolysis process. Knowing the percentage of possible condensable gas is significant before continuing with the thermochemical process. Parameters like heating rate, nitrogen flow rate, pyrolysis temperature, condensable temperature, and particle size are very important in determining the yield

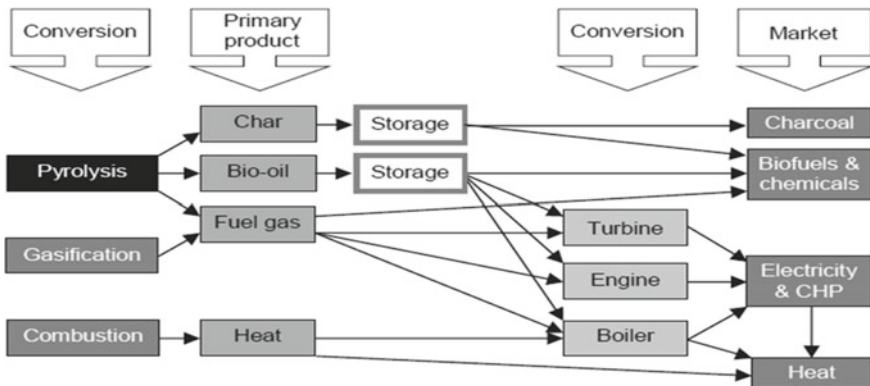


Fig. 1 Products from thermal biomass conversion—reproduced from [24]

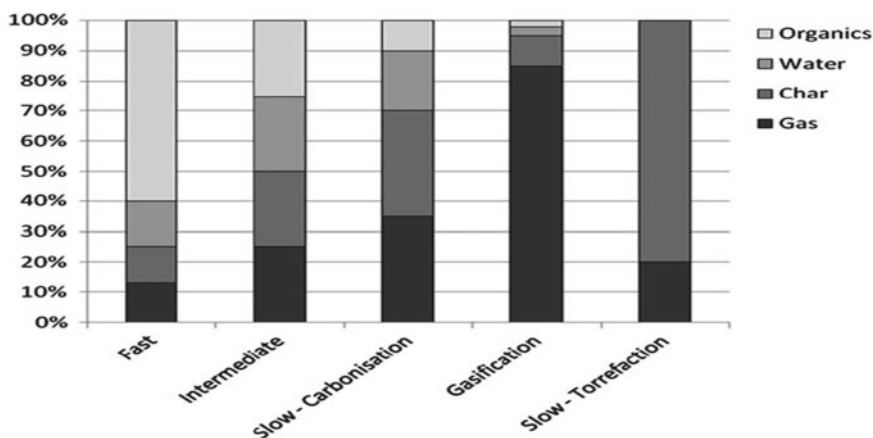


Fig. 2 Product yields from pyrolysis—reproduced from [28]

and quality of products [10, 23]. The process can be precisely controlled to produce the desired products. The pyrolysis products are significantly affected by the reaction temperature. Free radical formation occurs at a temperature below 302 °C, where depolymerization and elimination of water take place. At this temperature, carbonylation and carboxylation occur, CO and CO₂ evolve and char residue is the main product [23, 26].

Various reactors can be utilized to conduct the pyrolysis process. The most common are the fixed-bed and fluid bed reactors. The advantages of a fluid bed reactor are the temperature can be controlled precisely and a very efficient heat transfer to biomass can be achieved. Fast pyrolysis is effective with fluidized bed reactors because it applies high heating rates, rapid de-volatilization, and easy product collection [23]. Fixed bed fast pyrolysis is suitable for laboratory bench-scale experiments, and is often used by many researchers to investigate thermochemical conversion [23, 27].

3 Bio-Oil

Bio-oil is a low viscosity, dark-brown fluid with up to 15–30% water, contains many compounds, which can be grouped as acids, sugars, aldehydes, and furan, derived from the carbohydrate fraction; and phenolic compounds, aromatic acids, and aldehydes, derived from the lignin fraction [23, 26, 29, 30]. The composition percentages are water-insoluble pyrolytic lignin (25–30%), organic acids (5–12%), non-polar hydrocarbons (5–10%), anhydrosugars (5–10%), and other oxygenated compounds (10–25%), with the balance being water [26]. The pyrolytic oil's higher heating value is in the range of 13–17 MJ/kg. Typical properties of pyrolysis bio-oil and other fuels are given in Table 2.

Table 1 Typical product yields (dried wood basis) obtained from different modes of pyrolysis wood—reproduced from [24]

Mode	Conditions	Liquid	Solid	Gas (%)
Fast	~500 °C, short hot vapor residence time ~1 s	75%	12% char	13
Intermediate	~500 °C, hot vapor residence time ~10–30 s	50% in 2 phases	25% char	25
Slow—Torrefaction	~290 °C, solids residence time ~30 min	0% if vapours are burned	80% solid	20
Slow—Carbonization	~400 °C long vapor residence hours → days	30%	35% char	35
Gasification	~750–900 °C	5%	10% char	85

Table 2 Typical properties of wood pyrolysis bio-oil, No-2 Diesel fuel, and heavy fuel [23, 25, 26]

Physical property	Bio-oil	No-2 Diesel fuel	Heavy fuel oil
Moisture content (wt.%)	15–30	n.a	0.1
pH	2.5	n.a	n.a
Specific gravity	1.2	0.847	0.94
Elemental composition (wt.%)			
C	54–58	86	85
H	5.5–7.0	11.1	11
O	35–40	0	1
N	0–0.2	1	0.3
Ash	0–0.2	n.a	0.1
HHV (MJ/kg)	16–19	44.7	40
Viscosity	40–100 cp (315 K)	<2.39 cp (325 K)	180 cp

4 Challenges of Bio-Oil

The bio-oils problems such as high oxygen content and high-water yield, which lead to difficulties blending the product into conventional fuels are the main issues to overcome. The high oxygen content may also cause problems for the hydrogenation process and increase the consumption of hydrogen to produce additional water [31]. Bio-oils are also reported to have a much higher Total Acid Number (TAN) and ash content compared with normal crude oil [23, 32].

5 Bio-Oil Upgrading

Bio-oil can be upgraded in several ways. The oil quality can be improved physically, chemically, and catalytically. Physical upgrading of bio-oil includes filtration, solvent addition, and emulsions and was well-reviewed by Bridgwater (2012) as reported by Isa [23].

5.1 Chemical and Catalytic Upgrading of Bio-Oil

The characteristics of bio-oil like high density and high oxygen content are the main factors in improving the oil quality. The upgrading of bio-oil, so that it is comparable to conventional fuel, can be carried out in several ways, such as hydrotreating and hydro-cracking. The removal of oxygen as water by catalytic reactions using H_2 and known as hydrotreating, to improve product quality without appreciable alteration of the boiling range. The process is carried out at high pressure (up to 20 MPa) and temperatures up to 400 °C, producing a naphtha-like product [23, 26, 28]. By using hydrogen, the stability and fuel quality can be improved by decreasing the oxygenated compounds, as well as other reactive compounds [33]. The catalysts commonly used for hydrotreating are sulphide $CoMo/Al_2O_3$, $NiMo/Al_2O_3$ systems [23, 34]. The oil phase is hydrotreated and catalysed by sulphided $Co-Mo-P/Al_2O_3$ [23, 35].

Cracking can be conducted whereby complex organic molecules, such as kerogens or heavy hydrocarbons, are converted into simpler molecules such as light hydrocarbons, by the breaking of carbon-carbon bonds in the precursors. Hydro-cracking is a thermal process in which hydrogenation leads to the cracking process. Hydro-cracking is accomplished at lower temperatures than catalytic cracking—e.g., 260–425 °C but at much higher pressures 55–170 bars (5.5–17 MPa) by dual-function catalysts [23, 36]. The silica-alumina (or zeolite) catalysts are used in providing the cracking function. Wide ranges of products are expected to be produced as a result of combining catalytic cracking reactions with hydrogenation and the multiplicity of reactions. However, hydro-cracking is less popular than hydrotreating in the petroleum industry. Hydro-cracking is favoured for producing a light product, but it employs high temperatures and high hydrogen pressure to deal with acids that are not economical [23].

6 Pyrolysis Reactors

Several reactors have been reviewed and reported to explain the effectiveness of the pyrolysis processes by Isa [23]. Figure 3 illustrates a bubbling fluid reactor with an electrostatic precipitator. Bubbling fluid beds, always stated as just fluid beds, have

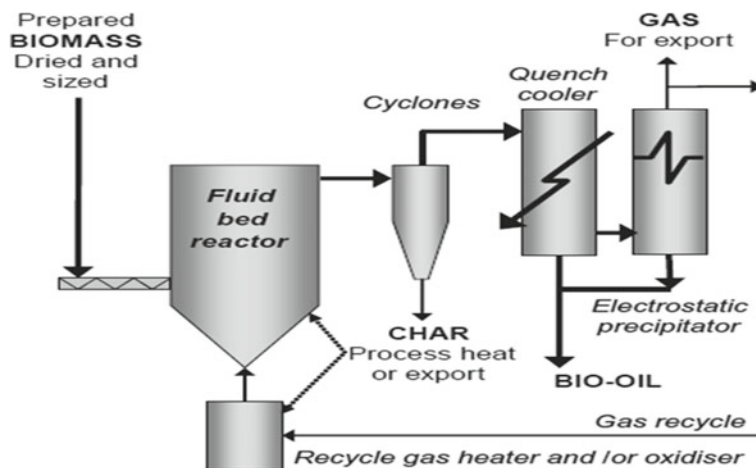


Fig. 3 Bubbling fluid bed reactor—reproduced from [27]

the advantages of being simple in operation, having precise temperature control, and having a good heat transfer to biomass particles generating from high solid density. In a fluidized bed, solid particles are held in suspension by an upward gas stream to establish a liquid-like gas–solid mixture. Heat transfer to the bed at large scales of operation has to be controlled appropriately because of the scale-up constraints of different methods of heat transfer, resulting in limited turn-down capability [37]. Fluid bed pyrolyzers give good performance with high liquid yields of 70–75 wt.% from wood on a dry-feed basis. Small biomass particle sizes of less than 2–3 mm are required to attain high biomass heating rates, with the rate of particle heating usually being the rate-limiting step [27]. This type of reactor is also simple to build and user-friendly to operate and scale up, obtaining high efficiency of heat transfer [31].

Ablative pyrolysis has a different concept from other fast pyrolysis methods, and its development has continued in several ways and was reviewed and reported by Isa [23]. Ablation shows the phenomena occurring when a solid material, subjected to a high external flux density, undergoes superficial melting and/or sublimation reactions [38]. The significant processes occur in the vortex and cyclone reactors where biomass particles are suspended in a high velocity flowing gas which after tangential introduction in the reactor, forces the particles against the heated reactor wall by centrifugal action [39]. Both reactors need huge volumes of motive gas relative to the biomass feed. In ablative pyrolysis, heat is transferred from the hot reactor wall to ‘melt’ wood that is in contact with it under pressure [27].

Once the wood is moved away, the molten layer vaporizes to produce a product very similar to that derived using the fluid bed systems. The pressure of the wood onto the heated surface has a very strong influence on the rate of the reaction, as well as the relative velocity of the wood and the heat exchange surface, and also the reactor surface temperature. The reactor has advantages as follows; large feed sizes

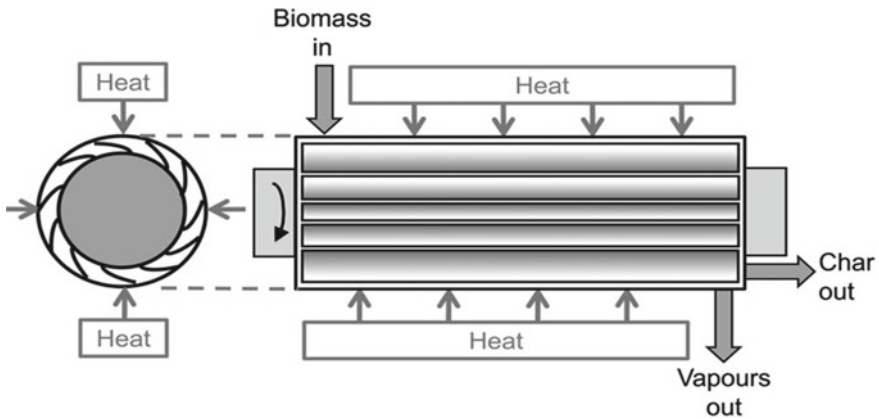


Fig. 4 Ablative fast pyrolysis reactor—reproduced from [27]

can be used and an inert gas atmosphere is not required so the processing equipment is smaller. However, the rate of bio-oil yield is highly influenced by pressure, the relative velocity of biomass on the reactor surface, and the reactor surface temperature [31]. Figure 4 shows the ablative reactor as reviewed by Bridgwater [27]. The principles of operating conditions for ablative pyrolysis can be conducted as follows:

1. High pressure of particle on the hot reactor wall employing centrifugal or by mechanical force.
2. High relative motion between the particle and the reactor wall.
3. Reactor wall $<600\text{ }^{\circ}\text{C}$.

Isa reported and reviewed the advantages of using microwave-assisted pyrolysis [23]. Microwave-assisted pyrolysis has the advantage to permit the careful control of pyrolysis parameters to produce high gas or oil yields. The operating parameters can lead and/or alter particular chemical reactions, resulting in different chemical yields of the volatiles/oils produced. The process uses different fundamental heating from all other pyrolysis techniques as the biomass particles are heated from within and not from external heat transfer. Microwave pyrolysis has been developed to reduce the long heating period by external heating which leads to a secondary reaction (a common problem faced in other pyrolysis processes). As a rapid pyrolysis process, microwave pyrolysis can avoid the formation of secondary reactions and enhance the quality of products produced. It also gives consistent heating of the sample due to volumetric heating of the materials [40].

The application of microwave heating to the pyrolysis process is responsible for new temperature distribution, higher heating rates, and for the appearance of unexpected physical behaviour fibre such as the ‘hot spots’ phenomenon, factors that increase the gas yield and ensure a higher syngas content [41]. In microwave heating, the power absorbed per unit volume, or power density (Pd), is given for a uniform electric field by the equation:

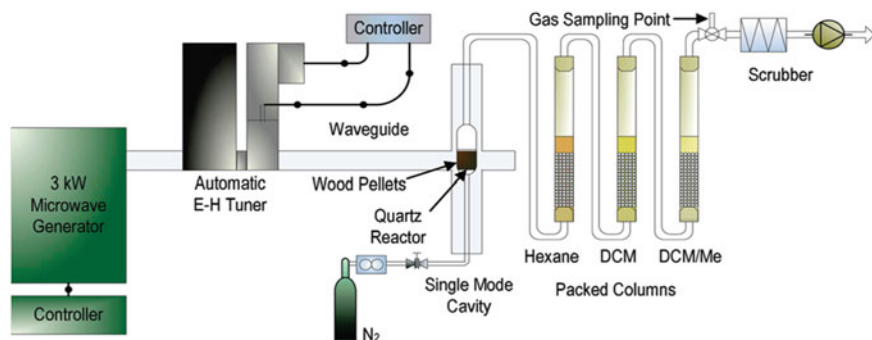


Fig. 5 Single-mode microwave pyrolysis system—reproduced from [42]

$$Pd = 2\pi f \epsilon_0 \epsilon'' |E|^2$$

where f is the microwave frequency, ϵ_0 is the permittivity of free space (8.85×10^{-12} F/m), ϵ'' is the dielectric loss factor, and E is the magnitude of the electric field. The loss factor represents the ability of a material to convert electromagnetic energy into heat. Materials with a relatively high value of ϵ'' are microwave-absorbent, whereas materials whose ϵ'' is close to zero are microwave-transparent [42]. It needs material with a high dielectric constant or loss factor. Water is a good example of this and will be driven off, then the particle heats up to start forming char. This is electrically conductive and eddy currents are generated, providing quick heating. Therefore, the control of a microwave system is significantly challenging [27]. Figure 5 illustrates a single-mode microwave pyrolysis system, from Robinson et al. [23, 42].

7 Historical Background on Biomass Hydrothermal Liquefaction

Many works on liquefaction have been carried out on numerous aspects to elucidate the fundamentals of biomass conversion through the hydrothermal process over the years [2, 43]. Furthermore, meetings organized by the International Energy Agency, where researchers and engineers find the best method under thermochemical conversion using biomass as a feedstock, have been held every 3–4 years since 1981; the reports produced from these conferences provide much information on hydrothermal biomass production [43]. The historical background of biomass hydrothermal liquefaction was reviewed and reported by Isa [23].

Direct liquefaction gained researchers' interest as the promising way to produce bio-oil and was foreseen as a 'suitable substitute' for fossil fuels, in the first half of the 1970s because of the oil crisis [2]. The obstacles of these early efforts were mainly caused by the high process prices and the lack of fundamental information

of the process, which led to the hiccup of early large demonstration plants built during that period. However, many kinds of research worldwide resulted in a clearer understanding of the process. Chan and co-workers reported that recent developments using waste biomass are promising routes to produce renewable energy in Malaysia [3].

Direct liquefaction as reported by Isa, is sometimes referred to as thermochemical conversion, thermal depolymerization, or simply liquefaction, the heat and pressure conversion process of producing liquid oil [23]. Indirect liquefaction, the H/C ratio is increased by venting H_2 to the mixing sample and the addition of a catalyst to produce synthetic crude oil. By contrast, indirect liquefaction produces a liquid fuel by gasifying organic materials to syngas, followed by synthesis to ethanol, methanol, or other chemical compounds. Indirect liquefaction (Fischer–Tropsch) has been used in producing methanol (CH_3OH or MeOH) and dimethyl ether (CH_3OCH_3 or DME) particularly involving coal as a feedstock [2]. The approach of liquefaction technologies can be a direct or indirect process. Numerous researchers have worked to improve the hydrogen-carbon ratio, the guidelines are as follows (a) For finished hydrocarbon fuels such as gasoline and diesel, H/C ~ 2 (molar basis) (b) For petroleum crude oil, the ratio ranges from 1.3 to 1.9 [23].

8 Direct Liquefaction

Recently, direct liquefaction can be conducted as an alternative conversion process to produce liquid fuels and biochemicals from solid biomass [44]. The use of water (hydrothermal liquefaction) or other solvents (solvolysis) under elevated temperature and pressure to convert the solid biomass into fragments of molecules, producing various types of organic compounds, which are known as bio-oil [3]. Isa in his work reviewed the importance of the liquefaction process particularly the effect of alcohol, water, and hydrogen donor solvents [2]. Parametric studies such as temperature, pressure, residence time, biomass particle size, heating rate, biomass-to-solvent ratio, and catalyst loading are broadly investigated on the yield and quality of bio-oil [3, 45, 46]. Liquefaction is recognized as a superior method for biomass thermochemical conversion and has an advantage on wet feedstocks as compared to the pyrolysis process which requires the biomass to be in dry condition. More importantly, utilizing water as a reactant as well as the reaction medium in the biomass conversion process will avoid the drying process' cost of wet feedstocks, which makes it a promising and suitable reaction medium for biomass liquefaction [2, 47].

Shuping and co-workers outlined advantages of the liquefaction process such as: (1) the presence of solvent could dilute the concentration of the products and can avoid the cross-linked reactions between hydrocarbon and aromatic compounds producing tar compounds, and (2) ability to conduct at low reaction temperature (less energy consumption) as compared to pyrolysis and gasification [2, 48]. Song et al. also reported the interesting benefit of using the liquefaction process is the

advantage to decrease the oxygen content of the products, which is quite significant as compared to the fast pyrolysis process [49]. The oxygen content for biomass was reported by previous researchers varies from 35 to 46 wt.% [2, 10, 49, 50].

8.1 The Effect of Alcohols

Makabe and Ouchi studied the effects of alcohol in conducting the liquefaction experiments using supercritical alcohol to convert the low-rank coal into liquid oil [51]. Aliphatic alcohols are reported by Kuznetsov et al. to be effective and suitable solvents for coal liquefaction [52]. The action of alcohol is considered to be influenced by the hydrogen donor activity and its alkylating ability [51, 52]. Fan et al. conducted solvolysis using many solvents and reported that ethylene glycol produced the highest conversion yield in the liquefaction process utilizing empty fruit bunch as a feedstock [21].

8.2 The Effect of Hydrogen Donor Solvents

Isa et al. reported the potential of hydrogen solvents in their work, particularly the importance of tetralin as a hydrogen donor solvent. Isa and co-workers also reported the mechanism of tetralin to donate 4 radicals hydrogen in liquefaction of biomass [45]. Liquefaction of biomass can be elucidated generally as hydrogenation when utilizing the solvents, but not molecular hydrogen [23]. Low-pressure molecular hydrogen can be used principally for deoxygenation for oil upgrading to form water. The idea of using hydrogen donor solvents is to propose a minimum process with the expectation of obtaining a high-quality liquid yield. Two mechanisms were reported to be involved: (1) The thermal biomass conversion promotes the bonding-cleavage. (2) Hydrogen atoms act to avoid repolymerization as a result of biomass degradation. The characteristic of solvents that can act as hydrogen donors as long as they have mobile carbon-hydrogen bonds with the capability to donate hydrogen and to stabilize the free radical of fragments biomass [2].

Pajak and co-workers reported that tetralin was used as a hydrogen donor reagent to compare various tars under high-temperature conditions with response to their hydrogen acceptance [53]. Pajak et al. conducted experiments, not exceeding 340 °C to prevent tetralin to decompose. Furthermore, the naphthalene formation is compared and presented in Table 3.

Table 3 Naphthalene formation (wt. %) in the reaction of Ziemowit coal-(A) and Pokoj coal-(B) with tetralin at 300 °C [23]

Time (hr)	5 (Mpa)		30 (Mpa)		50 (Mpa)	
	A	B	A	B	A	B
2	3.8	1.4	3.7	2	4.1	2
5	5.5	3.4	6.2	3.3	6.6	3.3
18	9.6	3.7	9.4	3.6	9.4	3.5

8.3 The Effect of Water

Water can act as a reactant and catalyst in hydrothermal biomass, and this causes the process significantly different as compared to pyrolysis [23]. The use of water as the reaction medium causes the hydrolysis reactions to occur and the rapid degradation of the biomass occurs. Isa et al. reviewed the importance of water under sub or supercritical conditions for liquefaction of biomass [2]. Furthermore, water's characteristics as an excellent solvent at high temperatures are significant to study. Under conditions close to the critical point, water has some significant properties. Among them is low viscosity with high solubility of organic substances, and subcritical water has an outstanding medium for homogeneity, leading to efficient reactions [2, 46, 54].

Subcritical water demonstrates significant properties to convert biomass under the condition where dielectric constant decreases from 78 Fm^{-1} at 25 °C and 0.1 MPa to 14.07 Fm^{-1} at 350 °C and 20 MPa [2]. Blaschek and co-workers reported when temperature increases and the dielectric constant decreases, it shows water molecules change from very polar to fairly non-polar [55]. Lavric and co-workers reported when going supercritical ($T > 374$ °C, $P > 22.1$ MPa), the values of density (0.2–0.7 g/cm^3), dielectric constant and ionic product of water lessening, and the supercritical water behaves as a non-polar solvent with high diffusivity and outstanding transport properties [23, 56].

The fundamental supercritical water oxidation (SCWO) applies temperatures above the critical temperature of water (374 °C) under oxidative conditions to produce thermal energy and target the CO_2 rich gas phase. Basically, the SCWO process was designed to be applied in the demolition of industrial waste materials [23]. The idea of producing CO_2 by utilizing SCWO has been established and reported [57]. However, there are reports on the constraints towards SCWO, one of the arising problems is salt precipitation, which occurs widely at high temperatures. Supercritical water gasification (SCWG) is another hydrothermal process that can be conducted for gasification. The SCWG is carried out to produce CO_2 , H_2 , and CH_4 under supercritical biomass gasification, but not oxidative conditions [23]. The condition for SCWG is thermal decomposition at 500 °C and heterogeneous catalysts are needed for product selectivity.

8.4 The Effect of Temperature

Temperature is one of the most significant factors influencing the liquid yield in the liquefaction process and was reviewed by Isa [23]. Liquid oil yields were reduced as impacted by temperature in hydrothermal media [58]. For example, Sugano and co-workers reported the product yields after liquefaction of eucalyptus with paper regeneration wastewater from 150 to 350 °C. It was found that the oil yield increased significantly from 200 to 300 °C, but the decrease in oil yield and increase in gas and water-soluble yields occurred at 350 °C. The liquefaction of rice straw in the reaction medium of sub- and supercritical 1,4-dioxane-water mixtures at temperatures of 260–340 °C gave oil yields between 30 and 50% [59]. This shows the temperature range for producing high liquid yields in hydrothermal media [58]. However, a suitable reaction temperature can increase the liquid oil yields. Mild solvent extraction (MSE) of white and red oaks at 350 °C has been conducted using anthracene oil as solvent, both red and white oak had 99% conversion with 28 and 68% solvent loss, respectively [60]. Table 4 shows the effect of catalytic hydrothermal biomass at various temperatures.

When the temperature supplied is sufficient than the activation energies for the biomass fragmentation and cleavage, extensive biomass depolymerization occurs. The reaction competition among fragmentation, hydrolysis, and repolymerization depends on the temperature during the liquefaction process [64].

Further, an increase in temperature to >450 °C inhibits biomass liquefaction. Solvolysis of pinewood with ethanol at 400 and 450 °C for 20 min, resulted in the oil yield decreasing from 26.5 to 19%. Very high temperature is not suitable in terms of operational cost and decreases the liquid yields. The secondary degradations and Bourdard gas reaction are very active at a high temperature which leads to the formation of gases. In addition, the act of free radical recombination reactions at high temperatures led to the charring process.

Table 4 Catalytic hydrothermal of biomass

Researchers	Temp (°C)	Biomass	Catalyst	Biomass (%)
Sun et al. [47]	280–360	Paulownia	Iron	~90
Karagoz et al. [61]	280	Pinewood	K ₂ CO ₃	~96
Bhaskar et al. [62]	280	Cherry (hardwood)	K ₂ CO ₃	~99
		Cypress (softwood)	K ₂ CO ₃	~95
Murakami et al. [63]	225–340	Activated sludge	Na ₂ CO ₃	~88–90
Akhtar et al. [1]	270	Empty palm fruit bunch	NaOH	~70–73

8.5 *The Effect of Residence Time*

Heavy oil yields from the liquefaction of biomass are greatly influenced by residence time [63, 65–67]. Yan et al. conducted liquefaction of sawdust at 300 °C using tetralin as a solvent and reported the highest oil yield obtained at 30 min [65].

Akhtar and Amin reported that short reaction times are expected to convert biomass effectively [46]. The rate of hydrolysis and decomposition is relatively fast in the supercritical reaction medium, therefore quick residence times are preferred [68]. The longer reaction time suppressed the bio-oil yield except for very high biomass to water ratios [69]. The negligible effect of residence time on liquid yields has also been reported [65]. It was found that the effect of residence time on oil yield was lesser than temperature [70]. The oil yield increases with the increase of residence time until the critical moment and tends to degrade to lighter products by condensation, cyclization [71].

8.6 *The Effect of Reaction Pressure*

The reaction pressure is a key influence to maintain the liquefaction process at a single-phase (sub- and supercritical liquefaction). Single-phase liquefaction can avoid large enthalpy inputs during the changing of solvent phases [31]. By maintaining pressure above the critical point in the process, the hydrolysis rate and biomass dissolution can be monitored, this may increase the reaction routes to give high oil or gas yields [46].

High pressure increases solvent density, the resulting high-density medium penetrates efficiently into molecules of biomass components, contributing to enhanced decomposition and extraction [23, 46]. Whenever the conditions of supercritical water are reached, the effect of pressure can have very little influence on liquid oil and gas yields [72]. Akhtar and Amin also reported the role of pressure on the properties of water in the supercritical region and stated that the effect of pressure on the solvent medium is very small and negligible [46].

8.7 *The Effect of Biomass Feedstock*

Biomass consists of cellulose, hemicellulose, and lignin, and these components act differently in the liquefaction process. Under hydrothermal conditions, hemicellulose and cellulose react more quickly than lignin, hence higher cellulose, hemicellulose content in biomass is a good indicator for high bio-oil yield.

Thermochemical liquefaction of Indonesian biomass residue has been investigated by Minowa and co-workers [73]. They reported the highest yield was produced using oil-palm shells; shells (coconut and oil-palm) gave a high oil yield of ~35%,

while petioles and leaf (*metroxylon*, oil-palm, and pineapple) had a low oil yield ~23%. Minowa and co-workers found the residue yield increased with the lignin content, the phenoxy radicals could be produced from the lignin in a hot state and they were able to condense and repolymerize to a solid mass.

Non catalytic and catalytic liquefaction of *P. massoniana* Lamb., *P. tomentosa* Carr. and *F. mandshurica* in water was carried out at five temperatures, 280, 300, 320, 340, and 360 °C as reported by Zhong and Wei [74]. A heavy oil yield of ~7–32% was produced. Zhong and Wei reported the yield of heavy oil generally decreases with increasing lignin content, as free phenoxy radicals are produced by thermal decomposition of lignin above 250 °C and that the radicals have a random tendency to form solid residue through condensation or repolymerization.

9 Potential of Biomass in Malaysia for Thermochemical Technologies

Malaysia is blessed with an abundant source of biomass due to its suitable climate for agriculture activities, generating a massive amount of waste every year [3]. Malaysia's rich agricultural sectors, most of them are underutilized, giving rise potentially to be used for producing energy. In the case of Malaysia, as highlighted by Energy Commission, the fundamental goal of energy security requires resource diversification in 20% of the energy mix by 2025 and requires efficient energy projects to achieve a 45% reduction target of greenhouse gas (GHG) intensity by 2030 [75].

Reviewing the historical development of renewable energy policies and initiatives serves as the baseline study to discuss the potential energy policy shift towards a sustainable renewable energy development future in Malaysia. Essentially, a renewable energy development plan could be categorized into three evolutionary phases which are; (i) Early Transition Phase (2000–2009), (ii) Acceleration Phase (2010–2019), and (iii) Sustainable Development Phase (2020–2029). The use of fossil fuels and causing carbon dioxide emission has been identified as the main cause leading to the global warming issue. Therefore, in a way to reduce the emission of greenhouse gases, the idea of substitution of fossil fuel with renewable energy should be conducted as soon as possible in terms of planning being the climate change solution as long as the renewable energy is truly developed in a sustainable way. In a country that has a huge amount of agricultural activities such as Malaysia; biomass can offer a very promising alternative feedstock for renewable energy. To increase the conventional energy supply, new sources for renewable energy will be encouraged and government incentives should be introduced to utilize biomass such as oil-palm, wood waste, and rice husk in thermochemical conversion.

Many works have been carried out by Malaysian researchers to convert Malaysian agriculture wastes into valuable products. Kabir and co-workers conducted a thermochemical process to convert oil-palm mesocarp fibre (OPMF) and palm frond (PF) to bio-oils and bio-chars using slow heating fixed-bed reactor [76]. They reported

the high heating values (HHVs) of OPMF-oil and PF-oil were, respectively, found to be 23 and 21 MJ/kg. It is a promising work although the upgrading processes seem needed to ensure compatibility for commercial use. The OPMF and PF contained 40.12 and 45.22 wt.% cellulose, 20.12 and 19.22 wt.% hemicellulose, and their lignin content is 30.33 and 31.24 wt.% lignin, respectively [76]. The high amount of holocellulose for OPMF and PF is a good indicator to be tailored to produce a high bio-oil yield. Co-pyrolysis is nowadays seen as a promising technique to be explored to produce high-quality bio-oil. Al-Maari and co-workers conducted a co-pyrolysis of palm wastes of empty fruit bunch (EFB) and palm frond (PF) with low-density polyethylene (LDPE) and polypropylene (PP) and found that the hydrogen generated from plastic promoted the decarboxylation of acids and decarbonylation reactions of carbonyls and sugars [77]. Co-pyrolysis of plastic with biomass permits modifying the composition of the solid, liquid, and gaseous products and adapting it as a liquid fuel [78]. Microwave dielectric properties have been studied by Salema et al. during the pyrolysis process [79]. This study was conducted to give new and insightful data on the dielectric properties of five different types of biomass generated from Malaysian agriculture (oil-palm shell, empty fruit bunch, rice husk, and coconut shell) and wood (sawdust) based industries). The efforts by Salema and co-workers will provide an extra option for the potential biomass in Malaysia to be used to produce renewable energy.

Traditionally, agricultural wastes such as rice husk, sawdust, and palm fibres were utilized in the downstream process to produce electricity for their respective processing mills [3]. Rice Mill factories in Kedah have utilized rice husk to power their boilers. Palm oil wastes give the best option for various utilisations on energy production in Malaysia. As the world's second-largest producer and exporter of palm oil in 2006, Malaysia's palm oil industry leaves behind a massive amount of biomass from its plantation and milling activity and currently produces an abundance of biomass in Malaysia with 85.5% out of more than 70 million tonnes [80]. The palm oil biomass also has a very good character and high potential to be used in thermochemical conversion for renewable energy sources, with calorific values in the range of 18–20 kJ/kg. The components from the palm oil biomass consist of empty fruit bunch, mesocarp fibre, shell, and palm kernel.

Biomass energy ranges from firewood to fuel (e.g., ethanol produced from sugarcane) and methane captured from landfills [81]. Biomass energy plays an important role in the energy supply of many developing and developed countries. In many developing countries, the proportion of biomass energy consumed ranges from 40 to 50% since these countries have large agriculture and forest area [82]. This has raised the world's total to ~13% of energy demand [83]. Sustainable biomass production from plantations is estimated to be in the range of 0.4–1.7 Mt yr⁻¹ for Malaysia, [84]. Based on the findings discussed in this chapter, it is definitely crystal clear that Malaysia has positioned herself on the right path to utilize biomass as a source for thermochemical conversion to produce renewable energy and this can set as a good example to other countries in the world that has massive biomass feedstock.

10 Conclusion

Malaysian agriculture wastes offer a high potential to be utilized as a feedstock for thermochemical conversion. Thermochemical conversion is seen as a promising technique for biomass conversion to produce renewable energy. Pyrolysis, co-pyrolysis, and hydrothermal liquefaction can be employed to convert biomass into biofuels and chemicals. Researchers are committed to finding ways to produce liquid yield from the thermochemical processes to ensure compatibility with the existing fossil fuels and are ready for commercial use. Malaysia has the capacity to use renewable energy resources to address the national energy and carbon reduction agenda.

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Bioethanol as a Potential Renewable Energy



Ku Syahidah Ku Ismail

Abstract Fossil fuels remain the largest source of transportation fuel, and the impact on the environment starts to show in the forms of climate change and environmental pollution. Bioethanol produced from biomass-based materials is good alternatives to cater to the depleting petroleum reserves and acts as a clean fuel when used as a mixture with gasoline. This chapter discusses the possible raw materials and processes for Malaysia to adopt if bioethanol is to be used as one of the fuels for transportation. Despite being an oil-producing country, Malaysia is blessed with agricultural crops and is in the correct position to move towards renewable biofuels from biomass. Thus a selection of feedstocks was proposed which were thought to fit Malaysia's climate and were the easiest to start with. The possible bioethanol production processes and potential microbes were described in general. Discussed also are the challenges and limitations to commercializing bioethanol as a blending fuel.

Keywords Bioethanol · Agricultural Crops · Challenges and Limitations

1 Introduction

As the demand for transportation fuel increases globally, the world is shifting towards renewable energy to mitigate the problems arising from fossil fuels consumption. Greenhouse gases, limited petroleum reservoirs, harmful transports emissions, and long-term effects on the environment were seen as threats to future generations, which led to the UN mandate on the Sustainable Development Goals (SDG). There are 17 goals designed by the United Nations General Assembly in 2015 to be achieved in the interest to realize a sustainable future by 2030. For instance, SDG 7 is devised to pursue development in renewable energy, as well as promote energy efficiency [1]. In achieving this SDG, biofuels are probably one of the most advanced alternative energy sources being scrutinized by researchers. Bioethanol is the most promising

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alternative biofuel to reduce the consumption of fossil fuels in the transport sector. The characteristics and benefits of bioethanol made it right to be blended with gasoline. Ethanol helps reduce carbon emissions by 80% compared to gasoline. Even though it has a 68% lower energy content compared to gasoline, its high oxygen level makes the combustion cleaner and reduces toxic substances to the atmosphere [2].

