Progress in biomass torrefaction: Principles, applications and challenges

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ABSTRACT

The development of biofuels has been considered as an important countermeasure to abate anthropogenic CO_2 emissions, suppress deteriorated atmospheric greenhouse effect, and mitigate global warming. To produce biofuels from biomass, thermochemical conversion processes are considered as the most efficient routes wherein torrefaction has the lowest global warming potential. Combustion is the easiest way to consume biomass, which can be burned alone or co-fired with coal to generate heat and power. However, solid biomass fuels are not commonly applied in the industry due to their characteristics of hygroscopic nature and high moisture content, low bulk density and calorific value, poor grindability, low compositional homogeneity, and lower resistance against biological degradation. In recently developing biomass conversion technologies, torrefaction has attracted much attention since it can effectively upgrade solid biomass and produce coal-like fuel. Torrefaction is categorized into dry and wet torrefaction; the former can further be split into non-oxidative and oxidative torrefaction. Despite numerous methods developed, non-oxidative torrefaction, normally termed torrefaction, has a higher potential for practical applications and commercialization when compared to other methods. To provide a comprehensive review of the progress in biomass torrefaction technologies, this study aims to perform an in-depth literature survey of torrefaction principles, processes, systems, and to identify a current trend in practical torrefaction development and environmental performance. Moreover, the encountered challenges and

perspectives from torrefaction development are underlined. This state-of-the-art review is conducive to the production and applications of biochar for resource utilization and environmental sustainability. To date, several kinds of reactors have been developed, while there is still no obviously preferred one as they simultaneously have pros and cons. Integrating torrefaction with other processes such as co-firing, gasification, pyrolysis, and ironmaking, etc., makes it more efficient and economically feasible in contrast to using a single process. By virtue of capturing carbon dioxide during the growth stage of biomass, negative carbon emissions can even be achieved from torrefied biomass.

Contents

1. Introduction

The development of renewable energy is considered as an imperative and essential countermeasure for resource and environment sustainability. Among developing renewable energy technologies, bioenergy has received more attention than other renewable energy resources such as solar energy, wind energy, geothermal energy, marine energy, and hydropower [1]. In recent years, there is a rapid growth in the installations of solar cells and wind turbines [2,3]. However, CO_2 emissions continuously rise while the atmospheric CO_2 concentration is higher than 410 ppm exceeding the safe global limits [4]. This implies that the anthropogenic activity from fossil fuel combustion still plays an important role in energy consumption, even though many efforts have been made in power generation from solar and wind energy.

Nowadays, bioenergy is the fourth largest primary energy source which is preceded by oil, coal, and natural gas [5]. Unlike solar and wind energy which are used solely for electricity generation, the development of bioenergy is mainly to produce biofuels that can be applied to heat and power generation as well as in the transportation sector. Biofuels are generated from the conversion of biomass which is produced from carbon dioxide and water through photosynthesis. From the viewpoint of energy storage, photosynthesis is regarded as a global process to synthesize biomass in which solar energy is stored.

Over the last several decades, biofuels based on biomass sources have evolved from first-generation biofuels produced from food crops, second-generation biofuels produced from inedible lignocellulosic biomass, third-generation biofuels produced from algal (macroalgal and microalgal) biomass, and then to fourth-generation biofuels through genetically engineered algal and microbial systems [5-7]. Biomass can be burned directly to generate heat and power. However, to extend its utility in industrial and other sectors, a variety of conversion technologies have been developed. As a whole, these technologies are categorized into (1) physical, (2) chemical, (3) biological, and (4) thermochemical conversion processes [8]. Biomass drying, separation, pulverization, and pelletization pertain to physical conversion. One of the notable chemical conversion is biodiesel production through transesterification. Biogas, biohydrogen, bioethanol, and biobutanol production can be fulfilled through fermentation, saccharification, or photosynthesis which are classified as biological conversion. Thermochemical conversion is a remarkable and the most important pathway for biofuel production, except for combustion where heat is the main product. The benefits of the thermochemical process are numerous: small footprint, efficient nutrient recovery, short reaction time, and the capability of handling a variety of wastes and blends, among others.

As far as solid fuels are concerned, coal has been widely employed in the industry because of its accessibility, low cost, stable supply, and high energy density [9]. However, the massive consumption of coal has given rise to several environmental problems such as local air and thermal pollution, regional acid rain, globally deteriorating atmospheric greenhouse effect, global warming, and climate change [10]. Compared to coal, biomass has several advantages as follows.

Biomass is an abundant energy resource that covers a large portion of land areas on the Earth's surface and has a short life cycle. Therefore, biomass is a potential candidate as an alternative fuel to coal.

Unlike solar and wind energy, bioenergy is an intermittence-free energy source in nature since biofuels from biomass can be properly stored in solid, liquid, or gaseous forms. This implies, in turn, that bioenergy is a stable backup energy resource.

The main growth-dependent carbon source for cells is atmospheric carbon dioxide, so biomass is usually noticed as a carbon-neutral fuel precursor. Moreover, biomass usually has lower sulfur and nitrogen contents compared to coal. This implies, in turn, that CO_2 emissions during biomass burning processes are more recoverable, along with fewer emissions of SO_x and NO_x [11]. Nevertheless, in the course of biofuel production, the carbon footprint in the chain of growing, harvesting, storing, transporting, and applying biomass should be considered.

However, solid biomass fuels are characterized by hygroscopic nature and high moisture content, low bulk density and energy density (or calorific value), poor grindability, low compositional homogeneity, and lower resistance against biological degradation and thereby storability [5]. Therefore, solid biomass is not a popular fuel for its application in industry. To overcome the aforementioned disadvantages, the development of torrefaction has received a great deal of attention in the last decade inasmuch as this thermochemical conversion technology can effectively upgrade biomass and improve solid biomass-derived fuel (biochar) quality.

The applications of torrefaction and upgraded biomass have been discussed in some papers [5,12–15]. However, the information on system integration and practical applications of biomass torrefaction in the industry remains insufficient. To provide a comprehensive review of the progress of torrefaction technology, the fundamentals of torrefaction are first introduced in this paper. This work highlights the treatment of biomass to enhance its material properties through a thorough discussion of the torrefaction process from operations, process parameters, reaction systems, commercialization, and environmental impacts. This study also aims to deepen the understanding of the torrefaction process towards commercialization and identify future research directions. A current trend in the development of torrefaction from academic studies and the up-to-date practical research from the viewpoint of patent strategy is then presented. Special attention is given to the system integration of biomass torrefaction in which the main components consist of feedstock, pretreatment, reactor, and post-treatment. The types of feedstock such as lignocelluloses, algal biomass, fermented residues, and wastes for torrefaction are introduced [16,17], while their pretreatments such as drying, pelletization, catalyst impregnation, and leaching are discussed. The reactor is a key facility to perform torrefaction in a system. A variety of reported and patented reactors and their characteristics are illustrated. As for the post-treatment, cooling, grinding, and/or pelletization are described. The mass and energy balances of a torrefaction system are also analyzed. Thereafter, potential applications of upgraded biomass (e.g., combustion, gasification, pyrolysis, ironmaking, and bio-adsorbent), current commercialization status, and cost analysis of torrefaction are addressed. Also, the carbon footprint and life cycle assessment of torrefaction processes are evaluated to quantify the impact of torrefaction upon the environment. Eventually, the challenges and perspectives of biomass torrefaction technologies are outlined to bridge the gap between the lacked knowledge in past review papers and future research.

2. Biomass thermal degradation

2.1. Thermochemical conversion technologies

Currently, the commonly utilized thermochemical conversion processes consist of combustion, pyrolysis, gasification, liquefac-
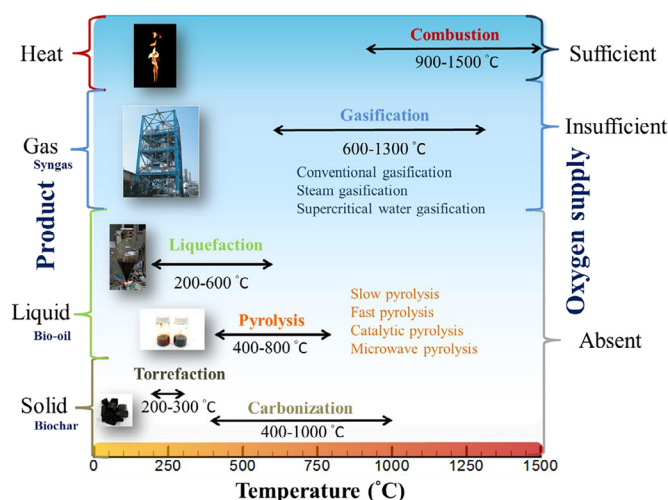
Fig. 1. A schematic description of biomass thermochemical conversion methods.

tion, carbonization, and torrefaction [5,18]. The operations of these methods depend on oxygen supply and reaction temperature, while solid, liquid, and gas biofuels are produced from these methods, except for combustion. The operating conditions of the aforementioned thermochemical conversion methods and their main products are summarized in Fig. 1.

The combustion of biomass, with sufficient oxygen or oxidant supply, possesses the merits of direct and easy operation as well as mature technique. Combustion technology has been applied in human lives such as heating and cooking for a long period. Combustion also played a key role in the Industrial Revolution to generate power through steam, and it is still a prominent factor for power generation at present. Almost all biomass materials can be applied in combustion as long as their calorific values are sufficiently high which can reduce the reliance on fossil fuels. Biomass burned alone or co-fired with coal has been applied for a long time [19]. Heat, rather than biofuels, is the main product from burning biomass where the operating temperature is normally between 750°C and 1500°C depending on feedstock, reactor, and combustion technology [19–21].

When biomass is burned in an environment with insufficient or starved oxygen supply, gaseous fuels or product gases are generated from the incomplete combustion of feedstock. Hydrogen (H_2) and carbon monoxide (CO) are two main products in the product gases, and both are spoken of as synthesis gas or syngas. In the product gases, certain amounts of carbon dioxide (CO_2) and methane (CH_4), as well as air pollutants such as H_2S, COS, CS_2, NH_3, and HCN, also exist [22,23]. The gasification temperature is generally between 600°C and 1200°C [24]. The gasification can be classified into conventional, steam, and supercritical water gasification [25], depending on the reaction environment. The comparison of the three gasification technologies is summarized in Table 1.

Instead of gaining gaseous biofuels, liquid biofuels are the main products from pyrolysis and liquefaction. In pyrolysis and liquefaction, the chemical reactions are triggered in an inert or oxygen-free environment. On account of no oxygen supplied, bonds in hydrocarbons in biomass are thermally broken and liquid bio-oils are obtained. In general, biomass pyrolysis is conducted at temperatures between 400°C and 800°C, and can be categorized into fast pyrolysis, slow pyrolysis, catalytic pyrolysis, and microwave pyrolysis where the fixed bed and fluidized bed reactors can be used [5,26]. The comparison of the four pyrolysis technologies is also listed in Table 1. Liquefaction, also known as thermochemical liquefaction or hydrothermal liquefaction (HTL), is a thermal process at a temperature range of 200-600°C to convert biomass into a liq-
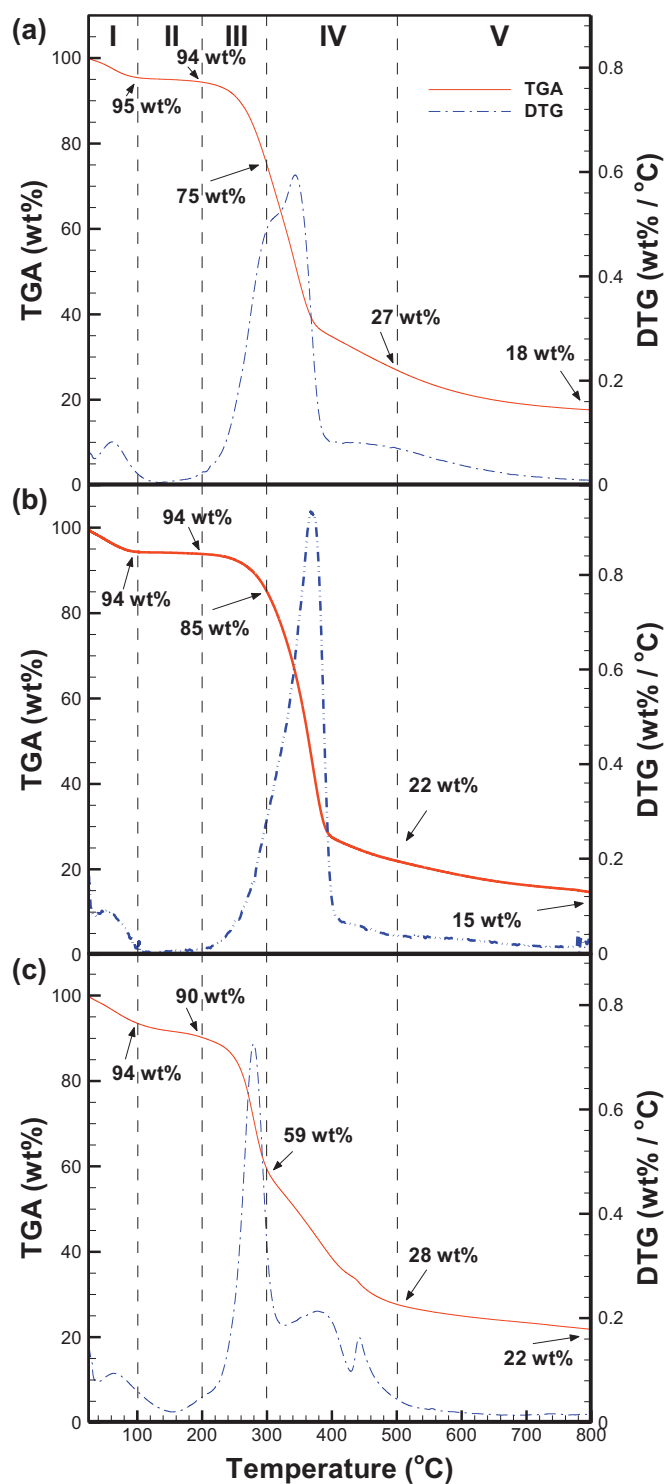
Fig. 2. Thermogravimetric analysis and derivative thermogravimetric curves of (a) bamboo, (b) *Camellia japonica*, and (c) microalga in nitrogen.

uid biofuel called bio-oil or biocrude. Unlike pyrolysis where the thermal degradation normally proceeds at the atmospheric pressure and vapors (including permanent gases and condensed liquids) are formed, the pressure in liquefaction (10-25 MPa) is high [18] to keep solvents such as water, acetone, or ethanol in the liquid phase [27]. This facilitates the chemical reactions for the feedstock in the liquid solutions.

Table 1
Comparisons of various gasification and pyrolysis technologies.

Gasification	Operating conditions				Product		Reference
	Temperature (°C)	**Gasification agent**	**Equivalence ratio (ER)**	**Pressure (MPa)**	**Primary gases composition (vol%)**	**Performance (%)**	
Conventional	400-1200	Air	0.15-0.4	0.1-1	H_2 (2-38), CO (10-36) CO_2 (5-65), CH_4 (1-15)	CC*:63-95 CGE**:53-75	[31-34]
Steam	600-1000	Steam	0-0.37	0.1-1	H_2 (21-83), CO (4-45) CO_2 (1-30), CH_4 (1-22)	CC: 42-124 CGE:33-80	[33,34]
Supercritical water	374-800	Water	-	22-50	H_2 (6-37), CO (0.1-22) CO_2 (26-51), CH_4 (2-52)	CC: 4-97 CGE:32-91	[31,35,36]

Pyrolysis	Operating conditions				Bio-oil yield	Reference
	Temperature (°C)	**Heating rate (°C min⁻¹)**	**Sweep gas flow rate (L min⁻¹)**	**Duration (min)**	**(wt%)**	
Slow	300-500	3.5-10	0.02-0.10	10-120	23-56	[31,37,38]
Fast	300-800	600-36,000	6.67-18.00	0.0017-60	18-77	[31,39,40]
Catalytic***	350-650	-	0.02-11.00	0.014-120	21-75	[41-43]
Microwave	250-800	-	0.05-20.00	5-60	9-70	[31,44]

* : CC: carbon conversion;

** : CGE: cold gas efficiency;

*** : Zeolite catalysts (i.e., ZSM-5, HZSM-5, SiO_2-Al_2O_3), modified zeolite catalysts (i.e., Co/ZSM-5, Ni/ZSM-5, Ga/HZSM-5), and metal oxide catalysts (i.e., MgO, CaO, ZnO) are widely used in catalytic pyrolysis [43].