1.1 Bioethanol: An Overview on The World’s Scenario

The world’s bioethanol production attained 115 billion L in 2019 [3], approximately 7.7% of the global gasoline demand [4]. In 2019, the largest bioethanol producers were the USA and Brazil (84% of the world production), followed by the European Union (5%), China (3%), India (2%), and Canada (2%). Prior to the COVID-19 pandemic, global bioethanol production was expected to escalate to 130 billion L by 2024 [4]. Figure 1 is showing the world’s ethanol production in 2020. A 13% decrease in 2020 was expected for bioethanol and biodiesel due to the pandemic, but a recovery is expected to resume once the pandemic subsides [4]. Demand for bioethanol is due to the awareness of reducing greenhouse gases (GHG) and the

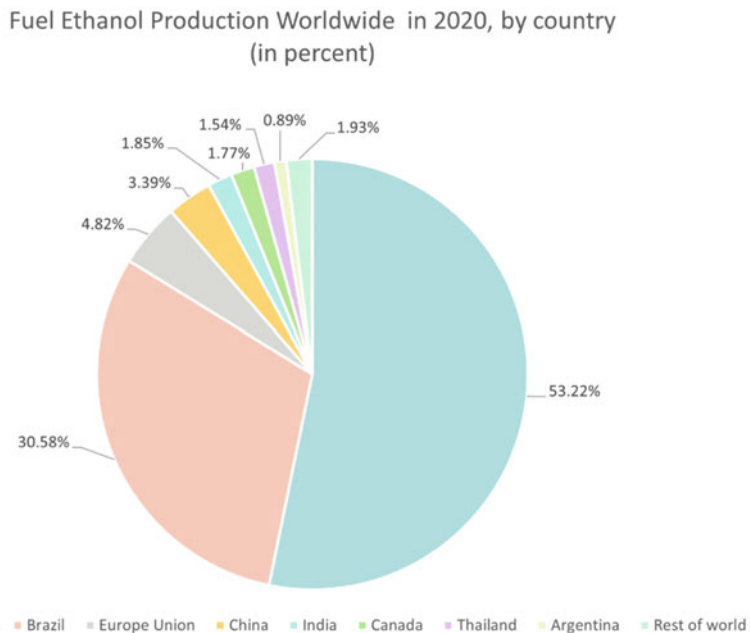


Fig. 1 Worldwide fuel ethanol production in 2020 [9]

interest to increase fuel efficiency [5]. It is expected to grow from USD 33.7 billion in 2020 to USD 64.8 billion by 2025.

In Brazil, ethanol was first tested as fuel in 1905. When the oil crisis caused a surge in the oil import price in the 1970s, Brazil's government initiated the Brazilian Program for Alcohol Fuel (Proalcool) to offer monetary assistance for sugarcane plantation expansion and mills construction. The ratio of ethanol-gasoline blend in cars was the highest (25%) compared to other countries [6]. For several years, Brazil was the largest ethanol producer, until the USA surpassed Brazil in the last decade.

Germany produced their biofuel from sugar beet pulp and grains and their production of bioethanol reached 700,000 tonnes in 2020 and was mostly used as fuel and basic raw materials for disinfectants due to the coronavirus pandemic [7]. The use of bioethanol succeeds in reducing 3 million tonnes of CO₂ from transportation emissions, equivalent to 1 million emission-free cars.

In Asia, China is leading in bioethanol production. As the fourth world's largest energy producer and user, its ministries and commissions have enforced the 'Implementation Plan for Expanding the Production of Biofuel Ethanol and Promoting the Use of Vehicle Ethanol Gasoline' in 2017. It was one of the significant efforts made to reduce carbon emissions, and increase the proportion of renewable energy from 10 to 30% in 30 years [8]. The implementation of renewable energy laws and development plans requires a substantial amount of financial support for such projects. By 2020, China plans to achieve nationwide usage of 10% ethanol (E10), and by 2025, renewable fuel production will focus on the commercialization of cellulosic ethanol [8]. It seems that cellulosic ethanol has a bright future in China.

As for Indonesia, they started producing bioethanol from molasses in 2007. However, the production stopped in 2010 due to political and economic issues. The drawback in production and use of bioethanol was seen inversely with biodiesel which contributed to a 5.7% increase of the total diesel consumption in the transportation sector in 2013 [10]. In 2010, bioethanol producers installed molasses-based ethanol plants with 339 million litres capacity. But lack of competitiveness in the sugarcane agro-industrial economy, low yields, gasoline fuel subsidies, and volatile international prices of petroleum have hindered domestic production and use of bioethanol in Indonesia [10].

Malaysia's neighbouring country, Thailand chose sugarcane molasses and cassava as their feedstocks to promote renewable energy as part of their national agenda to reduce oil imports. Their ethanol production from cassava and sugarcane molasses were 0.87 and 2.65 million litres per day, respectively [11].

1.2 Malaysia's Energy Policy

The strategic geographical area along the Strait of Malacca and the South China Sea made Malaysia blessed with abundant resources due to its tropical hot and wet weather throughout the year. The country has more than 160 million tonnes of biomass, including oil palm and timber waste, coconut trunk fibres, rice husks, sugar

cane waste, and municipal waste, annually [12] which could be potential renewable energy sources.

The Malaysian National Biofuel Policy in 2006 envisioned biofuel as one of the five energy sources for Malaysia, to improve the nation's prosperity and well-being. This is in line with the nation's Five-Fuel Diversification Policy, a national policy to promote renewable energy (RE) as the fifth fuel along with fossil fuels and hydropower. The National Biofuel Policy was implemented to encourage the production of biofuels, particularly biodiesel from palm oil, for local use and export. However, in 2007, the Government delayed the implementation of the whole biodiesel project due to the high price of refined, bleached, and deodorized palm olein. The Government of Malaysia then launched a new strategy to promote biofuel through the National Biomass Strategy 2020 in the year 2011. The strategy aimed to create higher value-added biomass economic activities that contribute towards Malaysia's gross national income (GNI) and create high-value jobs for the benefit of Malaysians. This approach outlined the production of bioethanol produced from lignocellulosic biomass, particularly the oil palm biomass as a starting point [13]. However, currently in 2021, the scenario of biofuel in Malaysia is still vague, where even the production of its biodiesel is far below capacity [14].

In terms of greenhouse gas (GHG), Malaysia plans to reduce the GHG emissions intensity of GDP by 45% by 2030. The GHG intensity level was at the equivalent of 317.63 tonnes of Carbon Dioxide (CO₂) and net emissions were at 50.48 tonnes. In the eleventh Malaysia Plan (2016–2020), it was outlined that the focus is to reduce the national dependency on fossil fuels while ensuring the development of reliable and affordable energy resources. The execution of the Renewable Energy Act 2011 and the implementation of the Feed-in Tariff (FiT) scheme demonstrated the aim of the country to explore and deploy RE as part of its national energy mix [15].

1.3 Current Status on Malaysia's Bioethanol Production

The research on bioethanol in Malaysia has gained attention due to its availability of tropical biodiversity and also the higher consumption of gasoline by vehicles rather than biodiesel. However, bioethanol production in Malaysia is currently at its infancy stage. Currently, there are only 2 bioethanol refineries, each operating in Perlis and Perak. Both biorefineries utilize sugarcane molasses from sugar mills, and their ethanol was mainly for consumption and industrial use. For example, the biorefinery in Perlis produces 5 million litres of ethanol per year, compared to the total imports of 15–20 million litres of ethanol per year [16]. The success of both companies reflects on the ability of such biorefineries to expand in producing ethanol fuel from agricultural wastes.

Bioethanol can be easily produced by the fermentation of sugars derived from starchy materials (first-generation bioethanol, 1G), lignocellulosic feedstocks (second-generation bioethanol, 2G), and algae (third-generation bioethanol, 3G). Microorganisms and enzymes act on sugars and/or starches found in plant parts,

undergo fermentation and convert them into alcohols such as ethanol or butanol. The fourth-generation bioethanol (4G) are expected to involve revolutionary developments in synthetic and systems biology in achieving carbon-negative rather than carbon neutral [1]. However, the 4G bioethanol is not discussed in this chapter.

2 Bioethanol from Sugars and Starch Feedstocks in Malaysia

The first-generation bioethanol was thought to be competing with food sources, but this has been the most successful form of biofuel and commercially available as showcased by USA and Brazil. Biofuels obtained from the conversion of feedstocks such as sugar and starch components of sugarcane, cassava, and sugar beet are classified under the 1G bioethanol. For Malaysia, the suitable raw materials if 1G bioethanol is to be produced could be molasses and starch from cassava.

In its simplest form, glucose can be converted to ethanol according to the following equation [17]:

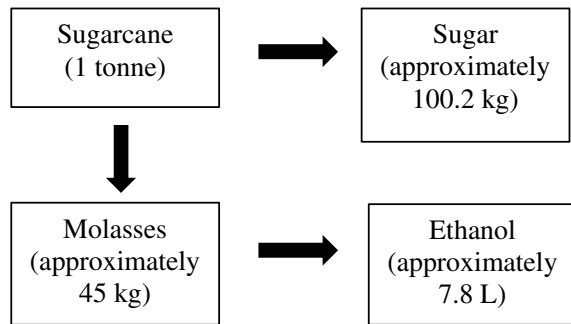


Based on this equation, the theoretical ethanol is expected to be 0.511 g/g glucose consumed. The rate of glycolysis is regulated by dissolved oxygen concentration. Optimum temperature and pH values for yeast are 30 °C to 35 °C and 4 to 6, respectively.

2.1 Molasses

Molasses is the low-value by-product of sugarcane refineries. Sugarcane stalks are first crushed in sugarcane mills, and the sugarcane juice will pass through multiple crystallization phases where crystal white sugar is formed. The final syrup when no more sugar can be produced is called 'molasses' which can be used as the feedstock for ethanol production [10]. Energy from sugarcane was well discussed in the literature [8, 18]. Molasses was used in several products such as polysaccharides, organic acids, and enzymes via microbial conversions [19]. Molasses from either sugarcane or sugar beets was found to be the most cost-competitive feedstock besides the lignocellulosic biomass [13]. It has been proven to be used in the production of bioethanol, as observed in other developing countries in Asia. Although Malaysia is not the biggest sugarcane planter, it has several sugar refineries in Kedah, Penang, Selangor, and Johor, which could supply the molasses as raw material. Figure 2 is showing the output of bioethanol production from sugarcane molasses based on

Fig. 2 Estimated output on bioethanol production from sugarcane molasses [20, 21]



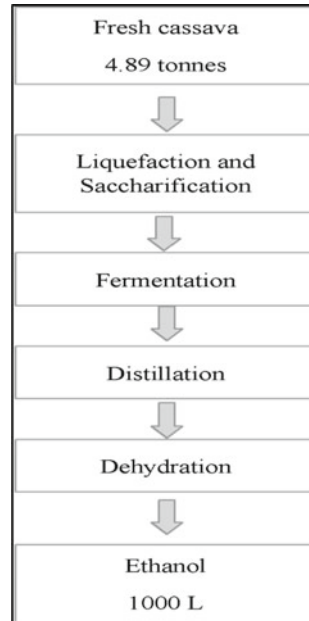
Ghani et al. [20]. It shows that 45 kg of molasses can be obtained from 1 tonne of sugarcane, and 7.8 L of ethanol can be produced from 1 tonne of sugarcane [21].

Pakistan managed to produce bioethanol from molasses alone and it is enough to replace around 7% of their total gasoline consumption [20]. Their sugarcane harvesting season involves traditional open-burning to burn the excess leaves which results in environmental pollution. However, the environmental sustainability of molasses-based bioethanol can be improved by mechanizing the harvesting method [20].

2.2 *Cassava (Manihot esculanta)*

Choices of crops suitable for ethanol production depend on the scenario of the country itself and also on issues such as food shortage, cost of production, as well as supply and demand. Rice and corns are a staple food for Malaysians, thus will rise economic concerns over the choices. However, cassava is also one of Malaysia's food crops but is not considered a staple since after World War II. There are also wide varieties of cassava that are not suitable for human consumption but are high in starch, which can be considered as feedstocks for ethanol. To improve the performance of cassava, the Malaysian Agriculture Research and Development Institute (MARDI) introduced a new cassava variety, Sri Kanji 1 capable of producing higher roots and starch compared with the normal variety of Black Twig. More specifically, Sri Kanji 1 can produce roots up to 92.9 t/ha with 30.5% starch content [22]. Another type of cassava variety is the Gajah variety which can reach 30–40 kg per tree. Cassava needs 61 MJ of energy for 1 kg of ethanol [23]. Compared to rice and corn, cassava is more tolerant to drought conditions, possible to be planted and harvested all year long, has high root (starch) productivity, continuous improvements of high yield varieties, fewer input requirements for planting and harvesting, high quantity and quality of carbohydrates, highest energy content per acre among starchy crops, and high ethanol yield per acre [22]. They can also be planted on marginal lands. From the environmental perspective, 1 L of Cassava Fuel Ethanol (CFE) could reduce GHG emissions by 73.2% [24]. Production of 1000 L of ethanol from cassava was well explained by Hanif et al. [22]

Fig. 3 Process flow for 1000 L of bioethanol from cassava [22]



as shown in Fig. 3. It starts by reducing the size of the cassava chips by grounding to increase the surface area. The ground cassava will then undergo liquefaction and saccharification of starch using α -amylase and glucoamylase enzymes, respectively, to release sugar. The sugar slurry will then undergo fermentation by bacteria, yeast, or other fermenting microorganisms to produce 15% ethanol. About 4.89 tonnes of fresh cassava is needed to produce 1000 L of ethanol [22].

2.3 Bioethanol from Lignocellulosic Biomass

Even though the USA produces bioethanol from corn starch, several of its conventional corn ethanol plants have installed technology to produce cellulosic ethanol from corn fibre residues, resulting in 2–4% of production coming from cellulosic feedstocks. Replication across the approximately 200 corn ethanol plants in the USA could increase cellulosic ethanol production to 1–2 billion L [25]. Many biomass sources in Malaysia can be used as a suitable feedstock for biofuels and at the same time avoid competition with the food supply. Figure 4 shows the availability of biomass in Malaysia. Malaysia produces 168 million tons of biomass annually, including rice husks, timber, coconut trunk fibres, oil palm waste, and municipal wastes [24].

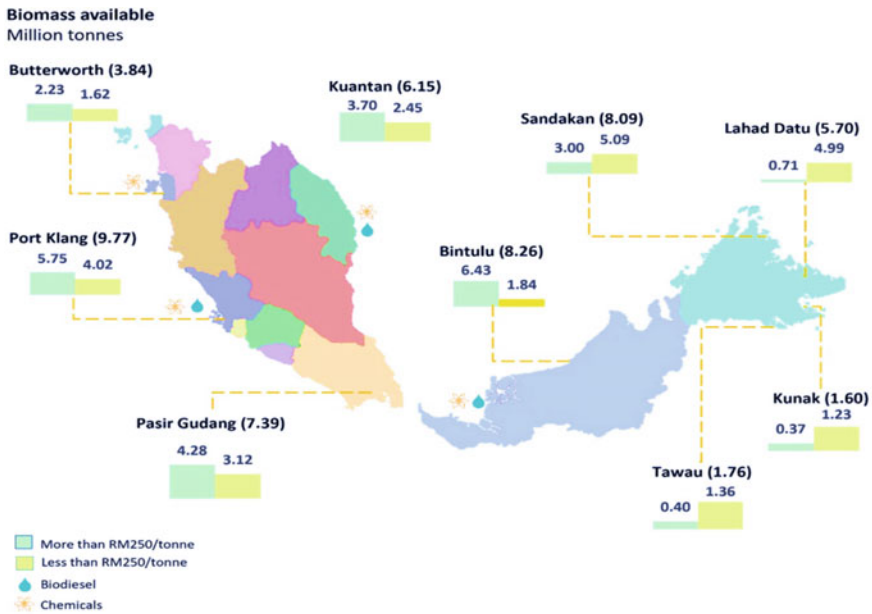


Fig. 4 Availability of biomass in Malaysia [26]

2.4 Oil Palm Feedstocks

Malaysia is the world's second-largest oil palm producer with more than 5.2 million ha planted areas [26]. Residues from the oil palm mills are the oil palm frond and trunks, empty fruit bunches, palm kernel shells, and mesocarp fibre, which mainly consists of cellulose (24–46%), hemicellulose (21–31%), and lignin (26–44%) [27]. The waste from palm plantation residues only was projected to be 100 million tonnes/yr by 2020 [28]. The palm oil mill effluent (POME) could be converted to 58 billion tonnes of bioethanol due to the high level of organic content. Bioethanol from oil palm feedstocks is economically feasible because the palm oil mills produce the waste biomass on-site and this can avoid the high feedstock and hauling costs [15]. Table 1 shows the comparison of ethanol production from oil palm and paddy. It shows that the theoretical ethanol production from oil palm residues is the highest using EFB, 4.3 million tonnes per year. The utilization of palm oil waste would have a minimal impact on agricultural prices and deforestation by utilizing the discarded lignin and water from distillation. A portion of the water can be recirculated, while the lignin can be combusted and converted into electricity and heat [4] [29], which is economic for an oil palm mill.

Table 1 Comparison between the properties of oil palm and paddy on bioethanol production [30]

Source	Oil palm			Paddy	
Scientific name	<i>Elaeis guineensis</i>			<i>Oryza sativa</i>	
Residue	Oil palm frond & trunk	Empty fruit bunches	Palm kernel shell	Rice husk	Rice straw
Annual production (tonnes) in Malaysia ^a	16,176,705	22,100,614	5,525,154	703,008	3,498,954
Theoretical ethanol production (tonnes) in Malaysia	2,889,215.91	4,262,539.49	626,876.42	109,003	629,550
Energy content (MJ/t)	19,930 for OPF; 19,257 for OPT	18,838	20,108	16,580	15,000–16,000

^a oil palm and paddy biomass production in 2014 and 2013, respectively

2.5 Paddy Wastes

Paddy is the second-largest crop planted in Peninsular Malaysia occupying 517,586 ha of land [26]. As shown in Table 1, the residues from paddy plantation; rice husks and rice straws were 703,008 and 3,498,954 t/yr, respectively. The potential ethanol production can be evaluated based on its primary compositions of cellulose and hemicellulose. On average, paddy contains 28–43% cellulose, 25–36% hemicellulose, and 12–24% lignin [2]. Researchers have proven that ethanol can be produced from paddy wastes and could easily eliminate the problem of open-burning after the harvesting season. However, the theoretical ethanol yield is lower compared to the ones using oil palm wastes.

2.6 Napier Grass

Another crop that has gained attention from researchers is Napier grass (NG). NG is a tall species of perennial tropical grass that is sturdy, deep-rooted, and requires low water and nutrients for growth. It was first introduced to Malaysia in the 1920s and many of its species are presently cultivated across the country such as Taiwan Napier, King Grass, Dwarf, and Red Napier [26]. The yield of NG in Malaysia is between 43.7 and 65.9 tonnes/hectare/year [26] and can be harvested four times a year [31].

The output energy from NG is estimated to be 25 times higher than the input energy consisting of the high amount of lignocellulosic material. The carbohydrate content in NG could reach up to 46.75% glucan and 18.58% xylan (dry weight) [32].

3 Bioethanol from Algae

Different from 1 and 2G ethanol feedstocks, algae cultivation does not require land or freshwater. The growth rate of macroalgae is a lot faster than land-based crops. There are over 10,000 species of macroalgae discovered, with only a few species being cultivated commercially [33]. Due to the technical issues of the high cost of delignification in 2G bioethanol, research was driven towards 3G feedstocks, which is algae. Macroalgae can be classified as brown, red, and green algae [34]. The brown and red macroalgae were cultivated in larger quantities than green macroalgae. Compared to lignocellulosic material which had to undergo vigorous treatment to remove lignin, algae has the advantage of the absence of lignin, making it a feasible option for carbohydrates. The carbohydrate in macroalgae is composed of two monosaccharides, which are D-galactose (56.2%) and 3,6-anhydrous-galactose (43.8%) [33]. After the hydrolysis process, these monosaccharides can be used as a substrate during the fermentation process for bioethanol production. The carbohydrate in microalgae cells can be extracted via enzymatic, acid, or solvent extraction and converted to bioethanol. Several carbohydrate-rich microalgae such as *Chlamydomonas reinhardtii* and *Chlorella vulgaris* are nominated as potential candidates for techno-economic analysis of bioethanol production [35]. Another example of macroalgae that can be found abundantly in South East Asia is *Eucheuma cottonii* which is the major commercial source of κ -carrageenan. Massive amounts of macroalgae cellulosic residues are generated after the extraction of κ -carrageenan [34]. If *Eucheuma* spp. was used as a feedstock for bioethanol production, the estimated bioethanol yields could reach up to 110,000 t annually.

4 Processes for Lignocellulosic Bioethanol Production

Biomass from plants is naturally recalcitrant, making it more complicated to be converted into bioethanol compared to starch. To release the sugars in the lignocellulosic materials, a pre-treatment step to break down the lignin, hemicellulose, and cellulose is required. The need to understand its molecular structure is a prerequisite to developing effective pre-treatment methods to destruct the lignin-carbohydrate complex (LCC). Prominent pre-treatment methods include physical pre-treatments, chemical pre-treatments, physicochemical pre-treatments, and biological pre-treatment [36]. The methods will not be discussed in detail but rather will focus on the process after pre-treatment itself, as long as the pre-treatment method produces fewer inhibitors (furfural, HMF, acetic acid) to improve yields of

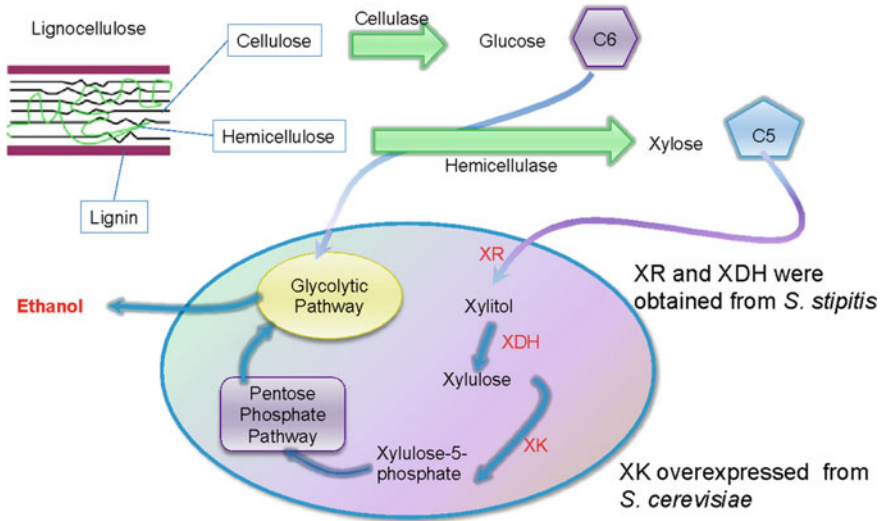


Fig. 5 Pathway of ethanol production by co-consumption of glucose and xylose

sugars, particularly sugars released during the hydrolysis of hemicelluloses. Hydrolysis using enzymes to release the sugars is then followed by fermentation by various functional microbes. After sugars are liberated, the processes described below are executed for ethanol production. For lignocellulosic materials, another sugar that can be converted to ethanol is xylose. The production of ethanol from xylose is described as follows [37]:

To ensure the utilization of sugars is maximized during the fermentation, genetic modifications on prominent yeasts such as *S. cerevisiae* proved successful. Figure 5 is showing the improvements made on *S. cerevisiae* to enable it to consume both glucose and xylose.

This was done by overexpressing the genes from *Scheffersomyces stipitis* encoding xylose reductase (XR) and xylitol dehydrogenase (XDH). Ethanol production was then enhanced by overexpressing the endogenous XK gene encoding glucokinase [38]. The construction of such strain could help in making fermentation highly efficient and cost-effective for Separate Hydrolysis and Fermentation (SHF), Simultaneous Saccharification and Fermentation (SSF), and consolidated bioprocessing.

4.1 *Separate Hydrolysis and Fermentation (SHF) and Simultaneous Saccharification and Fermentation (SSF)*

In the SHF process, the separation of the fermentation and hydrolysis process occurs in two different stages and separate tanks (Fig. 6).

This allows both processes to work at two different optimal operating conditions [39]. On the other hand, the SSF process combines both saccharification and fermentation in a single step. In terms of cost, SSF is cheaper due to the lower energy required, shorter processing time, and high ethanol yield. However, the cellulose component is hydrolysed into glucose by cellulases under optimal temperature, around 40–50 °C. Such high temperature cannot be tolerated by *S. cerevisiae* or *Z. mobilis*, which usually performs ethanol fermentation at temperatures generally below 35 °C [40]. Hence, a thermotolerant strain, as well as inhibitor tolerant strain, is highly anticipated. Also, it would be a more efficient process if the strains can utilize both glucose and xylose contained in the hydrolysate, as described earlier. The multi-stress tolerant strains can either be isolated from indigenous sources or were genetically modified to carry the desired phenotype. Table 2 is showing the ethanol yield via SHF and SSF processes, utilizing EFB as the raw material as described by Derman et al. [39]. The highest ethanol yield was obtained by treating the EFB with dilute acid and via SSF by *S. cerevisiae*.

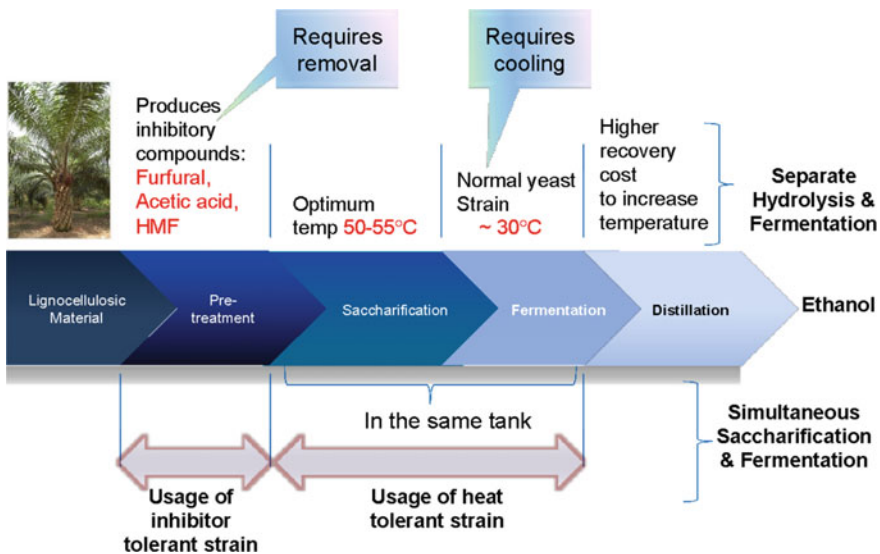


Fig. 6 Separate Hydrolysis and Fermentation (SHF) vs Simultaneous Saccharification and Fermentation (SSF)

Table 2 Ethanol yield from SHF and SSF using EFB [39]

Pre-treatment methods	Hydrolysis process	Fermentation process	Fermenting microorganisms	Ethanol production (g/L)
Formiline	Enzymatic hydrolysis (Cellulase and β -glucosidase)	SSF	<i>S. cerevisiae</i> CICC 31,014	83.6
Sequential acid/alkali	Enzymatic hydrolysis (Cellic [®] Ctec2 cellulase)	SSF	<i>S. cerevisiae</i> W303-1A	37.8
Alkali (15% w/v NaOH)	Acid hydrolysis (7% v/v H ₂ SO ₄)	SHF	Baker's yeast & yeast from loog-pang	6.23–8.49 (Baker's yeast) 0.05 to 0.21 (Loog-pang)
Dilute acid treatment (H ₂ SO ₄)	Enzymatic hydrolysis (Cellulast [®] 1.5L) and β -glucosidase (powder from almonds)	SSF	<i>S. cerevisiae</i>	386.61–497.07
Alkaline (10% NaOH)	Enzymatic hydrolysis (Cellic [®] Ctec2 and Cellic [®] HTec2 from Novozymes)	SHF & SSF	Dry yeast (<i>S. cerevisiae</i>)	402.39 (SHF)
Alkaline (2% NaOH)	Crude Cellulase cocktails from <i>Trichoderma asperellum</i> UPM1 and <i>Aspergillus fumigatus</i> UPM2	SSF	Baker's yeast	0.59
Acid treatment (H ₂ SO ₄)	Cellulase (Cellulast 1.5 L) and β -glucosidase	SSF	<i>S. cerevisiae</i>	-
Acid treatment (H ₂ SO ₄)	Two stages of dilute acid hydrolysis (H ₂ SO ₄)	SSF	<i>S. cerevisiae</i> and <i>Mucor indicus</i>	355.05 (<i>Mucor indicus</i>) 362.94 (<i>S. cerevisiae</i>)

some of the data were not reported

SHF: Separate hydrolysis and fermentation

SSF: Simultaneous saccharification and fermentation

4.2 Consolidated Bioprocessing (CBP)

Consolidated bioprocessing (CBP) advances the SSF process by incorporating a single organism or a consortium of organisms able to produce enzymes for hydrolysis

and simultaneous fermentation, all in one tank. This is one of the steps to debottle-neck the high production cost due to the use of external cellulase, usually produced by *T. reesei* [40]. The success of the CBP depends on the biocatalyst designed for the process. The pure strain or mixed culture must be able to synthesize and excrete cellulases to hydrolyse cellulose as carbon and energy sources to support their growth and metabolism. CBP combines the production of cellulases, enzymatic hydrolysis of cellulose, and ethanol fermentation of the resulting sugars in a single tank. However, no microorganisms in nature are capable of doing such work. Researchers began developing strains to fit the characteristics via genetic engineering; engineering cellulase producers with ethanol production, and engineering ethanologens with cellulase production [40]. So far, more attention has been focused on engineering *S. cerevisiae* with genes encoding glycoside hydrolases including cellulases and hemicellulases, but their expression is generally poor. In theory, CBP can completely eliminate the supplementation of cellulases. However, more fundamentals are to be elucidated to make it practical for cellulosic ethanol production. For example, the production of cellulolytic enzymes, hydrolysis of cellulose and hemicelluloses and fermentation of released sugars need to be well-coordinated through engineered strains. Furthermore, kinetic models of the heterogeneous enzymatic hydrolysis with mass transfer limitation and ethanol production need to be developed for the process optimization [40].

5 Application and Challenges for Bioethanol Production in Malaysia

The choices of bioethanol production processes depend on the raw materials chosen. Every raw material has its pros and cons to deal with, for example, concerns on the 1G and 2G bioethanol due to the competition with food supply and land usage, respectively. As long as the cost of production is feasible, and benefits the environment, bioethanol is one way forward to establish a clean fuel blend for Malaysia. Table 3 summarizes the advantages and disadvantages of the four bioethanol generations.

The easiest for Malaysia to start with is the 1G bioethanol as long as the starch feedstock used doesn't compete with food. The pre-treatment method is simpler and it can be fermented using the usual Baker's yeast, *Saccharomyces cerevisiae*. However, if the Technology Readiness Level (TRL) for 2G reaches maturity, it would be great to start with a small-scale production to cater to local energy needs.

Table 3 Summary of the advantages and disadvantages of bioethanol types for Malaysia

Bioethanol types suitable for Malaysia	Advantages	Disadvantages
First-generation bioethanol <ul style="list-style-type: none"> • Molasses • Inedible cassava 	<ul style="list-style-type: none"> • Direct use of waste from sugar mills • Feedstocks are ready to be used without complicated pre-treatment processes 	Cassava may require land and fertilizer, resulting in a reduced net energy ratio
Second-generation bioethanol <ul style="list-style-type: none"> • Oil palm • Rice straw • Sugarcane bagasse • Napier grass • Sago pith waste • Wood chips 	<ul style="list-style-type: none"> • Usage of residues from the whole plant results in higher energy produced per area of land • Some feedstocks can be grown on marginal lands 	<ul style="list-style-type: none"> • The technology available is still expensive for industrial production • Delignification is costly
Third generation bioethanol <ul style="list-style-type: none"> • Algae • Microalgae 	<ul style="list-style-type: none"> • Higher energy produced per area of land • Can be grown in wastewater, which will result in less use of fertilizer • Can be produced in an integrated biorefinery with other biofuels, e.g. Biodiesel 	Requires new technologies to convert algae into bioethanol
Fourth-generation bioethanol <ul style="list-style-type: none"> • Genetically engineered algae/microalgae 	It is predicted to be 'carbon negative' as it fixes more carbon than it produces [1]	Requires new technologies to convert algae into bioethanol

5.1 Technology Maturity Limitation

Malaysia's bioethanol technology has not been commercialized at a large scale due to several barriers. The ones operating in Perlis and Perak are operating based on the availability of molasses from sugar mills. The current bioethanol prices mean that current processes are not economically viable despite the availability of various technologies. Lignin hinders the bioconversion into glucose using enzymes, and the delignification process is costly. Most of the technologies are not feasible with the current bioethanol prices. Also, it is not feasible to be running a facility for a single product. A biorefinery should produce by-products that could be value-added to enhance the ROI. For example, lignin can be used as a raw material for the production of vanillin, while furfural is the starting raw material for Nylon 6,6 and Nylon 6 production [41].

5.2 Inadequate Infrastructure and Labour Cost

One key component for the success of biofuels in transportation is the establishment of adequate infrastructure. The supply chain infrastructure for biofuel needs to be convenient and efficient to reach the end-users for their daily usage. Biofuels blending and refuelling station infrastructures will need to be set up adequately together with complete transportation of biofuels supply network. Training of skilled workers, warranty of engines from manufacturers for the usage of biofuel blends, and technical support is deemed necessary.

5.3 Policy Enforcement and Sustainable Planning

It is high time that Malaysian policymakers realize the potential of bioethanol from various resources in the country. As an example, in Europe and Australia, the biofuel industry enjoys substantial excise tax and rebates. In Canada, subsidies for 1 L of ethanol from corn to substitute an equivalent litre of fossil fuel is also enough to buy a litre of the displaced fuel [1]. Planning for a sustainable future is anticipated and not to mention, financial support in research and development.

6 Conclusion

Bioethanol has great potential in Malaysia, especially in climate change mitigation. It offsets large amounts of GHG emissions that would help Malaysia achieve its GHG target. However, its production on a commercial scale is still in its infancy. Not to mention, financial support in energy crop farming, harvesting technology, as well waste treatment all need to be synergized and well-planned. To begin with, Malaysia could start with molasses as had been currently ongoing, or starch-based bioethanol production, which could later adapt the technology for lignocellulosic ethanol once the technology reached maturity. The bioethanol production should be produced in a biorefinery, close to the feedstock sources and have more by-products to cater for an economical process, ideally towards zero waste.

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Bioconversion of Malaysia Renewable Energy Resources to Biobutanol



Hafiza Shukor, Rafidah Jalil, and Noor Fazliani Shoparwe

Abstract Production of biofuel from renewable resources has gained interest to the government's, researchers and policymakers throughout the world due to the depletion of conventional fuels and environmental issues. As a country that is rich in various types of bioresources, Malaysia can be one of the top biofuel producers in Asia. Several types of biofuels can be produced from these resources, including biobutanol, four-carbon alcohol that has outstanding characteristics more similar to gasoline. Thus, this chapter will begin with an overview of biobutanol production and the possibility of Malaysia bioresources as a feedstock in biobutanol production. The role of the government in existing policies and action plans towards the development of Malaysia's renewable energy industry also has been analysed. Subsequently, several challenges and resolutions related to the development of biobutanol production were also addressed. The potential of biobutanol to replace gasoline and the economics of ABE fermentation in biobutanol production will be the last part of this chapter. Overall, this chapter will give a better understanding and view of the current situation on biobutanol production using Malaysia's renewable resources.

Keywords Biobutanol · ABE fermentation · Malaysia Biomass

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1 Overview of Biobutanol Production

Global conventional fossil fuel-based energy consumption has increased in line with the increase in world population. Additionally, the evolution of greenhouse gases has also increased significantly as a result of the use of fossil fuels that have led to global warming. The drastic rise in oil prices, the reduction of petroleum fossils and the growing awareness of environmental impacts such as greenhouses and acid rain, are the main reasons for the development of more economical and environmentally safe fuel production. Now, it is a focus for various parties, especially government's, researchers and policymakers to find and identify alternative energy sources that have the same or almost the same potential as new renewable fuels to replace these fossil fuels.

Over the decades, the use of non-fossil fuels from biomass sources through fermentation as a sustainable alternative fuel to reduce the adverse effects of fossil fuel use by providing cleaner energy sources has become increasingly focused. In addition, public awareness of the increasingly limited fossil fuel resources coupled with volatile world crude oil prices has opened the eyes of all parties to find suitable alternatives for the sake of universal survival. Basically, biofuel is a fuel based on existing biological resources that are mostly produced from combustible lignocellulose biomass that exists in the form of gas, liquid or solid such as bio alcohol, biodiesel, biogas (hydrogen) and solid biofuel are classified according to their respective categories based on differences in terms of chemical and physical properties [1]. Neutral biomass with less greenhouse gas (carbon dioxide) emissions than fossil fuels have a very significant impact on fuel production with several other advantages such as no use limit because it is renewable and its abundant resources around the world [2, 3]. Biofuels from renewable biomass sources provide excellent potential for fuel production because they can be produced by thermochemical or microbiological production methods.

As a tropical country and rich with huge renewable biomass resources, make Malaysia as one of the highly potential countries to produce various types of biofuels as a replacement for fossil fuels. Malaysia has produced 168 million tons of biomass annually and the most promising resources in Malaysia commonly come from palm oil mill residues, agricultural lignocellulosic waste and municipal wastes. Lignocellulosic-based biomass was the biggest type of bioresource available in Malaysia because 76% of the total land was covered by forests and agricultural fields. In this regard, Malaysia has become one of the most important references to biofuel technology in the world. Lignocellulose biotechnologies such as the use of hydrolysis enzymes to convert the complex structure of cellulose and hemicellulose in these lignocellulosic materials to simpler sugars have great potential to enhance the economic viability of biofuel production. The conversion process from lignocellulosic biomass to biofuels involves two main conversion processes, namely the treatment and hydrolysis process to simple sugars and then the fermentation process, namely the conversion of simple sugars to biofuels. The hydrolysis process is usually performed using enzymes to decompose the structure of cellulose and hemicellulose,

while the fermentation process is performed by either using yeast (*Saccharomyces cerevisiae*) [4, 5] or bacteria (*Clostridium* type) [6].

Compared to other types of biofuels, liquid alcohol fuels such as biomethanol, bioethanol and biobutanol which are commonly produced from agricultural waste can be used as a substitute for gasoline in the transport sector. However, biobutanol is more of a focus and attraction due to characteristics such as octane number, energy content and energy density that resemble the characteristics of gasoline. Biobutanol can be produced through the ABE fermentation process using solvent-producing clostridia-type bacteria that are capable of using various types of biomass as a cheap carbon source such as domestic waste, oil palm waste and agricultural waste [7]. In addition, the fermentation of ABE from renewable carbohydrate sources is the largest biotechnological process after fermentation producing ethanol by yeast [8]. The existing advantages of biobutanol have made it a new alternative fuel and its existence is capable of reducing the world's dependence on fossil fuels and at the same time capable of reducing greenhouse gas emissions [9, 10]. Therefore, efforts to improve efficiency in the production of biobutanol on a large scale are also expected to be able to provide a positive impact in terms of production costs. This chapter reviews the potential of biobutanol as one of the next-generation biofuels in Malaysia, comparison of several research and development are done using various types of Malaysia's bioresources and discusses the bioprocessing technologies and suitable strategies that have endeavoured to enhance biobutanol production from renewable biomass available in Malaysia.

2 Possible Malaysia's Bio-resources for Biobutanol Production

The development of the biobutanol production process started some time ago and it is divided into several generations based on the source and type of substrate used. The first generation of biobutanol production consists of food-based ingredients such as sugar (sugar cane), starch (potatoes) and oil (corn). However, the early stages of biobutanol production experienced problems in terms of ineffectiveness due to the conflict between food demand and as a source of substrate for fuel production. This situation results in high demand for this substrate and leads to increased prices for the substrate itself [11]. It is reported that the substrate cost for an ABE fermentation process contributes to approximately 63% of the overall process cost [12].

For sustainable production of biobutanol, economic considerations need to be given in the ABE fermentation process. Therefore, the use of substrates from lignocellulose material is seen to be able to provide a cost-effective impact in the production process of biobutanol [13]. However, the use of this lignocellulose material in ABE fermentation needs to go through several pretreatment steps to decompose the complex structure of this lignocellulosic material into a simpler form of sugar and can be used by bacteria in ABE fermentation [14]. Therefore, the next generation

of fuel production is beginning to move towards something cheaper, easier to obtain and can be reproduced such as lignocellulose material. Lignocellulose material is a type of material consisting of the structure of lignin, hemicellulose and cellulose. Nowadays, this lignocellulosic material becomes the focus for most researchers in producing more economical and abundant biofuels.

As a tropical country, Malaysia has large areas of natural land for biomass production. These biomasses from food crops, urban waste and forest residue could be used to generate valuable country biofuel. If Malaysia further utilized maximumly all of its bioresources, the country can be one of the biggest biofuel producers like Indonesia which currently being the third-biggest biofuel producer (producing 77 Terawatt-hours of energy in 2019) behind the United States (433 TWh) and Brazil (276 TWh) [15]. Therefore, many Asia countries including Malaysia have opted for biofuel as a potential; source of renewable energy and taken few initiatives to develop their bioenergy industry using these sustainable bioresources. In Malaysia, the rate of energy demand has increased due to industrialization and the increasing population (with an annual growth of 1.4% in 2018) and more than 70% of the energy demand was coming from the transportation sector [16]. This could be a problem for Malaysia in the next 40 years because of the depletion of fossil fuel resources [17]. It is reported that this country produces 168 million tons of biomass annually including rice husk, timber, coconut trunk fibres, oil palm waste and municipal waste. This could be a great insight into the future development of biofuel in Malaysia.

2.1 Palm Oil Mill Biomass

As one of the leading and second-largest palm oil producers in the world, Malaysia is producing an abundant amount of waste. In 2019, this country has produced 20 million tonnes of palm oil (MPOB, 2019) and is forecasted to produce 20.3 million tonnes in 2020. Due to the global outbreak of the COVID-19 pandemic, the production of palm oil declined to 19.14 million tonnes (<3.6%) with a total plantation area of 5,865,297 hectares [18]. Palm oil processing generated almost 90% of biomass after the oil extraction. Oil palm empty fruit bunch (EFB), palm oil mill effluent (POME), oil palm trunk (OPT), palm kernel shell (PKS) and palm kernel cake (PKC) are among residues produced after palm oil mill processing. Figure 1 shows the common types of palm oil biomass used in biobutanol production for research and development in Malaysia. Generally, palm oil mill biomass consists of 24–65% of cellulose, 21–34% hemicellulose and 14–31% lignin. The high cellulose and hemicellulose content of oil palm biomass makes it the most potential bioresource in Malaysia for the production of biobutanol.

Palm Oil Mill Effluent (POME) is wastewater generated from palm oil processing that contains a high level of organic nutrients but has environmental side effects if it is discharged into the environment. Annually, Malaysia will produce approximately 53–58 million tons of POME and this will be a great potential to be converted to useful products such as biofuels. The high composition of macro and micronutrients

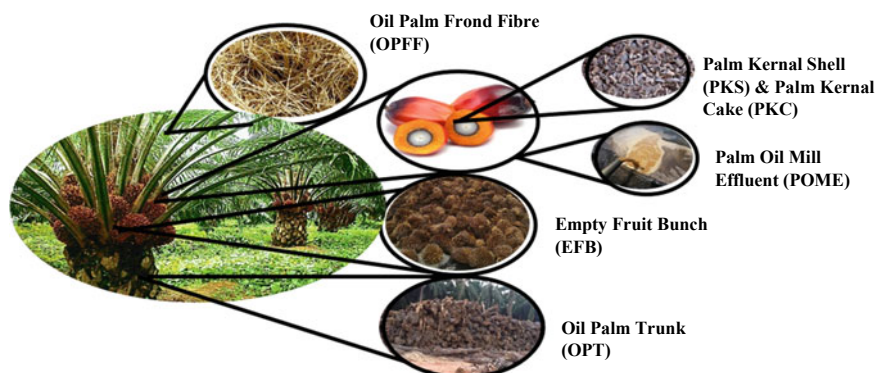


Fig. 1 Commonly types of palm oil biomass used in biobutanol production research and development in Malaysia

in POME makes it a promising medium in biobutanol production. Apposite to POME, empty fruit bunch (EFB), palm kernel cake (PKC), Palm Kernel Shell (PKS), Oil Palm Trunk (OPT) are some of the solid waste generated from palm oil processing that has been used previously in biobutanol production. Table 1 shows common types of palm oil biomass used for biobutanol production. In biobutanol production, most of this palm oil biomass has to go through the pre-treatment and hydrolysis before ABE fermentation to change the complex lignocellulosic form into simple fermentable sugars.

Therefore, as one of the important pillars of Malaysia's economy, the palm oil industry can channel its biomass generated as a new potential industry from the palm

Table 1 Malaysia palm oil based biomass for biobutanol production

Types of palm oil biomass	Microorganism	Biobutanol production (g/L)	References
Palm oil mill effluent (POME)	<i>C. saccharoperbutylacetonicum</i> N1-4	0.9	[19]
Palm kernel cake (PKC)	<i>C. saccharoperbutylacetonicum</i> N1-4	3.75	[20]
Empty fruit bunch (EFB)	<i>C. acetobutylicum</i> ATCC 824	2.75	[21]
Oil palm trunk (OPT)	<i>C. acetobutylicum</i> DSM 1731	12.76	[22]
Oil trunk fiber (OTF)	<i>C. beijerinckii</i> TISTR 1461	10.03	[22]
Decanter cake hydrolysate	<i>C. acetobutylicum</i> ATCC 824	6.04	[23]
Oil palm frond juice	<i>C. acetobutylicum</i> ATCC 824	9.24	[24]

Table 2 Malaysia agricultural biomass diversity in biobutanol production

Agricultural biomass	Clostridia sp.	Biobutanol (g/L)	References
Corn stover	<i>C. beijerinckii</i> P260	21.06 (ABE)	[11]
Corn stover	<i>C. acetobutylicum</i> ATCC 824	10.07	[27]
Corn cob	<i>C. acetobutylicum</i> SE-1	18.20 (ABE)	[28]
Sugarcane bagasse	Mix culture of Clostridial species	2.29	[29]
Rice straw	<i>C. acetobutylicum</i> NRRL B-591	1.40	[30]
Rice bran (RB) and de-oiled rice bran (DRB)	<i>C. saccharoperbutyl-acetonicum</i> N1-4	6.8 (RB) 7.10 (DRB)	[31]
Pineapple peel waste	<i>C. acetobutylicum</i> B 527	5.23 (ABE)	[32]
Mango peel waste	<i>C. acetobutylicum</i> NCIM 2878	10.5	[33]

oil industry. Malaysia's palm oil industry needs a strategy that will guide oil palm production towards sustainable palm oil production and development with a suitable incentive provided by the Malaysian government, this will motivate the other private sectors to get together for the growth of the biofuels industry in Malaysia.

2.2 Agricultural Biomass

Agricultural activities are also one of the important sectors in Malaysia and it has served as the backbone of Malaysia's economy which contributed up to 7.1% (RM 101.5 billion) to the national Gross Domestic Product (GDP) in 2019 and provided 16% to the population employment [25]. This sector generated 91% of the biomass amount at diverse variety types like lignocellulosic-based, starch-based and fibrous-based. Therefore, the source of the substrate from agricultural waste is found to have great value to be highlighted for the production of bioproducts, especially biobutanol compared to others [26].

The ability of solvent-producing *Clostridium* to produce biobutanol from various types of substrates from agriculturally based materials gives an advantage to the success of this process in finding cheaper alternative substrates and even being able to solve the problem of dumping of existing national waste. Table 2 shows the various types of agricultural waste that have been successfully used by Clostridia to produce biobutanol in ABE fermentation.

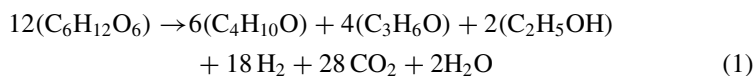
3 Biobutanol Production Process

Butanol can be produced through two processes, namely by chemical synthesis or by biological process (biobutanol). Chemically, butanol can be produced through three processes namely Oxo synthesis, Reppe synthesis or crotonaldehyde hydrogenation. Through the process of hydro formalization in oxo synthesis, carbon monoxide and hydrogen (syngas) are incorporated into carbon-carbon double bonds using Co, Rh or Ru as hydrocarbonyl substitute catalysts [34]. This process has been done commercially by producing aldehydes which will, in turn, be hydrogenated to produce n-butanol and iso-butanol as by-products depending on the reaction conditions (temperature and pressure) and the type of catalyst used.

For Reppe synthesis, butanol can be produced directly at low temperatures and pressures by a reaction between propylene, carbon dioxide and water in the presence of a catalyst [35]. However, the high cost is the main reason this process cannot be fully commercialized. Crotonaldehyde hydrogenation is a butanol synthesis process that has been commonly used for decades but is rarely used due to the high cost of using acetaldehyde. This process is the only chemical process that does not depend on petroleum. This process is capable of producing ethanol from biomass by dehydrogenating it to become acetaldehyde before the process continues [35].

The production of butanol through this chemical process only lasted until the mid-1970s when the oil crisis occurred. This oil crisis has led to the production of biobutanol through the fermentation process of ABE because of its advantages not only in terms of energy but also in the cost of production [36]. The tendency and concern for the production of biobutanol through fermentation can be seen when many reviews and comments were made afterwards regarding ABE fermentation as soon as the oil crisis in the 1970s [9, 35–38].

The production of ABE and its by-products through the fermentation process depends on the type of substrate and the type of solvent-producing *Clostridium* used. However, the basic equation (Eq. 1) of stoichiometric reactions is usually used for technical calculations to estimate the yield of biobutanol at the end of the fermentation process. It is a similar equation used in the ABE production process in China using cornstarch as the main substrate by standard *Clostridium* [39].



Biobutanol as four-carbon alcohol ($\text{C}_4\text{H}_{10}\text{O}$), is an end product in acetone-butanol-ethanol (ABE) fermentation that provides far superior advantages over bioethanol, including in terms of high calorific value for use in internal combustion engines, and corrosive properties low [13, 40]. Fermentation of ABE can be performed by various species of solvent-producing *Clostridia* bacteria under anaerobic conditions by using nitrogen gas to remove oxygen in the medium. Among the commonly used

types of Clostridia are such as *Clostridium acetobutylicum* [41], *Clostridium saccharobutylicum* DSM 13864 [39], *Clostridium beijerinckii* [40], *Clostridium tyrobutyricum* [42], *Clostridium saccharoperbutylacetonicum* N1-4 [43] and *Clostridium butylicum* [29]. This ABE fermentation process is mostly performed in cluster systems at temperatures between 30 to 35 °C and a pH range of 5.0 to pH 6.5 [44].

4 Biobutanol Fermentation Strategies

4.1 *Clostridium* sp. Improvement

Anaerobic bacteria known as Clostridia are a type of gram-positive bacteria that produce spores and are capable of producing biobutanol through a fermentation process called Acetone-Butanol-Ethanol (ABE) fermentation [45]. Compared to other microorganisms such as *S. cerevisiae* used for bioethanol production, Clostridia provides more advantages because it can use various types of sugars including glucose, mannose, fructose, sucrose, lactose and dextrin simultaneously while sugars such as xylose, galactose, arabinose, mannitol, raffinose and partial inulin which normally exists in hydrolysate which is a medium of lignocellulose material produced after treatment and hydrolysis [36, 44]. There are various types of Clostridia that are commonly used for biobutanol production such as *C. acetobutylicum* [46–50], *C. beijerinckii* [42, 44, 51–53], *C. thermocellum* ATCC 27405 [54], *C. saccharoperbutylacetonicum* N1-4 (ATCC 13564) [55–57], *C. tyrobutyricum* [58] and *C. saccharobutylicum* DSM 13864 [59].

C. acetobutylicum which was originally named BY was first successfully isolated by Weizmann in 1912 as the first culture successfully produced for solvent production. These cultures are used on an industrial scale to produce biobutanol for large production and can use starchy materials in the fermentation process [36]. *C. acetobutylicum* ATCC824 is a well-known and frequently used clostridia for ABE fermentation. *C. acetobutylicum* usually produces an ABE solvent in a ratio of 3: 6: 1 (acetone: butanol: ethanol) [36]. Compared to *C. acetobutylicum*, *C. beijerinckii* also has its own advantages of being able to produce good biobutanol yield and productivity when lignocellulosic materials such as hydrolysates from wheat straw, barley straw and starch are used [11, 26, 60].

The cell morphology of these Clostridia sp. strain under the microscope shows Gram-positive bacterial properties such as long rod-shaped or short rods with rounded ends and cells appearing solitary and sometimes in pairs typically measuring 0.4–0.8 μm × 3.1–6.2 μm [55, 61]. This strain is not only able to use various types of sugars such as pentose, hexose, cellobiose, lactose, maltose and starch but also able to use lignocellulose as a source of carbon in ABE fermentation such as sago [55], starch from cassava [62], palm kernel cake [57], rice bran [31] and palm oil effluent

[63]. Optimal growth for this species usually occurs in the temperature range of 30–37 °C and pH 6.5 to pH 7 [61].

However, the conventional *Clostridium sp.* are not able to stand the fermentation broth containing more than 2% of solvent or more than 15 g/L biobutanol produced due to product inhibition. Therefore, developing excellent strains that are resistant to biobutanol toxicity and hyper-biobutanol producing strains is an ideal solution for improving biobutanol fermentation. Thus, more effort is required to achieve a perfect solution. Despite recent advances in genetic engineering to produce a recombinant strain that can tolerate biobutanol toxicity, the improvement of strain with superior properties also can be achieved by using Adaptive laboratory evolution (ALE). ALE is a scientific approach used to artificially induce strain evolution based on a predetermined laboratory setting. It has been frequently used to gain insight into the basic mechanism of molecular evolution via adapting the microbial population under specific growth conditions during a long-term selection of stress. This method offers some major benefits as compared with classical genetic engineering but with some inherent limitations like efficiency issues. ALE has been applied to studies on various organisms, including microalgae, mammalian cells and viruses, to standard model organisms such as *E. coli* and yeast [64].

Many successful stories on the application of ALE on the improvement of microorganisms had been reported previously. The most recent achievement for strain improvement was achieved for *E. coli* which successfully mitigated acid stress using the ALE approach [65] and ALE also was applied to characterize and improve native methanol metabolism (methylotrophy) in *S. cerevisiae* [66]. On the other hand, Wang et al. [67] have successfully performed ALE for *Chorella sp* to remove phenol in wastewater. The resulting strain was obtained after 31 cycles for about 95 days and the strain could grow under 500 mg/L and 700 mg/L phenol without significant inhibition. The glucose-tolerant makes strain of *C. cohnii* [68] biodegradation of furfural by *Pseudomonas pseudoalcaligenes* CECT 5344 [69] and solvent stress cross-tolerance conferred to *Corynebacterium glutamicum* also has been successfully performed by ALE method [70]. At present, a study by Tian et al. [71] shows that growth adaptation in the chemostat using biobutanol tolerant of *C. thermocellum* has improved the strain tolerance up to 15 g/L from 5 g/L. This method shows a great improvement of biobutanol tolerance via growth adaptation. On the other hand, a maximum, 20.3 g/L biobutanol has been successfully produced by hyper biobutanol tolerant of *Clostridium acetobutylicum* JB200 which obtain from *C. acetobutylicum* ATCC 55025 after mutagenesis and adaptation in a fibrous bed bioreactor [72].

Mutagenesis of *C. acetobutylicum* species has been done since 1993 by Jain MK et al. [73] using *C. acetobutylicum* species that could generate ~3 g/L biobutanol. A mutant strain of *C. acetobutylicum* JB 200, in another way, could produce up to ~25 g/L [74]. On another hand, genetically modified *Clostridia sp.* also have been developed by a few researchers for the improvement in biobutanol production by inserting other types of microorganisms like *Saccharomyces cerevisiae* and *E. coli* with genes related to biobutanol [75, 76]. Nevertheless, many strains have

been successfully developed and modified, but they are still not adequate to achieve profitable process design without proper implementation of advanced bioprocessing techniques.

4.2 Simultaneous Saccharification and Fermentation (SSF) and Consolidated Bioprocessing (CBP)

Simultaneous saccharification and fermentation (SSF) is a well-known technology for the production of bioproducts by combining saccharification of biomass and fermentation process in the same reactor at the same time. Consolidated bioprocessing (CBP) is a technology in which enzyme production, biomass hydrolysis and fermentation process are conducted in the same reactor as a single process step by lignocellulosic microorganisms. Both processes have been applied as a strategy to reduce the number of steps in converting biomass into any bioproduct production.

The technology of the fermentation system for biobutanol production actually starts with separate saccharification and fermentation (SHF) for ABE fermentation because the fermentation process is strictly on anaerobic condition with a fermentation temperature between 30–37 °C and pH of 6.0–6.5, while the condition of the saccharification process by enzymes is between 50 and 60 °C with a pH range of 4.5–5.5. Towards reducing the processing time and energy consumption (cost-related), simultaneous saccharification and fermentation (SSF) technology have been introduced. It is proven that this technology is possible to be applied in ABE fermentation and even the combination of these to process generated a better yield and productivity even the saccharification has been conducted under a conditions similar to ABE fermentation (main process) by preventing substrate inhibition issues in ABE fermentation and thus improving the degradation of complex carbohydrate into simple fermentable sugars [77]. However, this technology faced low sugar concentration generated in the process. These happen when the substrate loading is limited to reduce sugars degradation product produced during the treatment. A previous study done by Ibrahim et al. [77] reported that SSF of 5% empty fruit bunch (EFB) generated sugars that noticeable as low for ABE fermentation (~30 g/L) still can produce high biobutanol yield as compared to SHF system using the similar initial sugar concentration and similar trend also happen in the SSF system using wheat straw in ABE fermentation [78].

Generally, consolidated bioprocessing (CBP) uses a single or co-culture microorganism that can do saccharification by producing an enzyme and can ferment the sugars produced for the production of the desired product in the same reactor. This strategy has been started previously for the production of biobutanol using starch-based biomass where the microorganism produces amylase to convert the complex form of starch into simple fermentable sugars and then used it to produce biobutanol. There is some *Clostridia* sp. that could produce a group of amylases enzymes by themselves like the *C. acetobutylicum* P262. This species has the ability to convert

various types of starch-based biomass like sago, potato, corn and tapioca into biobutanol using its α -Amylase and glucoamylase. A previous study showed that these enzymes could be produced by *Clostridial sp.* during the early lag stage of ABE fermentation (~within 4 h of fermentation) and can immediately do this saccharification process for cell metabolism [79]. *C. acetobutylicum* PW 12, a mutant of ART18 has been successfully converting cassava starch to biobutanol directly with 31% higher than biobutanol produced by wild type [80] while *Clostridium* BOH3 produced 17.8 g/L biobutanol (yield of 0.30 g/g) using cassava flour [81]. This technology has successfully reduced the overall process whereas the enzymes production, hydrolysis and ABE fermentation took only 48–72 h.

However, the application of CBP in lignocellulosic-based biomass to biobutanol is more challenging. The complex structure of lignocellulosic biomass compared to starch-based biomass make this technology more challenging and CBP on lignocellulosic-based biomass by *Clostridia* without co-culture or genetic engineering seems impossible. Therefore, several attempts have been conducted including genes that have been encoded for cellulase and celluloses sequence in the clostridial genome and growing the strain in the cellulosic environment. Lopez et al. [82] in his study show that *C. acetobutylicum* ATCC 824 have a significant level of cellulase activity when it was grown on xylose or lichenan [82] and *C. acetobutylicum* ATCC 824 only produced 3.73 g/L biobutanol after 8–12 h of fermentation using crystalline cellulose and filter paper as feedstock [83] while *Clostridium cellulolyticum* only produced 0.66 g/L of biobutanol even though it is already genetically modified [84]. The excellent finding has been discovered by Begum and Dahman in the year 2015 when 14.3 g/L ABE has been produced by clostridial fusant of *C. beijerinckii* with *C. thermocellum* and this special clostridium produced their cellulase enzyme up to 61.67 FPU/mL [85].

Therefore, further improvement and process modification would be an interesting research to be explored by other researchers. Process optimization of multiple biological processes in a single system reactor will be the most crucial step to be taken together with developing the new *Clostridia sp.* that can produce multiple enzymes during the hydrolysis process in the SSF or CBP system. Integrating the system with in situ product (butanol) recovery also could improve the yield in ABE fermentation by reducing product inhibition in the system. A total improvement of 72% was obtained when in situ recovery using gas stripping was implemented in SSF systems for biobutanol production from empty fruit bunch (EFB) [86]. A suitable process design could overcome all the challenges in biobutanol production.

5 Current Situation on Renewable Energy Production in Malaysia

Energy industries are one of the Greenhouse Gas (GHG) contributors in Malaysia other than transport, manufacturing, industrial process waste and agricultural sector. Therefore, in 2016, Paris Agreement (PA) was signed with The United Nations Framework Convention on Climate Change (UNFCCC) and committed to reducing its greenhouse gas (GHG) emissions by 45% by 2030 with several initiatives and programmes as stated in Table 3. It is expected that biobutanol could be one of the reasons for Malaysia to meet its greenhouse gas target.

Realizing the importance of renewable energy development in Malaysia towards reducing carbon emission, the Malaysian government has undertaken several initiatives and policies to drive renewable energy from the biomass industry forward. In the year 2000, Malaysia started to encourage manufacturing companies to use biofuel for electricity generation in the Fifth Fuel Policy under the 8th Malaysian plan. This plan aimed to generate 5% of country energy from renewable resources by 2005 and 70% of tax exemption for five years was given for any company invested in machinery for any palm oil biomass [88]. Between 2001 to 2010, Malaysia has introduced the Small Renewable Energy Power (SREP) Program to promote small-scale renewable electricity in Malaysia with the target to install up to 500 mV of renewable energy facilities. This policy allowed small renewable energy plants to sell their electricity produced to the national grid with 21 years of the license agreement and by the end of 2005, only less than 3% of its goals were achieved [89].

National Biotechnology Policy in 2005 with three phases of implementation phase: Phase 1 (2005–2010), focus on developing the foundation of biotechnology industry's growth, Phase 2 (2011–2015), towards achieving commercialization of biotechnology product and Phase 3 (2016–2020) towards transforming the industry to an important source of economics and wealth creation for the country [90]. About

Table 3 Malaysia's programme/initiatives towards reducing carbon emissions by 2030 [87]

Programme/initiatives	Programme target
Green Technology Master Plan 2017–2030	To transform Malaysia into low carbon and resource-efficient economy through the implementation of Green Catalyst Projects that would reduce 40% carbon intensity by 2020
Energy Efficiency Action Plan	Aims to reduce emissions of 13.113 million tonnes CO ₂ equivalent for the year 2030
Transportation Sector	The launching of the Mass Rapid Transit (MRT) phase one has successfully removed 9.9 million cars in 2017 and is estimated to remove additional 62–89 million cars between 2020 and 2030
Low Carbon Cities Framework	To introduce a carbon reduction blueprint within the local authorities and developers in making decisions on greener solutions

RM2 Billion has been allocated for this policy together with biotechnology research and development (R&D) implemented and this policy has petitioned Malaysia as one of the hotspots for bioproduct production for foreign investment [91]. In 2009, National Green Technology Policy was issued to accelerate the national economy and promote sustainable development. The growth of the green technology industry and biotechnology advancements will be enhanced by introducing Green Technology Financing Scheme (GTFS) that is worth RM 1.5×10^9 with a 2% interest subsidy and guarantee 60% on the green technology industry which has to attract foreign investment in the biomass-related industry [92].

Towards achieving a 20% Renewable Energy capacity mix with national electricity by 2025, Renewable Energy Policy and Action Plan were introduced in 2010 by the Ministry of Energy, Green Technology and Water. Several strategies have been done to overcome the main barriers to RE deployment in Malaysia and this policy has created a larger demand on local biomass resources and development of the bioenergy sector [93]. A system of feed-in tariffs for renewables energy generated from solar, biomass, biogas and hydro energy then been introduced in 2011 under Renewable Energy Act 2011 to strengthen the Renewable Energy Policy and Action Plan and from this, Malaysia RE (electric) generated from biomass and biogas resources has increased to 52.3 MW and 11.74 MW [94].

In 2012, the formation of Malaysia Biomass Industry Confederation (MBIC) was under Biomass Industry Strategic Action Plan 2012 [95] and 21 projects related to biomass were launched under Bioeconomy Program (BTP) [96]. This follows with National Biomass Strategy (NBS) 2020, a new wealth creation for Malaysia that has been started in November 2011 by Agensi Inovasi Malaysia (AIM) to promote the use of oil palm biomass and agricultural waste as a new industry instead of exporting to the open market [97]. Malaysia Industry-Government Group for High Technology (MiGHT) is then introduced to the Malaysian Biomass Industry Action Plan 2020 (MBIAP). This initiative focuses on biomass SMEs development in Malaysia.

The Green Technology Master Plan (GTMP) 2017–2030 is the latest framework from the Eleventh Malaysia Plan (2016–2020) under the Ministry of Energy, Green Technology and Water Malaysia to facilitate mainstreaming of green technology into the planned development of Malaysia. This plan targets installed RE mix installed capacity of 20% in 2020, 23% by 2025 and 30% by 2030. Several research and development activities are going in this direction for the future development of renewable biofuels. Biobutanol research is still less competitive compared with other biofuels like bioethanol and biodiesel. Therefore, the Malaysian government needs to review the policy enforcement for biobutanol whereas biobutanol could fill a gap in Malaysia RE policies and tighten the governance mechanism to motivate the biobutanol developers to sustain the growth of the biobutanol market in Malaysia. Lack of policies on gasoline that could be fulfilled by utilizing biobutanol fuels and will give an advantage. Government support via public research funding to universities and research institutions will be the massive effort in research and development on bioconversion technology from biomass to biofuels.

6 Challenges and Resolution in Biobutanol Production

Continuous depletion, increasing demand for energy sources and increasing prices of fossil fuels resources are the main factors for searching for alternative fuels from renewable resources [98, 99]. Moreover, global warming, climate change, instability of petrol price and severe environmental pollution due to consumption of fossil fuel for energy generation are also among several factors that influence the need for other options. High consumption of fossil fuel is the major contributor to the increase of carbon dioxide in the atmosphere [100]. In the early 20s, butanol has been used to produce butadiene as a feedstock for synthetic rubber production due to a shortage supply of natural rubber [101].

Biobutanol can be produced locally using various types of lignocellulosic materials as feedstock. Due to this, it has increased energy security as well as reduced GHG emissions by balancing the amount of carbon dioxide released to the atmosphere and indirectly reducing the effect of global warming [102]. Though, the cost of feedstock has a direct impact on the economy of the biobutanol production process. Hereafter, the selection for feedstock was shifted to lignocellulosic biomasses such as agricultural and forestry residues like rice straw, wheat straw, corn stover, waste wood and forestry waste [103]. Recent demand for fuels, the amount of biobutanol production globally has exceeded 1.2 billion gallons per year. Figure 2 shows the production of biobutanol per annum and the demand for butanol worldwide that has been increasing yearly from 2013 to 2023 in comparison with other types of fuels such as gasoline and advanced ethanol that has been produced using renewable resources. The biobutanol market has expanded 3% per year which accounts for

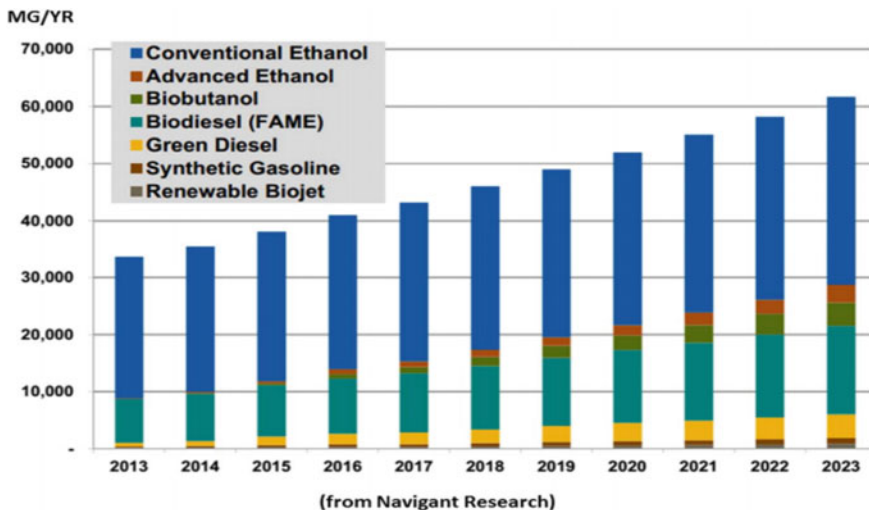


Fig. 2 Total biofuels production by fuel type, world markets: 2013–2023 [99]

Table 4 Comparison of biobutanol produced from Malaysian biomass

Type of biomass	Biobutanol yield (g/g glucose)	References
<i>Acacia mangium</i>	0.28	[104]
Palm kernel cake (PKC)	0.20	[105]
Oil palm frond juice	0.24	[106]
Empty fruit bunch (EFB)	0.13	[77]
Rice straw	0.27	[107]
Empty fruit bunch (EFB)	0.10	[108]

\$7–8.4 billion at the current price and estimated by 2020 is \$247 billion due to its advantages over bioethanol and biodiesel [99].

In Malaysia, many studies have been carried out to produce biobutanol from various types of lignocellulosic biomass. All of these studies were summarized in Table 4 to compare the types of lignocellulosic biomass that have been used as feedstock and the biobutanol yield. Al-Shorgani et al. [109] have studied the production of biobutanol using glucose as the substrate and found that the biobutanol yield was 0.27 g/g glucose using *Clostridium acetobutylicum* YM1. Results reported almost similar using the lignocellulosic biomass such as rice straw with biobutanol yield of 0.27 g/g glucose and 0.28 g/g glucose of biobutanol when using *Acacia mangium* as substrate.

6.1 Challenges as an Alternative Fuel

There are many challenges in biobutanol production as an alternative to fuel. The major challenges are the low yield of butanol, availability of compatible feedstocks, high cost of feedstock and product inhibition as well as product recovery [104, 109]. These hurdles could be resolved by using several genetic engineering techniques, metabolic engineering strategies and promising integrated continuous fermentation processes with efficient product recovery techniques [110]. During the biobutanol fermentation in an anaerobic condition and closed system, as the yield of product concentration is about 20 g/L, inhibition will occur where the biobutanol produced to inhibit the microbial growth of *Clostridium* species and indirectly will reduce the yield of biobutanol product [111, 112].

Generally, the production of biofuels such as biobutanol and bioethanol commercially will enhance the economic position of local workers by creating job and small business opportunities starting from the planting of the raw materials until the distribution of the biobutanol to the end-user by a consumer. Initially, first-generation biofuels such as bioethanol are produced from food sources that are also the source

material for the production of food and feed, so that there is a competitive use for them, which cannot be sustained for the long run. Therefore, it can affect the reduction of food supply and increase food prices [113].

Although the commercial production of biobutanol is growing rapidly, industries are still facing some challenges such as the development of biobutanol tolerant strain, overall production cost, the lower yield of product, sluggish fermentation and separation of microorganisms during and after biobutanol production via ABE fermentation and uneconomical product recovery. The application of nanocatalysts is one alternative to reduce the cost of feedstock and fermentation and improve biobutanol productivity [114]. Various types of nanocatalysts such as iron oxide, nickel cobaltite and zinc oxide have been used to enhance the biobutanol yield that provides a sustainable way by reducing the raw biomass processing as well as production costs and lowering down the harmful environmental impacts [115]. Table 5 shows some major industries that produce biobutanol at an industrial scale by utilizing modified microorganisms. DuPont and Bio Architecture Lab have invested around \$8.8

Table 5 Production of biobutanol by major companies in the world [99, 116]

Companies	Country	Production details
Gevo	CO, USA	Isobutanol from glucose using genetically modified yeast
Butyl Fuel, LLC	Columbus, USA	Biobutanol production with modified and patented <i>Clostridium</i> strain, able to produce high butanol (1.3–1.9 times higher) titer
Green biologics	Abingdon, UK	Biobutanol production with genetically modified strain (tolerate nearly 4% of butanol concentration)
Tetraviate bioscience	Chicago, USA	Biobutanol fermentation with mutated and patented <i>Clostridium beijerinckii</i>
Butalaco (bio-based innovations)	Zug, Switzerland	Genetically modified yeast with higher butanol-producing property and efficient utilization of C5/C6 sugars
Metabolic Explorer	Clermont-Ferrand, France	Using designed microorganisms for the production of butanol from lignocellulosic biomass
Cobalt Technologies	California, USA	Using non modified <i>Clostridium</i> (ABE fermentation in a continuous process) to break down components of plant matter including cellulosic, hemicellulosic and starch
Du Pont	Wilmington, Delaware, USA	Their process is based on the fermentation route of producing butanol using a variety of feedstocks

million in R&D activities for using seaweed biomass for commercial butanol production [114]. Like bioethanol, the production of biobutanol can be produced using the existing production facilities, thus the cost of production can be reduced [102].

6.2 Challenges in Downstream Processing

Visioli et al. [112] reported that the cost of biobutanol plant production is very dependent on the availability and price of the feedstock. Due to that, the expensive products will be generated using expensive raw materials as feedstock. The selection of raw material is important to reduce the production cost and reduce inhibition during the fermentation process.

The biobutanol recovery process after the fermentation process is the most expensive part of the biobutanol production process. Recovery of biobutanol via separation techniques are challenging where during the distillation process to separate the biobutanol, the formation of an azeotrope increases the energy cost. Azeotrope formed two liquid phases that occur above the solubility limit of biobutanol (above 55.5 wt.%). It is very difficult to separate using the conventional method and economically unfeasible. The most common method to recover biobutanol continuously such as adsorption, gas stripping, liquid–liquid extraction, pervaporation, supercritical extraction and flash fermentation process (Table 6). Among these methods, the pervaporation method using membranes is one of the most promising alternatives to conventional distillation. Without heating energy, the pervaporation process enables the efficient separation and concentration of the product in a single step and maintains the productivity of the microorganism to overcome product inhibition [117].

However, all of these separation methods have their advantages and disadvantages make it very difficult to select which is the best method or technique to recover the biobutanol yield. Mahapatra and Kumar [104] have summarized the major advantages and major drawbacks of several biobutanol recovery techniques as shown in Table 7.