Carbonization and torrefaction are practiced in an environment in the absence of oxygen, resembling pyrolysis, and liquefaction; however, they aim to produce solid fuels such as charcoke or biochar. In slow pyrolysis, the biochar (or solid char) yield is high, resulting from the slow heating rate and long residence time. In earlier literature, pyrolysis generally equates carbonization [28,29] where the reaction temperature ranges from 400°C to 1000°C. Charcoal produced from biomass carbonization can be applied in combustion as a solid fuel, in gasification as a feedstock, and in the metallurgical process as a reducing agent [30]. As for torrefaction, biomass is mildly pyrolyzed at temperatures of 200-300°C. The main target of torrefaction is to upgrade solid biomass as an alternative to coal.

2.2. Thermal degradation characteristics of biomass

Thermogravimetric analyzer (TG) is considered as a useful technique to access the thermal behavior and decomposition kinetics of biomass. Thermogravimetric analysis and derivative thermogravimetric (TGA & DTG) curves of bamboo (*Phyllostachys makinoi*) in nitrogen at a temperature range of 25-800°C are depicted in Fig. 2**a**. In examining the TGA curve, overall, the weight distribution of the biomass with increasing temperature can be partitioned into five different zones (i.e., Zones I, II, III, IV, and V). When the temperature is between 25°C and 100°C (Zone I), moisture or free-water in the biomass is vaporized and the drying process is carried out [45]. For the temperature between 100°C and 200°C (Zone II), the weight loss of the biomass is fairly slight (around 1 wt%). It follows that this zone is characterized by nearly chemically frozen. When the temperature is in the range of 200-300°C (Zone III), the thermal degradation of the biomass becomes obvious and the weight loss is 19 wt%. This significant weight loss is due to the biomass thermal degradation and devolatilization processes [46] in which a part of volatile matter (VM) in the bamboo is liberated. When the bamboo is heated at temperatures ranging from 300 to 500°C (Zone IV), the weight loss is 48 wt% and the weight of the biomass at 500°C is 27 wt%, revealing the most severe thermal degradation occurring in this zone. In other words, most of the VM is released and fixed carbon (FC) is retained in the solid residue. After the temperature is higher than 500°C (Zone V), the weight loss of the biomass with increasing temperature slows down. For example, when the temperature increases from 500 to 800°C, only 9% of the weight is lost from the heating. The low DTG curve corresponds to a continuous and slow loss of carbonaceous matters [47].

The TGA and DTG curves of *Camellia japonica*, an abundant wood in Taiwan, are shown in Fig. 2b. As a whole, the pyrolysis processes can also be characterized by a five-zone thermal degradation. The TGA curve in Zones I and II are stable, which are similar to those of bamboo. It indicates that the lignocellulosic biomass has insignificant thermal degradation before 200°C. The decomposition of *Camellia japonica* mainly takes place in Zones III and IV, approximately at temperatures of 230-410°C. The peak exhibited in Zones III and IV results from the thermal degradation of hemicelluloses and cellulose. The tail region of Zone IV and Zone V account for the degradation of lignin in the biomass.

The TGA and DTG curves of a microalga (*Chlamydomonas* sp. JSC 4) thermally degraded in nitrogen are shown in Fig. 2c. The weight loss characteristics of the microalga in Zones I and II are similar to those of bamboo. However, in Zone III (i.e., 200-300°C), the thermal degradation of the microalga becomes pronounced when compared to that of bamboo, stemming from the inherent difference in components between lignocellulosic biomass (i.e., cellulose, hemicelluloses, and lignin) and microalgal biomass (i.e., carbohydrates, proteins, and lipids) [48,49]. The weight losses of the microalga in Zones III and IV are 31 wt% and 31 wt%, respectively, showing the comparable devolatilization extents in the two zones. The peaks in Zones III and IV are mainly ascribed to the thermal degradation of polysaccharides, proteins, and lipids in the microalga, which had been identified in other studies by thermogravimetry-Fourier transform infrared spectrometer (TG-FTIR) and pyrolysis gas chromatography mass spectrometry (Py-GC/MS) [50,51]. When the microalgal biomass is heated in Zone V, its thermal degradation is not pronounced, as a consequence of continuous and slow decomposition of carbonaceous matters [52] or the secondary cracking and methanation of bio-oil [51], which cause 6% weight loss, resembling that of bamboo.

According to the TGA and DTG curves observed in Fig. 2, it is can be concluded that the thermal degradation mechanism of lignocellulosic biomass proceeds from drying or dehydration (Zone I), nearly chemically frozen (Zone II), mild pyrolysis (Zone III), severe pyrolysis (Zone IV), and then to carbonization (Zone V). But for the microalgal biomass, its thermal degradation characteristics

Table 2
Thermal degradation zones of bamboo, *Camellia japonica*, and microalga heated in nitrogen.

Zone	Temperature	Mechanism	Weight loss (wt%)		
	(°C)		**Bamboo**	**C. japonica**	**Microalga**
I	25-100	Drying or dehydration	5	6	6
II	100-200	Nearly chemically frozen	1	~0	4
III	200-300	Mild pyrolysis	19	9	31
IV	300-500	Severe pyrolysis	48	63	31
V	> 500	Carbonization	9	7	6

in Zones III and IV are in a comparable state. The weight loss values of the three biomass species in each zone are tabulated in Table 2. When the bamboo, *Camellia japonica*, and microalga are heated to 300°C, their total weight losses are 25 wt%, 15 wt%, and 41 wt%, respectively. Meanwhile, in the mild pyrolysis zone (Zone III), the weight loss values of the bamboo, *Camellia japonica*, and microalga are 19 wt%, 9%, and 31 wt%, respectively. These results reveal that volatiles in the biomass are liberated to a certain extent in the mild pyrolysis zone (Zone III). Nevertheless, for bamboo and *Camellia japonica*, around 75 wt% of solid residues remain after this heating process. Accordingly, the mild pyrolysis zone plays an important role in changing biomass properties from the thermal pretreatment. This motivates upgrading biomass using torrefaction (mild pyrolysis).

3. Torrefaction

3.1. Preliminary studies

As described earlier, solid biomass fuels possess several disadvantages so that their applications in the industry are limited [5]. In the last decade, the torrefaction has been widely developed since this technology can effectively promote the fuel quality of carbon-neutral solid. A survey of the journal paper number in Web of Science (Sciencedirect.com) made on January 19, 2020, using the keyword of "torrefaction" based on the Abstract, Title, Keywords, suggested more than 1623 papers had been published. Torrefaction and similar technologies such as roasting have been widely employed for wood treatment [53,54], coffee bean production [55], and enhancing the flavor and improving organoleptic properties of food [56].

Upon examining the articles, similar research focus can be observed such as torrefaction effects on biomass properties, energy densification, and solid and energy yields, followed by addressing the industrial, environmental, and agricultural applications of torrefied biomass such as combustion, ironmaking, pyrolysis, liquefaction, gasification, pollutant adsorption, and soil amendment [5,14,15,57,58]. Lately, more studies investigated the reaction mechanisms of torrefaction and the influence on biomass structures [59–62]. In addition, several studies attempted to understand biomass thermal degradation behaviors by conducting torrefaction kinetics [63–66].

3.2. Classification

The purpose of the torrefaction process is to upgrade biomass and produce solid fuels with better quality. To fulfill this goal, biomass is torrefied under dry or wet conditions, which are termed dry torrefaction and wet torrefaction, respectively. In dry torrefaction, biomass can be torrefied in dry and non-oxidative (inert) or oxidative atmospheres where the temperature is normally between 200°C and 300°C. In contrast, in wet torrefaction, biomass is upgraded by water and dilute acid solutions at temperatures of 180-260°C. In addition to the aforementioned two methods, biomass
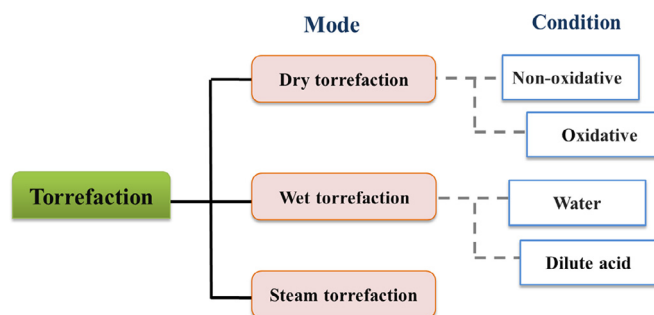
Fig. 3. Classification of torrefaction

can also be treated by steam to improve its properties. The classification of torrefaction methods is shown in Fig. 3.

3.2.1. Dry torrefaction

In non-oxidative torrefaction, nitrogen [59] and carbon dioxide [67] have been used as carrier gases, and the former is the most commonly utilized carrier gas to sweep biomass materials when they are thermally pretreated. As for oxidative torrefaction, attempts have been made using air [68], flue gas [69], and other gases containing different oxygen concentrations [70,71] as carrier gases to pretreat biomass. Owing to the presence of oxygen and exothermic reactions occurred in the thermal degradation, oxidative torrefaction has a higher reaction rate than that of the non-oxidative torrefaction [68], thereby shortening the torrefaction duration. Using air or flue gas to torrefy biomass can reduce operating costs because nitrogen separation from the air is not required. Fuel properties of biomass torrefied by a sweep gas along with low oxygen concentrations (<6 vol%) are close to those torrefied by nitrogen [71]. However, oxidative torrefaction obtains lower solid yield compared to the non-oxidative torrefaction [70–73]. It was also found that the higher heating value (HHV) of torrefied biomass decreases with increasing oxygen concentration when torrefied under the temperature of 300°C, [72]. The comparison of oxidative and non-oxidative torrefaction is highlighted and tabulated in Table 3.

3.2.2. Wet torrefaction

Instead of biomass upgraded in dry mediums, it can also be pretreated in wet mediums such as water and dilute acid to achieve biomass upgrading, and the produced solid is called "hydrochar". For biomass torrefied in hot compressed water or hydrothermal media, it has been addressed that no significant reaction of biomass occurred in liquid water when the temperature is below 180°C [74]. Consequently, wet torrefaction is normally operated under a reaction temperature between 180°C and 260°C with reaction time ranging from 5 to 240 min [66–68]. With increasing the temperature of the water, its properties would change dramatically, including dielectric constant, ion products, density, viscosity, and diffusivity [75]. These changes are conducive to biomass degradation under the liquid or aqueous phase. Therefore, wet torrefaction is usually operated under conditions close to the subcritical

Table 3

Comparison of non-oxidative and oxidative torrefaction.

Non-oxidative torrefaction	Oxidative torrefaction
Advantages	
◇Higher solid and energy yields	◇Lower operating cost (no N_2 separation cost)
◇Easier in temperature control	◇Lower heat supply
	◇Faster reaction rate
Disadvantages	
◇Higher heat requirement	◇Lower solid yield and energy yield (at high torrefaction temperatures)
◇Lower reaction rate	
◇N_2 should be separated from air	◇More difficult in temperature control

state. Besides, adding sulfuric acid [76], acetic acid [74], and other materials such as lithium chloride into the liquid water [74] had been performed to enhance wet torrefaction performance. When biomass is degraded in hot compressed water, some volatile acids are released into the solution [77], which further enhances the torrefaction process. For instance, when the treating temperature rises to 180°C, aldehydes and furfural derivatives would be formed as primary precursors for the formation of humins, resulting in the increment of solid products [78]. Recognizing that wet torrefaction treats biomass in a wet environment, no pre-drying process is required, implying that sludge, sewage, manure, and other wet biomass can be adopted as the feedstock in wet torrefaction [79]. The wet torrefaction process is similar to the dilute acid pretreatment [17,80,81]; therefore, xylose and glucose are likely to be produced and contained in liquid products that can be used for bioethanol production. Moreover, the degradation process proceeding in the liquid phase along with high pressure can accomplish the same improvement in the calorific value of fuels with dry torrefaction under much lower temperatures [76]. It also indicates that, compared to dry torrefaction, wet torrefaction can obtain higher energy densification with similar mass yield [82]. In the view of energy consumption, wet torrefaction does not require pre-drying, so it is more energy-saving in sampling compared to dry torrefaction. However, it is opposite in harvesting product processes, indicating that they have trade-off on energy consumption.

Another pronounced difference between dry and wet torrefactions is ash content in the upgraded biomass. Ash is considered as inert material in the course of dry torrefaction so that the ash content of the product would increase proportionally after torrefaction. However, the ash content in biomass is reduced if it is pretreated via wet torrefaction [83,84]. This is attributed to the dissolution of minerals in ash into the aqueous phase. The reduced ash content can prevent possible problems such as agglomeration, deposition, corrosion, fouling, and slagging [84] caused in hydrochar conversion processes.

3.2.3. Steam torrefaction

Aside from dry and wet torrefactions, steam torrefaction is also a torrefaction process using high-temperature and high-pressure steam explosion to torrefy the biomass [85]. The steam explosion was initially employed to produce bioethanol [86]. The process introduces high-pressure and high-temperature steam into a sealed chamber placing lignocellulosic feedstock and is usually conducted at temperatures of 200-260°C and a holding time of 5-10 min. The pressure is subsequently rapidly released which will cause steam to swell the lignocellulosic matrix and separate individual fibers along with slight loss of feedstock [87]. Low molecular weight volatiles in biomass are removed during the steam explosion, increasing the calorific value and carbon content of the product, and decreasing its mean particle size, bulk density, and equilibrium moisture content (EMC) [88–90]. In recent works, the studies of the steam torrefaction mainly concentrated on the characteristics of resultant solid products for manufacturing pellets [88–91]. The steam torrefaction also has the merits of enabling to in-

crease the calorific value, carbon content, and hydrophobicity at much lower temperatures and shorter treatment durations compared to dry torrefaction. Besides, the pellets derived from steam explosion treatment have elasticity and higher mechanical strength than those of the untreated pellets [88]. However, compared to pellets made from untreated biomass, the higher energy demand is required to make pellets from steam torrefaction, and more energy is required to push pellets out of the die [92]. The comparison between dry, wet, and steam torrefaction, including operating conditions as well as advantages and disadvantages, is summarized in Table 4.

3.3. Biomass constituents

3.3.1. Plant cell wall

Plant cell walls play an important role in defending against pathogens and insects to ensure the structural integrity of the plant. The structure, composition, and configuration of cell walls depend on cell type, cell wall layer, age, plant taxa, and tissue [93]. In general, plant cell walls can be split into three layers: (1) middle lamella; (2) primary cell wall; and (3) secondary cell wall. Hemicelluloses, cellulose, and lignin have different proportions and distributions in these layers. The schematic of the plant cell wall is shown in Fig. 4. The middle lamella is made up of the highest proportion of lignin. The primary cell wall is composed of pectin, hemicelluloses, and cellulose. The mature secondary cell wall contains most of the lignocellulosic biomass, but its organization and structure begin in the primary cell wall [94]. However, not all types of cells contain secondary cell walls. Based on the composition of polymers present and structure, the secondary cell wall can be divided into three parts (S1, S2, and S3). The S1 layer normally has a high concentration of lignin in secondary cell walls; the S2 layer contains more lignin than the S1 layer. The S2 layer also consists of the largest amounts of hemicelluloses and cellulose. In the secondary cell wall, cellulose chains are linked together by hydrogen bonding, and these linked cellulose chains form several parallel sheets that constitute the microfibril structure. Concerning the S3 layer, it has the least amount of lignin and forms the boundary of the lumen [95]. However, the integrated structures of cellulose, hemicelluloses, and lignin in plant cell walls are still not fully elucidated [96].

3.3.2. Hemicelluloses, cellulose, and lignin

Hemicelluloses (also named polyose), cellulose (a polymer glucosan), and lignin (a complex phenolic polymer) are the three main constituents in lignocellulosic biomass. Apart from these constituents, biomass also contains inorganic materials (also called ash) and organic extractives [5]. The relative proportions of these constituents depend on the nature of biomass. For instance, hemicelluloses contents (wt%) in hardwood, softwood, and agricultural biomass are 15-36 wt%, 11-27 wt%, and 22-35 wt%, respectively; cellulose contents in these materials are 39-54 wt%, 41-50 wt%, and 24-50 wt%, respectively, and lignin contents are 17-29 wt%, 27-30 wt%, and 7-29 wt%, respectively [97]. The relative contents

Table 4
Comparison of dry, wet, and steam torrefaction.