6.3 Resolution for High Yield of Biobutanol Production

Various approaches and strategies could be applied to enhance and increase the biobutanol product yield such as strain development, biomass pretreatment and saccharification, ABE fermentation and biobutanol recovery process [100]. Strain development through genetic engineering is the promising technology to improve biobutanol production where it could enhance biobutanol production, reduce biobutanol toxicity, increase biobutanol ratio, allow the strain to grow in a complex cellulosic substrate and develop new strain as a host for biobutanol production [100, 123]. The application of sugar-free solutions such as sugarcane juice and oil palm trunk sap that have high sugar content could enhance the yield of biobutanol as well as can reduce the cost

Table 6 Biobutanol separation method

Method	Findings	Reference
Pervaporation using membrane	<ul style="list-style-type: none"> • Type of membrane: poly (ether-block amide) with 5% and 10% (w/v) of carbon nanotubes • Productivity and yield increased about 20% in comparison with the pervaporation using a poly (ether-block-amide) only 	[118]
Gas stripping	<ul style="list-style-type: none"> • The gas stream must be added as a separating agent • The highest butanol selectivity is obtained when gas stripping is performed at 67 °C 	[99, 119]
Liquid–liquid extraction	<ul style="list-style-type: none"> • Water-insoluble organic extractant can be mixed with the broth in selectively separating the butanol • Oleyl alcohol and benzyl benzoate mixture has been increased the biobutanol productivity by 60% • 20% dacanol in oleyl alcohol, enhanced butanol separation by 72% 	[99, 120]
Perstraction	<ul style="list-style-type: none"> • Membrane separation technique using a suitable membrane that separates the broth containing butanol from extractant • Oleyl alcohol flows in silicon tubing to recover butanol. Substrate utilization increased from 60 to 601 g/L and butanol production increased from 11.5 to 147.4 g/L 	[99, 121]
Use of mixed extractants	<ul style="list-style-type: none"> • Low partition coefficient nontoxic solvent is mixed with a relatively toxic solvent with a high partition coefficient • The use of 20% decanol in oleyl alcohol allows effective extraction of ABE solvents while keeping aqueous phase concentration below toxic limits 	[122]
Liquid membrane	<ul style="list-style-type: none"> • The support for the liquid membrane was microporous polypropylene flat sheet (25 mm thick) • The solvent recovery increased the productivity two times, with a butanol concentration of 230 g/L in permeate (which is 30-fold higher than the fermentation broth) 	[122]
Adsorption	<ul style="list-style-type: none"> • use of silicate (with adsorption capacity of 85 mg butanol/g silicate) appeared to be more attractive as it could concentrate butanol solution from 5 to 790–810 g/L 	[116, 122]

Table 7 Biobutanol recovery techniques [103]

Method	Basic principle	Major advantages	Major drawbacks
Gas stripping	Gas purging	Simple, less clogging	Incomplete removal
Liquid–liquid extraction	Organic solvent contact	High capacity	Expensive
Membrane evaporation	Selective diffusion	Smaller membrane need	Clogging occurs
Perstraction	Membrane and solvent	High selectivity	Large membrane area
Adsorption	Hydrophobic adsorbents	High uptake capacity	Desorption is tedious

Table 8 Comparison of biobutanol and other fuels properties [101, 124]; *[102]; **[125]; ***[113]

Properties	Gasoline	Biobutanol	Bioethanol
Combustion energy (MJ/dm ³)	32	29	20
Evaporation heat (MJ/kg)	0.36	0.43	0.92
RON (Research Octane Number)	91–99	96	130
MON (Motor Octane Number)	81–89	78	96
Flash Point (°C)*	–43	35	17
Fire Point (°C)*	–23	45	26
Dynamic viscosity (mPa.s)*	1.11	2.50	0.98
Calorific value (MJ/Kg)*	47	37	30
Self-ignition temperature (°C)*	280	343	363
Density at 15 °C (kg/m ³)**	750	810	795
Oxygen content (% vol)**	< 2.7	21.6	34.7
Reid vapour pressure (kPa)***	75	17	6
Flammability (% v/v)***	0.6–0.8	1.4–11.2	3.3–19.0
Viscosity (mm ² /s) at 25 °C***	0.4–0.8	1.07	2.63

of production. This is due to the elimination of cost for biomass pre-treatment and saccharification process. This process is only applicable for lignocellulosic biomass where the cellulose and hemicellulose need to convert to simple sugars before being fermented into biobutanol. The biobutanol recovery process by in situ recovery and purification process has been well accepted as a promising technique to reduce biobutanol toxicity. It was reported that the biobutanol concentration in the fermentation broth could be increased by up to 2% by conducting this technique [100].

7 Potentials of Biobutanol to Replace Gasoline

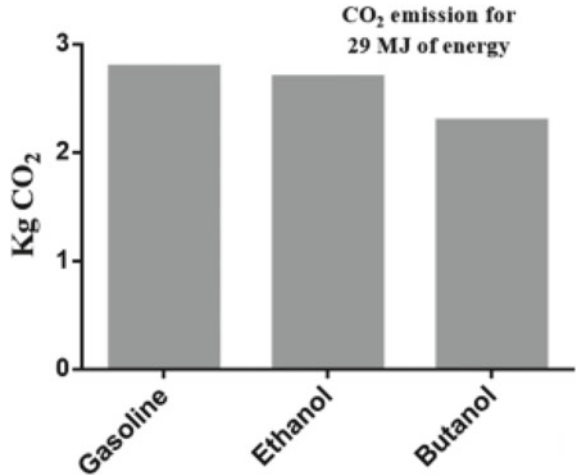
Commercially, alcohols products such as bioethanol, biobutanol and bioethanol have been used by the petrochemical industry as a fuel additive to improve their original quality. Table 8 shows the biobutanol properties in comparison with other types of fuels. According to Ha et al. [124] and Kaminski et al. [101], the properties of biobutanol are almost similar to the properties of gasoline that show its potential as fuel additives as well as biofuels. Biobutanol has high combustion energy (29.2 MJ/dm^3), low evaporation heat which enables to start motor engine easier during cold weather and decrease the ignition problems as well as is less corrosive compared to bioethanol [98]. Besides that, the low solubility of biobutanol in water decreases the possibility of groundwater pollution [122].

According to Shamsudheen et al. [102], biobutanol can be blended with gasoline up to 11.5% by volume. The application of biobutanol-gasoline blended fuel has the potential to reduce GHG emissions by 85% when compared to gasoline, therefore it is a viable and suitable alternative to gasoline. Besides that, biobutanol has lower water solubility, less corrosive nature which makes its distribution through existing pipelines comparatively easy in comparison with bioethanol and it can be blended with gasoline at a higher concentration (more than 15%) without any modification on the existing vehicle engines [98, 126]. Moreover, biobutanol contains 25% more energy than bioethanol. So that, mixtures of gasoline-biobutanol can be burned at any ratio of these two components and can also be used in pure form. Unlike bioethanol, biobutanol is less corrosive make it safe to supply, shipped and distribute using the existing pipelines system and filling stations [100].

Reid vapour pressure (RVP) is one of the important factors that need to take into consideration. This property is used to characterize the volatility and it is the industry standard practice to measure the vapour pressure. When the fuels have low RVP, it is associated with cold start problems and higher soot production, while high RVP fuels are associated with vapour lock. The issue of this vapour pressure can be controlled by the addition of fuel additives [113, 127]. From Table 8, the Reid Vapor Pressure of biobutanol is 7.5 times lower than bioethanol and 32 times lower than gasoline that shows that the volatility of biobutanol is lower and it is safer compared to gasoline and bioethanol [113].

Obergruber et al. [113] also reported that all engine fuels distributed in European Union (EU) market will comprise biocomponent to be blended with existing fuels such as gasoline. The consumption of bioethanol in the EU market is 21.90% which follows the European standard EN 228. In general, gasoline placed in the market must have a maximum oxygen content of 2.7% with an oxygen content of bioethanol is about 7.3% (v/v) and up to 11.7% (v/v) of biobutanol and 16% (v/v) in future without an engine modification. According to Hönig et al. [128], the oxygen content is kept in agreement with this standard if 12.5% volume of biobutanol is mixed with gasoline.

Fig. 3 Carbon dioxide emission for 29 MJ of energy for a different types of fuel [129]



7.1 Biobutanol Application as Engine Fuels

Although the biobutanol can be directly used as fuel either in pure form or blended with gasoline at a certain ratio, it is important to ensure that the properties of biobutanol meet the standard requirements. Exhaust emission release from engine fuels consists of undesirable combustion gases that were released and discharged into the atmosphere when the fuel combusts in the internal combustion engine. Excessive release of the gasses into the atmosphere will worsen the air quality, which can cause acid rain, health problems to humans and also cause damage to the ecosystem. The combustion gases are divided into two which nontoxic gases (nitrogen (N₂), water vapour (H₂O) and also carbon dioxide (CO₂) and toxic gasses that are very harmful such as carbon monoxide (CO) that was discharged from incomplete combustion, hydrocarbon (HC) exhibits from unburned fuel, nitrogen oxides, NO_x reveals from extra combustion temperatures, ozone (O₃) and also particulate matters (PMs). Despite that, the amounts of these emissions also depend on the engine design including operating conditions [102].

Table 9 shows the result of the emission test using SI engine using gasoline

Table 9 Emission test of SI Engine [102]

Type of gas	Biobutanol	Gasoline	Regulation value
Carbon monoxide (CO)	2.94	0.13	3.50
Hydrocarbon (HC)	4314	1212	4500
Oxygen (O ₂)	5.48	0.27	0
Carbon dioxide (CO ₂)	22.34	14.84	0

and biobutanol as fuels in comparison with regulation value. Shamsudheen et al. [102] also reported that during the road testing by riding the bike through various topographies and in varying speed conditions, a speed around 75 km/h without any issues has been achieved and its performance was found to be satisfactory. Hence, this fuel has the potential to substitute gasoline.

The combustion of 1 kg of biobutanol emits less CO₂ than that emitted by gasoline; to generate an equivalent amount of energy as that of biobutanol, a larger amount of bioethanol needs to be burned, which results in a higher amount of CO₂ emission as shown in Fig. 3 [125].

8 Other Applications of Biobutanol

Although it is well known that biobutanol has high potential as an alternative fuel, biobutanol can also be used as a feedstock to produce industrial solvents and specialty chemicals. Other than that, it also can be applied for the production of other products such as paints, coatings, resins, plasticizers, pharmaceuticals, food-grade extractants, chemical intermediates and herbicides as well as for perfume production, polymers such as butyl acrylate and butyl methacrylate [102, 129]. According to Fig. 4, statistical analysis that has been reported by Mordor Intelligence [129], biobutanol is mainly used as an intermediate for the production of butyl acrylates, which are further used in the production of paints and coatings, adhesives and textiles.

The production of paints and coatings is rising steadily in the global market, owing to its demand from construction, automotive and industrial coating applications.

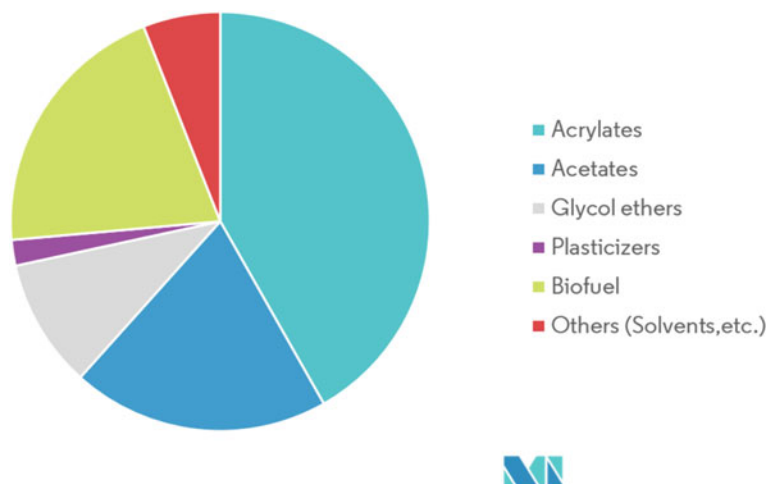


Fig. 4 Biobutanol market demand (volume share, %) by application in 2018 [129]

Besides that, adhesive demand is also rising, driven majorly by the growing construction and infrastructural activities, rising automotive production and increasing need for furniture. Butanol is also being used as a swelling agent for coating fabric in the textile industry and as an ingredient in eye make-up, lipstick and foundations in the cosmetics industry [100].

9 Conclusion

For biobutanol to be feasible to replace gasoline as an alternative fuel, the economics of the ABE fermentation process technology need to be evaluated in comparison with the fossil fuels market prices and the butanol prices available from the petrochemical industry [122]. According to Kushwaha et al. [114] and Dong et al. [130], the cost of biobutanol production from corn and soy molasses has been estimated to be \$4.41/gal and \$2.71/gal respectively. Dong et al. [130] have carried out cost analysis of biobutanol production using corn, soybean hull and soy molasses as feedstock with annual biobutanol production of 23,000 tons. It was found that biobutanol production from soy molasses is the cheapest with a production cost of \$2.71 per gallon, capital investment of \$9.1 MM and cost of the feedstock of \$10 per metric tonne.

Ibrahim et al. [100] have investigated that the cost of biobutanol production could be reduced by using low-cost feedstock as raw material like lignocellulosic biomass. However, there are still other factors that limit and lower the biobutanol yield such as pre-treatment of raw materials, low sugar concentration of lignocellulosic biomass, presence of inhibitors, strain capability and multiple end products that lead to low biobutanol concentration, yield and productivity.

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Recent Progress of Biodiesel Production



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Abstract Biodiesel is the most produced biofuel in the world. In Malaysia, biodiesel as a fuel was first introduced in the national policy in 2006. Crude palm oil (CPO) is the common feedstock for biodiesel production in Malaysia. Biodiesel is produced through transesterification, where methanol and an alkali catalyst are utilized to react with CPO, producing fatty acid methyl ester and glycerol. After subsequent downstream processes, biodiesel and glycerol are produced as the main product and by-product, respectively. The advancement of biodiesel research has resulted in many processes to produce biodiesel from various types of feedstocks. This chapter reviews biodiesel scenarios in Malaysia, covering the current biodiesel trend in Malaysia and processes in biodiesel synthesis in production plants. This is followed by the discussion on biodiesel standards and specifications for Malaysia usage. Current technologies in biodiesel production have been discussed, which consist of different types of catalysts, as well as advanced processes and technologies utilized in biodiesel synthesis. Finally, the conclusion has been drawn in the final section of this chapter.

Keywords Biodiesel · Transesterification · Palm oil · Catalyst

1 Biodiesel Trend in Malaysia

The first appearance of biodiesel in Malaysia's policy was in 2006 when the Ministry of Plantation Industries and Commodities tabled the National Biofuel Policy. The biodiesel research was led by the Malaysian Palm Oil Board (MPOB) and the Malaysian Biodiesel Association (MBA), which were established to represent the interest of the environmental-friendly biodiesel industry. Among the five thrusts listed by the ministry in the policy, biodiesel was mentioned in Thrust 1 and Thrust

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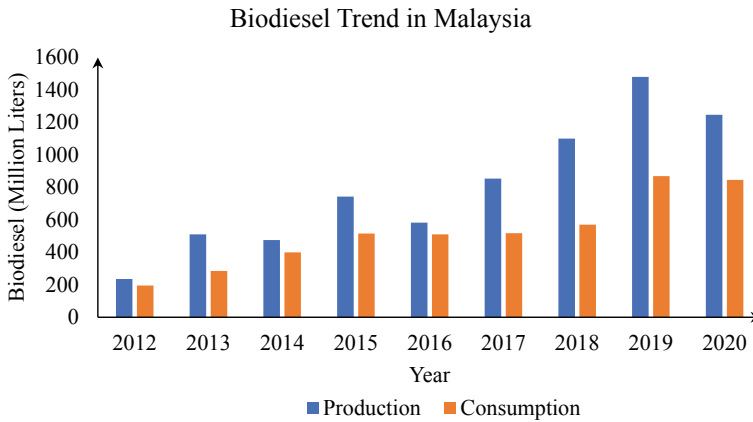


Fig. 1 Biodiesel production and consumption in Malaysia from 2012 to 2020 [2]

2. In Thrust 1 (biofuel for transport), the policy stated that diesel for land and sea transport must be in the mix of 5% processed palm oil and 95% of petroleum diesel, whereas, in Thrust 2 (biofuel for the industry), this B5 blend diesel must be used in firing boilers, construction machinery, and generators [1].

Malaysia is second to Indonesia in terms of crude palm oil (CPO) producers. Currently, CPO is a common feedstock for biodiesel production in Malaysia. Biodiesel production and consumption in Malaysia are shown in Fig. 1 [2]. Overall, the figure shows increasing trends in both production and consumption. It also shows that the local consumption of biodiesel is less than the volume of biodiesel produced, indicating that the surplus volume is not for Malaysia's consumption.

Malaysia has numerous biodiesel plants located mostly in Peninsular Malaysia, such as Vance Bioenergy Sdn. Bhd., PGEO BioProducts Sdn. Bhd., Nexsol (Malaysia) Sdn. Bhd., Sime Darby Oils Biodiesel Sdn. Bhd., IOI Bioenergy Sdn. Bhd., and KLK Bioenergy Sdn. Bhd. [3]. There was an integration of renewable energy into the energy fuel mix since 2020 when Malaysia introduced the Fifth Fuel Policy under the Eighth Malaysia Plan [4].

Biodiesel is recognized globally as an environmentally friendly fuel, and its consumption increased exponentially over the last decade [5]. As a result, the export of biodiesel becomes an important commodity in Malaysia. Figure 2 shows the statistics of Malaysia's biodiesel export volumes by the Department of Statistics Malaysia. Singapore is the top country for Malaysia's biodiesel export in Asia countries from the year 2019 to 2021 with an export value of 8609 MT, followed by China (6513 MT), Vietnam (210 MT), Thailand (1.5 MT), and Indonesia (0.78 MT) [6]. [7] reported that China is the largest biofuel producer in Asia. When the European Parliament (EP) decided to ban palm oil-derived biodiesel in 2018, there was a significant decrease in biodiesel export. However, based on increasing trends in both export values and biodiesel consumption, biodiesel is expected to continue receiving attention in ASEAN countries. The increasing trend in energy demand due

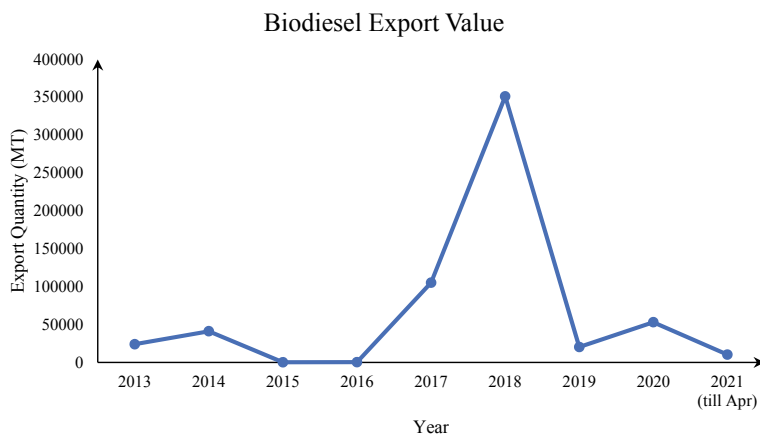


Fig. 2 Biodiesel export in Malaysia

to industrialization and the growing population in Malaysia may lead to fossil fuel depletion in the next 40 years [7]. Thus, in 2020, Malaysia introduced the mandate for the transport sector to manufacture biofuel with a 20% palm oil component (B20). In conjunction with the COVID-19 pandemic, Malaysia delayed the B20 palm oil biodiesel mandate to prioritize economic recovery [8]. However, the implementation of B20 biodiesel is still ongoing in Langkawi, Labuan, and Sarawak.

Edible and non-edible oils can be utilized as the feedstock for biodiesel production, including vegetable oil, waste animal oil, and waste cooking oil. The research of converting soapstock into biodiesel has received much interest worldwide. Currently, some local design companies, such as JJ-Lurgi Engineering Sdn. Bhd. and Oiltek Sdn. Bhd., are working to design biodiesel plants that utilize acid oil as the raw material [3]. Soapstock is the by-product of edible oil's chemical refining process that undergoes acidulation to split the soapstock into acid oil and acid water. Acid oil contains numerous fatty acid chains that are feasible to be used in biodiesel production.

Biodiesel production in local production plants is relatively simple, which uses sludge oil from palm oil mills as the primary feedstock. Used cooking oil is collected from domestic use and food and beverage industries, such as fast-food outlets and restaurants that produce feedstock for biodiesel production. Due to limited feedstock supply, the production is limited to about 20 tons per day [3]. In a general overview of biodiesel production, the pre-treatment process consists of raw material conditioning, where the feedstock is washed using a centrifugal separator and stored in a feed tank. In the production process, the feedstock is transferred to a reaction vessel. Methanol is simultaneously pumped into a vessel through nozzles and reaction temperature is controlled at about 60–70 °C under vacuum conditions. The reaction vessel is equipped with a recirculation pump that acts as an agitator, which continuously pumps the mixture and sprays into the vessel at different elevations. It provides sufficient mixing and mitigates the corrosion issue due to the properties of methanol.

The methyl ester produced is periodically sampled for quality records of iodine value (IV) and free fatty acids (FFAs). Excess methanol with a density of about 70–85% is collected in a vacuum system, where it will be further recovered in a methanol distillation column and recycled into the process [3]. Approximately 10% of used vegetable oil will be added to the storage tank and mixed with the biodiesel produced. Experimental results have proven that the mixing of used vegetable oil and biodiesel as the final product will produce comparable performance characteristics (i.e., oxygen content and calorific value) as compared to diesel fuel [9]. Before dispatch or delivery, the product will undergo a washing process, where the washed water at the bottom of the tank will be discharged to a wastewater treatment system and the oil with low density will be dispatched. Besides sludge oil, other biodiesel plants use palm fatty acid distillate as the feedstock [3].

2 Biodiesel Standards and Specifications for Malaysia Usage

The quality and applicability of biodiesel are governed by relevant standards and specifications. It is important to ensure that biodiesel is produced based on the requirement to ensure that its quality matches the expectation of end-users. The Standard and Industrial Research Institute of Malaysia (SIRIM) established the quality standards for biodiesel produced from palm oil in Malaysia in 2008 [10]. The European Standards (EN 14,214) has been the reference for producing Malaysia Biodiesel Standards (MS 2008:2008). Table 1 compares some biodiesel specifications between MS 2008:2008 and EN 14,214. There is not much difference between these standards, except for MS 2008:2008 which does not specify the value for cloud point. This is

Table 1 Biodiesel specification based on the standards used by Malaysia and the European Union [10]

Property	Units	MS 2008:2008	EN 14,214
Kinematic Viscosity @ 40 °C	mm ² /s	3.5–5.0	3.5–5.0
Density @ 15 °C	kg/m ³	860–900	860–900
Flash Point	°C	120 min	120 min
Cloud Point	°C	-	Location and Season Dependent
Total Acid Number	mg KOH/g	0.5 max	0.5 max
Cetane Number	-	51 min	51 min

Table 2 Properties of palm oil biodiesel and conventional diesel [11]

Property	Palm Oil Biodiesel	Diesel
Kinematic Viscosity @ 40 °C (mm ² /s)	4.56	2.28
Density @ 15 °C (g/mL)	0.877	0.827
Flash Point (°C)	196	64

because Malaysia does not experience cold weather that can lead to the formation of wax crystals in biodiesel, hence affecting biodiesel properties.

[11] compared the characteristics of biodiesel produced from palm oil via transesterification with conventional diesel. The chemical composition of the samples was determined using gas chromatography-mass spectroscopy. The properties of palm oil biodiesel and conventional diesel are presented in Table 2. From the table, all properties of palm oil biodiesel exceeded the properties of conventional diesel. Furthermore, by comparing the properties of palm oil biodiesel with the specified standards of MS 2008:2008 in Table 1, it can be said that palm oil biodiesel is suitable to be used in the local market.

3 Current Technologies in Biodiesel Production

Biodiesel, which can be produced from vegetable oils, is a suitable alternative to conventional diesel fuel. Vegetable oils are used as feedstocks for biodiesel production. However, vegetable oils cannot be used directly in diesel engines due to their high viscosity, and this characteristic can affect the performance of diesel engines, resulting in poor combustion. Therefore, vegetable oils need to be converted into biodiesel prior to use in diesel engines.

A common method to produce biodiesel is transesterification. In this process, triglycerides are converted into biodiesel in the presence of alcohol and a catalyst. The main product and by-product of transesterification are biodiesel and glycerol, respectively. The use of excess alcohol is preferred because transesterification is an equilibrium reaction. Hence, the reaction is pushed toward the product side, producing a higher biodiesel yield.

3.1 Catalysts

Catalysts are vital in biodiesel production. A catalyst accelerates a chemical reaction, but it is neither consumed nor permanently changed in the reaction. The presence of a catalyst allows transesterification to be conducted at moderate operating conditions with high biodiesel yield. In transesterification, the reaction rates increase in the presence of a catalyst; subsequently, the activation energy is lowered, hence initiating

transesterification. Various types and forms of catalysts have been studied to assist biodiesel production.

i. Homogeneous Catalysts

Homogeneous catalysts are conventional catalysts used for biodiesel production, which are in the same phase as the reactants and products. These catalysts can be divided into base and acid catalysts. Common homogeneous base catalysts are sodium hydroxide (NaOH) and potassium hydroxide (KOH). On the other hand, sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) are homogeneous acid catalysts used for biodiesel production. Despite excellent catalytic activities displayed by NaOH and KOH (e.g., high biodiesel yield and minimum reaction time), the formation of water as a by-product reduces the effectiveness of the process by lowering biodiesel yield [12].

Furthermore, feedstock containing high FFA amounts reduces the effectiveness of homogeneous base catalysts. Biodiesel yield is reduced as soap is produced via saponification due to the reaction between FFA and the catalysts. Due to this drawback, acid catalysts are more suitable for biodiesel production using feedstock containing a high percentage of FFA, such as H_2SO_4 and HCl. Water is the by-product of FFA esterification, with FAME as the main product. Esterification is usually conducted prior to transesterification if the feedstock has a high FFA level. Nevertheless, the use of acid catalysts is disadvantageous in terms of equipment susceptibility to corrosion problems and severe operating conditions are required for high biodiesel yield (e.g., high temperature and high catalyst concentration) [13].

ii. Ionic Liquids

Ionic liquids (ILs) have become the potential candidate in the search for greener catalysts in biodiesel synthesis. The utilization of ILs as solvents in biodiesel synthesis has been reviewed by Mohammad Fauzi and Amin [14]. Various combinations of cations and anions can be applied for producing, and commonly used cations and anions in ILs are presented in Fig. 3. One of the significant advantages of ILs is their recyclability in biodiesel synthesis, which shows excellent performance in subsequent runs of transesterification using recycled ILs even after several cycles. This property of ILs reduces production costs due to their recyclability, hence cementing their role as green catalysts for biodiesel production. Moreover, ILs can also be used as solvents for enzyme-catalyzed transesterification and catalyst supports, depending on the cations and anions present in ILs.

The immobilization of a bifunctional Brønsted-Lewis acidic IL on a magnetic support $Fe_3O_4@SiO_2$ was conducted for biodiesel production using *Koelreuteria integrifoliola* oil, which is a non-edible feedstock with a high acid value [15]. The biodiesel yield reached 93.7% at optimum conditions and in the presence of the catalyst. A magnet was used to separate the catalyst from the reactants after the completion of transesterification owing to the strong magnetization of the catalyst. In another study, the immobilization of an acidic IL sulfonic acid functionalized imidazolium hydrogen sulfate on the acidic organic-inorganic hybrid mesoporous material was performed using chemical grafting to produce a Brønsted-Lewis acidic

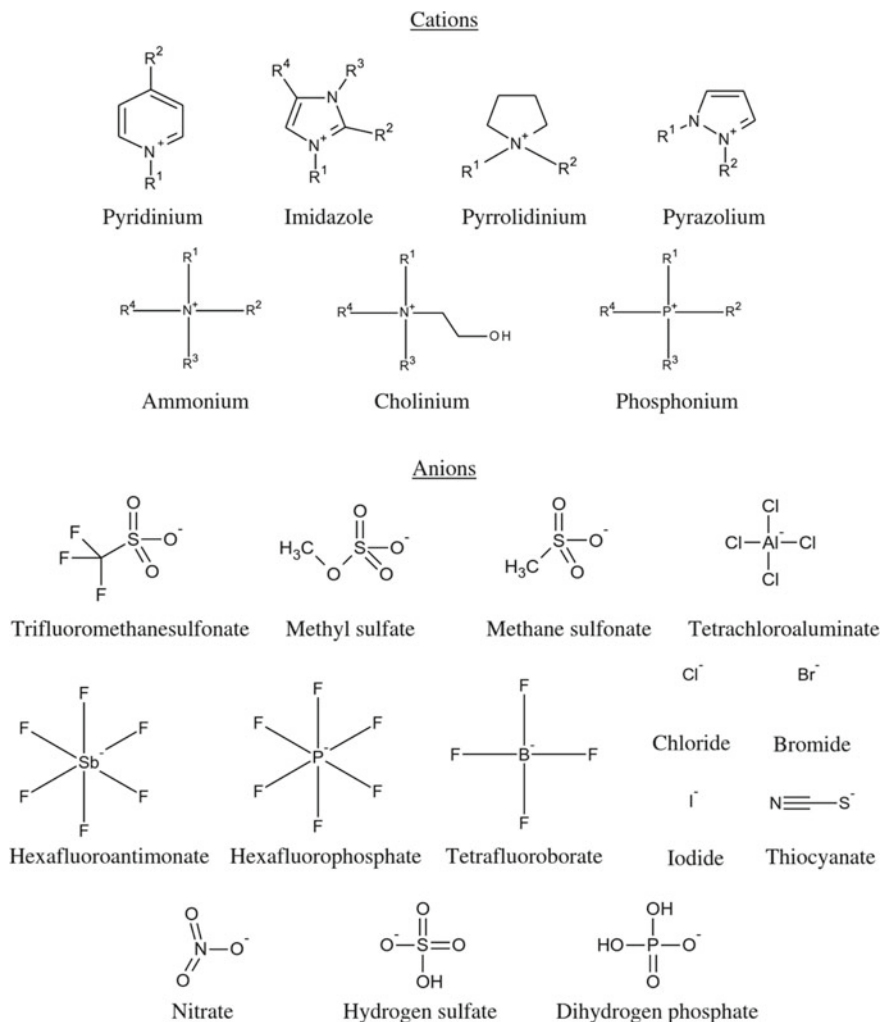


Fig. 3 Commonly used cations and anions in ionic liquids [14]

IL for biodiesel synthesis with soybean oil as the feedstock [16]. The biodiesel yield at optimum conditions was 98.9%. The catalyst possessed good acid–water resistance, which helped the catalyst maintain its catalytic activity for five subsequent cycles, where the biodiesel only dropped by 3.77% from the first to the fifth cycle, highlighting its ability to maintain high catalytic activity after recycling. Hosseini, Moradi, and Bahrami [17] converted soybean oil into biodiesel using a novel basic IL (chlorocholine hydroxide) prepared and immobilized on boehmite nanoparticles. The hydroxyl groups on the boehmite surface enhanced the basicity of the hybrid catalyst. A biodiesel yield of 95.2% was obtained by conducting transesterification

at 60 °C, compared to transesterification using acidic ILs that need to be conducted at higher temperatures to achieve high biodiesel yield.

iii. Heterogeneous Catalysts

Although homogeneous catalysts offer several advantages in biodiesel synthesis (e.g., such as low costs and high reactivity), homogeneous-catalyzed transesterification requires further stages of separation and washing after the reaction ends due to the same phase of the homogeneous catalysts and the reactants. Hence, the separation of the catalysts increases biodiesel production costs due to additional separation steps. The utilization of heterogeneous catalysts in transesterification can overcome this problem as the catalysts do not mix with the reactants during transesterification. The use of heterogeneous catalysts offers several advantages, including minimum wastewater generation during the reaction, catalyst recyclability, high glycerol purity, and easier separation from the reactants [12]. Even though heterogeneous catalysts require a longer reaction time than homogeneous catalysts, heterogeneous-catalyzed transesterification is economical as the catalysts are reusable in both batch and continuous processes with simple catalyst separation.

The utilization of heterogeneous catalysts for biodiesel synthesis was reviewed by Rizwanul Fattah et al. [18]. A heterogeneous base catalyst can be used to overcome the saponification problem during transesterification that complicates the separation of biodiesel from glycerol. Among the heterogeneous base catalysts that have been studied include alkaline earth and metal-based catalysts (e.g., magnesium oxide [MgO] and calcium oxide [CaO]), mixed metal-based catalysts (e.g., zirconium oxide [ZrO₂]), transition metal-based catalysts (e.g., zinc oxide [ZnO] and titanium oxide [TiO₂]), and hydrotalcite-based catalysts. Meanwhile, heterogeneous acid catalysts are less corrosive and toxic than homogeneous acid catalysts, with the former containing either Brønsted or Lewis acidity of different strengths. Studies on ion-exchange resins, heteropoly acid derivatives, sulfonic acid-based catalysts, and sulfated oxide-based catalysts have been conducted for heterogeneous acid catalysts in biodiesel production. Bifunctional solid catalysts have also been considered for catalyzing transesterification, where the catalysts have the dual functionality of a solid catalyst to deal with FFA content and a base catalyst to assist the conversion of triglycerides to biodiesel [12].

iv. Biomass-based Heterogeneous Catalysts

Recently, biomass-based solid catalysts have received much attention from researchers in transesterification and esterification for biodiesel production. Both base and acidic biomass-based catalysts have been studied to evaluate their performance in biodiesel synthesis, and the comparison is shown in Table 3. The cost to produce biodiesel can be reduced as the catalysts can be produced from renewable sources, and the catalysts are also non-toxic and widely available. Natural biological sources containing calcium and carbon have the potential for developing biomass-based heterogeneous catalysts. Waste shells are an excellent source of biomass for producing heterogeneous catalysts due to the presence of calcium carbonate (CaCO₃). Upon calcination at high temperatures, CaCO₃ is converted into CaO,

Table 3 Biodiesel synthesis using biomass-derived heterogeneous catalysts

Type of Biomass	Chemical Impregnation/Sulfonating Agent	Type of Feedstock	Optimum Transesterification/Esterification Conditions			FAME Y or C (%)	References
			T (°C)	t (h)	CL (wt. %)		
Egg Shell Waste	-	<i>Chlorella vulgaris</i> Biomass	70	3	1.39	10:1	92.03 (Y) [19]
Waste Snail Shell	-	Soybean Oil	25	2	3.00	6:1	98.00% (Y) [20]
Chicken Bone	Lithium Nitrate	Canola Oil	60	3	4.00	18:1	96.60% (C) [21]
Cork Biochar	Conc. H ₂ SO ₄	Waste Cooking Oil	65	6	1.50	25:1	98.00% (C) [22]
Oil Palm Empty Fruit Bunch	4-Benzenediazomium Sulfonate	Palm Fatty Acid Distillate	110	7	20.00	30:1	98.1% (Y) [23]
Coconut Coir Husk	Conc. H ₂ SO ₄	Waste Palm Oil	130	3	10.00	12:1	89.8% (Y) [24]

(T: temperature, t: time, CL: catalyst loading, MTOR: methanol-to-oil ratio, Y: yield, C: conversion)

which is a highly active base for biodiesel production. Chemical impregnation can be performed on base biomass-based catalysts to further enhance their catalytic activity, such as impregnation with NaOH and KOH. Acidic biomass-based heterogeneous catalysts can be produced via carbonization and pyrolysis, depending on the type of biomass used. The catalysts are often synthesized with sulfonating agents to increase their catalytic activity for biodiesel production. Concentrated H_2SO_4 is commonly used as the sulfonating agent due to the strong sulfonic acid sites ($-SO_3H$) provided for biomass-based heterogeneous catalysts.

3.2 Advanced Processes and Technologies

There are several disadvantages of conventional transesterification, such as harsh operating conditions, particularly those involving heterogeneous catalysts, and also excessive use of alcohols to drive forward the chemical equilibrium of transesterification toward the biodiesel. Numerous advanced processes and technologies have been studied and developed by researchers worldwide to overcome these drawbacks. Moreover, efforts have been made to enhance the feasibility of biodiesel production without affecting biodiesel productivity, including conducting biodiesel reaction and separation in a single unit, enhancing reactant solubility in transesterification, and improving operating conditions of conventional transesterification.

v. Reactive Distillation

Reactive distillation (RD) combines both chemical reaction and separation within the same apparatus. The technology utilizes a reactor for conducting chemical reactions and a distillation column for separating products in a single unit; thus, the technology offers low capital and operational costs due to the absence of additional operating units for the biodiesel separation step. Furthermore, this approach is useful for equilibrium-limited reactions, particularly transesterification, where this reaction is reversible; hence, the equilibrium needs to be shifted to the desired side (i.e., product) using an excess of reagent or by removing a volatile product via distillation. Among the important parameters for this technology are the number of total and reactive trays, as well as reboiler duty [25]. The reaction temperature increases with the increase of reboiler heat duty, which subsequently increases the transesterification reaction. Meanwhile, the number of total trays is vital for biodiesel purity. The residence time is influenced by the number of reactive trays, subsequently giving a positive effect on biodiesel synthesis.

Pradana, Hidayat, Prasetya, and Budiman [26] loaded potassium on activated carbon to synthesize a hybrid heterogeneous catalyst for biodiesel synthesis in an RD. The catalyst was chosen as it is environmentally friendly, low cost, and easy to be regenerated. The schematic diagram of the continuous RD used is presented in Fig. 4. In this study, palm oil was used as the raw material and methanol was used as the alcohol. Based on the parametric study involving reaction temperature, biodiesel conversion increased with temperature and time, and the highest conversion recorded

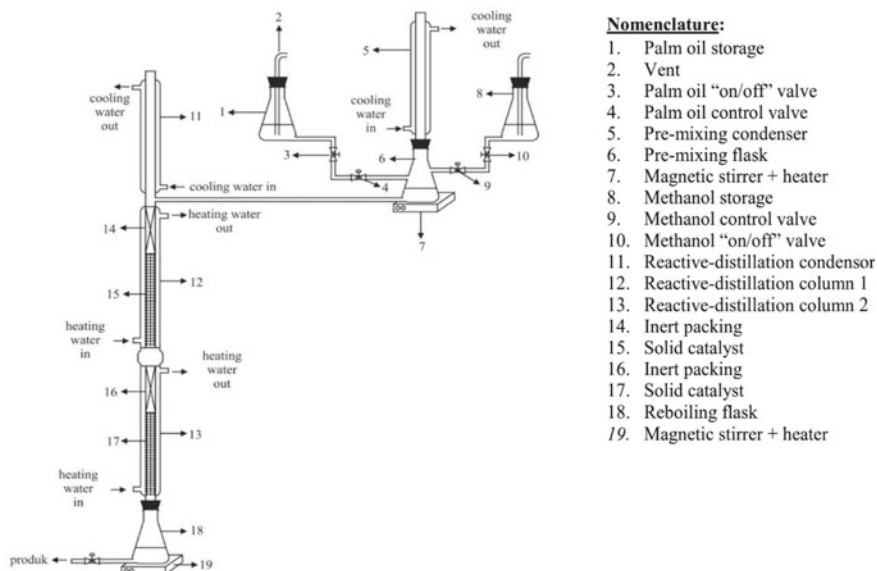


Fig. 4 Schematic diagram of continuous reactive distillation [26]

was 82.7%, which occurred at 60 °C. Higher reaction temperature increased palm oil conversion to biodiesel. However, the boiling point of methanol (65 °C) should be considered, as conducting the reaction above this temperature lowers the reaction rate as a result of methanol vaporization. Meanwhile, the highest conversion was observed for the methanol-palm oil molar ratio of 8:1.

Boon-anuwat, Kiatkittipong, Aiouache, and Assabumrungrat [27] utilized Aspen Plus® to simulate conventional transesterification in a continuous stirred tank reactor (CSTR) and RD in an RD column in the presence of homogeneous and heterogeneous catalysts. Soybean oil was chosen as the raw material in the process, with methanol as the alcohol. Sodium hydroxide and magnesium methoxide ($\text{Mg}[\text{OCH}_3]_2$) were used as the homogeneous and heterogeneous catalysts, respectively. For the homogeneous catalyst, RD recorded higher biodiesel purity and yield (97.3 wt. % and 98.3%, respectively) than the conventional process (96.8 wt. % and 97.9%, respectively). Furthermore, RD outperformed the conventional process for the application of the heterogeneous catalyst, where RD recorded biodiesel purity and yield of 97.0 wt. % and 97.5%, respectively, and the conventional process obtained biodiesel purity and yield of 98.2 wt. % and 92.7%, respectively. In terms of the energy required to produce a ton of biodiesel, the lowest energy required (153.0 kWh/ton biodiesel) was achieved by RD with $\text{Mg}(\text{OCH}_3)_2$, followed by RD with NaOH (183.2 kWh/ton biodiesel), conventional process with NaOH (368.6 kWh/ton biodiesel), and conventional process with $\text{Mg}(\text{OCH}_3)_2$ (829.5 kWh/ton biodiesel).

Mondal and Jana [25] simulated the feasibility of RD in algal oil conversion to biodiesel and compared the performance of the RD approach with a conventional

multi-unit system (i.e., CMS). The RD column behaviour was studied through the non-equilibrium stage approach, where the column consisted of a condenser at the top and a reboiler at the bottom. Meanwhile, the CMS is composed of a CSTR and a distillation column as separate units. From the simulation conducted using the MATLAB environment, the RD column achieved a higher algal oil conversion (i.e., 99%) than the CMS, and the molar compositions of biodiesel were nearly identical for both methods. Moreover, the CMS recorded an increase of 57.28% in capital investment compared to the RD column as the conventional distillation column consisted of more trays and a higher cost for installing a reactor. Furthermore, the operating cost increased by 40.14% compared to the RD column. A 40.11% reduction in the emission level of carbon dioxide (CO₂) was observed for the RD column, highlighting the potential of the column in reducing CO₂ emission to the atmosphere from fossil fuel combustion to operate the column.

vi. Supercritical Process

Triglycerides and alcohols are poorly miscible under normal conditions, limiting transesterification of feedstock into biodiesel. In this situation, more alcohols are used so that the equilibrium moves to the right (i.e., product side). This problem can be overcome with the utilization of supercritical fluids. A supercritical state is achieved when the pressure and temperature of the fluid exceed the critical temperature and pressure. The excellent solubility of supercritical fluids enhances the reaction rate of transesterification as the reactants dissolve in the fluid.

Supercritical carbon dioxide (SCCO₂) was implemented to synthesize biodiesel from soy sauce residue [28]. In this study, SCCO₂ was applied instead of the supercritical methanol approach as the alcohol requires a great deal of energy to achieve and sustain its supercritical state, thus limiting its large-scale applications. Biodiesel yield increased from 40 °C to 100 °C, but the yield decreased to 110 °C. A higher temperature enhanced the solubility of SCCO₂ with oil and methanol, improving the transesterification rate. However, the SCCO₂ solubility dropped at 110 °C due to the sharp decrease of SCCO₂ density; hence, less methanol and oil dissolved in SCCO₂ at this temperature, leading to decreased FAME yield. Biodiesel yield also increased with increasing pressure from 8 to 18 MPa, but there was not much difference in the yield for the reaction conducted at 16 MPa and 18 MPa. The density of SCCO₂ increased with increasing pressure, allowing more reactants to dissolve in SCCO₂. Moreover, SCCO₂ outperformed supercritical methanol transesterification for biodiesel production as the latter needs to be conducted at more extreme conditions (i.e., 425 °C and 30 MPa) to obtain higher biodiesel yield.

In-situ transesterification was conducted using *Schizochitrium limacinum* as the feedstock in the presence of various methylating agents (i.e., methyl acetate, methanol, and dimethyl carbonate) for biodiesel production [29]. The study also evaluated the reaction kinetics of transesterification for each methylating agent. The increase of methanol-to-algae ratio and pressure increased the conversion of microalgae to biodiesel, with the optimum parameters of 10:1 and 20 MPa, respectively. A higher inhibition of reaction was observed as the methanol used exceeded the methanol-to-algae ratio of 10:1, reducing the conversion to biodiesel. Meanwhile,

Table 4 Reaction rate constant and activation energy values for biodiesel production from *Schizochitrium limacinum* using different methylating agents [29]

Methylating agent	Reaction rate constant (s^{-1})	Activation energy (kJ/mol)
Methanol	5.0×10^{-4} – 9.7×10^{-4}	62.7
Dimethyl Carbonate	1.9×10^{-4} – 4.4×10^{-4}	56.6
Methyl Acetate	1.0×10^{-4} – 3.2×10^{-4}	54.0

there was an insignificant increase in biodiesel conversion as the pressure exceeded 20 MPa. The maximum temperature recorded for the microalgae and methanol system was 270 °C. Meanwhile, for the systems involving dimethyl carbonate and methyl acetate, the maximum temperature was 400 °C, where degradation occurred beyond this temperature. The reaction kinetic study considered the irreversible first-order kinetic model for all methylating agents for biodiesel conversion at optimum conditions, and the results are presented in Table 4. From the table, it can be concluded that methanol is the most preferred methylating agent in this study based on the highest reaction rate constant and activation energy.

Aghilinategh, Barati, and Hamadianian [30] produced biodiesel from *Chlorella vulgaris* using in-situ supercritical methanol in the presence of calcium oxide/titanium dioxide (CaO/TiO_2) as the nano-photocatalyst and subcritical water as the co-solvent. CaO was selected as the catalyst in this study. The sol-gel method was used for the preparation of the TiO_2 nano-catalyst, followed by the synthesis of CaO/TiO_2 by the photochemical method. Meanwhile, the microalgae cell wall can be disrupted using subcritical water, hence providing a more homogeneous medium for a higher reaction rate. Figure 5 illustrates the setup used for biodiesel synthesis. From the catalyst characterization, CaO/TiO_2 was successfully synthesized, and CaO did not leach at high temperature and pressure conditions due to the good attachment

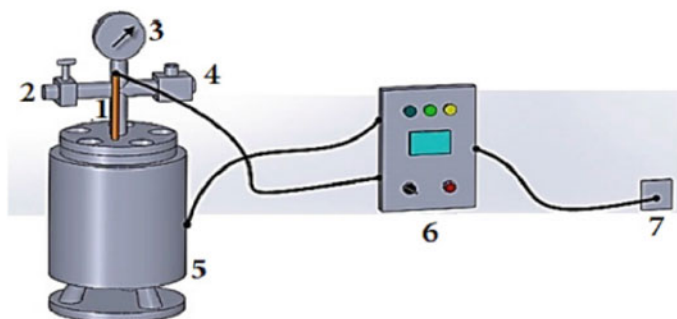


Fig. 5 The setup for biodiesel synthesis via in-situ supercritical methanol approach [30]; (1) Thermocouple, (2) outlet valve, (3) high-pressure gauge, (4) relief valve, (5) electric furnace, (6) power board, and (7) power outlet

of CaO to TiO₂, hence preventing the release of CaO into the product. From the results, the biodiesel yield for the transesterification conducted using CaO/TiO₂ was higher than the transesterification performed without the catalyst. Furthermore, the use of subcritical water and CaO/TiO₂ achieved the highest biodiesel yield among other experiments conducted. The catalytic activity of CaO and biodiesel yield could be enhanced even when a little water was used, as water could make the reaction medium homogeneous by dissolving the microalgae biomass and facilitate the mass transfer on the catalyst surface, thus enhancing transesterification and producing more biodiesel yield.

vii. Ultrasonic-Assisted Process

One of the limitations of conventional transesterification is the mass transfer limitation between reactants in the system due to the immiscibility of triglycerides and alcohol. An approach to overcome this limitation is by applying ultrasonic irradiation. The mixing efficiency between reactants can be improved using ultrasound within the frequency range of 20 kHz–2 MHz, where microbubbles are produced due to the cavitation effect [31]. The interfacial contact between the immiscible triglycerides and alcohol improves significantly due to microbubble formation, leading to an enhanced reaction rate of transesterification. Among the advantages of ultrasonic-assisted transesterification include shorter reaction time, lower alcohol-to-oil molar ratio, lower energy consumption, and higher reaction rate and conversion [32]. In addition, ultrasound-assisted transesterification can be carried out at lower temperatures than conventional transesterification to achieve high biodiesel yield due to the lower activation energy required to initiate the reaction.

Heterogeneous nano-magnetic catalysts were applied for biodiesel synthesis via ultrasonic-assisted transesterification of rapeseed oil [32]. In the study, ultrasonic radiation was used to enhance the transesterification reaction by conducting the experiment in an ultrasonic bath (power = 1 kW and frequency = 37 kHz). The catalysts (Li/Fe₃O₄ and Li/ZnO-Fe₃O₄) were prepared prior to biodiesel production, and from the results of the vibrating sample magnetometer, both catalysts showed the magnetic properties originating from Fe₃O₄, allowing better recovery via magnetic separation to avoid loss of catalyst. The highest biodiesel yield obtained for both catalysts was 99.8%, which was conducted for 34 min with 0.8% catalyst loading and the methanol-to-oil ratio of 12:1. This result highlights the significance of ultrasonic radiation, where the biodiesel yield of only 57.7% was recorded when the experiment was carried out at similar conditions but in the absence of ultrasonic radiation. Furthermore, ultrasonic-assisted transesterification requires a shorter reaction time (35 min) and lower temperature (35 °C) compared to conventional transesterification that is usually conducted in 60 min and at 65 °C to achieve high biodiesel yield.

Masri et al. [31] performed ultrasonic-assisted esterification of oleic acid in the presence of dicationic acidic ionic liquid (DIL) as the catalyst. The novel acidic DIL [CF₃SO₃]₂ was prepared prior to esterification, which contained trifluoromethane sulfonate as the anion and SO₃H-functionalized acidic group as the cation. Esterification of oleic acid was also conducted via conventional mechanical stirring for comparison purposes. From the results, the conversion of oleic acid achieved 89%

for ultrasonic-assisted esterification and 59% for conventional mechanical stirring, highlighting the high conversion obtained in the presence of ultrasonic irradiation. Furthermore, continuous ultrasonic irradiation was more significant for biodiesel conversion than pulsed ultrasonic irradiation as less mixing effect occurred in the latter due to less power supplied by ultrasound, hence hindering a good and rapid conversion. The optimization of oleic acid esterification was conducted using response surface methodology (RSM). Based on the optimization performed, the optimum conditions of temperature, reaction time, methanol-to-oil molar ratio, and catalyst amount of 59 °C, 83 min, 14.3:1, and 0.64 mol%, respectively, achieved 93.3% of conversion. Another added advantage of this process is the recyclability of $\text{DIL}[\text{CF}_3\text{SO}_3]_2$, where an insignificant reduction of conversion was observed when the catalyst was used in the subsequent reaction, which decreased from 93.11% in the first cycle to 89.03% in the fifth cycle.

Biodiesel production via in-situ transesterification has been reported extensively from 2010 onward [33–35]. One of the current in-situ reactive extraction of castor seeds was conducted by Thakkar, Shah, Kodgire, and Kachhwaha [36] for biodiesel production under ultrasound-microwave irradiation. Biodiesel production was assisted by microwave irradiation as the approach allowed a shorter reaction time to be applied than the conventional method. A hybrid reactor was used to supply ultrasound and microwave energy simultaneously. Meanwhile, the transesterification reaction was catalyzed by KOH and RSM was applied for the optimization of process parameters. Based on the predicted optimum yield, $93.5 \pm 0.76\%$ biodiesel was obtained by validating the optimum conditions, which was achieved at the methanol-to-oil molar ratio, catalyst amount, reaction temperature, and reaction time of 350:1, 1.74 wt. %, 43 °C, and 30 min, respectively. From the kinetic study conducted, the activation energies for in-situ ultrasound-microwave-assisted transesterification in the hybrid reactor and transesterification via conventional mechanical stirring were 28.27 and 38.92 kJ/mol, respectively. This finding highlights the ability of the in-situ process to provide lower activation energy in transesterification, hence enhancing the reaction rate. Moreover, from the castor oil extraction test, the in-situ hybrid system needed shorter time (1800 s) to achieve the extraction yield of 48–49% than the mechanical stirring system (2400–3000 s) for the extraction yield of 45–46%. This justifies the benefits of mass transfer enhancement due to the presence of ultrasound in the hybrid system.

4 Conclusion

The utilization of biodiesel as Malaysia's transportation fuel has been reviewed in this chapter. Malaysia is blessed with palm oil, which is the main feedstock for biodiesel production for this country. As the second-largest producer of palm oil in the world after Indonesia, the abundance of palm oil should be utilized for sustainable local production of biodiesel. Furthermore, palm oil biodiesel is suitable to be used in the local market because its properties meet the standards specified for Malaysia

usage (i.e., MS 2008:2008). Different types of catalysts, ranging from conventional homogeneous and heterogeneous catalysts to novel catalysts, including ionic liquids and biomass-based catalysts, offer various advantages for biodiesel synthesis. The presence of catalysts allows biodiesel to be synthesized in less harsh conditions. Moreover, advanced processes and technologies for biodiesel production improve the operating conditions of conventional transesterification, and the application of these technologies produces biodiesel with high yield and conversion. In conclusion, the availability of palm oil, coupled with the utilization of novel catalysts and advanced technologies, should be able to increase biodiesel production locally, thus highlighting biodiesel as Malaysia's transportation fuel.

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Critical Appraisal of Anaerobic Digestion Processes for Biogas



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Abstract Anaerobic digestion (AD) is a unique fermentation process that involves the bioconversion of waste materials to renewable energies catalysed by different microorganisms. Multiple AD techniques have been widely applied in different countries to convert wastewater, livestock manures and lignocellulosic materials (i.e. agro-industrial residues) into renewable biogas fuels (i.e. biohydrogen, biomethane and bioethanol). Among the different microbial conversions of organic biomasses, AD represents a green and economical choice owing to its efficiency in the carbon recovery process. Despite the escalating application of AD systems worldwide and the fast-developing fermentation technologies, several features including substrate pre-treatments, microbial strain selection and bioreactor configurations remain as a major challenge for its maximal application. This chapter aimed to provide a general overview regarding the AD system and its technical limitations as well as the potential of AD application in electricity generation, particularly in Malaysia.

Keywords Anaerobic digestion · Renewable resources pre-treatments · Biomass conversion · Bioprocessing · Affordable and clean renewable energy

1 Introduction

Anaerobic digestion technology has existed since the past few centuries and is considered as a useful technology for the generation of renewable energy and provides means to carter problems that arise due to low access to energy. Efficient conversion of organic matter in anaerobic digestion (AD) may be useful to form a combustible constituent called as biogas [1, 2], which is obtained from AD typically has a methane

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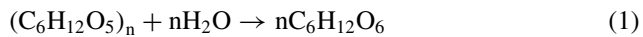
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content of 50–60% meanwhile if CH₄ achieve 55% content, the upper calorific value of 6.0 KWh/m³ at standard temperature and pressure (STP) [3]. There are several parameters that govern the production of biogas including pH, temperature, moisture content, substrate, nutrients, retention times, feeding modes and reactor configuration. Typically, these factors are optimized in a closed reactor tank or also known as a digester, wherein the biodegradation of separated waste is conducted. A proper digester is not only essential to ensure the optimum condition for the AD process, but it will also directly influence the final CH₄ yield. In Malaysia, AD is widely applied for commercialization purposes in palm oil mill industries of which palm oil mill effluent (POME) is converted into biogas through the anaerobic process [4]. The utilization of renewable biogas does not only benefit large-scale society, but it may also overcome some environmental issues including global warming as well as climate change. These issues will be further discussed in this chapter.

2 Background of Anaerobic Digestion

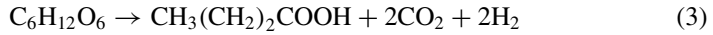
2.1 Hydrolysis Process

Fundamentally, hydrolysis is formed by a chemical reaction that occurs between H⁺ and OH⁻ which involves the breakdown of water. This process is often used to catalyze the breakdown of larger polymers such as organic polymers into soluble monomers. For example, in waste biomass digestion, cellulose is hydrolysed to release monomers i.e. glucose via enzymatic reactions [5]. This phenomenon is facilitated by hydrolytic bacteria [2] as interpreted in Eqs. (1) below [1]. As revealed by [6], hydrolysis is not the limiting step in solid anaerobic digestion but the mechanism behind that plays an important role in the process via the utilization of acetate, propionate, butyrate and glucose.



2.2 Acidogenesis Process

The second process in anaerobic digestion is performed by acidogenic bacteria that will ferment the product formed by the hydrolytic reaction to organic acids including volatile fatty acid (VFA) with hydrogen being produced as a by-product [2]. Equations (2) and (3) exemplified the reaction that occurs through degradation and conversion to VFA, ethanol and H₂ by acidogenic bacteria [1, 7]. During fermentation in the digestive tank, this bacterium accumulates in an acidic environment while creating ammonia [8].



2.3 Acetogenesis Process

The intermediate products such as lactate, ethanol, propionate and butyrate process will be further oxidized by acetogenic bacteria to more—reduced, to acetate and H_2 [2, 8]. Equations (4) and (5) below represent the stage of acetogenesis, in which products of the acidic phase are converted into acetate (CH_3COO^-) and hydrogen (H_2) [1, 7]. Most acetogenic bacteria are gram-positive which are spores-forming *Clostridium* or the non-spore-forming *Acetobacterium*. In addition to these bacteria, there are specialized groups of strictly anaerobic microorganisms that are ubiquitous in nature [8]. The efficiency of biogas production vital equally rely on this process since 70% formation of methane (CH_4) through reduction of acetate (CH_3COO^-) and about 11% formation of H_2 [1].



2.4 Methanogenesis Process

This process involves the conversion of acetate to CO_2 and CH_4 by methanogens and can be found in a variety of anaerobic ecosystems and as a terminal step in a microbial organic matter [9]. Table 1 differentiates the characteristics of anaerobic organisms

Table 1 Main characteristics of anaerobic organisms [12]

Parameters	Acidogenic and acetogenic organisms	Methanogenic organisms
Growth rate	High	Slow
pH	Low sensitivity	High sensitivity
Temperature	Moderate sensitivity	High sensitivity
Toxic agents	Moderate sensitivity	High sensitivity
Volatile acids	Low sensitivity	High sensitivity
Redox potential	Low sensitivity	High sensitivity

between methanogenic, acetogenic and acidogenic. Figures 1 and 2 provide an overview of the general processes that happen in anaerobic digestion including hydrolysis, acidogenesis, acetogenesis and methanogenesis processes [10].

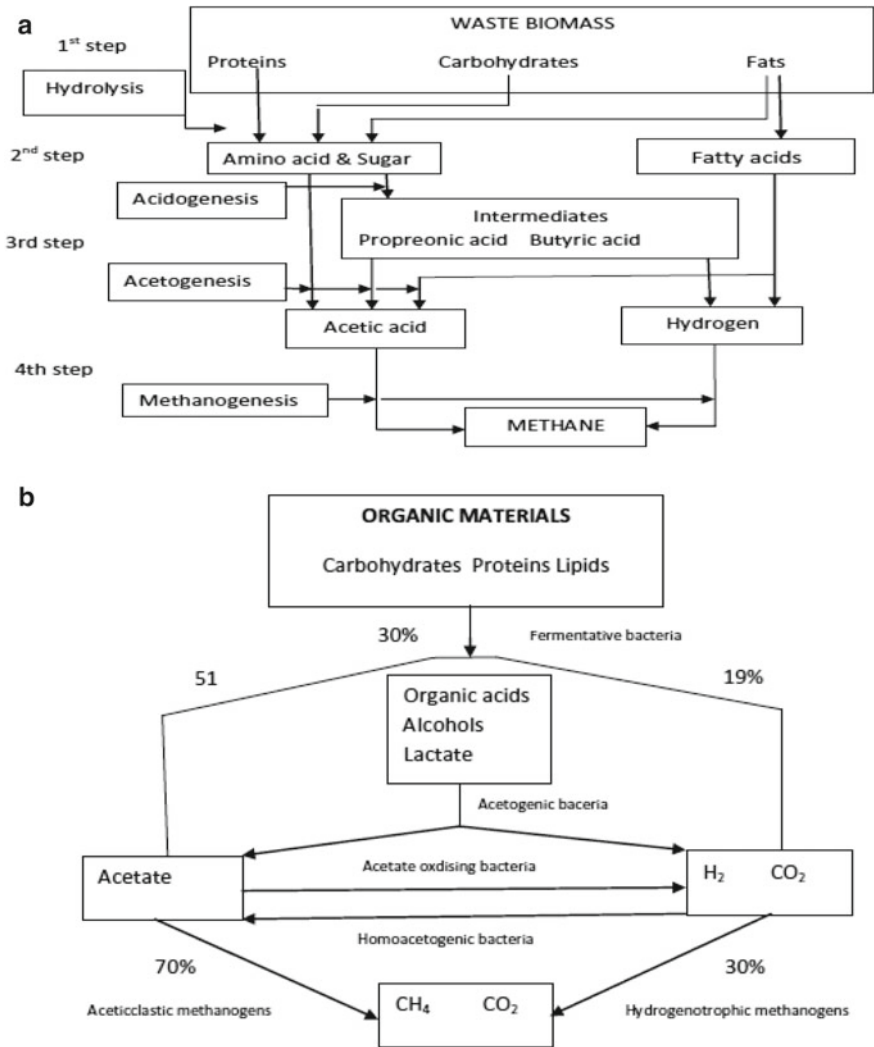


Fig. 1 a Carbon flow diagram of the biogas process. b Schematic diagram of four major steps involved in waste biomass hydrolysis and biogas production [8, 11]

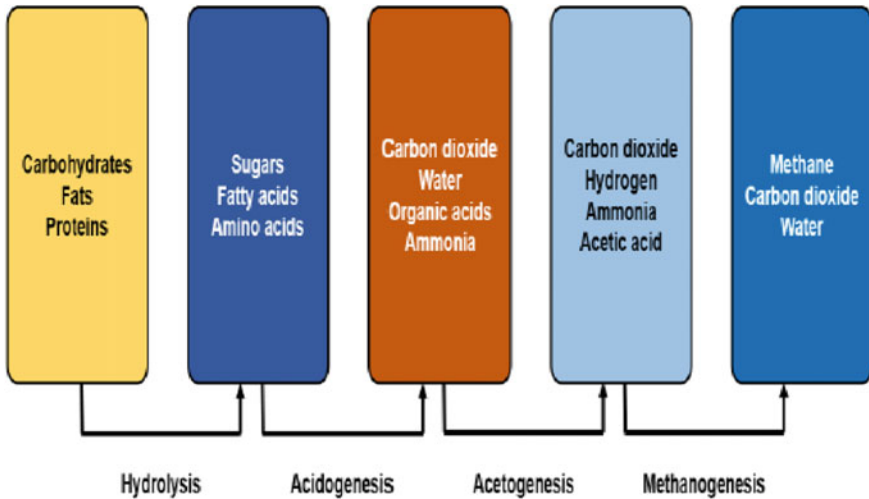


Fig. 2 Process of aerobic digestion [10]

3 Parameter Affecting Anaerobic Digestion

There are physical parameters that must be monitored and controlled to ensure functionality and stability of biological processes which are pH, temperature, moisture content, substrate, nutrients, retention times, feeding modes and reactor configuration [13]. The optimum pH value differs from each phase of reaction in AD. Firstly hydrolysis at a pH range of 6.0–8.0 can provide an optimum working condition for hydrolytic microorganisms [14]. Next is suitable pH during acidogenesis reaction shifting from 4.0 to 8.0 which significantly influences the VFA products [15]. Strong inhibition of VFA products occurs when the pH is below 4.0 whereas acetogenesis reaction works in anaerobic conditions with optimal performance depicted within a pH range from 6.0 to 6.2 [16].

Moreover, the digestion rate will be significantly affected by the environmental temperature condition. A slight change in the temperature may affect bacterial growth and activity, hence leading to a drop in biogas production [17]. Besides, temperature plays a critical role in the state of substrates such as the solubility, ionization equilibria and metabolic rate. In general, the increase of temperature has benefits in enhancing reaction rates [18]. Hence [19] highlight an important part which is facultative thermophile growth usually extends from the thermophilic (>45 °C) into mesophilic (25–40 °C) ranges. These two ranges are usually used as the operating temperature for the AD system. In addition, literature also reported that biogas formation was excessively produced in these two ranges of temperatures. While thermophilic AD was shown to produce higher biogas production in a short time, it is more difficult to operate, expensive, unstable and requires higher energy input as compared to the mesophilic condition. This is probably because the higher the temperature, the higher

the possibility for the accumulation of inhibitory substances such as NH_3 that can slow down or disrupt the digestion process. Thus, mesophilic AD is more preferred due to its stability and low energy consumption [17, 20]. Nevertheless, mesophiles are less sensitive to environmental changes [21, 22].

Enhancement of AD due to high moisture content affects the rate of dissolving degradable organic matter, while lower moisture content results in a deficit in bacterial activities due to physiological response to water stress. Research conducted by [23] reported that the production of CH_4 increased the moisture content between 60 and 80%. Moisture content can be represented by total solid (TS) held in the digesters, wherein it can be classified into dry digesters and wet digesters. Dry digesters have up to $\text{TS} \geq 20\%$ feedstock and a solid concentration of about $\text{TS} \geq 15\%$ [24]. Solid particles play the role as a nutrient source and also as supporting media. Microorganisms can attach and penetrate through particles [25]. Wet digesters have $\text{TS} \leq 15\%$ feedstock and are well known in the wastewater treatment field. Microorganisms are maintained in suspension within the liquid [16]. Although wet AD was found to produce more biogas and requires less complicated equipment [26], this approach needs large quantities of water and digestion volume [27]. As for dry AD, it uses less energy consumption and is more stable than wet AD but it requires more complex equipment and potential accumulation of inhibitory compounds that may affect biogas production [26, 28, 29].

Substrate formation may vary in type and complexity which provides a carbon source for the bacterial activities. Carbohydrate is the most suitable substrate when degraded will provide around 600–700 L of biogas per kg matter with 50% or more CH_4 content [19, 23]. Besides carbohydrates, fat is also demonstrated as an excellent substrate and can produce the highest CH_4 yield; due to hardly being soluble in water and difficulty to blend into the digestion process, fat must undergo pre-treatment in order to become more readily accessible to the bacteria [13, 19].

Requirement for bacteria on nutrients for their cellular metabolism remarkably affects AD and consequently biogas production. It has been noted that the amount of nutrient level from different elements; carbon:nitrogen:phosphorus:sulphur at 600:15:5:3 are suitable for the methanogenesis process [23]. A balance between macronutrients and micronutrients is compulsory for microbial synthesis and microbial activities, respectively [30].

Retention time means the time at which the feedstock remains in the digester and plays a vital role in bacterial growth. There are two measurements of retention time: hydraulic retention time (HRT) and solids large-scale retention time (SRT). Wilkinson and Kennedy (2012) found that HRT will differ for each substrate; 14–30 days for dry processes and around 3 days for wet processes HRT. Measurement of the concentration of bacteria can be identified by SRT of which high SRT indicates a larger population of biomass retained within the system [13].

The next parameter is the feeding modes which can be divided into a batch or continuous processes. The continuous process was shown to have constant and high production of biogas compared to the batch process [31]. However, it requires a more complex technology especially in terms of internal fluidity to ensure smooth feedstock feeding and removal [32].

Table 2 Key parameters of performance and operation of an anaerobic biogas power plant system [13, 16]

Parameters	Symbol	Unit	Optimal value/range	Determination
Pressure	P	mbar	N/A	Measurement during operation
pH	pH	–	6.5–7.5	
Temperature	T	°C	37–51	
Gas quantity	V	m ³ / day	N/A	
Methane fraction	CH ₄	%	50–70	
Moisture content	MC	%	60–80	
Carbon to nitrogen ratio	C/N	–	20–30	
Nutrients	C:N:P:S	–	600:15:5:3	Calculation from operation data
Retention time	RT	days	15–30	
Hydraulic retention time	HRT	days	15–30	
Solid retention time	SRT	days	>20	

The last essential parameter is the reactor configuration. Typically, the AD process can be structured as a one-stage, two-stage, or multi-stage reactor, depending on the AD process, which either occurs in the same or separated digesters [33]. The reason for different types of reactor stages designs is most likely because to ease research in terms of optimizing, controlling and investigating the intermediate steps of the digestion in order to improve the biogas yield [34]. A two-stage reactor is shown to achieve better performance than a one-stage reactor based on biogas throughput, rate of production and total energy recovery [35]. However, the cost of construction, operation and maintenance for each reactor increased with the number of stages configured in the reactor [34]. Nevertheless, nowadays, the use of multi-stage reactors continues to grow due to the high biogas production, shorter fermentation period and degradation rate [26, 36].

In summary, several parameters have been shown to influence the AD process (Table 2). Thus, it is crucial to choose an appropriate digester and maintain it regularly to ensure that the quality of biogas produced is suitable for future application, particularly in Malaysia.

4 Biogas Digester

Several microorganisms have been utilized in the anaerobic digestion process which may not only facilitate the production of biogas but also help to reduce the risk of human infection that might be potentially derived from livestock waste. This is because improper management of waste may cause significant risk to the environment and public health through the released pathogen and toxic chemicals to the groundwaters or soil [37]. Since the microorganisms are anaerobic and require certain

nutrients to grow, a proper tank is needed to ensure the optimum growth of these microorganisms. This optimum environment is maintained and controlled in a reactor tank, wherein the biodegradation of separated waste is conducted. Several digesters have been designed and developed to accommodate a great deal of biogas demand, including garage-type, fixed dome, floating and balloon-type biogas digesters (Table 3, Fig. 3). These 4 types of digesters are common in developing countries and details of each digester have been described by Vögeli et al. (2014). Although they can be constructed in different sizes, the principal design elements are the same.

Among the four digesters, the garage-type (Fig. 3a) is the only dry digestion system that operates in dry (high total solid content, >15%) and batch-mode conditions. This digester is designed with an airtight door which helps to seal the waste in a simple garage-like digester. After the door is closed, the percolation system is activated, wherein it will sprinkle percolate over the biomass and help to ensure even dispersion of AD bacteria in the system. The percolate will be collected in a storage tank and re-sprinkled over the biomass regularly. Usually, the percolation system is halted a few days before digestion process termination to let the dewatering process of digestate material take over. At the end of the digestion process, the reactor is flushed with CO₂ from an engine to prevent the generation of an explosive gas/air mixture [38, 39].

As for floating-drum digester, fixed-dome and balloon-type digesters, they are known as wet digestion systems that can operate in wet (low total solid content), continuous-mode and mesophilic conditions. The floating-drum digester (Fig. 3b) is usually designed with a cylindrical digester constructed underground while the

Table 3 Type of digester [32]

Types of digester	Garage-type	Floating-drum	Fixed-dome	Balloon-type
Special design	Consist of a tank containing percolation fluid	Contains underground digester and mobile gas-holder	Sealed, dome-shaped, fixed gas-holder and a displacement pit	Contain plastic or rubber digester bag to store gas
Advantages	<ul style="list-style-type: none"> • Simple design • Easy to treat digestate 	<ul style="list-style-type: none"> • Easy to construct and operate • Constant gas pressure • Stored gas is visible 	<ul style="list-style-type: none"> • Low setup cost • Long life-span • Less space • All parts fixed 	<ul style="list-style-type: none"> • Low setup cost • Easy to set up, maintain and transport • Shallow installation depth
Disadvantages	<ul style="list-style-type: none"> • Gas tightness-difficult to open • The material must not be moved or turned during the process 	<ul style="list-style-type: none"> • Short lifespan • Expensive material • Require regular maintenance • Steel corrosion 	<ul style="list-style-type: none"> • Fluctuating gas pressure • Hard to repair • Require a skilled technician 	<ul style="list-style-type: none"> • Short lifespan • Easy to break • Variable gas pressure • Unstable

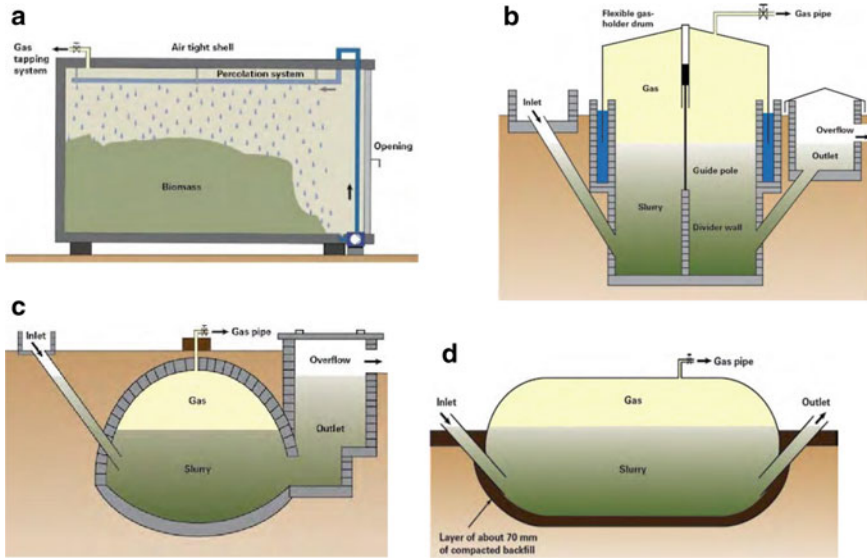


Fig. 3 Schematic diagrams of different types of digesters; **a** Garage-type, **b** Floating-drum, **c** Fixed-dome and **d** Balloon-type [39]

movable, floating gasholder (drum) is above the ground. However, a smaller system can be built fully on the ground. The produced gas will be collected in the drum with the rises or falls of the drum serving as a good visual indicator of the quantity of the gas generated. Additional weight can be added on top of the gasholder or a guiding frame can be installed inside the gas drum to increase the gas pressure and prevent the tilting of the drum.

Compared to floating-drum, the fixed-dome digester (Fig. 3c) consists of an immovable gas holder and is designed with a close dome-shaped digester. The gas produced is stored in the upper part of the reactor and its pressure varies depending on the gas production and consumption. This is because, when the outlet gas valve is closed, the gas pressure increases, pushing the digestate into the compensation tank, while decreasing when it is open. Like the floating-drum digester, it is built underground to protect the digester from extremely low temperatures.