	Dry torrefaction	Wet torrefaction	Steam torrefaction
Operating conditions	200-300℃	180-260℃	200-400℃
	10-240 min	5-240 min	5-120 min
	1 atm	1-200 atm	1-40 atm
Advantages	Easier operation	Lower reaction temperature	Suitable to wet biomass
	No post-drying	Suitable to wet biomass	No pre-drying
	Continuous production	No pre-drying	Higher pelletability solid products
		By-products in liquids	
		Lower ash content in hydrochar	
Disadvantages	Pre-drying	Post-drying	Higher energy consumption
	Higher ash content in biochar	High-pressure operation	High-pressure operation
		Corrosion of reactor by inorganic salts	
		Challenge in continuous production	
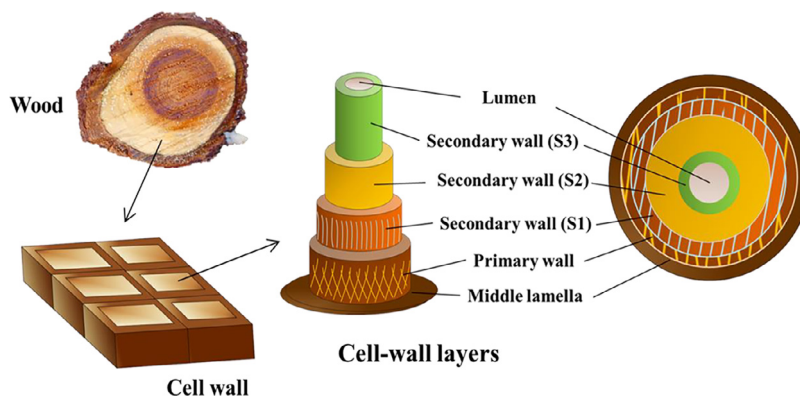
Fig. 4. Illustration of the plant cell wall in woody biomass
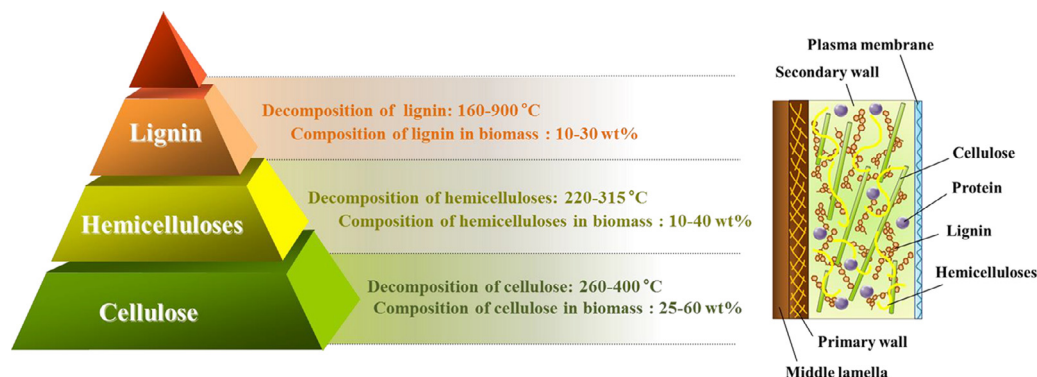
Fig. 5. Contents and properties of cellulose, hemicelluloses, and lignin in lignocellulosic biomass.

of three constituents in biomass are roughly ranked as cellulose > hemicelluloses > lignin. The detailed contents of cellulose, hemicelluloses, and lignin in biomass as well as their molecular formulas and thermal decomposition temperatures [5] are shown in Fig. 5.

The components and structures of hemicelluloses, cellulose, and lignin are extremely different from one another. Hemicelluloses, denoted by $(C_5H_8O_4)_m$, contains branched mixtures of various polymerized monosaccharides (such as glucose, xylose, galactose, mannose, arabinose, and glucuronic acid) where m is polymerization degree with values of 100-200. Hemicelluloses have higher reactivity than cellulose in that the braches, including acetic acid and glucuronic acid, inhibit the constitution of hydrogen bonds [75]. The decomposition temperature of hemicelluloses is between 220℃ and 315℃. Hence, when biomass is torrefied, a drastic impact on hemicelluloses is always observed. [59].

Cellulose, represented by $(C_6H_{10}O_5)_m$ with m of 7,000-12,000 is a linear homopolysaccharide composed of β-D-glucopyranose units linked by (1, 4)-glycosidic bonds [85]. Cellulose shows a higher carbon content than those of other lignocellulosic components that respond to major energy content in biomass [98]. Cellulose molecules strongly tend to form inter- and intra-molecule hydrogen bonds which shape crystalline micro-fibrils were surrounded by amorphous cellulose [79], resulting in the higher thermal stability of cellulose than that of hemicelluloses [75]. The decomposition temperature of cellulose is normally between 260 and 400℃, where the initiation period has been explained as the formation of "active cellulose" through the depolymerization process [99,100].

Lignin, denoted by $(C_9H_{10}O_3 \cdot (OCH_3)_{0.9-1.7})_m$ [101], is a highly branched, three-dimensional, and polyphenolic substance which consists of an irregular array of variously bonded "methoxy-" and "hydroxy-" replaced phenylpropane units [102]. Lignin in lignocellulosic biomass acts as a binding substance for hemicelluloses and cellulose structures [79]. During the densification or pelletization, it also works as a glue. The glass transition temperature of lignin is between 135℃ and 165℃ [103]. When the temperature during

Fig. 6. A schematic of different stages during dry torrefaction.

densification is higher than the glass transition temperature and the moisture content is between 10 wt% and 15 wt%, lignin in biomass softens and further enhances the inter-particles binding. The m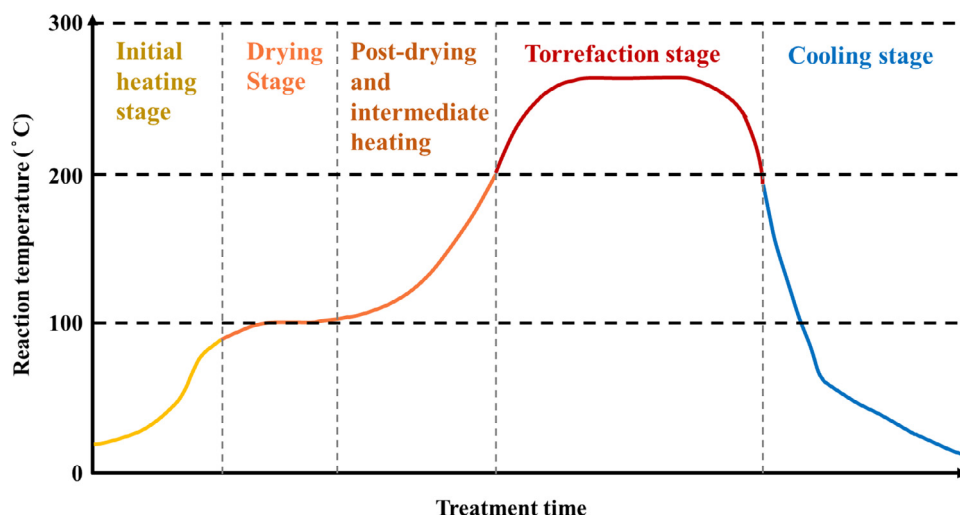ain part of lignin is thermally stable; thus, to complete the degradation of lignin requires sufficient time and relatively high temperatures. Even if lignin softens at temperatures as low as 80-90°C [104], its thermal decomposition temperature is in the range of 160-900°C [99,100].

As a whole, hemicelluloses are less structured than cellulose and their sugar composition varies widely among different tree species. Cellulose is mainly responsible for the structural strength of biomass, and it plays an important role in providing a supporting fibrous mesh which is reinforced by lignin polymers [105]. The lignin biopolymers and other compounds are the fillers in woody tissue making it a complex substance. On account of these inherent differences in composition and structure, the properties among the three constituents are different from each other. The hydrophobicity of cellulose is medium, while those of hemicelluloses and lignin are low and high, respectively [97]. Cellulose is characterized by the endothermic reaction when it is pyrolyzed; however, thermal degradation becomes exothermic if the charring or char formation process is significant [106]. In contrast, the exothermic reaction is exhibited when hemicelluloses and lignin are thermally degraded [32,99]. The calorific values of cellulose and hemicelluloses are approximately 17 and 18 MJ kg^{-1}, while it is between 23.3-26.6 MJ kg^{-1} for lignin [97]. Based on these HHV results, it indicates that the lignin content is positively correlated with the quality of the torrefied product.

3.4. Biomass property variation from torrefaction

There are several kinds of torrefaction processes as mentioned earlier. However, non-oxidative torrefaction is the major method used to pretreat solid biomass and has a high potential for its application in the industry. Therefore, the attention of the present study is paid to the non-oxidative torrefaction. For non-oxidative torrefaction, the entire biomass torrefaction process is split into five stages: (1) initial heating; (2) drying; (3) post-drying and intermediate heating; (4) torrefaction; and (5) cooling, [107], as illustrated in the Fig. 6. The five stages are described as follows [108].

In the initial heating stage, the biomass is heated until it reaches the desired temperature of the drying stage. Meanwhile, the moisture inside the biomass gradually evaporates at the end of this stage.

In the drying stage, the temperature holds constant until the critical moisture content is reached, while free water of the biomass is evaporated at a constant rate. The rate of water evaporation starts to decrease when reaching the critical moisture content.

In the post-drying and intermediate heating stage, the biomass is heated to 200°C. Physically bound water is removed while the resistance against mass and heat transfer is within the biomass particles. The biomass is almost free of water content at the end of this stage. Some mass loss can be expected during this stage, as a consequence of the evaporation of light organic compounds.

The torrefaction stage contains a heating period and a cooling period. The biomass is torrefied when the reaction temperature exceeds 200°C. This stage is operated under constant temperature called torrefaction temperature. Devolatilization starts during the heating period, continues during the period of constant temperature, and stops during or after the period of cooling.

In the cooling stage, the temperature of the torrefied product is cooled from 200°C to room temperature or the desired final temperature. There is no mass loss during this period, while some evaporation of adsorbed reaction products may occur.

As described earlier, raw biomass is known by its: (1) hygroscopic nature; (2) high moisture content and high atomic H/C and O/C ratios; (3) low calorific value; (4) poor grindability; (5) large volume or low bulk density; (6) higher biological degradation; and (7) non-homogeneity. Recent researches suggest that the aforementioned drawbacks of raw biomass can be overcome once torrefaction is applied to solid biomass. In other words, the torrefied biomass possesses the following characteristics: (1) higher hydrophobicity or water-resistivity; (2) lower moisture content and atomic H/C and O/C ratios; (3) higher calorific value; (4) better grindability; (5) higher bulk and energy densities if densification process is employed; (6) lower biological degradation; and (7) higher homogeneity in biomass.

The change in biomass properties during torrefaction is ascribed to some reaction mechanisms involved and coupled. These mechanisms include the dehydroxylation of hemicelluloses [109], the deacetylation and decarboxylation of xylan-containing hemicelluloses polymers [110], partial depolymerization and demethoxylation from cellulose (shortening of cellulose macro-fibrils) and lignin [111], etc. The mass loss of biomass from thermal degradation results in decarbonization, dehydrogenation, and deoxygenation in biomass [112-114]. The relevant mechanisms that occurred during biomass torrefaction and the resulting change in properties
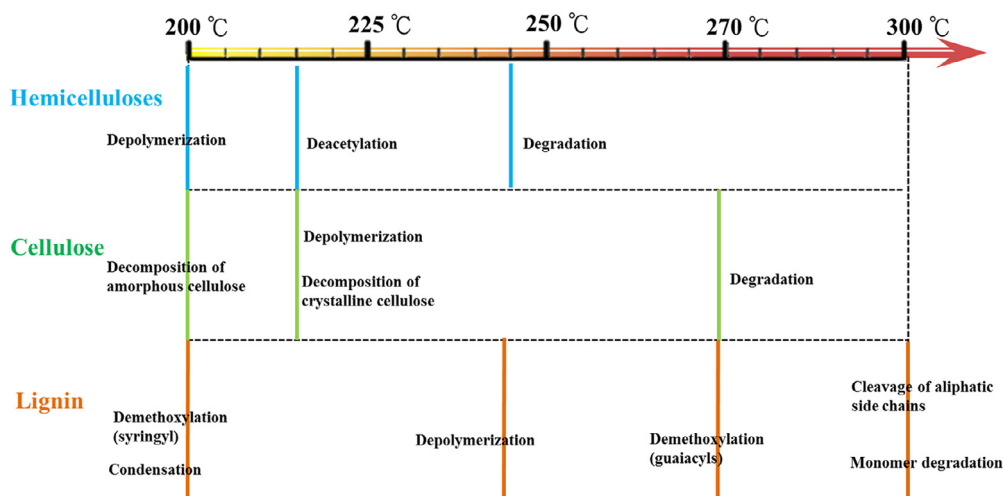
Fig. 7. Reaction mechanisms occurred in the course of biomass torrefaction.

Table 5
Physicochemical transformation and property variations of biomass before and after torrefaction

Raw biomass	Physicochemical transformations	Torrefied biomass property
High moisture content	◇Dehydration	Low moisture content
Hygroscopic	◇Dehydration	Hydrophobic
	◇Dehydroxylation	
	◇Decomposition of amorphous cellulose	
	◇Apolar tar in pores	
Higher O/C and H/C ratio	◇Less extent decarbonization	Lower O/C and H/C ratio
	◇Dehydrogenation	
	◇Deoxygenation	
	◇Deacetylation	
	◇Demethoxylation	
	◇Devolatilization	
Lower calorific value	◇Dehydration	Higher calorific value
	◇Carbonization	
	◇Dehydrogenation	
	◇Deoxygenation	
	◇Dehydroxylation	
Poor grindability	◇Hemicelluloses decomposition	Improved grindability
Higher biodegradation and poor storability	◇Hemicelluloses decomposition	Lower biodegradation and higher storability
	◇Lignin modification	

are illustrated and tabulated in Fig. 7 and Table 5, and the property variation of biomass from torrefaction is described below.

Torrefaction of lignocellulosic biomass involves the degradation of hemicelluloses, cellulose, and lignin at different temperature stages. Biomass initially degrades from150 to 200°C, due to dehydration and removal of light volatile [5,115]. When the temperature reaches 200°C, the degradation of hemicelluloses occurs, including deacetylation and depolymerization reactions. The deacetylation leads to the formation of acetic acid, which would catalyze the further depolymerization of low-order carbohydrates, as well as condensation and degradation in lignin [116,117]. The amorphous phase of cellulose starts to decompose at around 200°C to increase the relative crystallinity of biomass, while the crystalline phase of cellulose begins to decompose and the depolymerization of cellulose occurs at temperatures higher than 270°C [118].

Lignin has a complicated and large structure compared to hemicelluloses and cellulose. Lignin is an amorphous tridimensional polymer consisted of three basic units; they are p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units, respectively [119]. During biomass torrefaction, the softening of lignin starts at 160-190°C, the cleavage of α- and β-aryl-alkylether linkages occurs between 150°C and 300°C, and the cleavage of aliphatic side chains occurs at around 300°C. The cleavage of linkages leads to the removal of methoxyl groups (also called demethoxylation). Furthermore, the

significant depolymerization occurs when the reaction temperature is beyond 300°C [117,120].