As for the balloon-type digester (Fig. 3d), it comprises a heat-sealed, weather-resistant balloon-like bag that acts as both a digester and gas holder at one. Usually, the gas is collected and stored at the upper part of the balloon, while the digestion process occurs at the bottom. Its limitation is the absence of a stirring device, making digestate mixing difficult. Similar to the floating-drum digester, additional weight can be added to the balloon to increase the produced gas pressure, but cautions need to be taken to avoid any damage to the balloon. Additionally, since it is quite fragile, it is important to protect the balloon from direct solar radiation or animals [39].

The digester is usually designed based on the parameters described in Sect. 2.2, including total solid content, feeding mode, temperature and reactor configuration

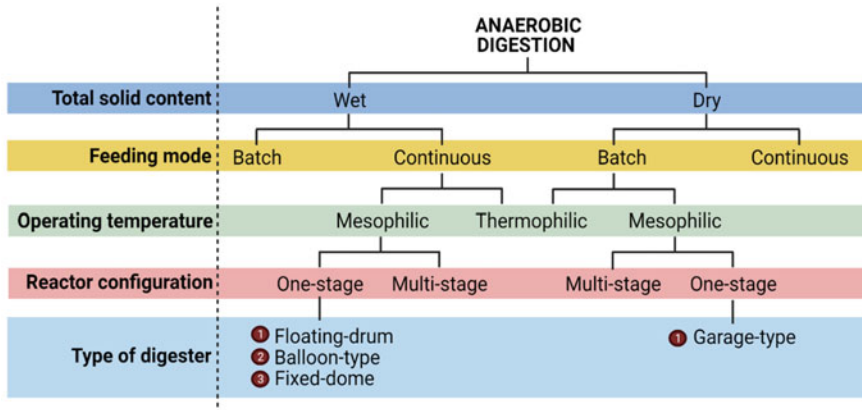


Fig. 4 Selection of biogas digester types based on several factors. Types of digesters can be selected based on total solid content, feeding mode, operating temperature and reactor configuration (adapted from [39]) (Created with Biorender)

Table 4 Some common maintenance activities for biogas digester [42]

Maintenance activities	Reason	Frequency
Sludge removal	To remove excess sludge	Every 1–2 years
Pump cleaning	To avoid clogging	Every 3–6 months
Iron packing replacement	To remove corrosive H ₂ S	Every 6–12 months
General engine maintenance	To ensure proper fluid levels	Every week
Preventative engine maintenance	To ensure proper electrical, fuel and air intake	Every month
Valve leak checks	To avoid a safety hazard	Every 6–12 months
Pipe leak checks	To avoid leaking	Every 6–12 months

[39, 40]. These factors will not only influence the types of digesters used but can also be shown to affect the biogas output [41] (Fig. 4).

4.1 Maintenance of Biogas Digester

Digester needs to be maintained regularly to ensure maximum biogas production. It can be done by the workers themselves or via recruitments of some service providers. Examples of the common maintenance activities for biogas digester and its frequency are listed in Table 4.

Thus, it is crucial to choose an appropriate digester and maintain it regularly to ensure the quality of biogas produced is suitable for future application. However,

before the biogas can be applied to various gas appliances, they require further treatments to improve the heating value of the end product. These additional treatments or also known as biogas scrubbing utilized several cleanings or upgrading steps such as the removal of carbon dioxide (CO₂), water vapour and hydrogen sulphide (H₂S) that might affect the quality of biogas.

5 Biogas Processing

Biogas, a combustible gas, can be generated not only from food waste and organic waste but also from animal manure and slurries through a process known as anaerobic digestion (AD) [43]. As described in the previous section, this microbial process comprises several sub-processes known as acidogenesis, acetogenesis and methanogenesis occurring within an optimized and controlled airproof reactor tank known as an anaerobic digester. The biogas produced can be either used directly or further cleaned and processed to increase the heating value of the end product especially for the use as renewable natural gas or to fulfil the requirements for several complex gas appliances, including boilers, vehicles and engines. These cleaning and polishing steps involved the removal of CO₂, hydrogen sulphide, water vapour and other remaining gases; compression and conversion of methane to hydrogen (Fig. 5). The final product generated through this cleaning and upgrading process is biomethane, containing 95–99% methane (CH₄) and 1–5% CO₂.

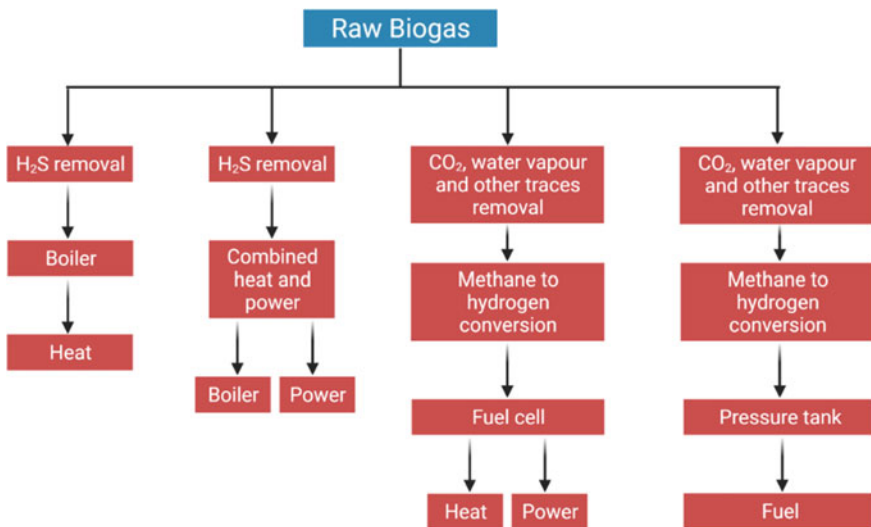


Fig. 5 Example of biogas application and their cleanup process. Other examples of biogas utilization are to generate heat, power and fuel. These end products require several cleaning and polishing steps, including hydrogen sulphide (H₂S), carbon dioxide (CO₂), water vapour and other traces removal; and methane to hydrogen conversion (adapted from [44]). (Created with Biorender)

5.1 CO₂ Removal

The raw biogas consists of 3:2 ratios of methane to carbon dioxide (CO₂) as the main gas component. It also contains other minor constituents such as oxygen (O₂), hydrogen sulfide (H₂S), nitrogen (N₂), siloxanes, carbon monoxide (CO), volatile organic compounds (VOCs) and ammonia (NH₃) [43]. However, the raw biogas produced can be upgraded to improve its quality, comparable to natural gas through several procedures, including CO₂ removal. Usually, in a simple biogas application such as the heater, CO₂ will not be removed and retained in biogas as it will pass through the burners [45]. However, for a more complex application, such as in a vehicle, CO₂ is consistently removed to improve the biogas calorific value.

Four main techniques have been designed for CO₂ removal, including absorption, adsorption, separation and biological methane enrichment. The summary for each technique has been described in Table 5.

Table 5 The percentage of CH₄ loss, advantages and disadvantages of techniques for removal of CO₂ [43]

Technique		CH ₄ loss (%)	Advantages	Disadvantages
Absorption	Physical	<4	<ul style="list-style-type: none"> • Low operation and maintenance cost • Simple process • High CH₄ purity 	<ul style="list-style-type: none"> • Need large quantities of water and external heat • High energy consumption • Easy to contaminate
	Chemical	<1	<ul style="list-style-type: none"> • High CO₂ removal • High CH₄ purity • Rapid process than physical 	<ul style="list-style-type: none"> • High energy consumption • Pre-treatment required • Salt precipitation and poisoning of amine
Adsorption	Pressure swing	<4	<ul style="list-style-type: none"> • Low energy consumption • High CH₄ quality • No chemical used 	<ul style="list-style-type: none"> • Complex process • Pre-treatment required • Required steam to improve gas quality
Separation	Membrane	<1	<ul style="list-style-type: none"> • Environmentally friendly • Low energy consumption • Low cost • Simple process 	<ul style="list-style-type: none"> • Pre-treatment required • Low CH₄ quality • High membrane selectivity
	Cryogenic	<2	<ul style="list-style-type: none"> • High CH₄ purity • Environmentally friendly 	<ul style="list-style-type: none"> • Expensive • Pre-treatment required • High energy consumption • Undeveloped technology

In recent years, CO₂ content in biogas was used as a feedstock to generate chemical material, rather than being removed. Several techniques have been outlined for this purpose, including methanation reaction [46] and hydrogen-assisted methanogenesis [47]. Methanation reaction or also known as the Sabatier reaction occurred between CO₂ and H₂ to generate methane and water. The drawback of this approach is the need to use a thermally stable catalyst that can only function at low temperatures [48]. For instance, Ni-based catalysts are frequently studied for industrial purposes due to their low cost and ease of availability, but their activity is lessened in low temperatures, affecting the efficiency of the reaction. Another approach is through hydrogen-assisted methanogenesis, wherein CO₂ conversion to methane depends on the use of H₂ by hydrogenotrophic methanogens. However, this method requires an optimum concentration of H₂ to ensure the proper reaction occurs. Besides, it may also inhibit syntrophic acetogens activity which is crucial for butyrate and propionate degradation [49]. Nevertheless, compared to the common CO₂ removal technique, the biogas produced through this approach is less efficient for electrical generation [43].

5.2 Water Vapour Removal

In raw biogas, apart from CO₂, the remaining components such as water vapour are undesirable and considered impurities [50]. The water vapour content in raw biogas usually accounts for 5–10% and its production is temperature-sensitive, wherein the lower the raw biogas temperature, the lower the percentage. This water must be removed as it may decrease the calorific value (NCV) of biogas, clogging the pipeline and contributing to the production of highly corrosive acids by reacting with H₂S [50]. To date, several separations or removal techniques have been designed to reduce the moisture content. Among the techniques are adsorption with silica gel or dehumidification with glycol, both of which are classified as drying techniques. Besides that, other methods have been applied, including condensation.

Compared to condensation, the drying technique utilizes the principle of absorption, adsorption, heating and cooling. For absorption, glycol is used as a drying agent to absorb water because it can significantly reduce the dew point from –5 to –15 °C [51]. Besides, it also can regenerate at 200 °C, making it suitable for both continuous or batch-type operations [52]. Alternatively, another method used silica gel, magnesium oxide, activated carbon or alumina adsorption, which can reduce the dew point to –40 °C [44].

As for condensation, it is less efficient than drying methods as it only decreases the dew point to 0.5 °C. It involves multiple physical drying methods such as demisters, cyclone separators, water traps and moisture traps [45]. Demisters separate liquid particles with 0.5–2 nm wired mesh, while cyclone separators separate water droplets through centrifugation. The moisture traps method promotes water removal by decreasing the temperature through expansion [53]. Additionally, water can also

be discarded through electric cooling or by designing the underground pipeline with water traps [54].

Nevertheless, these water removal methods are expected to give a higher yield of CH_4 and meet the technical instruction provided by the main gas engine manufacturers [55].

5.3 Hydrogen Sulfide Removal

Hydrogen sulfide (H_2S) needs to be routinely removed from raw biogas to avoid any formation of corrosive sulphuric acid that will decrease the performance of the appliance [56]. Even at low concentration, H_2S was found to significantly decrease CH_4 conversion as low as 20% [57] and can promote deactivation of the catalyst by competing with CH_4 for the active site of the catalyst [58, 59]. The separation of H_2S can be achieved through various methods but the most employed method is adsorption. H_2S removal through adsorption can be done chemically using activated carbon or metal oxide.

Adsorption using activated carbon is commonly explored by the researcher due to its high adsorption capacity, even with a little amount of H_2S , and rapid kinetic reaction [60]. This method requires oxygen to oxidize H_2S to elemental sulphur that would bind to the surface of activated carbon [61]. However, the normal or virgin activated carbon is a weak catalyst with low H_2S adsorption efficiency. Thus, to increase its catalytic performance and total load, the activated carbon can be impregnated with some chemicals such as sodium hydroxide, potassium hydroxide [56, 62], iron [63], potassium carbonate or zinc oxide (ZnO) [53] as catalysers. This impregnation strategy is commonly applied by the industry as it can increase the removal capacity up to 120–140 kg $\text{H}_2\text{S}/\text{m}^3$ [45]. Nevertheless, this approach is expensive, reduces the ignition temperature of the carbon and is difficult to regenerate [53]. Another adsorbent such as metal oxides also has been used in the forms of iron fillings, iron pellets and iron sponges, which offered regeneration properties [64]. However, it is expensive, highly chemical-intensive and may promote the release of pollutant sulphur dioxide (SO_2), which restricts the use of this method on a large scale [65].

Another approach for H_2S removal is absorption, which can be done through physical or chemical scrubbing. Physical scrubbing such as water scrubbing or adsorption, whereas chemical scrubbing use sodium hydroxide to reach a large scale with H_2S to form the insoluble salts, Na_2S or NaHS [66]. The next method is biofiltration which applied the use of microorganisms such as *Thiobacillus* and *Sulfolobus* to oxidize H_2S in the presence of oxygen. This biological degradation method can be implemented inside the digester or by using a trickling filter, packed with the microorganism. Although this method shows high efficiency in removing H_2S by more than 99% [67], it may also cause excessive biomass accumulation on the surface [68].

Collectively, these additional steps are necessary to ensure the quality of biogas produced suitable for biofuel application in Malaysia. However, some concerns

related to environmental issues such as global warming domineered its potential, making it is less favourable among researchers. Thus, it is crucial to fully profile both the advantages and disadvantages of biogas to justify its future application.

6 Biomethane and Biohydrogen as Future Biofuel and Its Application in Generating Electricity in Malaysia

The current trend on global energy consumption based on non-renewable resources (including fossil fuel, coal and natural gas) indicates a progressive escalation for the next few decades [69, 70]. This inclination is a reflection of the rapid evolution of industrialization and technological development in urbanized countries i.e. the United States of America, the European Union, Japan and China [69]. Likewise, escalating energy consumption has also been observed in Malaysia in parallel with the progressive urbanization and development of the country [71]. Nevertheless, the non-renewable energy supply is forecasted to deplete as a result of excessive source consumption over its reproduction [72]. Moreover, fossil fuels such as coal emit more pollutants and carbon dioxide to the atmosphere, resulting in tremendous environmental contamination and global warming problems [70].

Overall, the electricity and heating sector contribute to the highest carbon dioxide emission followed by transportation, industry, residential, other energy industries, commercial, utilities, agriculture and fishing industrial sectors [70]. In Malaysia, a prodigious amount of carbon dioxide has been emitted to the environment during its transitional stage from an agriculture-oriented economy to become an industrialized country [73]. Given that a balance between industrialization and a healthy environment is pivotal, a promising transition from non-renewable energy combustion to a more environmental-friendly approach using renewable bioenergy including biomethane and biohydrogen has been practised in several industrialized countries worldwide to mitigate greenhouse gas (GHG) emissions and solve the climate change issue [74]. Aiming to embrace a similar green energy utilization concept, the Malaysia government also has enforced several measures including the implementation of laws and regulations to promote the application of renewable energies such as biohydrogen and biomethane in the country.

Biohydrogen and biomethane are renewable carbon-neutral energy sources and are considered as a key development for sustainable global energy supply [75, 76]. Both biogases represent an alternative for fossil fuels as they can overcome the environmental problems and challenges associated with fossil fuel consumption. Unlike conventional fossil fuel, the thermochemical reaction of hydrogen leads to the generation of powerful explosive energy (142 kJ g^{-1}) while producing water as the by-product [77, 78]. Given the non-polluting nature of hydrogen consumption, the versatile energy source is commonly used as a feedstock in the chemical industry as well as a “future fuel” to generate energy and electricity for vehicles and boilers [79]. In addition, hydrogen can be used in electrical energy storage (EES) power plants

that can store excess energy during off-peak hours while releasing the stored energy during peak hours [79]. Given the tremendous benefits of hydrogen utilization in economic development, the industrial sector as well as to the environment, Malaysia has allocated huge funding for research and development (R&D) (approximately RM 40 million or USD 11.4 million) involving the application of hydrogen fuel cell to generate electricity in vehicles.

Furthermore, a strategic collaboration between the industrial and academic institutions for example The Institute of Fuel Cell, Universiti Kebangsaan Malaysia (IFC-UKM) and the Institute of Hydrogen Economy, Universiti Teknologi Malaysia (IHE-UTM) has been established to accelerate the government's mission and achievement to promote green plus sustainable energy consumption [80, 81]. While Malaysia's effort seems in the right direction, the utilization of hydrogen fuel cells as a renewable energy source is still in its infancy. A synergetic collaboration and information sharing with the other pioneering countries such as Japan, Korea and The United States would certainly benefit the government on the adoption of hydrogen as part of green energy sources [80].

Biomethane is another renewable energy product that is biologically derived from biogas produced by microorganisms through anaerobic digestion or microbial fermentation using different organic biomass i.e. agricultural wastes, manures, slurries and oil residues as well as through bioelectrochemical systems or electromethanogenesis [82]. The main combustible biogas normally consists of a mixture of methane (typically 55–80%), carbon dioxide and a small quantity of hydrogen sulphide and other trace gases. Therefore, several cleaning steps using different technologies are conducted to obtain a pure biomethane gas such as chemical-physical precipitation, adsorption of hydroxide or metal oxides, internal biological desulfurization, biological filters, physical or chemical adsorption, membrane separation and adsorption on activated carbon [83].

The biomethane has properties potentially equivalent to methane (with the heating value of 55.5 MJ kg^{-1}) [84] that can be used as vehicle fuel, or injected into the natural gas grid or to generate electricity and heat in power plants while reducing the amount of carbon dioxide emitted to the environment compared to the natural gas. Due to its significant importance as a green energy source, the number of upgraded biogas plants in urbanized countries such as in Europe has escalated from 187 in 2011 to 435 in 2015 [85]. Following a similar path, several biogas plants have been constructed in Malaysia. For example, a multi-process facility based on the Waste Recovery and Regeneration System (REGEN System) was built adjacent to Havys Oil Mill Sdn Bhd in Palong, Negeri Sembilan with an attempt to convert crude palm oil mill waste to multiple beneficial by-products including biogas [86].

Nevertheless, the utilization of biomethane as renewable energy to generate electricity in Malaysia seems in a sluggish state due to the irregular supply of waste biomass, the low efficiency of combustion technology and poor interconnection infrastructure [87]. While the application of both biohydrogen and biomethane as green energy sources in Malaysia is still challenging, both biogases successfully contribute to the generation of electricity supply in Malaysia, indicated by a promising escalating trend as displayed in Fig. 6 [88].

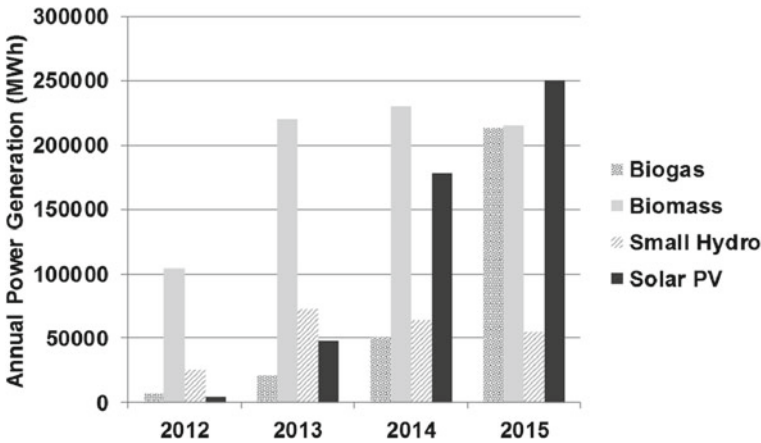


Fig. 6 Annual power generation (MWh) of commissioned renewable energy installation. Data was constructed by [88] based on the website of the Energy Development Authority

6.1 Driving Force of the Biogas Industry Development in Malaysia

6.1.1 Malaysia Aims to Embrace Sustainable Energy Production via a Green Environmentally Friendly Approach

Heavy reliance and exploitation of fossil fuel have raised concerns on energy insecurity as the non-renewable source is projected to deplete within 60 years. Furthermore, intensive utilization of those energy sources leads to increasing GHG emission that contributes to global warming, increased sea water level, and climate change [79]. In response to the threatening scenario, Malaysia as a committed government has provided an excellent effort to adopt environmental-friendly technologies and green initiatives at both local and international levels to achieve a green sustainable economic and industrial development. Under the Paris Agreement 2015, Malaysia together with the other 194 countries agreed to control the global rising temperature to below 2 °C and restrain the warming to 1.5 °C above the pre-industrial level [89]. Furthermore, Malaysia also agreed with the policy to decrease the greenhouse gas emission (GHG) of gross domestic production (GDP) by 45% in 2030 relative to the year 2015 [90].

A transition to the utilization of renewable energy in Malaysia had been initiated since 1999 when the Four-Fuel Diversification Policy had been revised to Five-Fuel Diversification Policy with the inclusion of renewable energy as part of the energy sources after oil, natural gas, coal and hydropower (Table 6) [91]. In addition, the Small Renewable Energy Power (SREP) and the Biogen Full Scale Model Demonstration Project that displayed the feasibility of biomass and biogas power generation projects connected to the grid was also launched in 2001 and 2002 to attract active

Table 6 Summary of energy policies in Malaysia

Year	Policy and acts	Key features
1974	Petroleum Development Act	Establishing and regulating a national corporation (PETRONAS) for the exploration and utilization of national petroleum resources, including its function, rights, and exclusivity for all connected operations
1975	National Petroleum Policy	Managing the oil and gas business to ensure a sufficient supply at acceptable rates to fulfil national economic development goals while maintaining ethical governance of national resources
1979	National Energy Policy	Maintaining appropriate, sustainable, cost-effective and efficient energy use from both traditional and renewable sources
1980	National Depletion Policy	Managing national oil reserves to avoid overexploitation because of augmented production capacity
1981	Four Fuel Diversification Policy	Enhancing the National Depletion Policy of 1980 in terms of avoiding an over-reliance on oil as a primary energy source. Gas, hydropower and coal should all be included in the energy mix
1990 (Amendment 2001)	Electricity Supply Act	Protecting the interests of residential and commercial gas customers in terms of sufficient supply at reasonable costs, installation, licencing, infrastructure and safety
1999	Five Fuel Diversification Policy	Augmenting National Energy 1979 by expanding the energy mix to incorporate renewable energy in addition to oil, gas, coal and hydropower
2001 (Amendment 2010)	Energy Commission Act	Establishing the Energy Commission, which will be charged with regulating energy supply activities and enforcing energy supply legislation, as well as encouraging renewable energy and non-renewable energy conservation

(continued)

Table 6 (continued)

Year	Policy and acts	Key features
2005	National Biofuel Policy	Providing incentives to encourage the use of biofuels, as well as making a biodiesel blend with 5% diesel and 5% palm oil available
2009	National Renewable Energy Policy and Action Plan	Promoting and diversifying energy mix through the use of renewable resources to achieve electrical supply stability and sustainable socio-economic growth
2011	Renewable Energy Act	Funding for the creation of a specific tariff structure to encourage the production of renewable energy and related activities

participation by the private sectors in the small power generation investment using the renewable energy sources [88, 91, 92].

6.1.2 Conversion of Overwhelming Agricultural Biomass to Renewable Energy (Biogas) and Beneficial Digestate

Along with the growing industrial sector, Malaysia is blessed with fertile land that can be exploited intensively for agriculture. A total of RM 101.5 billion (7.1%) of Malaysia GDP in 2019 was contributed by the agricultural sector of which oil palm was the main contributor (37.7%) followed by the other agriculture sources (25.9%), livestock industry (15.3%), fishing (12%), forestry and logging (6.3%) and natural rubber (3%) [93]. As a resource-rich country, Malaysia has abundant agricultural biomass such as oil palm wastes, woods, paddy residues and livestock manures that can be exploited to produce biogas and generation of electricity. An average of 53 million m³ of palm oil mill effluent (POME) are generated from the palm oil processing industry per year that can cause hazardous contamination to the rivers attributed to its high chemical and biological oxygen demand (COD and BOD respectively) [94].

Approximately, 3.66 million tonnes of paddy residue are abandoned in the field whilst this number is predicted to increase progressively because of technology development in the agriculture system [95]. Owing to the reserved bioenergy within the carbohydrate-rich agricultural wastes, those residues are applicable as feedstock to produce biogas through the AD system [94, 96]. The dark fermentation system is catalysed by different obligate or facultative anaerobic microorganisms including thermophiles i.e. *Thermoanaerobacterium thermosaccharolyticum* [97], *Caldicellulosiruptorsaccharolyticus* and *Thermotoga* sp. [98, 99] and several other aerobic

bacteria including *Bacillus* sp., *Aeromonas* sp., *Pseudomonas* sp. and *Vibrio* sp. [77]. A higher biohydrogen yield was produced through the fermentation of organic biowastes compared to the wastewater, indicating the potential of agriculture residue as a good substrate for biogas production.

Aside from the biogas production, the digestate product from the anaerobic digestion can also be exploited as biofertilizer or natural compost owing to its considerable amounts of nitrogen (in ammonium form) and macro- and micronutrients that are essential for plant growth and development (Fig. 7) [100, 101]. The utilization of organic biomass in the AD not only benefits the government in terms of green renewable energy supply but also reduces the accumulation of waste residues, odour removal and inactivation of microbial pathogens within the abandoned waste [102].

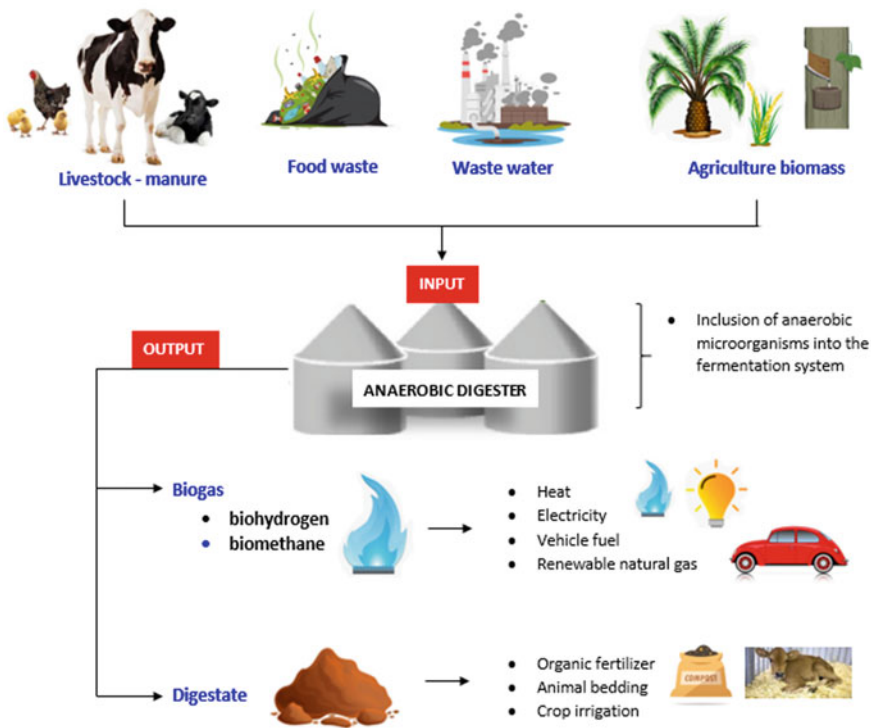


Fig. 7 Different organic biomass i.e. livestock residues, food waste, wastewater and agriculture residues can be used as feedstock for AD by microorganisms to produce biogas and digestate as the final product

6.2 Current Technologies on Biogas Production

The decomposition of organic biomass through anaerobic digestion involves four-stages critical processes i.e. hydrolysis, acidogenesis, acetogenesis and methanogenesis [101] (see details in Sect. 2). The advanced technology development allows the anaerobic fermentation procedures to be catalysed in different bioreactors such as photobioreactors, dark fermentation bioreactors, microbial electrolysis cells, hybrid bioreactors and multistage bioreactors [77].

However, the diversity and complexity of macromolecules (such as cellulose, hemicellulose and lignin) within the organic biomass, sludge or agricultural residue represent a major constraint that might diminish the substrate susceptibility to microbial degradation and enzymatic reaction [103].

Furthermore, as certain bacteria grow at a slow rate, a long fermentation period is required for biomass degradation by those microorganisms. Hence, the raw materials need to be pre-treated to facilitate microbial degradation to enhance biogas production. Several pre-treatment procedures are performed to improve the biodegradability of the biomass during the fermentation process for example substrate milling to reduce substrate particle size [104], oxidative ozonation to solubilize solids (i.e. lignin) in sludge [105], sodium hydroxide to reduce total content of phosphorous [106], steam explosion and ultrasonic techniques to disintegrate the biomass structure [84, 107] and biological treatment using cellulase or protease-secreting fungi or bacteria i.e. *Bacillus* sp. to improve liquefaction of the fermented residue [108]. Overall, it has been observed that the pre-treatment processes resulted in improved anaerobic digestion, diminished retention time and increased biogas production [109].

Other than the pre-treatment process, co-digestion involving simultaneous fermentation of more than one biomass has been proven in producing higher biogas yield [102, 110]. This is because co-digestion may result in the improvement of chemical or biological interaction within the system, enhancing the buffering system and the nutrient requirement for microbial growth, promoting synergetic interaction among the degrading microorganisms as well as reducing the effect of inhibitors in the fermentation system [102].

Whilst the type of bioreactors, substrate and microorganisms are the key components in AD, the physical and chemical conditions of the fermentation system also need to be improved to maximize biogas production. Physical conditions, for example, optimal pH and fermentation temperature, are crucial for microbial growth as acidic conditions and excessive environmental heat may result in microbial death and deterioration of biogas yield [102]. Methanogenic microorganisms grow well in neutral to alkaline condition (pH 7–8.5) while some bacteria favour specific environmental temperature range i.e. psychrophilic; 10–20 °C or less than 30 °C, mesophilic; 30–40 °C and thermophilic; 50–55 °C or even reaching 60 °C. On the other hand, chemical parameters i.e. carbon (C) and nitrogen (N) ratio (C: N) also serve as a critical factor that determines the efficiency of anaerobic digestion and biogas production.

Carbon is required as a large scale for the bacteria while nitrogen is pivotal to support microbial growth. A ratio of C: N; between 20:1 and 30:1 is always applied in the digestion system for optimal operation. The inappropriate C: N ratio will result in slower microbial growth or excessive ammonia accumulation, thus leading to microbial demise and deteriorated biogas generation [102, 111, 112]. Given that optimal physical and chemical fermentation conditions are crucial for efficient biomass decomposition and biogas production, AD bioreactors are generally equipped with mixing impellers to maintain the homogeneity of the substrate and even dissemination of nutrients, pH and temperature condition within the fermentation system [113].

6.3 Environmental Issues of Biogas Production

While the main mission for biogas utilization as a renewable energy source is to serve as an alternative for fossil fuel consumption and to mitigate the global warming phenomenon, the anaerobic digestion process is also associated with the generation of greenhouse gases (GHG) including carbon dioxide, methane and nitrous oxide [114, 115]. Even though that GHG emission is more likely resulting from an inappropriate bioreactor system and open storage of digestate, this issue is still controversial thus affecting the community acceptance of biogas production through anaerobic digestion as well as its utilization in daily life [114]. Nonetheless, it is worth evaluating the impact of biogas production on global warming case by case to reveal the big picture of biogas potential and its benefits to the globe.

6.3.1 Carbon Dioxide Emission

Hazardous compounds and air contaminants such as carbon dioxide are released to the environment during biogas generation through diffusive emission as well as during the combustion process in vehicles or power plants. The oxidation of methane during biogas combustion leads to the generation of carbon dioxide. Moreover, inappropriate biomass transportation and digestate storage or its utilization as biofertilizer may also contribute to the release of carbon dioxide into the atmosphere [114]. For example, a large quantity of GHG including carbon dioxide is emitted from open ponds and tanks containing palm oil mill effluent (POME) in Malaysia [94]. Worryingly, the elevation of atmospheric carbon dioxide does not only contribute to global warming but also affects human health resulting in severe inflammation, reducing cognitive ability, bone demineralization, kidney problem, oxidative stress and endothelial failure [116]. However, the utilization of biogas has indirectly resulted in the reduction of fossil fuel utilization leading to a less anthropogenic greenhouse effect on the environment [114]. Furthermore, recent technologies using retrofit SYS-I to SYS-III have been developed to capture carbon dioxide from being emitted during biogas production [117].

6.3.2 Methane Emission

A large quantity of methane is produced during biogas generation and uncontrollably released to the atmosphere predominantly from the conventional ponding system [118]. In Malaysia, the rate of emitted methane ranges from 0.15 to 0.042 L g⁻¹ of POME which is higher compared to the other biomass [94]. Due to financial constraints, POME is commonly treated in open anaerobic or aerobic ponds. This common practice leads to the release of methane into the atmosphere hence resulting in a catastrophic impact on the environment [119]. From a health perspective, a low concentration of methane is not considered as harmful to human wellbeing. Nevertheless, methane is still a greenhouse gas whose global warming impact is 28–36 higher compared to carbon dioxide [114]. Therefore, the most powerful strategy to produce clean biogas production is through the utilization of an integrated bioreactor instead of the traditional ponding system [78].

6.4 Nitrous Oxide Emission

Nitrous oxide as a by-product of nitrification and/or denitrification processes is another greenhouse gas that is released during biogas production. The release of nitrous oxide also can significantly contribute to the global warming problem. However, as indicated before, the impact of biogas plants on GHG emissions including nitrous oxide could be reduced through the utilization of a closed bioreactor or proper digestate storage [114].

7 Conclusion

Biogas is produced using anaerobic digestion technology and can be considered a significant resource for satisfying global energy demands. This chapter compiles all the existing literature on biogas and anaerobic digestion into a single document. Reviewing previous studies on anaerobic digestion for biogas production by selected authors, stating the processes, stages and necessary parameters of anaerobic digestion for biogas production, as well as discussing the application and maintenance of biogas digesters, the chapter's objectives were met. Biogas production efficiency is determined by the type of feedstock utilized as well as the size of the biogas digester. The issue of temperature is one of the most important factors to address in this technology since a high temperature is necessary for biogas output; hence, insulation is essential to maintain temperature stability and minimize temperature variations. Furthermore, several variables influence anaerobic digestion processes; these elements must be considered for improved biogas generation. As a result, the environmental concerns and applications of biogas generation were briefly explored in this chapter.

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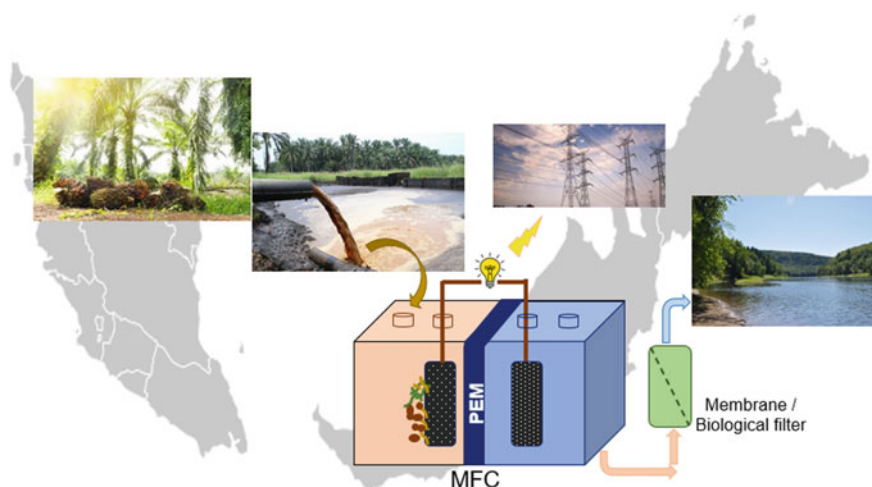
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Current Status on Microbial Fuel Cell (MFC) Technology



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Abstract



Agricultural and industrial activities in Malaysia have adversely impacted environmental quality leading local researchers to mobilize their expertise and resources to protect the environment from this alarming situation. The palm oil industry, for instance, generates an abundance of wastes (such as palm oil mill effluent [POME]), which calls for effective technological tools to reduce these recalcitrant wastes from spreading further. Microbial fuel cell (MFC) is an emerging technology for wastewater treatment and electricity generation simultaneously, which appears to be the

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most advantageous solution for these environmental concerns. This chapter reviews the prospects of MFC research with a special emphasis on the current MFC status in Malaysia. It begins with an overview of MFC principles, electron transfer mechanisms, and bio-electrochemical performance. Following that, a review of the recent MFC developments and activities by Malaysian researchers is discussed with an emphasis on POME utilization. This chapter concludes with several resolutions to the main challenges researchers and scientists are facing regarding the scalability of MFC for electricity recovery and wastewater treatment.