3.4.1. Color change

The color of the feedstock is an intuitive indicator that changes when the feedstock is thermally degraded [121]. The colors of the samples are measured by a colorimeter based on the three-dimensional CIELAB (Commission internationale de l'éclairage, L* a* b*) color space, which has been adopted to quantify the color change of treated biomass. In the CIELAB color space, the vertical coordinate for lightness L* represents the position on the black-white axis (L*=0 for pure black and L*=100 for pure white). The chromatic coordinates a* and b* are characterized by the position of a horizontal plane. The chrome value of a* stands for the position on the green-red axis (+a* for red and -a* for green), while the chrome value of b* responds the position on the blue-yellow axis (+b* for yellow and -b* for blue). The equation for the total color difference ΔE* is given as $\Delta E = \sqrt{(\Delta L^2 + \Delta a^{*2} + \Delta b^{*2})}$[122]. For instance, the color of raw wood chips (*Cryptomeria japonica*) (Fig. S1a) is close to yellow, which has higher L*, a*, and b* values. The L*, a*, and b* values of wood chips decrease after they are torrefied at a low temperature of 250°C, that changing their colors from yellow to light brown (Fig. S1b). When the biomass is torrefied at a higher temperature of 300°C, the wood chips further turn their color to dark brown with even lower L*, a*, and

b* values (Fig. S1c). The color change of biomass depends on the conditions of torrefaction. It has been found that the color change of biomass from brown to black occurs at the temperature range of 150-300°C [115]. This primarily results from the changes in the chemical composition after torrefaction. The color change of torrefied wood can be attributed to several reactions. Firstly, the decomposition of hemicelluloses generates byproducts with different colors. Secondly, the acceleration of the color change of torrefed biomass is attributed to several factors such as the oxidation reactions, the crosslinking reactions, and the condensation reactions from the cleavage of lignin β-O-4 ether bonds and aromatic methyl groups in lignin which lead to the formation of oxidative products like quinones. Thirdly, the enzyme-mediated (Maillard) reactions between polysaccharides (such as amino acids, sugars, and phenolic compounds) occur in thermal degradation. Lastly, the oxidative reactions between the extractives (in woody biomass) and atmosphere in the process of torrefaction are triggered [123–126]. This color change also implies the partial carbonization occurring at the wood surface during torrefaction.

3.4.2. Transformation of hygroscopicity to hydrophobicity

The raw biomass is hygroscopic owing to its inherent hydrogen-bonded to the hydroxyl groups of the cell wall components that can easily absorb the water [127,128]. The normal moisture content of biomass ranges from 30 to 60 wt%, based on the period of storage, time of harvest, type, method (e.g., shedding) storage conditions (such as temperature and humidity), and storage location (indoor/outdoor) [129]. The Fourier Transformation Infrared (FTIR) analysis suggests that hydroxyl groups of raw biomass will be partly destroyed through dehydration [109,130] and dehydroxylation [109] reactions of hemicelluloses and cellulose in biomass [124,128]. This reduces the content of hydrogen bonding which results in the hydrophobic characteristic [131,132] and the drastic reduction in the EMC [133,134] of the torrefed biomass. The reduction of absorbed water improves biomass durability [135].

The hydrophobicity of biomass can be identified through the tests of contact angle and EMC where the change in the wettability of biomass before and after torrefaction is evaluated [53,135,136]. The profiles of EMC (with conditions of 65% humidity for 6 h) and contact angle tests of poplar wood before and after torrefaction are shown in Fig. 8. The figure suggests that EMC decreases from 5.72% (raw wood) to 3.27% (torrefed at 230°C), accounting for a 42.8% decreasing degree in EMC (Fig. 8a). The sessile drop technique is the most common method to measure the contact angle by observing a drop deposited on a solid surface [135]. It has been pointed out that small contact angles ($< 90°$) correspond to a hydrophilic surface (with hygroscopic property), while large contact angles ($> 90°$) correspond to a hydrophobic surface (with low wettability) [137]. Fig. 8b shows that the water droplet is absorbed into the raw wood rapidly, as a consequence of its hygroscopic nature. Specifically, the contact angle is around 65° in the beginning and becomes 0° at around 4 s. In contrast, the contact angle of the torrefed woods can keep for a long time and are always greater than 90°. The results unanimously suggest that the higher the torrefaction temperature, the greater the contact angle. When the torrefaction temperature increases from 200 to 230°C, the contact angle increases from 94° to 107°.

The hydrophobic behavior of torrefed biomass can also be evaluated by TGA curves. The weight loss of torrefed biomass between 25 and 100°C is minimal when compared to its raw biomass, whose storage conditions were controlled under 25°C with 65% relative humidity [138]. It has been reported that the formation of hydrophobicity has a highly linear correlation with the removal of hydroxyl groups and the formation of micropores [109]. Moreover, increasing torrefaction severity can enhance the hydrophobicity of the torrefed sawdust [139]. The formed tar condensing
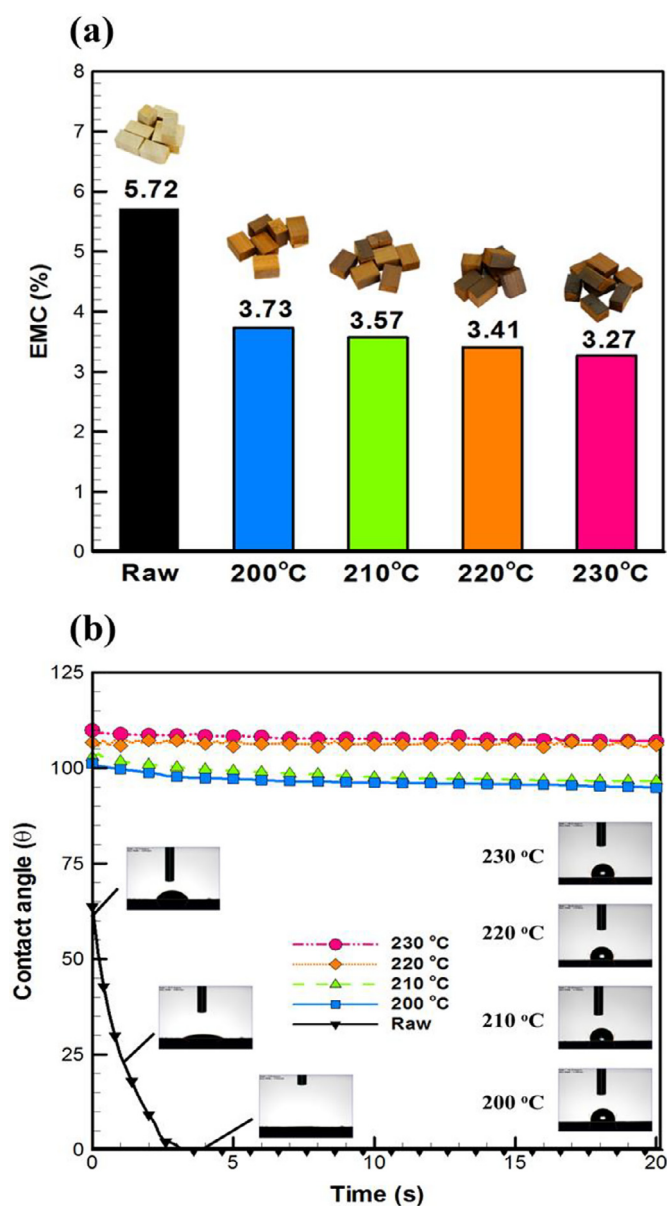
Fig. 8. Profiles of equilibrium moisture content (EMC) (with conditions of 65% humidity for 6 h) and (b) contact angle of poplar wood before and after torrefaction (temperature: 200-230 °C, duration: 1000 min).

inside the pores can lower the saturated moisture content in torrefied biomass and also inhibit the moist air passing through the solid. Owing to the apolar character of condensed tar, it can also prevent the condensation of water vapor inside the pores [133]. In summary, dehydration, dehydroxylation, and tar condensation are responsible for the transformation of hygroscopic biomass into hydrophobic biochar, and the aforementioned mechanisms are illustrated in Fig. 9.

3.4.3. Atomic H/C and O/C ratios (van Krevelen diagram)

The van Krevelen diagram is a graphical plot to show the atomic hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) ratios of fuels, especially for the solid fuels such as biomass, lignite, peat, charcoal, and coal [14,15], as shown in Fig. 10. For fuel with higher energy density, the trend for the atomic H/C and O/C ratios becomes lower. Compared to coal, biomass has higher VM content and lower FC content. For example, the VM content in coal and biomass are normally in the ranges of 0.5-50 wt% and 67-88

Fig. 9. Mechanisms causing hygroscopic transformation of biomass from torrefaction.

Fig. 10. *van Krevelen* diagram of various fuels.

3.4.4. Calorific value

The main elements in biomass are carbon (C), hydrogen (H), and oxygen (O) which construct hemicelluloses, cellulose, and lignin; and a small amount of nitrogen (N) and sulfur (S). When burning the biomass, the major heat release is attributed to the oxidation of carbon. Hydrogen is also a crucial heat source in the combustion of biomass, but hydrogen in biomass is mostly present as either C-H bonds or O-H bonds. The oxygen contained in biomass is beneficial to combustion, but a higher oxygen content in the biomass reduces its calorific value. Therefore, torrefaction is utilized to remove the undesired elements (H and O) in the solid products, achieving calorific values close to that of coal (25-35 MJ kg^{-1}) [141]. Additionally, biomass with higher ash content has a lower calorific value. The carbon, nitrogen, and sulfur contents in biomass are lower compared to that of coal, while its hydrogen and oxygen contents are higher. Besides, the high moisture content in biomass leads to a lower calorific value compared to coal. The summary of the fuel properties of raw biomass, torrefied biomass, and coal are depicted in Fig. 11.

3.4.5. Biological degradation

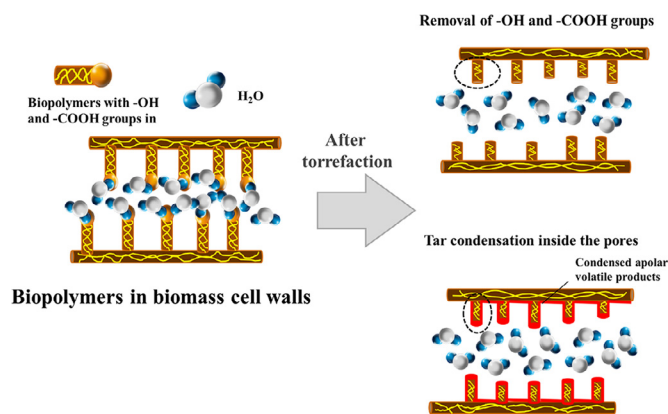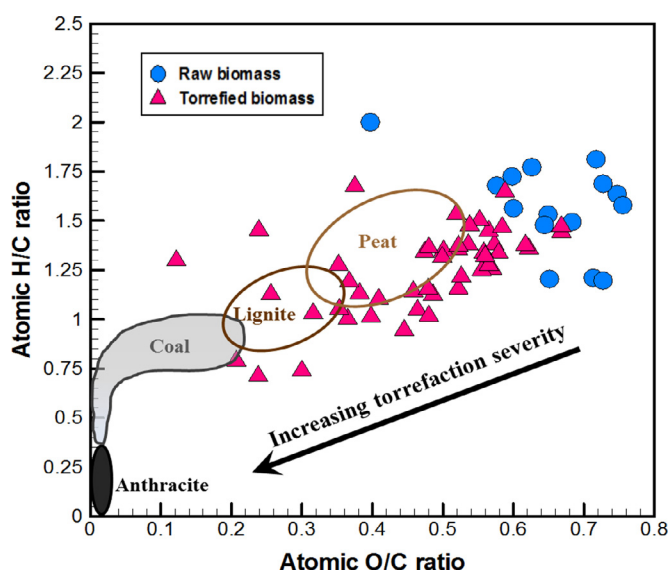Raw biomass inherently shows poor durability to fungi (**Fig. S2**) After biomass undergoes torrefaction, the torrefied biomass possesses a higher resistance to microbial degradation. With regard to the biological degradation of torrefied biomass, several studies have been pointed out that torrefied lignocellulosic biomass can increase its durability [136,142,143]. After torrefaction, the important degradation of hemicelluloses, which are generally considered as an important nutritive source for the development of wood-rotting fungi, leads to the improvement of durability. Meanwhile, the ineffectiveness of fungal peroxidases to degrade lignin can be explained by the modification of the lignin network, which is unable to be recognized by fungi.

Overall, four factors justify the improved durability of torrefied wood against fungi [136]: (1) improvement of the hydrophobic characteristic of biomass, which limits the absorption of water into the biomass and the growth of fungi; (2) the new volatile products are polynuclear aromatic hydrocarbons derivatives of phenanthrene, acenaphthylene, and polyaromatics compounds [144] generated during torrefaction can act as fungicides; (3) the modification of wood polymers leads to a non-recognition of the polymers by enzymes involved in fungal degradation; and (4) the profound degradation of hemicelluloses from torrefaction results in less nutritive source for fungi growth.

3.4.6. Grindability and reactivity

Grindability improvement of torrefied biomass is an important upgrading of biomass for the post-application. After torrefaction, the cell-wall structures are represented with bigger ruptures and bigger pores, elucidating the significant collapse of the cell walls [145]. This is attributed to the release of VM during torrefaction [146]. Because the cell walls are destroyed, it is easier to grind the torrefied biomass, thereby improving the grindability. This improvement in the grindability is crucial for fuel application. Specifically, better grindability of material is conducive to saving more energy if the biomass is pulverized into small particles [147].

The energy required during the grinding process of torrefied biomass could be significantly decreased by 40-88% when compared to the grinding of raw biomass [148]. Wang et al. [149] evaluated the grindability of torrefied Norway spruce stem wood, stump, and bark. The grindability of Norway spruce was significantly improved after torrefaction. They indicated that the energy required for grinding torrefied stem wood and stump under 225°C of torrefaction could be reduced up to 50% compared to untreated samples. Phanphanich and Mani [150] evaluated the effect of torrefaction on the grindability of wood chips (WC) and logging

wt%, respectively. The FC contents in coal and biomass are 46-92 wt% and 0.5-20 wt%, respectively [5]. When biomass undergoes torrefaction, the dehydration and devolatilization processes proceed. This results in the removal of moisture and light volatile fractions that contain most of the H and O inside the biomass [140]. The liberation of these materials leads to decarbonization, dehydrogenation, and deoxygenation reactions [112,113], that is, some of the atoms C, H, and O are lost from the thermal pretreatment. Nevertheless, the decarbonization extent in torrefaction is smaller than the dehydrogenation and deoxygenation extents. As a consequence, relatively more carbon remains in torrefied products, and the atomic H/C and O/C ratios thus decrease.

Based on the chemical formulas of hemicelluloses, cellulose, and lignin shown in Fig. 10, their atomic H/C ratios are 1.67, 1.6, and 1.19-1.53, respectively, whereas the atomic O/C ratios in cellulose, hemicelluloses, and lignin are approximately 0.83, 0.80 and 0.47-0.36, respectively. [5]. Most of the hemicelluloses and partial cellulose in biomass are thermally decomposed by torrefaction, depending on the torrefaction severity, whereas biomass with lower atomic H/C and O/C ratios relatively retains more lignin. This also corresponds to the trend of decreasing the two ratios with increasing the torrefaction severity.

Fig. 11. Fuel properties of raw biomass, torrefied biomass, and coal.

Fig. 12. Grindability of sugarcane bagasse at (a) 200 °C, 225 °C and 250 °C, 275 °C and 300 °C (at 30 min) (b) 200 °C, 225 °C and 250 °C, 275 °C and 300 °C (at 60 min). Reprinted from the reference [151] with permission of Elsevier Copyright © (2019).

residues (LR). The results indicated that the specific energy consumption for grinding torrefied biomass could save up to 10 times for torrefied WC, and up to 6 times for torrefied LR when compared to that of raw biomass. They also suggested that the specific grinding energy consumption was linearly correlated with torrefaction temperature. The particle size distributions for raw and torrefied sugarcane bagasse in comparison to four reference coals have been determined [151], as presented in Fig. 12. The ground samples were sieved with mesh sizes from 53 to 600 μm, and the retained mass of each mesh was calculated based on original dried sample mass. The reduced particle sizes of sugarcane bagasse could stand for the improved grindability of sugarcane bagasse and significantly decrease the energy consumption during biomass grind-

ing. Thus, the consumed energy of grinding biomass undergoing torrefaction can be largely reduced.

Hardgrove grindability index (HGI) is a common indicator to examine the grinding scale of biomass for milling and to evaluate the difficulty of grinding a solid sample into the powder [152]. The HGI depended on the torrefaction severity wherein the higher the HGI value, the easier the grinding [153]. It was found that a high HGI of torrefied beech was featured by moderate or easy grinding when the mass loss of beech was higher than 30% from torrefaction. After grinding, the particle shape and size of the ground torrefied biomass has been significantly reduced with enhanced bulk and energy density [147]. Because of this, the ground torrefied biomass shows an excellent application for fuel pulverization and co-firing in power plant or gasification.

The recognition of fuel reactivity such as ignition and burnout is of the utmost importance when torrefied biomass is used as a solid fuel [154]. The ignition and burnout temperatures of torrefied biomass are raised compared to its raw counterpart, stemming from the devolatilization and depolymerization during the torrefaction [155]. Li et al. [156] examined the combustion properties of biochar from the torrefaction of *Miscanthus floridulus* and Australia coal by TG. The ignition and burnout temperatures of Australia coal (447 and 887°C) were both higher than those of biochar (266 and 489°C). They also evaluated the combustion characteristic index (S) of Australia coal and biochar. A higher S value of fuel stood for its better combustion performance. The S value of biochar (49.70) was much higher than that of Australia coal (0.87). The higher S value of the biochar was ascribed to its lower ignition and burnout temperatures and higher mass-loss rate. Mi et al. [157] investigated the combustion and pyrolysis behaviors of torrefied wood, torrefied bamboo, and their blends. They discovered that the torrefied biomass had higher combustion and pyrolysis peak temperatures, as a consequence of removals of moisture and volatile, as well as thermal degradation of hemicelluloses, cellulose, and lignin from torrefaction. They also found that there was no synergistic effect during combustion and pyrolysis of the different blends. Chen et al. [113] examined the combustion performance of various torrefied biomass materials in a drop tube furnace. The examinations from the burnout and R-factor of the samples suggested that a higher burnout was reached and more volatile products were released with raw and torrefied biomass at 250°C than at 300°C. The results of R-factors from the examined fuels demonstrated that torrefied biomass facilitated the gas-phase or solid-phase combustion. Ndibe et al. [158] examined the co-firing characteristics of torrefied biomass (50%) and coals (50%). The results showed that the torrefied biomass blended fuels could be ignited faster, but generated more elongated flames with higher volatile yields. This created a more elongated combustion zone compared to the intense and short coal flame.

3.5. Torrefaction parameters

The performance of torrefaction is affected by some factors such as temperature, duration, and carrier gas flow rate and its composition, particle size, the presence of the catalyst, etc. The influences of these parameters on torrefaction performance are described below.

3.5.1. Temperature

Torrefaction temperature is the most important parameter among the operating parameters. The thermal decomposition temperatures of hemicelluloses and cellulose are in the ranges of 220-315°C and 315-400°C, respectively, while torrefaction is operated at temperatures of 200-300°C, it is thus known that the operating temperature has a significant influence on the results of torrefaction. Torrefaction can be categorized into light torrefaction (200°C to 235°C), mild torrefaction (235°C to 275°C), and severe torrefaction (275°C to 300°C), according to torrefaction temperature [102]. During light torrefaction, moisture and light (or low molecular weight) volatiles in biomass are released. Hemicelluloses in biomass are the most active components among hemicelluloses, cellulose, and lignin. Hemicelluloses are thermally degraded to a certain extent during light torrefaction, whereas cellulose and lignin are only slightly or hardly affected [130]. Therefore, the weight loss of biomass after light torrefaction is not pronounced and its energy density or calorific value increases only slightly. When biomass undergoes mild torrefaction, hemicelluloses decomposition and volatile liberation are facilitated. Hemicelluloses are substantially depleted and cellulose is also consumed to a certain extent. In the case of severe torrefaction, hemicelluloses are

almost depleted completely and cellulose is thermally degraded to a great extent. Among the constituents, lignin is the most difficult to be thermally degraded and its weight loss within the temperature range of orrefaction is low. Hemicelluloses and cellulose are the main constituents of biomass. Owing to the substantial removal of hemicelluloses and cellulose from biomass by severe torrefaction, the weight and energy yield of biomass usually decrease vigorously, even though the energy density of the fuel is greatly enhanced.

3.5.2. Reaction time (duration)

Apart from temperature, torrefaction time or duration is another important factor in evaluating torrefaction performance and severity. Torrefaction is normally conducted for several minutes [57,159] to several hours [145,160]. The calorific value of resultant solid fuel or biochar is enhanced by torrefaction, and an increase in duration raises the carbon content and heating value in the biomass. For instance, the torrefaction of wood briquettes operated under 250°C for 0.5, 1 and 1.5 h showed that the calorific values of the biomass increased from 20.0 to 22.7 kJ kg^{-1}, while the longer torrefaction duration would take more energy for the thermal pretreatment [133]. The results of TG [59] showed that the rapid thermal degradation of biomass occurred at torrefaction time less than one hour, and tended to be very slow beyond one hour. Consequently, torrefaction duration is normally controlled within one hour. An overview of the typical operating ranges of temperature and residence time, the impacts of reaction temperature on the properties of biomass prevails over the treatment time. Different combinations of temperature and residence time can be used to reach a given torrefaction degree, as expressed by the weight loss [159]. On the other hand, the crucial properties of the torrefied product such as HHV and saturated moisture uptake can be correlated by the weight loss or torrefaction severity of biomass [132,159]

3.5.3. Particle size

The particle size is one of the important parameters for biomass torrefaction [161,162]. Biomass has poor heat conductivity, while the temperature gradient across the particle will influence the biomass pyrolysis mechanism [52]. In general, smaller particles can promote the heat and mass transfer to keep the relatively constant temperature within them during pyrolysis, thereby enhancing bio-oil production by restraining the char formation and secondary cracking of vapors [163]. On the other hand, large particles will inhibit bio-oil formation. The main output for pyrolysis normally is bio-oil rather than biochar. However, particle size reduction (milling or grinding) can be costly and significantly increase the overall cost of the biomass pyrolysis operation. It will be a trade-off issue between the cost and efficiency of the pyrolysis process when regarding particle sizes.

The experimental results showed that increasing particle length could enhance mass and energy yields, but opposite with particle diameter [164]. The particle size had an impact on the torrefaction severity, especially under high temperatures [161]. During torrefaction, although the temperature gradient for particles with sizes smaller than 1 mm is very small, the torrefaction reaction rate is affected by internal diffusion from generated vapors inside the particles. The torrefaction of wood sawdust with different particle sizes (0.25-0.5, 0.5-1.0, and 1.0-2.0 mm) in a continuous slot-rectangular spouted bed (SRSB) reactor was studied by Wang et al. [162]. They found that larger particle size limited the performance of the reactor. When the particle size increased, the solid yield of torrefied biomass was decreased, leading to a decrease in the energy yield. Bates and Ghoniem [165] developed a comprehensive one-dimensional model to describe the torrefaction of a single woody biomass particle. For a larger size biomass sample, the

heat released from chemical reactions during torrefaction caused significant intraparticle gradients and accelerated the degradation of the biomass. In addition, because of the rise in the reaction rate at higher temperatures, the sensitivity of torrefaction to particle size also increased.

3.5.4. Carrier gas

In general, the torrefaction is performed in an N_2 atmosphere. Recently, some studies evaluated the effects of different carrier gases, such as CO_2, air, flue gas, etc., on torrefaction performance [67]. It was reported that the CO_2 as a torrefaction medium could promote the thermodegradation of biomass and the thermal cracking of the released volatile compounds during torrefaction [67,166]. Hernández et al. [167] performed the torrefaction of sewage sludge under N_2 and CO_2 in a TG-FTIR. Their results indicated that the presence of CO_2 exhibited reactive behavior during torrefaction, resulting in an increase of the decomposition rate and shifting the characteristic degradation peak to a lower temperature around 7°C. The effect of CO_2 on the torrefaction of woody biomass in a temperature range of 200-300°C was explored [67]. It revealed that the CO_2-torrefied biomass demonstrated a more significant increment of surface area, ascribing to the formation of pores in the samples compared to N_2-torrefied biomass.

Regarding the boundaries for limiting O_2 percentage, the supply of the O_2 percentage is mostly less than 15% [168–170]. In general, the air in the atmosphere consists of 21% of O_2. The high percentage of O_2 will lead to the combustion process rather than the torrefaction process. The main purpose of adding O_2 is to enhance the torrefaction reaction. The oxidative torrefaction of biomass involves not only thermal decomposition and devolatilization of biomass but also the exothermic oxidation reactions [169,171]. The reaction rates of oxidation reactions are normally faster than the decomposition reactions and devolatilization, leading to the reduction of the torrefaction duration [171]. The effects of oxygen concentrations (2, 6, 10, and 21%) on the torrefaction of *Eucalyptus grandis* at 240 and 280°C were evaluated by Rousset et al. [172]. The results suggested that the effects of the oxygen amount on the solid yield and torrefied product properties were more marked under a torrefaction temperature of 280°C. The torrefaction of oil palm fiber pellets (OPFP) in inert and oxidative atmospheres showed that the oxidative torrefaction resulted in higher FC and lower VM in torrefied OPFP when compared with the non-oxidative torrefaction [170]. This is due to the higher reaction extent of VM in the course of oxidative torrefaction. Uemura et al. [173] conducted the torrefaction of oil palm empty fruit bunches (EFB) in a batch reactor under a flue gas atmosphere (9 vol% O_2 +12 vol% CO_2 + 71 vol% N_2). They pointed out that a decrease in the solid yield and an increase in HHV were obtained after torrefaction, as a consequence of enhanced decomposition by O_2 and CO_2 in the flue gas. The relevant studies concerning the effects of carrier gas on torrefaction are summarized in Table S1.

3.5.5. Carrier gas flow rate

Some studies have investigated the effect of flow rate (or superficial velocity) on torrefaction [68,174]. The results revealed that the superficial velocity of the carrier gas played no role in the torrefaction performance in the inner conditions [68,175]. Asadullah et al. [176] examined the effect of sweeping gas (N_2) flow rate on palm kernel shell torrefaction. The gas flow rate was controlled from 100 mL min^{-1} to 1000 mL min^{-1}, providing the superficial velocity from 3.5 cm min^{-1} to 35.0 cm min^{-1}. They reported that the increase of the superficial velocity helped to move out the volatile products during torrefaction. However, the solid yield was almost unchanged with the variation of the superficial velocity. This observation implied that the torrefaction performance was dominated by heat and mass transfer in biomass rather than on the biomass surface. In contrast, when biomass underwent oxidative torrefaction, increasing air superficial velocity diminished the solid yield, regardless of the torrefaction temperature [68]. It implied, in turn, that the oxidative torrefaction of biomass was controlled by the surface oxidation.

3.5.6. Catalyst

Studies have shown that inorganic metals in biomass could play a role as catalysts in the thermochemical processes of biomass, thereby influencing char formation [177], distribution of pyrolysis products [178], gasification [179], and combustion [180]. Alkali metals and alkaline earth metals have attracted attention as promising catalysts for the thermochemical conversion of biomass [181]. Recently, some researchers have examined the influences of inorganic metals on biomass torrefaction [182,183]. Relevant experimental results pointed out that potassium or sodium was catalytically active in the degradation of biomass during torrefaction [183]. The effects of potassium on torrefaction performance by a thermogravimetric analyzer addressed that the mass loss of woody biomass increased with rising K^+ concentration [183]. At higher torrefaction temperatures (270 and 280°C), the catalyst effect was more significant. During torrefaction, potassium plays an important catalytic role in the thermodegradation of cellulose in biomass, involving two pathways:(1) cleavages of C-H, C-C bonds, and glycosidic linkage, and (2) cleavage of hydrogen bond [184]. The effects of K_2CO_3 addition on the condensable species during wood torrefaction were studied by GC-MS [185]. The results indicated that the potassium enhanced the formation of acetol and acetic acid. The number of lignin derivatives, like syringol and 4- vinylguaiacol guaiacol, also rose with increasing impregnated K_2CO_3 concentration. The catalytic effects of potassium were examined on biomass torrefaction at 150°C to 300°C by TG [186]. The results revealed that with the same mass loss, at least 28% of time reduction for the torrefaction of K^+-impregnated biomass was observed, and the maximum time saving could achieve 93%. However, it has been found that potassium was less influential on hemicelluloses. The insignificant impact on hemicelluloses from the addition of potassium could be due to that single polymers are not affected in the same way as in the whole biomass where potassium could affect the interaction between biopolymers [185,187].

3.5.7. Performance index

The torrefaction performance is highly corresponding to torrefaction severity (TS) [31], which is mainly dominated by torrefaction duration and temperature. Recently, numbers of indexes, such as torrefaction severity index (TSI), severity factor (SF), weight loss (WL), torrefaction severity factor (TSF), energy-mass co-benefit index (EMCI), and upgrading energy index (UEI), have been defined to evaluate torrefaction performance. WL, generally calculated with a dry basis, is the most widely used index to represent TS in that an increase in torrefaction duration or temperature gives rise to higher WL. Meanwhile, the influence of TS on the FC [188] or carbon content [189], HHV [188,189], the enhancement of HHV [190], color change [145], hygroscopicity [145], and energy yield [191] can also be evaluated by WL. In some cases, WL is replaced by solid yield to indicate TS [192].

TSI is developed to identify the torrefaction degree and is defined as:

$$\text{TSI} = \frac{WL}{WL_{\text{ref}}} \tag{1}$$

where WL and ΔWL_{ref} stands for the weight loss of the sample at a certain torrefaction operation and a reference operation, respectively. ΔWL_{ref} is based on the highest TS condition, normally at 300°C for 60 min. According to this definition, the value of TSI is in the range of 0-1. In the study of Chen [193], they performed the

torrefaction of microalga residue (*Chlorella vulgaris* ESP-31) for 15-60 min at 200-300°C, and the results revealed that the TSI gradient versus duration was smaller than that versus temperature. According to the observation, they reported that torrefaction temperature showed a more significant influence on the solid yield compared to treatment duration.

SF was initially introduced to determine the extent of biomass pretreatment by aqueous solvent or steam [194,195], and was defined as [196,197]:

$$SF = \log\left[t \times exp\left(\frac{T_H - T_R}{14.75} \right) \right] \qquad (2)$$

where t is the pretreatment time (min), T_H is the reaction temperature (°C), and T_R is the reference temperature (=100°C). Recently, some studies have adopted SF to evaluate the performance of the steam explosion [198] and torrefaction [196]. In the study of Lee [196], SF was adopted to account for the effect of TS on the biopolymers in the biomass. When the SF value was low, torrefaction had an important effect on the degradation of hemicelluloses, but not on cellulose or lignin.

Concerning to TSF, it was suggested by introducing a time exponent in SF:

$$TSF = \log\left[t^\alpha \times exp\left(\frac{T_H - T_R}{14.75} \right) \right] \qquad (3)$$

In the above formula, the value of T_R could be adjusted for finding a more suitable reference temperature to describe the impact of torrefaction. Moreover, by introducing a time exponent α, the thermodegradation nature of biomass to torrefaction conditions was taken into account, and its optimum value, namely, α_{opt}, could be acquired. Chen et al. [192] evaluated the TSF of different torrefied biomasses (spent coffee grounds, Chinese medicine residue, *Arthrospira platensis* residue, *C.* sp. JSC4), and determined the α_{opt} values of the materials with T_R=0°C. The results indicated that the optimum time exponent (α_{opt}) in TSF with maximizing R^2 value was between 1.6 and 3.0. These values suggested the larger influence of duration on TS when compared to SF.

Unlike WL, TSI, SF, and TSF, EMCI and UEI are used to evaluate the torrefaction outcome in terms of energy production and material storage. EMCI is represented by the difference between the energy yield and the solid yield [100]. Physically, a higher EMCI value stands for the torrefied product with higher energy yield and lower material volume, which is conducive to fuel production with storage due to smaller volume. Lu et al. [100] evaluated the torrefaction of oil palm fiber (OPF) and eucalyptus in nitrogen and air atmospheres. They found that, for the torrefaction of OPF in N_2 and air, the maximum values of EMCI were 19.0 and 7.7, respectively, and at 300°C and 250°C, respectively, indicating that the optimum operations occurred at the two temperatures. Concerning eucalyptus torrefaction in N_2 and air, the optimum operations developed at 325 and 275°C where the EMCI values were 18.9 and 14.0, respectively.