Keywords Microbial fuel cell · Palm oil biomass · Wastewater treatment

1 Overview of Microbial Fuel Cell

The energy derived from fossil fuels has faced critical challenges due to its limitations to meet the global clean energy demand. Fossil fuels, such as oil and gas, are forecasted to be depleted by the year 2042 [1]. Thus, there is an urgent need to find alternative renewable sources of energy. A microbial fuel cell (MFC) is considered as one of the alternative renewable sources owing to its potential for converting organic waste into electricity and treating wastewater simultaneously [2]. The interest in MFCs has grown vastly in recent years due to their mild operating conditions and use of relatively inexpensive materials or freely available biomass. Although the industrial application of MFCs has yet to be realized due to its low electrical power output, small-to-high scale MFC studies have increased significantly over the years based on the reported literature around the world.

M.C. Potter was the first scientist to discover that bacteria could produce electricity through his observation using *E. coli* in 1911 [3]. These electroactive bacteria, also known as exoelectrogenic bacteria, are the main feature in MFC responsible for electron production through oxidation of organic substrates in an anode chamber. Examples of exoelectrogens normally identified in MFCs include *Geobacter*, *Pseudomonas*, *Shewanella*, and many more. The electrons will be transferred via an external circuit to reach a cathode chamber. The protons resulting from substrate oxidation disperse through the proton exchange membrane (PEM) and combine with the final electron acceptor (mainly oxygen) in the cathode to form water, thus completing the circuit.

MFC has undergone many transformations as compared to early-years conventional double-chamber and single-chamber MFC (Fig. 1 a & b). In the double-chamber configuration, anode and cathode chambers are separated by the PEM to allow the flow of protons from the anode to the cathode while avoiding oxygen diffusion to the anode chamber. On the other hand, the cathode of a single-chamber configuration is exposed directly to the air with improved electron acceptance or oxygen reduction reaction (ORR) by a catalyst. Carbonaceous and metal-based catalysts, such as activated carbon and Pt/C catalysts, are widely used in a single-chamber MFC due to their high surface area and accelerated ORR.

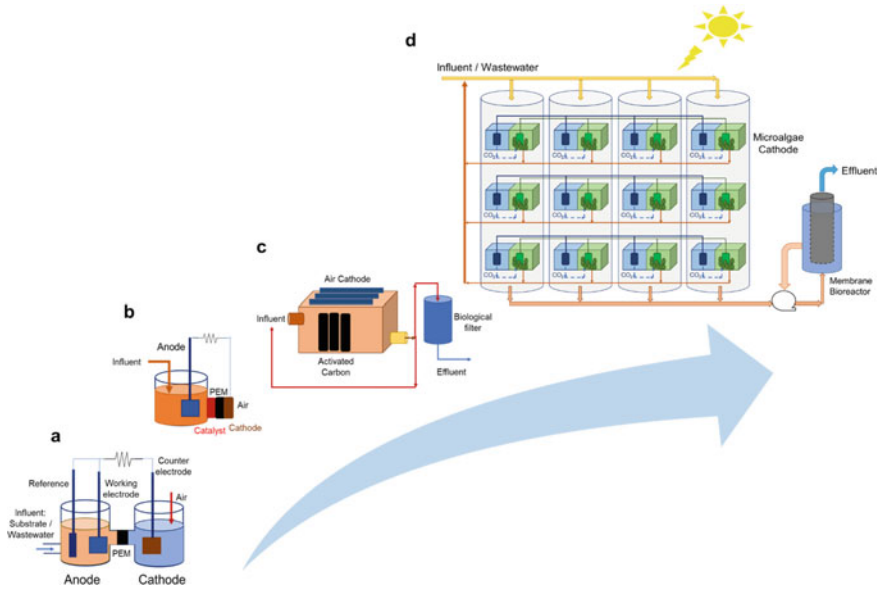


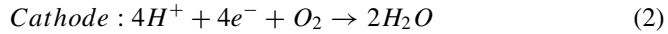
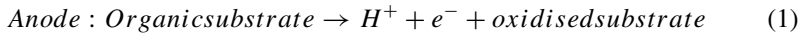
Fig. 1 Evolution of MFC configurations over the years: Conventional double-chamber and single-chamber MFCs (a & b), circulated air–cathode MFC (c), and advanced stacked-microalgae MFC (d). *PEM: Proton exchange membrane

Several improvements have been made on the double- and single-chamber MFCs, for instance, by integration of membrane bioreactor and consolidation of multiple MFC reactors in series or parallel (Fig. 1 c & d). These improved designs with a systemic circulation of the influent and effluent have optimized the MFC performances up to 5-folds for power generation and COD removal. Also, the use of microalgae as a biocatalyst for oxygen reduction in the cathode has significantly increased voltage generation while minimizing the release of CO₂ to the environment as a result of substrate oxidation in the anode. Other MFC elements, such as electrode and PEM materials, microbial biofilm attached to the anode surface, and MFC reactor design, have also significantly contributed to the overall MFC performance in the current generation and waste removal.

2 Operating Principle of Microbial Fuel Cell

Based on Fig. 1, the anode chamber consists of microbes, organic substrate, and anode electrode under anaerobic conditions. Meanwhile, the cathode chamber contains a cathode electrode and electron acceptor (i.e., oxygen) [4]. The exoelectrogenic microbes inside the anode chamber will metabolize the substrates for energy production while generating carbon dioxide (CO₂), electrons, and protons [5]. The flow of

electrons produced in the anode to the cathode based on Eqs. 9.1 and 9.2 is the result of the metabolic reaction of organic substrates through the citric acid cycle [6].



2.1 Electron Transfer Mechanism

Two mechanisms govern the electron transfer by bacteria: direct and indirect electron transfer mechanisms. The direct electron transfer mechanism is only achieved by the exoelectrogenic bacteria that directly transfer electrons via cytochromes or pili, whereas the indirect electron transfer mechanism involves the addition of a mediator. The microbes respiring near to the electrode surface use cytochrome to pass the electrons, whereas the cells in the biofilm distant from the electrode surface use pili [7] (Fig. 2). Some examples of pure culture bacteria that can be used to oxidize substrates in MFCs without mediators are *Geobacter sulfurreducens*, *Shewanella putrefactions*, *Bacillus subtilis*, and *Escherichia coli* [8].

For indirect electron transfer, a mediator serves as an electron shuttle from bacteria cells to the electrode [9]. The mediator can either be secreted naturally by the

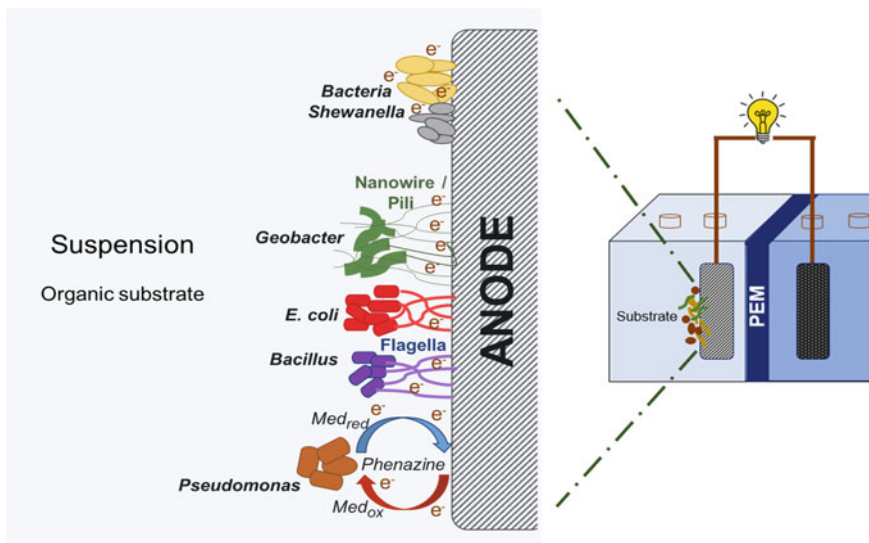


Fig. 2 Electron transfer mechanism in MFC

microbes or by adding artificial mediators to the system [10]. The electron mediators will penetrate the bacterial cells, capture the electrons from the metabolic reactions, and pass these electrons to the anode surface through an affinity-driven process [11]. Several natural and synthetic mediators responsible for electron shuttles include phenazine, thionine, methyl viologen, 2-hydroxy-1,4-naphthoquinone, methylene blue, humic acids, and anthraquinone-2,6-disulfonic acid [12]. However, these mediators have some disadvantages, such as toxicity and expensive [13]. Therefore, a mediator-less MFC has become more favorable compared to the MFC that uses a mediator.

2.2 Electrochemical Performances of Microbial Fuel Cell

Electrochemical reactions and performances of MFCs can be examined through several parameters, including current density, power density, polarization curve, Coulombic efficiency (CE), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) represented by a Nyquist plot. The electrons and protons generated by redox reactions result in the production of voltage. Voltages produced by the MFC can be measured directly by multimeters, voltage metres, and potentiostat [14]. The recorded voltage, V will be divided by the external resistance value, R to obtain the current value, I based on Ohm's law ($I = V/R$). The voltage and current values will be used to derive the power output ($P = IV$). Power density is the key parameter used to describe electricity generated by the MFC and it can be calculated by dividing the power with the electrode surface area, W/m^2 .

Polarization curve can be constructed by changing the external resistance where maximum power and internal resistance can be observed from the curve that consists of power, potential, and current profiles [15]. Apart from power generation, it is also important to recover as many of the electrons stored in the biomass as possible to optimize them as electrical current [14]. The percentage of electrons recovered from the oxidation of organic matter is known as CE (Eq. 9.3). CV, a recurring profile that comprises oxidation and reduction peaks, is widely used to study the electron transfer mechanism between biofilms and the electrode surface [16], the performance of novel electrode materials [14], and redox reaction at the surface of the electrodes [17, 18]. EIS can be used to measure the MFC internal resistance, including ohmic resistance (resistance from the membrane, solution, and electrode materials), charge transfer resistance, and diffusion resistance [19].

$$CE = \frac{8 \int_0^t I dt}{FV\Delta COD} \quad (9.3)$$

where the value of 8 is a constant associated with chemical oxygen demand (COD) reduction (based on oxygen's molecular weight [32 g/mole], containing four electrons exchanged per mole of O_2), I is the current produced in a time interval, F is the

Faraday's constant (96,485 C/mole–electrons), V is the volume of anode chamber, and ΔCOD is the change in COD over time (t).

3 Current Development of Microbial Fuel Cell in Malaysia

Studies on MFCs have been reported as early as 1983 [20]. However, due to lack of attention and interest in the subject, studies on MFCs failed to expand over decades. Only in 2003–2004, it was confirmed that an MFC system could generate electricity while treating domestic wastewater to practical levels [20]. From that point onwards, MFCs have continuously gained considerable attention throughout the world and its popular subject category in energy fuels started to evolve dramatically.

In Malaysia, several prominent scientists have taken up this challenge to establish research and development centres and institutes to explore this emerging technology. As a support for the government plan in Fuel Diversification Policy, the Fuel Cell Institute of Universiti Kebangsaan Malaysia (UKM), the first research institute in Malaysia conducting research on fuel cell and hydrogen energy, was established on 1 July 2006. Under the leadership of Prof. Dato' Ir. Dr. Wan Ramli Wan Daud, one of the most prominent researchers in Malaysia, this institute has successfully progressed with a number of interdisciplinary research groups focussing on MFC, hydrogen production, CO₂ reduction and biosynthesis, wastewater treatment, ceramic and material research, and water desalination. It could be said that this initiative has also opened up more research interests among Malaysian researchers to explore MFCs in various specializations, including constructed wetland MFC, plant MFC, MFC based on forestry residue, solid waste, and sewage sludge, to name a few. These scientific efforts are also in agreement with the global initiative of Sustainable Development Goals (SDGs): (6) Clean water & sanitation, (7) Affordable & clean energy, (9) Industry, innovation, & infrastructure, and (13) Climate action. Table 1 lists some of the research projects and activities on MFC studies that have been conducted or in the ongoing phases. It should be noted that the information in Table 1 is basically gathered through online observation and the listed projects/activities might be conducted by other non-listed Malaysian universities/institutes as well. This data is only a general representation of active projects in MFC which dynamically progress from time to time across Malaysian universities and institutes, without any bias on the report.

3.1 Overview of Research on Microbial Fuel Cell Using Palm Oil Waste in Malaysia

MFC has been well studied by Malaysian researchers over the last decades. The richly available agricultural by-products or biomass in Malaysia, especially palm

Table 1 Projects and research activities on MFC in Malaysia

No	Projects/Activities	Research Institute/University	References
1	<ul style="list-style-type: none"> • Study on electrochemically active microbes, optimization of operating conditions, and electron transfer mechanism • Wastewater treatment—domestic and palm oil mill effluent (POME) sludge treatment • Electrode materials and design • Proton exchange membrane design 	Malaysian universities/Institute	[21, 22]
2	<ul style="list-style-type: none"> • Hydrogen energy production using microbial electrolysis cell (MEC): <ul style="list-style-type: none"> - Comparison to conventional water electrolysis - Biotic and abiotic cathodes • CO₂ reduction and biosynthesis—production of formate, acetate, butyrate, etc • Ceramic materials—properties of separator (pore size, ionic strength, selectivity, and permeability) • Water desalination—microbial desalination cell for purifying water from saline content • Ti/Ni-based alternative cathode MFC 	Fuel Cell Institute, UKM	[23–27]
3	<ul style="list-style-type: none"> • Membrane-less MFC • Benthic MFC <ul style="list-style-type: none"> - Marine sediment MFC for heavy metal remediation - Xylene, Benzene Biodegradation Soil MFC - Soil contaminant remediation • Graphene oxide anode MFC for metal removal 	Universiti Sains Malaysia	[28–34]
4	<ul style="list-style-type: none"> • Carbon nanotube-based electrodes MFC • Polysulfone membranes for MFC applications • MFC enhancement by mutagenic bacteria • Activated carbon-based MFC • Integrated adsorption hybrid-MFC 	<ul style="list-style-type: none"> • Universiti Malaya • Universiti Teknologi Malaysia • International Islamic University Malaysia • Universiti Malaysia Sarawak • University Tunku Abdul Rahman 	[35–40]
5	<ul style="list-style-type: none"> • Up-flow constructed wetland MFC using floating plant • Caffeine removal by double-chamber electrocatalytic MFC • Integrated MFC using Polypropylene activated carbon • Chlorophenol degradation by OPEFB based Electrode MFC 	Universiti Malaysia Perlis	[41–45]

(continued)

Table 1 (continued)

No	Projects/Activities	Research Institute/University	References
6	<ul style="list-style-type: none"> • Photocatalytic MFC—catalyst geometry for CO₂ reduction • <i>Pseudomonas</i> + <i>Klebsiella</i> The substrate-inoculum mechanism in MFC 	Universiti Malaysia Pahang	[46–49]

oil biomass, have directed much research interest towards the developmental MFC topics. There is an increasing trend of studies on MFCs using palm oil wastes in Malaysia, as depicted in Fig. 3. These data show that the research and development of MFCs in Malaysia have increased dramatically over the years, particularly in the use of readily available palm oil-based biomass. This initiative could help to resolve ongoing national debates about palm oil mill wastes, including liquid POME, solid residues in the form of biomass, and greenhouse gas emissions, all of which have had a severe impact on Malaysia's environment [50]. These data are also indicators of the effort demonstrated by Malaysian researchers to transform palm oil wastes into sustainable biofuel/bioenergy as envisioned by the National Biomass Strategy (NBS-2020).

POME has been the leading material used in MFC research, especially as substrates or sources of microbial inoculums to operate MFC reactors [47, 49, 51, 52]. POME is a liquid sludge produced through crude palm oil extraction from fresh fruit bunch and clarification process, which contains extremely high biological

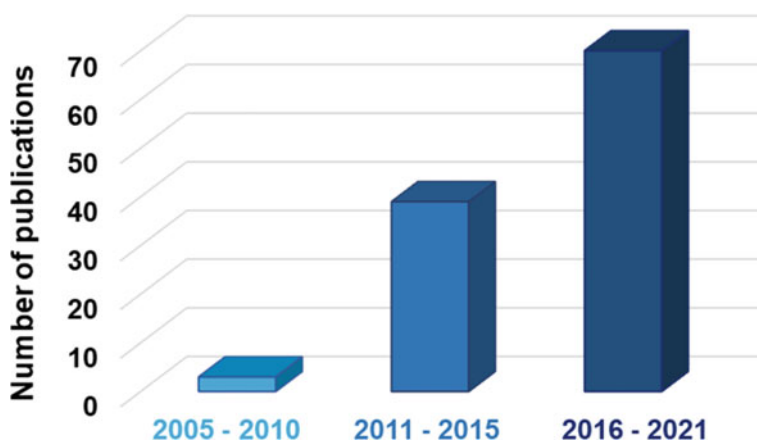


Fig. 3 Number of publications on MFCs using palm oil wastes in Malaysia. * Single database search engine by **Google Scholar** was used for publication search. Multiple search engines were avoided to prevent the redundancy of publication data. The data on publication numbers were collected up to April 2021. The publication types include journal articles, conference proceedings, theses, policy frameworks and reports, book chapters, and others. The data might vary from one search engine to another

oxygen demand (BOD) (about 25,000 mg/L), COD (can be up to 54,000 mg/L) and other contents of oil, grease, and total suspended solids. POME is also discharged with unpleasant characteristics, for example, strong odour, acidic, and high effluent temperature [50]. Hence, POME needs to be treated urgently and efficiently due to these non-environmentally friendly properties. Current and typical POME treatment in Malaysia is by using an anaerobic digestion (AD) system that generates biogas as a by-product [50]. This biological treatment is preferable due to its low energy requirement, the reduced release of unpleasant odour, and relatively high biogas generation. As POME is subjected to highly stringent wastewater treatment regulations, various treatment approaches have been considered for polishing of POME, including advanced oxidation process, physicochemical treatment, membrane filtration and bioreactors, and adsorption as the extension to the anaerobic ponding system. However, these treatment methods are relatively expensive and demand high energy consumption when dealing with huge volumes of POME generated.

Therefore, MFC appears to be a preferable method in treating POME due to its milder operating conditions, no energy consumption (as MFC itself is an energy supplier), and very minimal sludge production as opposed to AD. Interestingly, POME serves as a good source of organic matter, including lipids, carbohydrates, minerals, proteins, and nitrogenous compounds [53], which become valuable nutritional feed for bacteria in MFCs. In addition, POME is found to contain diverse microbial populations that are significantly suitable for biofilm development to power the MFC. Among principal microbial genera/families discovered in POME and proven to generate a high electrical current in MFC include *Pseudomonas*, *Escherichia*, *Bacillus*, *Klebsiella*, *Enterobacter*, and many more [54, 55]. These exoelectrogenic bacteria have tremendous potential for electrical power generation and can also effectively treat POME by reducing COD levels by up to 95%.

Other parts of palm oil residues have also been utilized in MFC studies, such as palm oil empty fruit bunch (EFB) [56] and oil palm trunk sap [33, 55]. These parts are generally used as substrates for biofilm growth or as sources to extract microbes for electricity generation in MFCs. Further attempts could exploit other parts of palm oil wastes (e.g., EFB fibre). The fibre consists of carbon-based cellulosic materials that can be potentially transformed into MFC electrodes. This is because carbon-based electrodes have demonstrated excellent MFC performances, as reported in most studies. Carbon-based electrodes are normally used in MFC reactors, including carbon cloth, carbon brush, carbon mesh, carbon paper, and modified carbon materials (e.g., activated carbon, carbon nanotubes, and graphite) [57]. These carbon-based electrodes are proven to improve bacterial adhesion to anode surface, thus increasing the power output in MFC systems.

3.2 *Microbial Fuel Cell Development and Design Using Palm Oil Biomass for Electricity Generation and Waste Removal*

Previous studies have reported multiple advanced designs of MFCs aiming to improve power attainment and optimize waste reduction. In this subchapter, several advanced development and designs of MFCs using Malaysian palm oil biomass as the main support for microbial function are briefly discussed, as presented in Table 2. Most of the reported studies used laboratory-to-pilot scale MFC setup for electricity generation and contaminant/COD removal. No higher scales of MFC construction for industrial application have been reported thus far. The highest power density achieved by the MFC using palm oil biomass is in the order of tens of Watts per metre cubic (W/m^3) by diverse electroactive microbial strains. The MFC could also achieve $> 90\%$ COD/BOD removal and demonstrated good performance to reduce other organic compounds and metals as well. These achievements are very promising for a relatively small device like an MFC reactor, and future attempts are highly demanded of higher-scale MFC construction for industrial wastewater treatment applications.

4 Challenges and Resolution Perspectives in Microbial Fuel Cell Application

Over the years, the practical hindrances to scaling up MFCs have become the major issue highlighted in most MFC studies. These challenges include low power attainment, high operating cost, complex industrial wastewater, and the flexibility of microbial anode or biofilms that drive MFC operations. Other technical problems, such as the high cost of cation exchange membranes and highly designed electrodes, biofouling problems, and associated internal resistances and power losses, which could reduce MFC performance, are worthy of being highly considered [59].

Basically, a laboratory-scale MFC (10^{-6} to 10^{-3} m^3) must be scaled up by several orders of magnitude to a scale suitable for wastewater treatment (1 to 10^3 m^3) [60]. Furthermore, a feasible operation should consider all scalable elements, such as modular or stacked MFC systems for reduction of operating cost and simple maintenance. This subchapter discusses only two main challenges and resolutions by current MFC progress in order to have a clearer prospect on these emerging issues.

4.1 *Low Power/Voltage Attainment*

Although the electrical current generation from MFCs has recently improved and achieved minimal power targets by small laboratory-scale systems, higher voltage is needed at least to power electronic devices. Firstly, a series of stacked MFC designs

Table 2 Current designs and development of MFCs and their performance using palm oil biomass

MFC types/Designs	Electrode materials	Palm oil Biomass	Electroactive microbes/Biofilms	Current/Power output	COD/Waste Removal	References
<ul style="list-style-type: none"> • Single chamber-air cathode • Cubic plexiglass (25 mL) 	<ul style="list-style-type: none"> • Anode: Carbon brush • Cathode: PACF 	POME as anode inoculum	<i>Klebsiella varicola</i>	1.7 W/m ³	COD: 43%	[47]
<ul style="list-style-type: none"> • Single chamber-air cathode (500 mL) 	<ul style="list-style-type: none"> • Anode: Carbon cloth with AC • Cathode: Pt-based with MPL and GDL 	POME	Unidentified	344 mW/m ²	COD: 92% BOD: 91%	[40]
<ul style="list-style-type: none"> • Single chamber-air cathode (5.65 L) • MFC-GAC hybrid adsorption system 	<ul style="list-style-type: none"> • Anode: Tubular MFC-adsorption hybrid brush • Cathode: Graphite fibre brush 	POME as anode inoculum	Unidentified	55 mW/m ³	COD: 91% BOD: 93%	[39, 58]
<ul style="list-style-type: none"> • Double chamber 	<ul style="list-style-type: none"> • Anode: Fabricated L-GO/ZnO • Cathode: Graphite rod 	OPEFB Oil palm trunk sap	<i>Lysinibacillus, Klebsiella pneumoniae, Leucobacter</i>	1.35 mW/m ²	Pb ²⁺ : 91%	[55]
<ul style="list-style-type: none"> • Double chamber (450 mL) • Borosilicate glass 	<ul style="list-style-type: none"> Anode/cathode: PACF 	POME	<i>Pseudomonas aeruginosa, P. mendocina, P. viridivida, Acinetobacter schindleri, Actinobacillus capsulatus, and Brevibacterium paucivorans</i>	22 mW/m ²	COD: 70%	[52]
<ul style="list-style-type: none"> • Double chamber (100 mL) • Polyacrylic sheets 	<ul style="list-style-type: none"> Anode/cathode: Carbon graphite 	POME	<i>P. aeruginosa</i>	451.3 mW/m ²	COD: 13%	[54]

PACF: Polyacrylonitrile carbon felt; AC: Activated carbon; MPL: Microporous layer; GDL: Gas diffusion layer; GAC: Granular activated carbon; L-GO: Lignin based graphene oxide; OPEFB: Oil palm empty fruit bunch

have been proven to yield higher voltage that could further promote the practical use of MFCs. The voltage across the circuit will be accumulated from all connected cells with a similar current flow throughout MFC systems. A three-series stacked MFC construction in continuous mode operation improved voltage generation up to 2.12 V and power of 3.16 W/m³. In a 40-individual air–cathode MFC series, the voltage and power increased significantly from 1.1 V to 4.9 V and from 5.8 mW/m² to 2,500 mW/m², respectively. It is interesting to note that the series and parallel MFC operations also influenced the microbial community profile. The dominant species found in the unconnected single MFC system were *Bacillus* and *Lysinibacillus* and after converting the single-mode to series and parallel connections, other microbial strains like *P. aeruginosa* and *Bacilli* classes dominated the anode chamber [61].

Secondly, the harvesting of low power generation by MFCs has led to the emergence of new hybrid systems developed by integrating MFCs with external fabricated harvesting systems based primarily on supercapacitors [62, 63]. Recently, supercapacitor-based electrode MFCs have been proven to show better performance, which is mainly attributed to their excellent material properties [64]. This novel capacitance-based MFC has significantly improved ORR kinetics along with the increase of power density by 140% by using the combination of carbon nanotubes and carbon nanofibers (CNTs/CNFs) electrodes. A stable catalytic activity was also achieved without a reduction in voltage over 60 days [65].

Other than MFC hybridization, modelling and simulation work on MFC operation seem to be useful tools to overcome its main performance drawbacks. An optimization study is necessary to reduce technical constraints and costs of MFC materials and operation, as well as to increase MFC performance. Much scientific effort has been made to optimize MFC systems in order to achieve low-cost operation and provide sustainable energy [66]. However, over the last decade, only a small number of studies have been reported on modelling and mathematical optimization of MFCs, which might be due to the intricacy of simulation works that require a vast number of preliminary data. It is just over recent years that multiple works dealing with MFC modelling have increased [67]. Several phenomena that are still hidden deep inside the anodic environment of exo-electrogenicity that can be best explored by the modelling approach are the mass transport surrounding and inside the cell, microbial growth, phase of matters, layers and boundary conditions, anode and cathode reaction kinetics, and the electrochemical behaviour of the cell [66]. Due to well-established MFC technology among scientific communities, an increase in the number of modelling approaches pertaining to MFC optimization is expected in the near future. It is believed that this effort will increase our understanding of this system to improve its performance through cost-effective means.

4.2 Flexibility of Anode Biofilms

Anode microbial biofilm is the key component to drive the current generation in an MFC system. Previous studies have shown significant changes in the composition of microbial communities on improving MFC power output [68]. However, the low extracellular electron transfer rate from the electrogenic biofilm to the electrode surfaces still limits the practical application of MFCs [69]. In addition, MFC operation will become more complicated when dealing with real industrial effluents or typical environments (e.g., sediments, wetlands, marine environments, and lagoons) [59]. The bacteria kinetics are hardly interpreted in diverse microbial consortia and the biofilm interface with electrode has still not been fully described [70], especially in a multitude of microbial species (either electroactive or not) [68]. Finally, the microbial electrochemistry for biofilm formation, interspecies communication, metabolic pathways governing substrate oxidation, and the influence of microbial colonization still require careful elucidation to entirely understand the bioelectrochemical phenomena in the MFC reactors [71].

Genetic modification of biofilms can be a potential approach to enhance MFC power performance through biofilm-electrode surface interaction. Molecular biology techniques, such as “knock-in” and/or deletion/repression/overexpression technology, can be used to genetically trace the potential and appropriate bacteria to acquire exoelectrogenic properties. This is important to ensure that there are no harmful and transmittable properties of genetically modified organisms [68]. It is also critical to avoid escapism where the modified bacteria without promoter compounds (arabinose, tetracycline, and other compounds that trigger strong promoters) are released to the environment and destroyed by autolysins [68]. Several cutting-edge chemical and molecular biological analysis techniques have been studied to modify the properties of bacteria, including chemical modification of microbial cells, gene regulation, mutagenesis, or overexpression of key genes that enhance the electrogenic potential of the bacterial community composition. For example, chemically polyethyleneimine-treated *P. aeruginosa* biofilm was found to accelerate electron transfer, resulting in twice the maximum power density compared to that of the non-treated biofilm [72]. Through genetic manipulation, the main redox-active compounds secreted by exoelectrogenic bacteria, which are responsible for mediating electron transfers from biofilms to the electrode surface, could be improved. The extracellular electron transfer was improved in *P. aeruginosa*-inoculated MFCs after the modification of the phenazine-1-carboxamide synthesis pathway [73].

Apart from modifying the genes of potential bacteria to enhance exoelectrogenic properties, the surface chemistry and morphology of electrodes could also be modified to achieve better bacterial adhesion [5]. In principle, oxygen has always been the main oxidant at the biocathode due to its considerable concentrations and high reduction potential. Several studies have demonstrated that the utilization of metallic oxidants (e.g., U, Cd, Cr, and Cu) could be reduced to a less toxic oxidation state [74] by metal-reducing bacteria (MRB). The ORR problems in the cathode could be compensated with the stable and flexible genetically modifiable MRB.

5 Conclusion

MFC appears as a highly promising technology for electricity generation and wastewater treatment and is foreseen to be developed for real industrial applications in the near future. Recent data suggest that MFC has the potential as the most preferred sustainable technology owing to its unique capability to recover bioelectrical energy. Various scientific works, especially in Malaysia, have proven that this technology offers potential prospects for power generation and wastewater treatment by the use of richly available biomass, for instance, palm oil wastes. However, more studies are required to develop a sustainable higher-scale MFC system that can endure multiple operational and technical hindrances to significantly improve MFC performance. In addition, MFC systems should also be well-customized to tolerate high-strength wastewater containing multiple refractory and toxic compounds, especially in the Malaysian wastewater system. Other key elements of MFC, such as microbial cultures, substrates/biomass, physicochemical parameters, MFC setups, and electrode materials, are important to be appropriately designed to optimize its electrical power and waste degradation capabilities. Besides, the efforts to hybridize the MFC system with other existing wastewater treatment technologies should be maximized in order to enhance the prospects of MFC for industrial applications.

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Renewable Energy: The Past and the Future



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Abstract The application of renewable energy such as bioethanol and biodiesel as a fuel substitution is a promising approach to reduce the dependency on fossil fuels. However, several aspects need to be improved, mainly on the product yield and economic processes. This chapter discussed the challenges hindering the progress of renewable energy, particularly bioethanol and biodiesel in Malaysia. Several current innovations and technologies for the advancements of second, third and fourth generations were subsequently reviewed based on their potentials to improve the feasibility of bioenergy production. In addition, the implementation of previous and current renewable energy programmes to increase their uptake in the country was highlighted. The effect of initial programmes, including the Small Renewable Energy Programme (SREP), UNDP-GEF Biomass Power Generation and Demonstration (BioGen) Project, Malaysian Building Integrated Photovoltaic (MBPIV) Project and the Economic Transformation Programme (ETP), as well as the recent Feed-in Tariff (FiT), Self-Consumption programme (SELCO) and Net Energy Metering (NEM) programmes on the progress of RE application in Malaysia was deliberated. Ultimately, the impact of RE empowerment towards achieving the goals outlined in Malaysia's Sustainable Development Goals was concluded.

Keywords Renewable energy · RE Programme · Sustainable Development Goals · Energy Security

1 Introduction

Renewable energy (RE) was identified as the fifth fuel in the Malaysian Five-fuel Diversification Strategy in 2011, which had further diversified the energy mix in

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Malaysia. In 2018, it was reported that 4.2% of the electricity generation mix was occupied by RE with 1450 MW of installed capacity [1]. Solar and biomass energy has become the most promising RE in Malaysia [2]. According to Salleh et al. (2020), solar energy is topping the chart with a 47% or 430 GWh share in the energy generation mix, followed by biogas and biomass with 25% and 22% which is equivalent to 224 GWh and 198 GWh of the energy generation mix, respectively [2]. RE such as bioethanol and biodiesel are seen as promising biofuels to be produced in Malaysia due to their rich palm oil resources and suitable weather for microalgae cultivation. However, the biggest challenges for the production of this RE rely on the product yield and economic feasibility of the process. Therefore, research and innovations focussing on biomass-based energy could stimulate the development of bioenergy and subsequently increase its share in the energy generation mix. In addition, innovations in technology are required to ensure bioenergy plays a role in the reliable, affordable, and sustainable energy system of the future.

2 Challenges and Barriers

2.1 Bioethanol

Bioethanol can be classified into several categories; first generation, second generation, third generation, and the latest is the fourth generation; based on different raw materials and production steps involved [2, 4, 5]. Hence, each category faces different problems and challenges that have to be resolved to achieve higher productivity and make it economically viable. First-generation bioethanol is produced from sugars and starchy material; for example, sugarcane, maize, molasses and wheat [5, 6]. These sugar sources are converted into bioethanol through ethanolic fermentation, involving microorganisms commonly *S. cerevisiae*. Although the production step is simple and direct, the yield depends on the availability of the crop. Large amounts of fertilizers are needed to increase the crops yield, hence contributing to the high cost of raw materials [7, 8]. Moreover, the utilization of food sources as raw materials has created an issue of food competition [9]. From the environmental aspect, the utilization of fertilizer and land was recognized as major contributors to high environmental problems, such as global warming [10, 11].

Unlike the first-generation bioethanol, second-generation bioethanol is derived from non-edible sources such as lignocellulosic material, consisting mainly of cellulose, hemicellulose and lignin [12]. The employment of cellulosic residues, especially from the agricultural and wood industry, is considered a green approach because it is based on non-food sources, thereby minimizing the release of greenhouse gases [13]. Various agricultural residues could be used for this purpose, such as sugarcane bagasse, corncob, rice straw and husk, wheat straw, oil palm biomass and many more [8]. Besides being abundantly available, this biomass is also relatively cheap [14].

However, the problems in lignocellulosic bioethanol are low yield and highly expensive hydrolysis processes [7]. The conversion of lignocellulosic biomass into sugars before fermentation is challenging due to its complex and recalcitrant structure. Pretreatment to alter its native structure is necessary to provide higher enzyme penetration during enzymatic hydrolysis, hence improving the hexose and pentose sugars production [8]. Among the pretreatment approaches currently adopted at the existing bioethanol biorefineries are dilute acid and steam explosion, yielding more than 90% (g/g substrate) of sugar [15]. However, the cost of pretreatment and enzymes is very high. Through economic analysis, it was reported that sugar recovery contributed about 40% of total production cost, with enzyme alone accounting for 22% [12, 15]. Hence, the selection of the most efficient pretreatment method is crucial as it helps to reduce enzyme loading and improve the economics of bioethanol production. Besides that, the lack of microorganisms capable of converting hexose and pentose sugars is also a problem. The natural *S. cerevisiae* only consumes hexose sugars, mostly glucose, thereby limiting the sugar yield. Other microorganisms such as *Pichia stipitis*, *Kluyveromyces marxianus*, and *Candida shehatae* are capable of fermenting pentose sugars [5]. Hence, the development of more robust industrial strains which could consume both hexose and pentose sugars is highly desired [7].

The generation of bioethanol by utilizing algal biomass is called third-generation bioethanol [5, 16]. With sufficient light, carbon dioxide and nutrients, microalgae produce a high amount of lipid and carbohydrates, which can be further extracted to be used for the generation of bioethanol, biodiesel and biohydrogen [3]. However, low biomass yield hinders its application at the industrial scale. Moreover, high energy inputs are required in the harvesting of biomass. Hence, a cheaper and energy-efficient approach is required to make the process more feasible [3]. The advancement of third-generation bioethanol is considered as the fourth generation, where it involves genetically engineered biomass feedstocks, such as algae, trees, and plants with improved carbon-storing and release ability [17].

Another issue that contributed to the economic problem of bioethanol is the requirement of highly concentrated bioethanol, more than 99% for application as biofuel, hence an energy-consuming distillation process is needed [7]. Furthermore, several limitations related to the properties of bioethanol also limit its application as a biofuel. Unlike gasoline, bioethanol is hygroscopic and has a low boiling point; it may vaporize in engines during hot conditions and result in vapour lock. Therefore, modifications of the current engine system are necessary to avoid problems like corrosion and dissolution inside the engine [18].

From a larger perspective, as Malaysia moves towards the bioeconomy, it is vital to ensure adequate control of the agricultural biomass in terms of quality, amount and punctual transportation from the farming site [13]. A feasible production comprises excellent logistics for biomass delivery. A direct approach would be by developing an integrated biorefinery, where the infrastructure could be shared between the existing plant or mill and the biorefinery for the production of new products (e.g., chemicals and biofuels). For instance, the integration of lignocellulosic bioethanol biorefinery in the existing palm oil mill appeared to be economically promising for scaling

up [19]. Besides simplifying the process, this approach would also increase the competitiveness of existing plants.

2.2 Biodiesel

Like first-generation bioethanol, biodiesel is also considered a first-generation biofuel. It is generated through transesterification of animal fats or plant oil, such as soybean oil, yellow grease and used as cooking oil. In Malaysia, biodiesel is produced mostly using crude palm oil (CPO) as it is among the major commodities in the country. For this reason, its market is significantly influenced by the fluctuations of CPO's, hence maintaining a stable biodiesel market is challenging [20]. It was reported that the unsteady market value of palm oil was one of the contributing factors to the failure in achieving the aim of B5 biodiesel scheduled in the National Biofuel Policy [18]. Unstable CPO market price creates an inconsistent market supply of CPO, therefore affecting the biodiesel industry. In order to boost biodiesel utilization, the B7 (7% blending in biodiesel) programme was introduced in 2016 by utilizing it in industrial sectors for electricity generation [20].

Moving forward, B10 (10% blending in biodiesel) programme was announced in 2019 to further support the biodiesel producer. Similarly, the issue of the unstable market price of CPO was one of the major challenges [20]. Furthermore, the increasing demand for CPO created a significant price gap between palm oil and biodiesel. The rise of CPO price increases the cost of biodiesel production and makes the product more expensive; hence, it is considered incompetent to compete with crude oil (petroleum). It was reported that the biodiesel market would only be competent if the price of crude oil is above 50 United States Dollars (USD) [21]. In 2020, the price of crude oil dropped to as low as USD 37 per barrel [22]. Moreover, unlike B5 and B7 programmes, the B10 programme failed to convince the carmakers to provide vehicle warranty due to insufficient information to support its safety in the fuel delivering system [20]. Consequently, the consumer needs to bear any adverse effect due to its application in the vehicle. To solve this issue, the government is working with other government agencies like the Malaysian Palm Oil Board and Malaysia Automotive Association to continually convince the vehicle manufacturer by providing more evidence through their research work [20]. The continuous support from the vehicle manufacturer, not only assists the implementation of the B10 programme, but also the B15 programme which began in 2021.

3 Technologies and Innovations

Advancements in science and biotechnologies have accelerated research in biofuels production from engineered microbes and plants through metabolic engineering approaches. Each generation of biofuel is utilizing engineered microorganisms in

producing superior workhorses to directly fabricate desired products in fulfilling the needs of future fuels. The following sections will further discuss the roles of genetically modified microbes in generating biofuels and enhancing the efficiency and productivity of microbial strains for industrial uses.

3.1 *Advancements in the Second-Generation Biofuels*

Bioethanol from lignocelluloses traditionally produced in separate tanks for hydrolysis and fermentation. This approach is known as separate hydrolysis and fermentation (SHF). This conventional process is now simplified to simultaneous saccharification and fermentation (SSF) and most currently, the approach is refined to consolidated bioprocessing (CBP). These current approaches allow enzymatic hydrolysis and fermentation in the same reactor as shown in Fig. 1. They involve less equipment, which will subsequently reduce the overall production cost [23]. The SSF process is often successful when combined either with autohydrolysis or dilute-acid pretreatment. Cellulases and xylanases are the enzymes used in SSF to catalyze the breakdown of lignocelluloses into sugar monomers for microbial fermentation. These enzymes are inhibited in the presence of glucose, xylose, cellobiose and other oligosaccharides, thus reducing the sugar yield [24] and has become the limiting factor in SHF. The major difference between SSF and CBP lies in the hydrolytic enzymes. SSF involves the addition of hydrolytic enzymes concurrently when performing the fermentation, therefore overcoming the end-product inhibition. CBP advances a step further as the microbe itself produces the enzymes internally. Thus, CBP incorporates these processes in a single step. An engineered microbial strain with high enzyme secretion activity and high fermentation capacity is desirable for the development of the CBP process.

Conventional yeasts used in the production of ethanol such as *Saccharomyces cerevisiae* are very robust in terms of their tolerance to industrial inhibitors produced from extreme processes in the pretreatment of lignocellulosic hydrolysates. However, the major drawbacks of these yeast strains are their inability to utilize pentose sugars, as well as not growing well in the cellulosic and lignocellulosic biomass. Therefore, a versatile microorganism that can withstand high temperature, high ethanol concentration and the presence of inhibitory compounds in hydrolysates is highly anticipated for a successful CBP implementation.

In a study conducted by Amoah and colleagues, they successfully constructed a yeast capable of expressing five cellulase genes, consisting of cellobiohydrolase I (*CBHI*), cellobiohydrolase II (*CBHII*), β -glucosidase (*BGL*), endoglucanase (*EGII*) and xylanase (*XYNII*) for consolidated bioprocess ethanol production. They proposed the δ -integration method for screening of the optimal cellulase ratio produced by the CBP yeast. Their results depicted that the optimal cellulase ratio varies in different biomass, suggesting its importance to breed CBP yeast having optimal cellulase ratio for designated biomass. The bred CBP yeast was capable of producing 0.93 g/L of ethanol from ionic-liquid pretreated bagasse and 0.71 g/L of ethanol from Laubholz

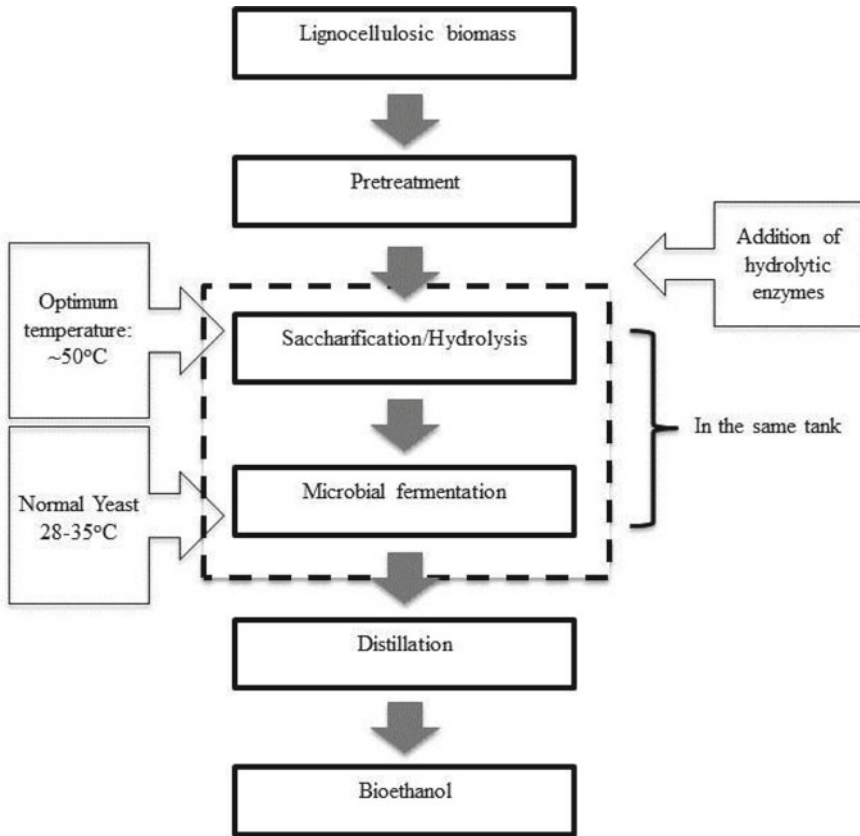


Fig. 1 Scheme of bioethanol production. Saccharification and fermentation (SSF) occur in a single tank simultaneously while CBP advances further by incorporating microbes capable of producing hydrolytic enzymes

unbleached Kraft pulp (LUKP) [25]. In another report, Singh et al. reported an anaerobic thermophilic isolate of *Clostridium sp.* DBT-IOC-C19, which was isolated from Himalayan hot springs. This isolate could convert cellulosic and hemicellulosic into bioethanol, lactate and acetate in a single-step conversion. Additionally, they discovered that after varying the cellulose concentration, the isolated strain can utilize cellulose up to 10 g/L. The degradation kinetics of Avicel by the DBT-IOC-C19 strain at 5 g/L and 10 g/L was 94.6% and 82.74%, respectively within 96 h of fermentation [26].

The attractiveness of CBP is due to simultaneous hydrolysis of lignocelluloses and single-step fermentation without the addition of external enzymes. This approach is also promising in reducing the processing cost. Tian et al. had used an engineered *Clostridium thermocellum* in the production of ethanol through consolidated bioprocess. The strain produced ethanol at a remarkable temperature of 55 °C and

was engineered in their central metabolic pathways to produce only ethanol. In this research, 60 g/L of crystalline cellulose was utilized as substrate and yielded 0.39 g/g of ethanol, which is 75% of the theoretical yield [27].

To date, the research in this area is still ongoing and a rightful candidate is yet to be discovered for CBP implementation. Although there have been numerous reports on the bioethanol-producing microorganisms, their ability to co-ferment sugars, low ethanol yield as well as low tolerance to chemical inhibitors, ethanol and high-temperature fermentation remain the major challenges [28]. Hence, microorganisms with the ability to ferment pentose and hexose sugars simultaneously to bioethanol and possess multiple stress tolerance are still investigated in line with the demanding process.

3.2 *Advancements in the Third-Generation Biofuels*

The main ideas of solar fuels focussed on generating energy from sunlight. Sunlight is captured and stored in material as chemical bonds. When needed, these chemical bonds can be hydrolyzed and produce fuels. The idea of making fuels from sunlight is the basis of photosynthesis and the ground for third-generation biofuels, which are manipulated micro/macro-algal biomass to produce fuels. In the presence of sunlight, the algae produce oxygen and sugars or other materials from water and carbon dioxide which can then be used as sources of fuels.

Being a perfect candidate for the third-generation biofuels, microalgae offer several advantages such as fast growth rate, carbon-neutral, the high production rate of lipids (oils) and high photosynthetic yield. Terrestrial plants normally contribute about 0.5% of solar energy to biomass while the observed yields for microalgal are approximately 3% to 8% [29]. The percentage compositions of protein, carbohydrates and lipid of algal biomass in dry weight are shown in Table 1. The compositions of microalgal biomass vary among species. Microalgae such as *Nannochloropsis granulate* (B) (CCMP-535) has the highest lipids content of 48% while *Chlorella sp.* and *Dunaliella salina* are among the species that have the highest protein content (53–57% dry weight).

Lipids, carbohydrates and proteins found in microalgae biomass have the potential to be converted into other different bioproducts (Fig. 2) [30]. The potential applications of algal biomass are vast. Lipids and carbohydrates can be extracted to produce biofuels such as biodiesel, bioethanol, biohydrogen and biomethane while carbohydrates and protein can be utilized as fertilizers, nutritional supplements, cosmetics, and feed. It is advantageous to implement microalgae as feed-stocks for biofuels production since it is not a staple food crop for either humans or animals. In addition, microalgae do not occupy lands for agriculture and require saline water for their cultivation. Microalgae species are normally classified into four main groups; green algae (Chlorophytes), red algae (Rhodophytes), blue and green algae (Cyanobacteria) and other algae (Chromophytes). The most widely studied among them are the Cyanobacteria, Bacillariophyceae and Chlorophytes, producing

Table 1 Compositions of protein, carbohydrates and lipids in different species of microalgae biomass [30][31]

No	Microalgal species	Lipids	Carbohydrates	Proteins
1	<i>Acutodesmus dimorphus</i> (UTEX-1237)	18.8	38.6	28.1
2	<i>Botryococcus braunii</i> (A) (UTEX-572)	34.4	18.5	39.9
3	<i>Botryococcus braunii</i> (B) (UTEX-572)	24.9	30.6	39.1
4	<i>Chlamydomonas reinhardtii</i>	21	17	48
5	<i>Chlorella sorokiniana</i>	12	22	24
6	<i>Chlorella sp.</i>	15.7	25.2	53.3
7	<i>Dunaliella salina</i>	6	32	57
8	<i>Nannochloropsis granulate</i> (A) (CCMP-535)	23.6	36.2	33.5
9	<i>Nannochloropsis granulate</i> (B) (CCMP-535)	47.8	27.4	17.9
10	<i>Neochloris oleoabundans</i> (UTEX-1185)	15.4	37.8	30.1
11	<i>Porphyridium aeruginosum</i> (UTEX-755)	13.7	45.8	31.6
12	<i>Porphyridium cruentum</i>	9–14	40–57	28–39
13	<i>Prymnesium parvum</i>	22–39	25–33	28–45
14	<i>Scenedesmus dimorphus</i>	16–40	21–52	8–18
15	<i>Spirogyra sp.</i>	11–21	33–64	6–20

vast varieties of commercial products such as biomass feedstocks, fatty acids, β -carotene, carotenoids, docosahexaenoic acid (DHA), eicosapentaenoic acid (EPA) proteins and carbohydrates.

The major hurdle in the conversion of algal biomass into other products is the reliance on complex, technologically challenging and expensive processes. Initially, the algal biomass is hydrolyzed into its main components of lipids, carbohydrates and proteins by either extraction or fractionation technology. Then, these extracted components are converted into desired products through transesterification, fermentation, anaerobic digestion, transesterification, and pyrolysis or gasification. For instance, bioethanol production from microalgal species requires cultivation process, harvesting and drying, saccharification of the biomass to liberate sugars and fermentation by yeast to convert the sugars to bioethanol. The production of biodiesel from microalgae necessitates the extraction of lipids after biomass drying, followed by a transesterification process to produce fatty acids methyl esters (FAME) (biodiesel).

Biodiesel and bioethanol can be co-produced since the microalgal biomass consists of both lipids and carbohydrates. Normally the lipids are extracted to produce biodiesel and subsequently, the biomass residuals are pretreated and fermented to bioethanol. The co-production of biodiesel and bioethanol from microalgae *Chlorella sp.* KR-1 was demonstrated by Lee et al., and the microalgal species accumulated 38% (w/w) of lipids and 36% (w/w) of carbohydrates. The extraction of lipids was performed at 60 °C using dimethyl carbonate and methanol (7:3, v/v) as solvents under magnetic stirring for 12 h. Then, FAMES were produced by lipase-catalyzed transesterifications and approximately 250–298 mg of FAMES/gramme of microalgal

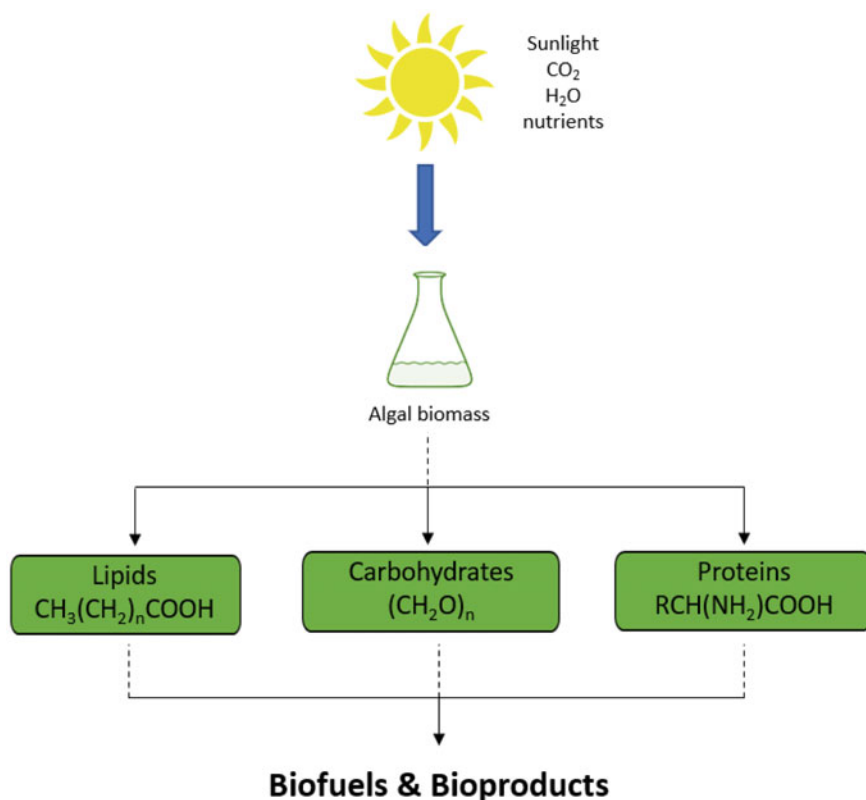


Fig. 2 Potential applications of algal biomass. Adapted from [30]

biomass was obtained. The residual biomass was then used for saccharification and bioethanol production. Enzymatic treatment with Pectinex enzyme yielded 76.9% of monosaccharides while chemical treatment with 0.3 N HCl yielded 98.2% of monosaccharides.

The process produced 0.4 g ethanol/g fermentable sugar and 0.16 g ethanol/g residual biomass [32]. Besides that, *Chlorella* UMACC050 has also been isolated from Malaysia. This isolate showed a very high content of fatty acids between 34.53 and 230.38 mg L⁻¹ d⁻¹, making it a potential candidate for biodiesel production [33].

The co-conversion of biodiesel and bioethanol has also been produced by psychrophilic microalgae. The psychrophilic microalgae can be found in the coldest region on earth such as the Arctic and Antarctica. Due to harsh environments, the microalgae evolved to adapt to such surroundings and offers special compounds that are native to cold habitats such as antifreeze proteins, polyunsaturated fatty acids, antioxidants and UV radiation-screening compounds [34, 35]. Therefore, the psychrophilic microalgae are potentially useful as alternative feedstocks for biofuel

production and other bioproducts. Lipids from the psychrophilic biomass are high in polyunsaturated fatty acids, thus contributing to its fluidity at a very low temperature. Such characteristics could be useful for biodiesel applications in the cold regions or winter because at very low temperatures, the FAMES molecules tend to crystallize and agglomerate, subsequently clogging fuel lines and filters [36]. Recently, Kim et al. isolated an Arctic Sea ice microalgae identified as *Chlamydomonas sp.* The researchers had used freeze-dried samples and the extraction was performed using Lewis's method. The total yield of FAMES extracted was 165.4 mg/g of dry cell weight. Subsequently, the carbohydrates content was estimated to be 50.3% (w/w) while the residues after biodiesel extraction were used to produce bioethanol. Hydrolysis of starch using sonication and addition of enzymes (AMG 300L; amyloglucosidase) produced the highest bioethanol concentration with 0.22 g/g of residual biomass. Collectively, the research produced 300 mg of biofuel per gramme of dried biomass, thus making these findings the highest psychrophilic biofuel producer to date [37].

On the other hand, thermotolerant microalgae may also be useful in hotter regions. In order to establish outdoor microalgae cultivation in hot environments, strains that are tolerant to high light intensity, high temperature, seawater environments are required. Exploration of indigenous strains that can fulfil these requirements are highly investigated. *Picochlorum* is one of the genera that has been identified to have broad thermotolerance, resilience to high light intensity, halophilic, fast doubling time and a compact genome architecture [38, 39]. In 2019, Dahlin et al. characterized an isolate of *Picochlorum renovo sp. nov.*, that is thermotolerant, halophilic with high-productivity, therefore possesses the potential to be cultivated outdoors [40]. Other than that, *Desmodesmus sp.* F2, *Coelastrella sp.* F50, *Micractinium sp.* and *Geitlerinema sulphureum* are among microalgae species that have been reported to have thermotolerant ability [41]–[43].

According to Franz et al. tropical regions serve as suitable locations for microalgal cultivation compared to temperate climate regions due to longer daylight hours and stable temperatures annually [44]. Hence, the tropical weather of Malaysia is promising for large-scale cultivations of microalgae for biofuels production. Microalgae have exhibited remarkable potentials to be cultivated in Malaysia than other types of feedstocks due to the tropical climate, longer daylight hours, high biomass productivity and economic supply of nutrients [45]. However, the mass cultivation of microalgae in Malaysia is still in the infancy phase. According to the microalgae-biodiesel study of Malaysia, large-scale cultivation of microalgae may only be economically feasible when it is integrated with other industries such as aquaculture farming or industrial wastewater treatment plants. Therefore, value-added products can be produced along with microalgae cultivation for biofuels [46].

Biofuels are seen as better alternatives to conventional fuels to a large extent. In comparison to the first-generation biofuel that utilizes food crops as feedstocks, the third-generation biofuels focussed on the generation of biofuels from microalgae. Biofuels produced from microalgae are much cleaner than the combustion of fossil fuels. Since microalgae are capable of assimilating CO₂ during growth, the combustion of fuel produced by microalgae is regarded as a carbon-neutral process. However,

the major challenge in the conversion of algal biomass to biofuels is the economic feasibility of the process. Currently, the production of algal biofuel is still not cost-effective compared to conventional fuels. Nonetheless, there are promising discoveries on the ability of some genetically modified microalgae species in accumulating up to 70% of lipids in their dry weights [30]. The development of superior strains that can meet all industrial requirements is highly anticipated and the search for such strains is still ongoing. Advancements in genetic engineering tools and biotechnological approaches are essentials in the discovery of superior microalgae species capable of producing higher yields at feasible costs.

3.3 *Fourth-Generation Biofuels*

The fourth-generation biofuels are derived from the third-generation biofuels. The fourth-generation biofuels focus on enhancing the efficiency of converting solar energy into chemical energy via photosynthesis, which is the basis for microalgae cultivation. Investigation on the photosynthesis and metabolic pathways to enhance the photosynthetic process, as well as to increase light penetration in potential microalgal strains are performed using genetic and metabolic platforms in the fourth-generation biofuels [47].

Although microalgae are regarded as better alternatives to produce biofuels as mentioned earlier in Sect. , the production of biofuels from microalgae is still considered uneconomical compared to the first-generation biofuels. These are mainly due to low biomass yield, high cost of lipid or carbohydrate recovery and downstream processing, limitation in light penetration in dense microalgae cultivation systems and growth inhibition of microalgae by a combination of high dissolved oxygen and intense sunlight [48]. Therefore, some of these technical barriers could be potentially resolved through metabolic and genetic engineering. The development of high yield, lipid-rich microalgae, oxygen-tolerant species, and improvement of certain lipid types for efficient photosynthesis in microalgae are progressing in producing superior strains of microalgae for future fuel efficiency.

Basically, genetic engineering in microalgal strains is possible and relatively easier than genetic manipulations in crop plants that existed in multiploidy. The haploid nature of most microalgal at different vegetative stages and the absence of cell differentiation make it easier to manipulate genes [49]. However, the progress of genetic or metabolic engineering of these organisms has been delayed due to the knowledge gap on genes and genome sequence of microalgae. The improvements of microalgal species are now picked up after the establishment of *Chlamydomonas reinhardtii* (model organism) full genome sequence in 2007, with subsequent advances in genome sequencing platforms, strain developments and genome editing technologies [50].

In 2016, Yamaoka et al. identified a plastid-targeted 2-lysophosphatidic acid acyltransferase (*CrLPAAT1*) gene from *Chlamydomonas reinhardtii*. This gene is

responsible for forming phosphatidic acid by acylating the *sn*-2 position of 2-lysophosphatidic acid. Phosphatidic acid is known as the first precursor in the biosynthesis of all acylglycerol lipids in the cell. It was reported that under nitrogen-deficient conditions, the expression of this gene can increase the lipid content by more than 20% in *C. reinhardtii*. The gene *CrLPAATI* is native in *C. reinhardtii* and can be targeted to improve lipid content in microalgae [51]. Besides the expression of the *CrLPAATI* gene to improve lipid content, a knockdown of the pyruvate dehydrogenase kinase (PDK) gene was also reported by Ma et al. [52]. PDK is the enzyme that deactivates the pyruvate dehydrogenase complex (PDC), whereas the latter is known to catalyze the reaction of converting pyruvate into acetyl-CoA. As demonstrated in *Arabidopsis*, the PDC activity can be inactivated by the overexpression of the *Brassica napus* PDK gene, resulting in the decrease of seed oil content. These events motivated Ma et al. [52] to conduct the study. Specifically, the knockdown of the antisense PDK gene in *Phaeodactylum tricornerutum* resulted in the increment of neutral lipids of up to 82% in the mutant strain [52].

In order to improve light-harvesting systems in microalgae, Polle et al. disrupted *Tlal*, a gene that encodes for the chlorophyll antenna size regulation in *C. reinhardtii* by insertional mutagenesis. The resulting mutant was a truncated light-harvesting chlorophyll antenna size. Under mass culture conditions, the mutant strain revealed a higher efficiency for solar conversion and higher photosynthetic productivity compared to the wild type [53].

The fourth-generation biofuels that make use of genetically engineered feedstocks are seen as a promising candidate to replace fossil fuels. Genetic improvement of microalgal strains towards efficient solar conversion, high photosynthetic productivity, rapid biomass production and high yield of lipids content are highly anticipated in the search for new alternative fuels. However, research progress in Malaysia on fourth-generation biofuels is rather scarce. Therefore, the opportunities to participate in this area of research are immense. Support in terms of funding and policies from the government, as well as investments from industries, are highly encouraged to expedite research in the fourth-generation biofuels.

4 Renewable Energy Programs

The effort to elevate the RE status in Malaysia began a long time ago and is still progressing. Among the early programmes include the Small Renewable Energy Programme (SREP), the UNDP-GEF Biomass Power Generation and Demonstration (BioGen) Project, the Malaysian Building Integrated Photovoltaic (MBPIV) Project and the Economic Transformation Programme (ETP) [54]. Looking back, the Malaysia Renewable Energy Policy and Action Plan were introduced under the 10th Malaysia Plan in 2011, with a projected RE capacity of 985 MW or 5.5% from 2010 to 2015 [54]. The goals were to improve the contribution of RE to the electric power generation mix, assist the development of the RE industry, and generate a cost-effective and environmentally safe RE for upcoming generations. Subsequently, the

Sustainable Energy Development Authority (SEDA) was established and has been responsible for the implementation of the RE programmes in Malaysia since then. As part of the plan, the Feed-in Tariff (FiT) was introduced to increase public awareness on RE and it is continuing thus far. In 2018, the revised RE plan was announced by the government, whereby a 20% RE capacity mix was targeted to be achieved by the year 2025 [55]. Half of this target is expected to be fulfilled by the solar energy generation system, whereas the remaining will be contributed by other RE technologies. Henceforth, in addition to FiT, other programmes involving the application of solar technology was offered by the SEDA to attract more RE consumers, including the Self-Consumption programme (SELCO) and Net Energy Metering (NEM).

4.1 Small Renewable Energy Program (SREP)

The Small Renewable Energy Program (SREP) was introduced on 11 May 2001 along with the 8th Malaysia Plan, with the target to instal 500 MW of RE facilities by 2010 [54, 56]. This project aimed to motivate the RE project developers and assist in RE generation in Malaysia. Moreover, it enables the independent small RE power plant to sell their electricity, generated from either biomass, municipal waste, biogas, solar or wind to the grid. As of March 2010, the total approved project was 43 with a total capacity of only 275.15 MW, including Jana Landfill Sdn Bhd in Puchong, Selangor and TSH Bioenergy in Tawau, Sabah, utilizing biogas and empty fruit bunch as their fuel source, respectively [32, 54]. However, this programme failed to achieve the targeted capacity due to technical restraints, a prolonged endorsement procedure, absence of supervision, omission of investors, and the lack of initial viability. In addition, disapproval from the national utility Tenaga Nasional Berhad and incomparable electricity rates with the exact production expenses further contributed to its poor performance [56].

4.2 The UNDP-GEF Biomass Power Generation and Demonstration (BIOGEN) Project

The United Nations Development Programme (UNDP) and the Global Environment Facility (GEF) were implemented to aid the BioGen project in 2002. The objectives were to develop an efficient RE production system for the palm oil industry. Moreover, it aims to reduce the emission of GHG and methane coming from fossil fuel utilization and decomposition of unused biomass from the oil palm industry [54]. By utilizing empty fruit bunches, the produced electricity could be sold to the public, generating additional income. Bandar Baru Seriting Biomass Project and Felda Besout POME Biogas Project were initiated under the BioGen project. However, both projects failed to meet their target with an efficiency of only about 16% [54].

4.3 *The Malaysian Building Integrated Photovoltaic (MBPIV) Project*

To boost the application of photovoltaic for electricity generation, the MBIPV project was launched, beginning in 2005 for five years [54, 57]. Supported by the GEF and UNDP, the commencement of this project helped to improve the overall energy efficiency, without losing the building aesthetics. The photovoltaic systems were installed at different locations throughout the country, with a total of 97 sites and an overall capacity of 857.92 kWp [58]. As part of the project, the SURIA 1000 was introduced for property developers to encourage the extensive utilization of solar photovoltaic systems on properties or buildings. Furthermore, the housing and commercial sectors would have opportunities to safeguard the environment and join in RE initiatives. Nevertheless, following four years of monitoring, a few problems were reported by the Photovoltaic System Monitoring Centre (PVSMC) on the grid-connected photovoltaic systems, caused by technical and environmental issues [58]. Moreover, the economic analysis demonstrated that this project was expensive, hence several modifications are required to make it cost-effective and applicable [54].

4.4 *Economic Transformation Programme (ETP)*

The Economic Transformation Programme was introduced in October 2010, as part of the National Key Economic Areas (NKEA) to boost the national economic performance and become one of the high-income countries by 2020. Overall, four entry points projects were identified under the ETP, including enhancing energy efficacy, strengthening solar power capability, advancing nuclear-based power production and exploiting Malaysia's hydroelectricity capacity [57]. In summary, electricity was identified as the prime energy for the country's fiscal development. With that, Malaysia intended to become one of the top photovoltaic panel producers by 2020 [54]. This goal was successfully achieved as in 2017, Malaysia was announced as the third-largest producer of solar photovoltaic cells and modules worldwide [59]. Furthermore, based on the Malaysian Solar Photovoltaic Roadmap announced in 2017, the country is expected to be the centre for solar cell business by 2030. The focus on renewable energy including biomass, biogas, solar photovoltaic and mini-hydro was further continued in the 11th Malaysia Plan, as well as on energy security to certify sustainable management of energy resources.

4.5 Feed-In Tariff (FiT)

Based on the findings of the MBPIV Project, the Feed-in Tariff was introduced in Malaysia in 2011. The execution of the Feed-in Tariff was initiated after the enactment of the Renewable Energy Act (2011) and Sustainable Energy Development Authority Act 2011 under the 10th Malaysia Plan. With the aim to turn renewable energy into a feasible and promising long-term investment for businesses, industries and individuals [57], this programme was supervised by the Sustainable Energy Development Authority of Malaysia (SEDA) under the Ministry of Energy, Green Technology and Water. Besides that, this programme also aids in implementing RE economically, where 1% from the electricity tariff from the user is employed for the growth of the RE [54]. Different tariff rates were introduced, ranging from RM0.22 to RM0.53 per kWh (as of 1st January 2020), based on the category of renewable resource used/RE technologies, the fixed capacity of the RE installation, and the date of complete RE installation connected to the grid and set for RE generation. In addition, bonus FiT rates are given to RE installation that meets certain criteria [60]. The FiT rates were comparable with those charged by Tenaga Nasional Berhad to the domestic consumer for electricity (non-RE), ranging from RM0.22 to RM0.57 per kWh.

4.6 Self-Consumption (SELCO) Programme

The SELCO programme was initiated particularly for the generation of electricity for own usage using solar photovoltaic, without involving the exportation of excess electricity to the grid. The purpose is to help in reducing the individual, commercial and industrial consumer's electricity bill [60]. The solar system could be installed at the location of interest without having to apply for the NEM quota, hence it is time and cost-saving. However, the drawbacks are that any excess energy will be wasted as the solar system is not connected with the grid. Hence, it is important for the consumers to choose the suitable size system to be installed and wisely plan their energy usage upon installation. Due to this reason, this programme is recommended for individuals or companies with constant electricity usage.

4.7 Net Energy Metering (NEM) Scheme

The Net Energy Metering Scheme (NEM) was first introduced in 2016 to boost the RE application, with an allocation of 500 MW up to the year 2020 [60]. Through this scheme, the excess energy after being utilized by consumers is exported to TNB at a certain displaced price. This programme was continued by the initiation of NEM 2.0 in January 2019 by SEDA and Energy Commission (EC), under the

Ministry of Energy and Natural Resources (KetSA). The true net energy approach was applied, where surplus solar photovoltaic energy can be transferred to the grid on a “one-to-one” offset basis. To further encourage the solar energy uptake and due to massive response from the photovoltaic industry, the NEM 3.0 was launched in December 2020 (effective from 2021 to 2023). With more than 5000 MW quota allocation, this scheme provides more chances to instal a photovoltaic solar system and save electricity bills. There are their categories under NEM 3.0; NEM Rakyat, NEM GoMEn and NOVA programmes [60]. NEM Rakyat is special for individual consumption, whereas NEM GoMEn is for government ministries and entities. A similar approach was applied in both programmes where extra energy will be sent to the TNB grid and consumers can use the credit received to offset part of the electricity bills. However, in the NOVA programme, excess energy could either be transferred through the supply system to the Distribution Licensee (e.g., TNB) or up to three selected premises. The accredited worth of the transferred energy would help to reduce the electricity bill of the premises.

5 Sustainable Development Goals

In 2015, all member states under the United Nations had adopted the Sustainable Development Goals (SDGs) as a shared guide to end poverty, protect the planet and reduce inequalities by 2030, so that the world population would enjoy peace and prosperity. There are 17 goals for SDGs as shown in Fig. 3, which includes no poverty, zero hunger, clean water and sanitation, climate action, affordable and clean energy, and sustainable cities and communities.

Among the 17 goals indicated in the SDGs, SDG 7 which is affordable and clean energy is the most related to the empowerment of RE. SDG7 focuses on ensuring that people of the world would have equal access to reliable, affordable, modern and sustainable energy. According to data obtained by the United Nations [61], about 789 million people in the world have no access to electricity. It is important to note that electricity is the most basic necessity and a well-established energy system power-up all sectors. Economic sectors, healthcare, education, communications, agriculture, infrastructure and high-technologies industry requires the use of electricity, thereby highlighting the significant impact if electricity supply is lacking. Conventional fossil fuels such as petroleum, coal or natural gas have been primarily used for energy production for a long time. However, fossil fuel burning has contributed approximately 60% of total global greenhouse emissions. If no action is taken to mitigate greenhouse gases, this situation may accelerate global climate change and negatively impact natural ecosystems. Therefore, energy efficiency and the use of RE could contribute to slowing down climate change and reducing disaster risks.

Investing in renewable energy resources could help to boost transformation from using conventional fossil fuels to safer, reliable, affordable, and sustainable energy systems. Implementation of lignocelluloses or algae biomass as feedstocks for biofuels production, adopting clean energy technologies and infrastructure, as well



Fig. 3 Seventeen goals of Sustainable Development [58]

as engaging in energy-efficient practices may facilitate these transitions. To date, renewable energy has been making incredible progress driven by policy support, innovation, and technological advancement, though the development is not homogeneous across countries and sectors. This is mainly due to governmental policy, financial challenges and technological barriers. Therefore, to achieve SDG 7, vigorous efforts are needed to increase energy efficiency and increase the composition of RE in the global energy mix. Apart from that, governmental policies are encouraged to continuously adapt to the current market conditions, so that the energy can be obtained at a cheaper price and the efficient integration of RE energy into the system.

In realizing the SDG7 along with other SDGs and the 2030 agenda, Malaysia has set up the plans, policies, laws and regulations to better protect and ensure sustainable use of natural assets. The strategies and achievements have been presented to the United Nation’s High-Level Political Forum (HLPF) in 2017 and again in 2021 under Malaysia’s Voluntary National Review (VNR) to reaffirm Malaysia’s commitments. Malaysia realized that organization of resources including preparing the manpower, capacity building and physical spaces as well as funding is crucial to ensure the success of SDGs implementation. Therefore, the implementation of SDGs in Malaysia is aligned with the five-year national development plan starting

with the Eleventh Malaysia Plan (11MP), 2016–2020, then continuing with the Mid-Term Review (MTR) of 11MP, 2018–2020. Currently, Malaysia is at the Twelfth Malaysia Plan (12MP), 2021–2025 and will be followed by the Thirteenth Malaysia Plan (13MP), 2026–2030 [62].

Moving forward, Malaysia has incorporated the 10–10 Malaysian Science Technology Innovation and Economic Development (10–10 MySTIE) Framework in the 12th Malaysia plan (2021–2025) in line with the implementation of SDGs. The framework integrates 10 global science and technology drivers with 10 socioeconomic drivers in the country, so that science, technology, innovation (STI) and social sciences can complement each other. The 10–10 MySTIE framework was designed to support the National Policy of Science, Technology and Innovation (DSTIN) 2021–2030 in transforming Malaysia from technology users to technology developers. Additionally, the 10–10 MySTIE framework aims to serve as a catalyst or platform to translate research into transformative outcomes for the community. One of the key socio-economic drivers being stressed in this framework is energy and national STIE niche areas, which has been identified including diversified renewable energy, energy storage system and microgrid [63]. Thus, with the assistance from the 10–10 MySTIE framework, more research projects in the renewable energy area could be brought to commercialization, which will help to accelerate RE implementation to 20% of the total Malaysian energy mix by the year 2025 [55], ultimately achieving the SDGs agenda by the year 2030.

6 Conclusion

Renewable energy is certainly a promising option for the replacement of fossil fuels worldwide. However, there are still challenges and barriers which need to be resolved before its full implementation as a sole energy source could be achieved. The application of more efficient approaches for biofuel production through the advancement of the technologies helps to improve the economics and environmental impact of the RE system. Looking from Malaysia's perspective, the initiation of previous and ongoing RE programmes by designated authorities has contributed to promoting RE utilization in the country. Clearly, Malaysia is committed to becoming one of the main technology developers in this area, as proven by the integration of various RE strategies in the national agenda. It is believed that with full commitment and continuous support from all parties, the execution of future programmes such as 10–10 MySTIE would be a success, hence leading to the accomplishment of Malaysia's SDGs.

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