The UEI is a ratio of the torrefaction energy yield (based on HHV) to the energy input (supplied electricity, kWh) into the torrefaction system [199]. From this definition, an increase in UEI means higher energy efficiency of a torrefaction process, as a result of higher energy yield or lower energy input. The results of biomass waste (coffee grounds and microalga residue) torrefaction by conventional and microwave heating showed that the UEI value by microwave torrefaction was higher than that by conventional torrefaction in light torrefaction, as shown in Fig. 13. From the results of UEI, the microwave torrefaction presented higher energy efficiency and shorter duration than conventional torrefaction [200].
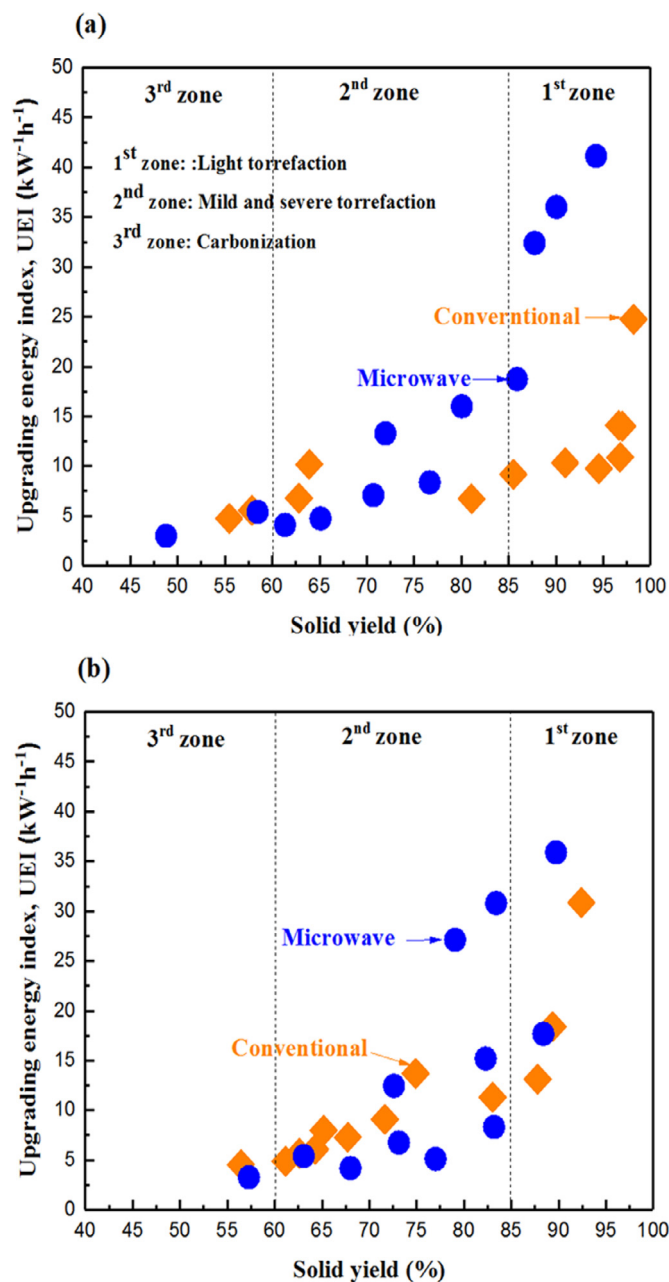
Fig. 13. Profiles of UEI versus the solid yield of (a) coffee grounds and (b) microalga residue with different torrefaction treatment measures.

3.6. Torrefaction kinetics

Thermal degradation of biomass in course of torrefaction involves a series of complex chemical reactions. The decomposition of lignocellulosic biomass mainly happens at cell walls which are primarily comprised of hemicelluloses, cellulose, and lignin [201–203]. The degradation of microalgal biomass relates to the decomposition of carbohydrates, proteins, and lipids [7,31]. The kinetic analysis is an efficient way to recognize the characteristics of biomass thermodegradation [204,205]. In general, there are two basic modes adopted for biomass pyrolysis kinetics: isothermal kinetics and non-isothermal. According to these two basic modes, several different models such as the one-step model (or called model-free) [206], the two-step model [5], the multi-step model [207], and the multi-components model [119,208] have been developed (**Fig. S3**).

For the thermodegradation kinetics of biomass torrefaction, the isothermal pyrolysis kinetics is generally applied to describe the degradation mechanisms of biomass [209,210]. Chen and Kuo [64] developed a one-step torrefaction kinetics model to predict the thermal decompositions of xylan, cellulose, and lignin at 200-300°C. The proposed values of the reaction order on xylan, cellulose, and lignin, and are 9, 3, and 1, while the corresponding activation energy values are 67.83, 124.42, and 37.58 kJ mol^{-1}, respectively. The reaction rate is proportional to the order of the concentration of a single reactant in the kinetics theory. The higher reaction order of a reaction implies that the reaction can be triggered more easily. Therefore, the degradation rate of xylan is much higher than those of cellulose and lignin. Chen et al. (2014a) evaluate the kinetics for non-isothermal and isothermal torrefaction of *Scenedesmus obliquus* (CNW-N). The results revealed that the reaction severity of non-isothermal torrefaction was higher than that of isothermal torrefaction at the same average temperature.

A non-linear regression method was used to determine the torrefaction kinetics of *Ceiba pentandra* (Araba) and *Alstonia congensis* (Ahun) from the one-step model [211]. The results indicated that the reaction orders of Araba and Ahun were 2.15 and 2.28, while the corresponding activation energies were 134.45 kJ mol^{-1} and 143.38 kJ mol^{-1}, respectively.

A multi-step model was adopted to investigate the kinetics of aspen by torrefaction as studied by Klinger et al. [212]. The evolutions of various chemical species were predicted based on the degradation of hemicelluloses. The proposed kinetics model could accurately establish the dynamic profiles of gaseous products at the initial stages of torrefaction (up to 30% mass loss) in the temperature range of 260 to 300°C.

Torrefaction kinetics for different wood species (eucalyptus, locust, and spruce) in the temperature range of 210 to 290°C with long treatment duration were studied by Cavagnol et al. [207]. A variety of multi-step series reaction mechanisms were explored from the literature (one, two, and three-step models) for the determination of kinetic parameters. They reported that the two-step model provided an acceptable accuracy for the mass loss predictions in the course of torrefaction. The kinetics for isothermal torrefaction of industrial solid wastes (oilcloth and PVC) was determined by an independent parallel reaction (IPR) model [213]. The results revealed that a high heating rate was more efficient for the non-isothermal torrefaction of the oilcloth waste. In contrast, PVC waste pretreated with a low heating rate could achieve more energy saving.

The isothermal pyrolysis kinetics is widely applied for biomass torrefaction by the two-step model, as tabulated in Table S2, which is related to the release of volatiles, and intermediate and char formation [214]. The solid-phase pseudo-components (A, B, and C) represent the initial raw biomass (A), intermediate (B), and final char or residual (C), while V_1 and V_2 stand for the volatile products. The reaction rate constants are denoted by k_1, k_2, k_{V1}, and k_{V2}. Di Blasi and Lanzetta [214] firstly developed the two-step kinetic model, and reported that the reaction occurred at the first step was attributed to the degradation of hemicelluloses and extractives removal. While the second step reaction accounted for the decomposition of hemicelluloses, cellulose, and part of lignin [215]. The rate equation of each reaction was assumed to be the solid reaction and first order [216]. The reaction rate constant k (s^{-1}) for every reaction was calculated using the Arrhenius law, expressed as $k_i = A_i \exp(\frac{-Ea_i}{RT})$, where $i = A$, B, C, V_1, and V_2. In the Arrhenius equation, A_i is the pre-exponential factor, Ea_i is the activation energy of component i, R is the universal gas constant, and T is the absolute temperature. Sheng et al [216] obtained the torrefaction kinetics of wood chips in a pilot-scale reactor by using the two-step model. They established a correlation between the HHV

and the predicted mass yield to estimate the energy yield of torrefied chips. A two-step kinetic model was introduced to describe the mass loss dynamics during spruce torrefaction with different contents of impregnated potassium (K) [217]. For the cases with different concentrations of K, they adopted the same activation energy but different pre-exponential factors for the rate constants to have the kinetics, and the calculated results had good agreement with experiments. In the study of Silveira et al. [218], the torrefaction kinetics of poplar wood boards by a two-step scheme with a three-stage approach was evaluated. They pointed out that the root-mean-square deviations of the direct approach and the three-stage approach were 0.363 and 0.235, respectively, implying 35% of improvement by the proposed three-stage approach. The kinetics for the torrefaction of woods (poplar and fir) in a semi-industrial reactor was determined through the two-step model [219]. The obtained kinetics were applied for the predictions of elemental composition (C, H, and O) in the woods during torrefaction. The elemental H and O in poplar and fir significantly decreased when the reaction temperature was higher than 170°C, resulting from a devolatilization reaction in the course of torrefaction. Based on the predicted C, H, and O in the woods, the extents of decarbonization (DC), dehydrogenation (DH), and deoxygenation (DO) were also evaluated. Because of the higher intensity of devolatilization in poplar during torrefaction, the intensities of DC, DH, and DO were all larger than in fir.

4. Torrefaction reaction systems

Overall, the reaction system of biomass torrefaction for producing carbon-neutral fuels to replace coal consists of a feeding unit for feedstock, a pretreatment unit, a reactor, and a post-treatment unit. The details of each aforementioned unit are tabulated in Table 6.

4.1. Feedstock

In recent studies concerning biomass torrefaction, a variety of biomass materials have been adopted as the feedstock. Lignocellulosic biomass or energy crops (e.g., bamboo, pine, spruce, willow, eucalyptus, banyan, larch, beech, birch, wood briquettes, and wood pellets, etc.) are the most important and commonly used materials for the feedstocks of torrefaction. The torrefaction of agricultural residues and forestry wastes (e.g., sawdust, bagasse, coffee residue, rice husk and straw, wheat straw, oil palm empty fruit bunches, etc.) has also been investigated. However, to prevent the imbalance of the food supplies and forest vegetation worldwide, the sources of feedstock from non-agriculture biomass or even unusable wastes are promoted recently. Third-generation biofuels from algal biomass, including microalgae and macroalgae, are gaining more attention in the bioenergy field, owing to its rapid growth rate, high carbon fixing efficiency, and higher yield per unit area than terrestrial biomass [31,220].

In addition to the aforementioned first to third-generation biofuels, the waste-to-fuel technology is developed recently. For instance, municipal solid waste (MSW), food waste, industrial waste, sewage sludge from municipal and industrial wastewater, and dairy manure have also been investigated as the torrefaction feedstock [221]. In the overview of the literature, torrefaction is a promising technology to transform versatile feedstocks into biofuels. The torrefaction conditions and results (i.e., heating value and energy yield) on different feedstocks are summarized in Table S3.

The recognition of the basic properties of biomass plays an important role in pretreatment choice and the thermodegradation. In general, the basic characterizations of biomass include proximate analysis, calorific analysis, elemental analysis (ultimate analysis), fiber analysis, composition analysis, and metal analysis. The

Table 6
Descriptions of a torrefaction reaction system.

Process	Description
Feedstock selection and analysis	The selection of the feedstock will lead to different outcomes. The basic characterizations are thus required to identify the compositions of the feedstock, mainly including proximate analysis, elemental analysis, and composition analysis, etc.
Pretreatment adoption	To enhance the efficiency of the torrefaction process, pretreating the feedstock is an essential step. For instance, the drying process to remove the intrinsic water and grinding the feedstock to increase the particle reaction area are the common pretreatments adopted before torrefaction.
Reactor selection	Various types of reactors have been developed maturely such as batch types or continuous types. Each type of reactor has its advantages and disadvantages, and the selection of the reactor depends on the requirement and purpose of the user.
Post-treatment of the products	To further enhance the qualities of torrefied products in terms of higher energy density, convenient transportation, and handling, post-treatment such as densification is thus operated.

requirements of the analyses depend on the nature and source of biomass.

The proximate analysis consists of the measurements of moisture, VM, FC, and ash, which can be performed using an oven or furnace by following standard methods for different kinds of feedstock, as provided in Table S4 [222]. The thermogravimetric analyzer can also be employed to conduct the proximate analysis with a small amount of feedstock [223,224].

The calorific analysis includes the HHV and the lower heating value (LHV) where their difference is from the latent heat of the water. The HHV of a sample can be measured directly using a bomb calorimeter. Alternatively, several predicted formulas can be used to calculate the HHV and LHV of feedstock based on the results of elemental analysis and/or proximate analysis [225].

The elemental analysis normally includes the measurements of carbon (C), hydrogen (H), nitrogen (N), oxygen (O), and sulfur (S) in a feedstock. When dairy manure [226,227], food waste [228,229], or sewage sludge [230,231] are used as feedstock, the contents of the phosphorus (P) and chlorine (Cl) are also determined through the use of X-ray fluorescence (XRF) spectrometry [232] to avoid the formation of pollutants in the products. From the fuel point of view, proximate, calorific, and elemental analyses are essential to understand the basic properties of biomass. In some cases such as biowaste or sewage sludge [233], metal analysis including the determinations of sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), copper (Cu), zinc (Zn), chromium (Cr), lead (Pb), and nickel (Ni) are also present using atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectroscopy (ICP-OES), or inductively coupled plasma mass spectrometry (ICP-MS).

When lignocellulosic biomass is used as the feedstock, the fiber analysis, consisting of the measurements of cellulose, hemicelluloses, and lignin, will be performed, following the Van Soest method, or ASTM E 1758-01 with Klason lignin method [234-236]. The torrefaction of lignocellulosic biomass is significantly affected by these three basic components. Generally, the motives of torrefaction are to remove light VM in biomass which is mostly contained in hemicellulose and part of cellulose, and generate higher energy density products. Hence, a feedstock with higher hemicel-

lulose content renders lower solid yield compared to lower hemicellulose content [59,237].

The composition analysis of algal biomass is performed to measure the contents of carbohydrates, proteins, and lipids [190,238,239]. The thermal decomposition behavior of feedstock is also a common analysis that can be conducted via a TG [67,101,240,241]. The sample will be heated from 105°C to an elevated temperature of about 900-1000°C under nitrogen or air atmosphere, mostly with a flow rate of 100 mL min^{-1}, to observe the pyrolysis and combustion phenomenon, respectively. The results from TG can provide useful information on feedstock for its torrefaction. The aforementioned analyses for different kinds of feedstocks are summarized in Table S5.

4.2. Pretreatment

After receiving the feedstock, several pretreatment processes can be performed to control the physical and chemical conditions of biomass for the subsequent torrefaction process. The basic pretreatments of feedstock include drying, grinding or pelletization, alkali and alkaline earth metals (AAEMs) impregnation, ionic solution and bio-solution treatment, leaching or water washing (or demineralization),

The drying process is usually conducted by storing samples in an oven at temperatures of 50-105°C for 8-24 h to remove the surface and bound water to obtain the dry-basis samples [60,224,237]. Drying is considered as the major energy consumption process. To avoid excess energy input during the drying process, volatiles generated from torrefaction, so-called torgas, can be combusted to partially supply heat for the processes of torrefaction and the predrying of biomass. The flue gas can also be used to directly or indirectly heat biomass. The dried samples are ground by a shredder or mill machine, followed by subsequent sieving to obtain desired particle sizes. Some studies already reported that the smaller particles are easier to undergo thermal degradation, based on better conductive and convective heat transfer rates from the reactor wall [161,242]. When large biomass is torrefied, the volatile diffusion will be constrained, and consequently, the properties of the derived products are non-uniform.

Pelletization has been widely used to increase the densification of biomass since the derived pellets are easily transported and handled. The pelletization step was introduced as a pretreatment process before the torrefaction of five biomass materials (wood chips, coniferous barks, olive pips, straw, and pine pellets) to enhance the energy density and water-resistivity of pellets [243]. The results showed that torrefied pellets had better water-resistivity and higher energy yield (∼90%) compared to torrefied sawdust. Adopting pelletization prior to torrefaction could obtain higher energy density and water-resistivity products, and even be more energy efficient [244].

The AAEMs (e.g. K, Na, Ca, and Mn) have been known for having catalytic effects on the thermal degradation of biomass such as pyrolysis and gasification [183,245,246]. Therefore, several studies investigated the catalytic effects on the biomass torrefaction by doping or impregnating methods [182,183]. Danish wheat straw and spruce wood chips were impregnated 2 wt % KCl and K_2CO_3, respectively, before the torrefaction process [182]. The TG results indicated that the addition of K could effectively catalyze the decomposition of hemicelluloses and cellulose, in terms of moving the degradation peaks to lower temperature. The grindability tests also gave positive results, in which the torrefied products from alkali-impregnated samples had higher particle reduction than untreated ones, while the enhancement of KCl-impregnated torrefied products was better than that of K_2CO_3-impregnated one. Shoulaifar et al. [183] adopted both doping and impregnating methods to study the catalytic effects of K, Na, Ca, or Mn on the TG torrefaction of two kinds of coniferous wood (spruce and pine), one deciduous wood (aspen), and one herbaceous biomass (miscanthus). A similar tendency with the aforementioned studies was reported that when the concentrations of K, Na, and Mn increased, the mass loss increased as well, whereas Ca had no obvious effect [182,183]. The tendency in hemicelluloses and cellulose degradation with increasing K concentration in biomass was also observed.

Additionally, there were studies on organic solutions (ion liquids (ILs) or bio-solution) to pretreat lignocellulosic biomass before torrefaction, aiming to modify the indigenous structure of the biomass and to enhance the degradation reaction. Sarvaramini et al. [247] impregnated the feedstock with three kinds of imidazolium-cation based ILs (Emim OTf, Emim BF_4, and Hmim NTf_2), instead of mineral acids solutions (H_2SO_4, HCl, and HNO_3) to avoid the formation of poisonous emanations. The Emim OTf and Emim BF_4 ILs showed the effective improvement in the degradation of cellulose, due to the increasing the decomposition rate and moving the decomposition temperature forward. Conversely, these ILs had no noticeable effects on the degradation of hemicelluloses and lignin. Most of the torrefied products from the impregnated feedstock contained higher energy densities (based on HHVs), while the energy yields were lower compared to those without pretreatment. Bamboo was pretreated with a bio-solution (natural organic enzyme-7F) to improve the efficiency of the torrefaction process [248]. The results indicated that the solution-treated bamboo prior to grinding could obtain better-quality torrefied products, due to the enhancements on the reaction rate during torrefaction and the energy density of the products.

However, the remained alkali metals (K and Na) in torrefied products would interact with silica, sulfur, or chlorine during combustion and cause slagging and fouling of the equipment [249,250]. Therefore, several studies [224,235,245] used the washing (leaching) process by water and organic solutions [251] (e.g., ammonium acetate, hydrochloric acid, and nitric acid) to wash the inherent metals of biomass before torrefaction, so-called demineralize. The ash content of all demineralized and torrefied products (1.0-10.1 wt%) decreased significantly compared to those (3.5-13.1 wt%) without demineralization [245]. The ash fusion behavior of torrefied products was also improved by using the washing pro-

cess. Kasim et al. [224] performed acid leaching coupled with torrefaction to convert palm empty fruit bunches (EFB) into quality-improved solid biofuel. The results indicated that the pretreatment of demineralization could improve the properties of the resultant biofuel, in terms of the increasing mass yield, energy yield, and carbon content, which might be attributed to the lack of natural catalyst mitigating the decomposition of the biomass. Moreover, it was observed that the demineralization effectively reduced the AAEMs content and oxygen content.

4.3. Reactor

Nowadays, torrefaction technologies are developed based on already existing reactor concepts, designed for other processes such as drying, pyrolysis, or gasification. These reactors are adopted and modified for the torrefaction process. The reactor type is classified by the movement of the feedstock, the means of heat transfer, and the assisted media. The developed reactors in commercial companies or scale-up laboratories consist of (1) fixed bed reactor; (2) rotary drum reactor; (3) screw reactor; (4) microwave reactor; (5) moving-bed reactor; and (6) others such as torbed reactor, belt drier, multiple hearth furnace, vibrating electrical elevator and reactor (REVE), rotating-packed bed reactor, and spouted-bed reactor. There is no best reactor design suitable for any feedstock, hence, the proper selection of the reactor is essential based on the given feedstock.

The fixed bed reactor is a common torrefaction apparatus (**Fig. S4a**) used in laboratories for preliminary tests [252–254], owing to its merits of simple setup and low cost. It is mainly composed of a glass or stainless steel cylindrical tube to put the tested samples, a furnace to supply heat, temperature measurement devices like thermocouples to detect the sample and reactor temperatures, and a cooling unit to condense vapors or gaseous products. Nitrogen is used as a carrier gas to provide an inert environment in the course of torrefaction, and the gas flow is typically horizontal to blow out volatiles. Nevertheless, the disadvantages of the fixed bed reactor involve difficult sampling as well as poor heat transfer and temperature controlling, which limits its scalability and commercialization.

Rotary drum dryer is a heating device with high temperatures, originally used as the material heating and drying equipment. Since the rotary drum dryer is also a type of conveying equipment, it is thus beneficial for the development of a continuous torrefaction system, as shown in **Fig. S4b**. A continuous rotary drum reactor system normally consists of a feeding unit by using a screw feeder, a rotary reactor unit heated by an external heater, and a product collecting unit. Owing to the continuous rotating of the reactor, the conductive heat transfers between the wall and samples, and within biomass can be achieved effectively. The rotary drum bed had a lower solid yield compared to convective and fluidized reactors when operated under the same torrefaction conditions [255]. The rotary drum bed has the disadvantages of low thermal efficiency, owing to indirect heating, less plug flow, and limited scalability compared to other types of reactors.

A screw-type reactor, also called auger reactor, is a proven technology mainly composed of one or more auger screws transporting the feedstock through the reactor (**Fig. S4c**), which is also considered as a continuous reactor. Indirect heating is a typical method adopted in this type of reactor by using a medium inside the hollow wall or hollow screw. Direct heating has been investigated recently with various concepts to enhance its thermal efficiency. Concerning the operation of torrefaction with the screw reactor, several crucial parameters need to be considered, including the degree of filling, screw frequencies, and residence time. Improper controlling conditions may cause the blockage of the process ow-

ing to the agglomeration of particles and poor-qualities products [256,257].

Microwave torrefaction reactors (**Fig. S4d**) use the high-frequency electromagnetic irradiation, for blasting the water molecules or dielectric materials inside biomass and resulting in an increase of their internal energy or temperature. The microwave reactor employs electromagnetic waves, which can operate at a specific frequency range of 300 MHz to 300 GHz. There are two main mechanisms to describe electromagnetic microwave radiation: dipolar polarization and ionic migration. Typical industrial microwave reactors usually operate at a frequency of 2.45 GHz, which has been proven to be both effective and relatively achievable. The microwave reactor is different from other reactors that utilize direct heating. In a direct heating system, by contrast, biomass is heated externally, such that heat from the heat carrier (gas, solid, liquid, or reactor wall) initially contacts the surface of the particles and then is conducted into their center. This mode of heating is less efficient because biomass is a poor thermal conductor, whereas the microwave heating occurs simultaneously throughout the samples. The microwave irradiation produces efficient internal heating of biomass particles, while the heating depends on the ability of the materials absorbing the impinged microwaves. Generally, the power adopted in microwave-assisted torrefaction of various feedstocks is ranging from 150 to 400 W, corresponding to the heating rates within 10 to 135°C min^{-1} [258–260]. However, the heating rate of the torrefaction process will be controlled below 50°C min^{-1} to avoid insufficient reaction time and non-uniform products.

The moving-bed reactor has advantages of compact and simple design, as well as a high heat transfer rate via the heat-carrying gaseous medium, as displayed in **Fig. S4e**. Biomass particles enter a hopper at the top of the reactor and are fed in by the control of a screw conveyor, while the heating gas flows counter-currently from the bottom of the reactor to heat the feedstock [261]. The feedstock is subsequently treated by drying and torrefaction along the temperature gradient of the vertical column. The flow rate of the feedstock and the reaction duration will influence the height of the column. With the optimized conditions, the short residence time can be achieved. Owing to the high fill percentage of the moving-bed reactor, the pressure drop is severe compared to other types of reactors. It is thus essential to consider the operating cost of the blower in optimizing the process design when a moving-bed reactor is chosen.

The toroidal bed reactor (**Fig. S4f**), abbreviated as Torbed reactor, was developed and patented by Torftech cooperation. Typically, this technology has merits of accurate control of processes requiring gas-solid contact and higher temperatures than those experienced in conventional equipment. The principle of a Torbed reactor is the toroidal flow of the bed which has a refractory-lined and insulated chamber. Heat is carried via a gaseous medium which is blown in from the bottom of the reactor at a high velocity (50 to 80 m s^{-1}) passing stationary angled blades. The injection angles result in a flow with a horizontal and vertical velocity vector, which lifts and moves the feedstock in a horizontal motion at the same time. The toroidal motion allows a higher gas speed, which reduces the boundary layer between solid particles and gas. Owing to its high heat transfer rate and well mixing of the feedstock, the reaction duration of the Torbed reactor (around 80 s) is far shorter than that of other types of reactors. Therefore, it can provide novel and cost-effective means for processing a very wide variety of different materials.

The multiple hearth furnace consists of a series of circular hearths placed one above the other and enclosed in a refractory-lined steel shell, as shown in **Fig. S4g**. The system can be divided into a drying zone and a torrefaction zone. Biomass is dried in the drying zone utilizing a drying gas flow and subsequently is tor-

refied in the torrefaction zone. In this process, part of the drying gas flow containing water vapor is discharged from the drying zone and heated in a heat exchanger and then at least partially returned to the drying zone. Furthermore, part of the torrefaction gas flow evolved in the torrefaction zone is discharged from the torrefaction zone and fed to a combustion assembly for combustion. The resulting exhaust gas is used to heat the drying gas flow in the heat exchanger and is introduced into the torrefaction zone. Biomass is stirred and moved in a spiral path across each hearth by a vertical rotating shaft that goes through the center of the furnace. Biomass is fed to the top hearth, passing across it and then, through the drop holes to the hearth below with the temperature gradually increases one layer after another from 200 to 300°C. Biomass passes continuously over and across each hearth to the bottom of the furnace where the product is collected.

A robust, simple, and modern technology, REVE (as shown in **Fig. S4h**), modified from the concept of roasting various food ingredients such as peanuts, barley, or soya was developed by REVTECH. Few studies have presented the application of this integrated technology with high capacity in biomass torrefaction [243,262]. Four types of biomass (wood chips, pine barks, olive pips, and straw) were torrefied under temperatures between 240°C and 300°C, residence time up to 30 min, and mass flow rate between 10 to 140 kg h^{-1} [262]. The elemental analysis, HHV, and grindability of torrefied products were performed to evaluate the feasibility of this technology. Due to the plug-flow, homogeneous heating, and well-mixing characteristics of the REVE, the obtained products had good uniformity, improved grindability, and high energy yields with 68.6 to 89.4%.

A novel concept of reactor design, rotating packed bed (RPB) has been proposed to enhance the mass transfer of the reactants during the treatment, which has two main advantages: (1) increasing centrifugal force to obtain a high gravity (Higee) environment and (2) the elongated path of the carrier gas in the RPB. Pillejera et al. [263] first adopted RPB in the bamboo torrefaction process as displayed in **Fig. S4i**. The bamboo was torrefied with three temperatures (206, 255, and 300°C) at a fixed holding time (30 min). Three different rotating speeds (0, 900, and 1800 rpm) were conducted in the RPB reactor, which could correspond to the dimensionless G number of 0, 58, and 234, respectively. The G number could quantify the average centrifugal force (g) for each rotating speeds (rpm) [264]. The results showed that the G number has a significant influence in the solid yield, enhancement factor (EF) of HHV, and energy yield of the torrefied products for the temperatures of 206 and 255°C. On the contrary, the effect of G number on these quantities was slight when the process operated under 300°C. It was explained that the influence coming from the high temperature was greater than the force induced by the rotor, hence, implied that there existed a threshold value for the increase or decrease in torrefaction parameters at varying temperature and rotating speed.

The spouted bed is originally developed to strengthen the gas-solid contact with coarse particles and has been extensively applied to biomass pyrolysis and gasification [265,266]. The spouted bed is capable of handling large (>1 mm) particles such as typical biomass particles. Moreover, spouted bed reactors can provide excellent particle-particle and particle-fluid heat transfer. The SRSB reactor, as shown in **Fig. S4j**, is relatively easy to scale up compared to conventional spouted beds. Its potential applications in a torrefaction process owing to the excellent gas-solid heat and mass transfer performance [267]. In their study, the sawdust particles were torrefied in an SRSB torrefaction reactor at four temperatures (240, 270, 300, and 330°C), three feeding rates (220, 440, and 710 g h^{-1}), and a residence time of 50 min. The results found that the weight loss increased from 14.2% to 29.4% when the temperature was raised from 240 to 330°C. This increase was associated with

a greater degree of devolatilization at higher temperatures. Higher weight loss was also obtained at a lower feed rate because of the longer residence time of the biomass particles. In contrast, a higher feed rate led to a less vigorous movement of the biomass particles owing to biomass accumulation in the reactor. This could also have affected the heat transfer rate and resulted in a lower weight loss. Based on the introduced reactors, their advantages, disadvantages, and current situations are summarized in Table S6.

4.4. Post-treatment

When the torrefaction of the feedstock is completed, the reactor will subsequently undergo the cooling step, usually cooled down to below 80°C under an inert atmosphere to avoid the self-ignition and combustion of the solid products. The resultant products of torrefaction including gaseous, liquid (condensate), solid products, and tar will be collected. The solid products can be post-treated to enhance their fuel properties. The main post-treatment of torrefied solid product is densification by pelletization, aiming to promote it as a promising biofuel in terms of transportation, storage, and handling. Additionally, the enhanced energy density of pelletized torrefaction products can be utilized in co-combustion with coal. Using pelletization as a post-treatment of torrefied products has been studied by the Energy Research Centre for the Netherlands (ECN) in 2005, and it proposed a TOP (torrefaction and pelletization) process. Afterward, several related studies were performed successively [132,161,244,268,269].

A single pellet press or pellet mill can be applied to produce torrefied pellets. Owing to the low water content ($<1\%$) of torrefied products, preconditioning by adding water content (5-13%) or binder to samples was usually adopted before pelletization. Generally, around 0.5-1 g of samples are pelletized into one pellet under die temperatures of 70-170°C, compression of 125-300 MPa, and holding times of 10-60 s. Additionally, particle size, torrefied feedstock, and remained constituents (hemicelluloses, cellulose, and lignin) will also affect the performance of pelletization. Peng et al. [161] performed torrefaction (temperatures of 250 and 300°C; residence times of 15 and 30 min) and further pelletization with three particle sizes of pine sawdust (0.23 mm, 0.67 mm, and 0.81 mm). The densification analysis indicated that the pellet derived from greater particle sizes had higher water content, Meyer hardness, and energy consumption. The pellets from wheat straw torrefied at a higher temperature (300°C) had unfavorable properties of poor mechanical stability and lower density compared to those obtained from lower torrefaction temperatures [269], which was also observed in other studies with different kinds of feedstocks [132,161,268]. This phenomenon, spring back effect, may stem from the greater reduction in intermolecular bonding and available hydrogen bonding under severe torrefaction [270,271]. Moreover, the static friction showed a vigorous increase during the compression of torrefied samples when the torrefaction temperature increased to 300°C [269,270], which indicated that energy consumption would also increase [244].

To overcome the drawback of torrefied products, the addition of binder and increasing die temperature had been adopted to promote the properties of the torrefied pellets. Increasing die temperature from 170 to 230°C could enhance the density of the torrefied pellets comparable with untreated pellets [132]. The energy consumption for compression of torrefied pellets would be 50% higher than that of untreated pellets. Ghiasi et al. [244] applied a 7 wt% binder (wheat flour) with torrefied products (Douglas fir wood chips) for subsequent pelletization. The results showed that the supplementary of the binder could reduce the energy consumption of torrefied pellets from 1164 to 461 kJ kg^{-1}, which was even lower than that of untreated pellets. However, some studies used a high level of binders, which did not meet the guidelines ($<4\%$) of the

International Organization for Standardization (ISO) [132,272,273]. The lower bulk density and durability were also found in starch-type binders, which would lower the qualities of pellets. Therefore, further development of these shortcomings is required to accelerate the commercialized path.

5. Applications and commercialization

5.1. Applications of torrefied biomass

5.1.1. Co-firing and combustion

Studies have shown the potential fuel acted by torrefied biomass for firing and co-firing with coal in existing large-scale facilities such as pulverized coal boilers [274,275]. From the viewpoint of sustainable development, net CO_2 emissions could be significantly abated by consuming biomass in co-firing systems [276]. Li et al. [277] employed a CFD model to simulate the co-firing of coal and torrefied biomass in a pulverized coal boiler. Five different torrefied biomass proportions of 0% (coal only), 25%, 50%, 75%, and 100% on a thermal basis were taken into account. They reported that 100% torrefied biomass could be fired in the boiler, without causing an obvious reduction in the efficiency and fluctuation in boiler load. In the study of Xue [278], they indicated that the co-firing of torrefied biomass reduced fuel segregation compared with the co-firing of raw biomass, and this was mainly stemming from the more combustion heat and higher reactivity of the torrefied material. Meanwhile, the thermal oxidation behavior of torrefied biomass was similar to coal combustion, resulting from the reduction of the H/C ratio in the torrefied biomass.

Lasek et al. [279] examined the combustion of torrefied willow in a bubbling fluidized-bed combustor. They revealed low SO_2 emissions (the measurements were based on a 6% O_2 concentration) level during the combustion of the torrefied biomass. This observation was mainly ascribed to the low sulfur content in the torrefied biomass. According to their results, the SO_2 concentrations in the flue gas generated from the combustion of torrefied willow, Polish lignite, and Polish hard coal were 2, 293, and 1184 ppm, respectively. Ohlemüller et al. [280] studied a 1 MWth pilot plant coupled with chemical looping combustion (CLC) of hard coal and torrefied biomass. During their co-combustion (coal: biomass $= 50/50$), the total carbon capture efficiency (η_{CC}) could reach 66%, leading to a 122% CO_2 reduction when considering carbon from the coal.

5.1.2. Gasification

Biomass gasification is a potential thermal process in which the feedstock is converted into a gas product in an oxygen-starved environment where synthesis gas or syngas, namely, H_2 and CO, is the main products [281,282]. On account of the improved properties of torrefied biomass such as higher calorific value and lower volatile content, the gasification efficiency can be improved and tar formation can be lowed [283].

Chen et al. [281] adopted numerical simulations to compare the gasification of raw bamboo, torrefied bamboo, and coal in an entrained-flow reactor. The most appropriate equivalence ratio (ER) values for the gasification of raw bamboo, torrefied bamboo, and coal were shown to be 0.692, 0.434, and 0.357, respectively. The cold gas efficiency of torrefied bamboo (54.52%) under the optimum conditions was higher than that of raw bamboo (28.98%) by a factor of 88%, and the gasification performance of torrefied biomass was closer to that of coal (80.82%) when compared to that of raw bamboo. It was thus summarized that torrefaction is a promising technique to improve the properties of biomass for enhancing gasification performance. Yang et al. [284] studied the co-gasification of *Eucalyptus globulus* and torrefied *Spirulina platensis*

pellets in a bubbling fluidized bed reactor. The two samples pertained to woody biomass and microalgal biomass respectively, the capacity of the reactor was 30 kW. They discovered that the H_2 and CH_4 concentrations in the product gas initially decreased followed by slightly increased with increasing mass ratio of the torrefied microalgal pellet. On the other hand, the inverse tendency was exhibited for the CO concentration of the product gas and its LHV. Huang et al. [285] evaluated the syngas production from the co-gasification of wet sewage sludge and torrefied birch. They revealed that the use of torrefied birch under high torrefaction severity led to high H_2 and CH_4 production, and gave rise to the decrease in CO_2 and CO formation. The maximum yield of H_2 from wet sewage sludge and torrefied birch co-gasification was 32.17 mol kg^{-1} at 1100 K.

Zhang et al. [286] examined the co-gasification of coal and torrefied biomass (woody wastes and agricultural residue) in CO_2 and the synergy between the coal and torrefied biomass by a thermogravimetric analyzer. They found that the CO_2 gasification reaction of the torrefied biomass was substantially higher than that of the parent biomass. Compared to the coal and raw biomass blends, the co-gasification of the blends had higher synergy. Kuo et al. [287] examined the influence of the calcium looping (CaL) process on the co-gasification of torrefied bamboo and coal in a power plant. Two different schemes (pre- and post-CaL) were investigated, and the results suggested that the pre-CaL case was suitable to design a process for co-generating hydrogen and electricity with a higher efficiency along with low CO_2 emissions. In the post-CaL, the CO_2 capture efficiency could reach 93-97%, which was higher than that of the pre-CaL (86-91%), thus concluding that the post-CaL case could provide an approach for a co-gasification power plant having nearly zero CO_2 emissions.

5.1.3. Pyrolysis

Recently, torrefaction is considered as an efficient alternative pretreatment method for pyrolysis-derived bio-oil production [288,289]. Bio-oils produced from the pyrolysis of torrefied biomass contain lower water content and higher carbon content than those from raw biomass pyrolysis [290]. Bu et al. [291] examined the co-pyrolysis of low-density polyethylene (LDPE) and torrefied rice straw by microwave heating. They reported that the bio-oils from the torrefied biomass had a lower water content, and the main compositions in the bio-oil were phenols, ketones, hydrocarbons, esters, and alcohols. Louwes et al. [292] investigated the fast pyrolysis of torrefied hardwood. The underlined that though the bio-oil yield significantly decreased from 44 wt% (raw material) to 31 wt% (treated material), the bio-oil obtained from the torrefied biomass presented higher quality in terms of oxygen content, decreasing from 45.7 to 37.2 wt%), and HHV, increasing from 19.1 to 23.1 MJ kg^{-1}) when compared with the bio-oil from virgin biomass. Chen et al. [293] investigated the two-stage thermodegradation of hemicelluloses, cellulose, and lignin to evaluate the effect of torrefaction on pyrolytic products. According to the Py-GC/MS analysis, the analysis revealed that inherent pentose units and O-acetyl of hemicelluloses were decomposed into furfural and acetic acid during torrefaction, and therefore the pyrolysis bio-oil of torrefied hemicelluloses contained lower acetic acid and furfural contents. In contrast, the influence of torrefaction upon cellulose was insignificant, due to the high thermal stability of the crystalline structure in the cellulose. As for lignin, a pronounced influence on its pyrolysis was observed when lignin underwent severe torrefaction at 300℃, resulting in an increase in aromatic compounds in the course of pyrolysis. In summary, pyrolysis-derived bio-oils from torrefied biomass are normally characterized by lower organic acids, furfural, and aldehydes as well as higher hydrocarbons, phenols, furans, ketones, aromatic, anhydrous sugars, aliphatic groups, and carbonaceous residues [294].

5.1.4. Ironmaking

The iron and steel industry consumes about 20% of the annual industrial energy requirements and constitutes 6.7% of the global CO_2 emissions [30]. Because of that, improving energy efficiency and reducing CO_2 emissions during ironmaking processes have been covered extensively in recent years [295]. To avoid the excessive usage of fossil fuels, biomass is a potential alternative to coal in iron ore agglomeration, metallurgical coke production, and pulverized coal injection in the tuyeres of blast furnaces [296].

The blast furnace is the most crucial and commonly employed facility to produce hot metal in the ironmaking industry [113]. High-quality coke is normally used as the reducing agent for the direct reduction process of iron oxides to produce pig iron in the blast furnace [9]. In the study of Proskurina et al. [297], they reported that it was possible to use torrefied biomass for replacing coal in pulverized coal injection (150-200 kg ton^{-1} hot metal) for the production of iron. Wang et al. [298] simulated the replacement of pulverized coal by biomass into blast furnaces for CO_2 reduction. They estimated 115.7 GWh year^{-1} of energy saving potential and 6.4% of CO_2 reduction by torrefied biomass. Chen et al. [113] discovered that biochar produced torrefaction at the temperature of 300℃ was quite comparable with the high-volatile bituminous coal used in blast furnaces for ironmaking. Ubando et al. [299] analyzed iron oxide reduction by graphite and torrefied forest residue through TG. They found that the iron oxides reduced by the torrefied biomass were more pronounced in the low-to-medium-range temperatures with an onset temperature of 300℃, while the iron ore reduction by graphite occurred at temperatures higher than 950℃). This work was later on expanded by Ubando et al. [296] who evaluated the use of torrefied microalgal biomass as a reducing agent in ironmaking. Their results indicate that the use of torrefied microalgal biomass has lowered the initiating reduction temperature of iron oxides when compared with other biomass-based reductants.

5.1.5. Adsorbent for pollutants

Biochar recently is regarded as an environmentally-friendly and sustainable material for removing inorganic and organic pollutants [300,301]. Meanwhile, the use of biochar to adsorb contaminants is more cost-saving compared to conventional adsorbents with higher costs [57]. The performance of biochar in contaminant adsorption depends on its physicochemical properties such as specific surface area, pore sizes, surface functional chemistry (e.g., -OH, -CH, and C=C), and the mineral content in ash [300,302].

De Jesus [303] evaluated the adsorption performances of two different torrefied biomass materials (coconut waste and orange waste) to remove polycyclic aromatic hydrocarbons (PAHs). The adsorption tests were examined using a mixed solution of benzo(k)fluoranthene, benzo(a)anthracene, benzo(b)fluoranthene, and benzo(a)pyrene, dibenzo(a,h) anthracene, abbreviated by BkF, BaA, BbF, BaP, and DahA, respectively. Their results indicated that the removal percentages of PAHs by torrefied coconut waste and orange waste were 47.09-83.02% and 23.84-84.02%, respectively. Abdelhadi et al. [219] produced biochar from olive mill solid waste (OMSW) torrefied at 350℃ and 450℃ for heavy metal (HM) removal. The biochar yield was 24–35% with surface area in the range of 1.65-8.12 m^2 g^{-1}. They pointed out that the OMSW biochar demonstrated high HM removal performance which was better than that of commercial activated carbon (CAC). The removal efficiencies of lead and copper by CAC were 54% and 74% respectively, while the efficiencies for other HMs were less than 30%. For HM removal by the biochar, the removal efficiencies of Pb and Cu were greater than 80% and lower than 20% for selenium (Se) removal.

Li et al. [302] evaluated the performance of torrefaction char (TC) adsorption for methylene blue (MB) and uranium (U(VI)) re-

moval. The results suggested that the maximum U(VI) and MB adsorption capacities by the TC were greater than 100 mg g^{-1} and 350 mg g^{-1}, respectively. They also found that the adsorption performance of the TC would be affected by the torrefaction atmosphere. The MB adsorption was more profound when employing TC from N$_2$, whereas the U(VI) adsorption was more pronounced when using TC from air. They also suggested that the TC was a promising material for water pollution control because of the low treatment temperature, simple preparation, and high adsorption capacity.

5.2. Commercialization

To move the torrefaction system forward into the market, the applications of patents are one of the essential paces to safeguard the invention against other companies. According to the statistics of the European patent office (EPO) from 1 January 1970 to 21 January 2020, there were already 393 torrefaction-related patents published worldwide. It can be observed that vigorous growth occurred since 2007. Europe (EU) has most publications with 158, accounting for 51% of total publications, while the United States (US) ranked second with 106 publications (34%). Regarding the invention patent, the US has the most publications with 93, followed by China and Canada having 31 and 27 publications, respectively. Concluding the invention patent by continent, North America has 120 patents, followed by the EU and Asia where they both have 31 patents.

On the other hand, the techno-economic analysis is required to evaluate the feasibility of the entire system in terms of performance, costs, benefit, risk, and uncertainty. In addition, price stability and predictability are important to mitigate risks related to investments that are required for torrefied pellet production.

Svanberg et al. [304] proposed a techno-economic system model to analyze the costs of the torrefaction supply chain under Swedish conditions. The model was constructed by four parts: (1) a supply system to a torrefaction plant; (2) a complete energy and mass balance of drying, torrefaction, heat generation, and densification; (3) capital expenditures (CAPEX) and operating expenditures (OPEX); and (4) a distribution system to the gate of an end-user (combined heat and power plant, CHP). Their results showed that the cost for the entire supply chain was 31.8 €/MWh$_{LHV}$ under the base case of 200 kton$_{DS}$/year torrefaction plant, where the supply system contributed 59.5% of the system cost, the production cost to pellets accounted for 31.0%, and the distribution system for only 9.48%. The analysis of the scale-up suggested that the production system had higher cost reduction (50% reduction) than that of the distribution system (16.5% reduction) when increasing the torrefaction plant size from 25 kton$_{DS}$/year to 200 kton$_{DS}$/year. It was also found that even a highly efficient setup of a drying system still consumed lots of heat and thus contributed to the highest costs in the production system. However, the costs of the distribution system were much lower among the entire system, resulted from the higher energy density of torrefied densified biomass being more efficient during transportation and handling [244,305]. The sensitivity analysis showed that the profound-effect parameters consisted of the amount of biomass, biomass premium, forwarding, and transportation cost, biomass moisture content, drying system, and mass yield.

Thrän et al. [306] adopted the BioChainS tool (Biomass-to-end-use Chain Simulation tool) to evaluate the production costs of torrefied wood pellets against the raw wood pellets. The simulation displayed that the larger production plant (500,000 Mg a^{-1}) fed with cheaper biomass feedstock (15 MWh^{-1}) could achieve lower production costs of 29 € MWh^{-1} compared to the base condition operated under production plant with 72,800 t a^{-1} output density. Furthermore, the annual cost of co-firing of coal with 30 wt% tor-

refied pellets (2-3 M€ a^{-1}) was much lower than that of coal with 30 wt% raw wood pellets (12-13 M€ a^{-1}), implying that large-scale production plants coupled with co-firing with coal could achieve economical utilization of torrefied pellets.

Chai et al. [307] optimized the production costs of three biofuels, including conventional pellets, moderately torrefied pellets, and severely torrefied pellets in terms of the depot capacity and biomass moisture capacity. The optimized production costs for three cases were between 7.03-7.17 US$/GJ$_{LHV}$ with depot capacity between 82-92 MW$_{LHV}$. It was found that the production costs had no significant difference among the three scenarios when increasing the capacities beyond 60 MW. The optimized biomass moisture contents ranged from 32 to 40 wt%, depending on the demand for biomass or its derived combustible gas used for drying and torrefying biomass. The results also indicated that the biomass cost, consisting of the field price of biomass, mass loss during on-site drying, and interest costs incurred during on-site drying, accounted for the most cost of the total production costs, which was consistent with the study of Svanberg et al. [304].

Agar et al. [308] compared the production costs of torrefied pellets and conventional pellets by integrating the economic analysis with the results of the literature. The results showed that the annual production cost of the torrefied pellets (6.11 M€) was less than that of conventional pellets (7.05 M€), while the specific costs of torrefied pellets (95.54 € t^{-1}) were less than that of conventional pellets (88.09 € t^{-1}). The crucial parameters affecting the tow processes were loan amortization, utilities, logistics, and transport. Regarding the sensitivity results, the study suggested that (1) investment costs must be reduced by more than 17%; (2) the LHV (as received) of pellets must be improved by more than 8%; and (3) the bulk density (as received) must be improved. In the overview of the techno-economic analysis, the costs of torrefied pellets are getting close to raw wood pellets, indicating that it will be a comparative product in the fuel market. The economic analysis of the torrefaction processes introduced above is summarized in Table S7.

The commercial development of torrefaction is in its early phase. Several technology companies and their industrial partners are moving towards commercial market introduction, which can be found in Table S8). The general view is that most of the demonstration plants have technical problems that have delayed their commercial operation. Several thousand tonnes of torrefied pellets have been produced by European and US companies, mainly for large scale co-firing tests at coal power plants.

6. Environmental performance

Torrefaction has gained much attention not only due to the inherent benefits of upgrading biomass but also because of its sustainability advantages. Much of which can be accounted through the environmental impacts generated from the life-cycle of torrefied biomass from cultivation to processing up and combustion, as shown in Fig. 14. The environmental impact evaluation of torrefaction for different biomass feedstocks is essential to reduce the underlying impact of the process and its supply chain. The resulting assessment and recommendations lead to the sound strategic design of the production of bioenergy products.

6.1. Life cycle assessment

Life cycle assessment (LCA) is a known methodology for identifying the environmental impacts of systems and products. LCA was developed in conformance with the International Organization for Standardization (ISO) standards [309,310] that consist of four main stages. Firstly, the goal and system boundary definition provides information on the functional unit and the scope of the assessment. Secondly, the inventory of the system or known as the life-
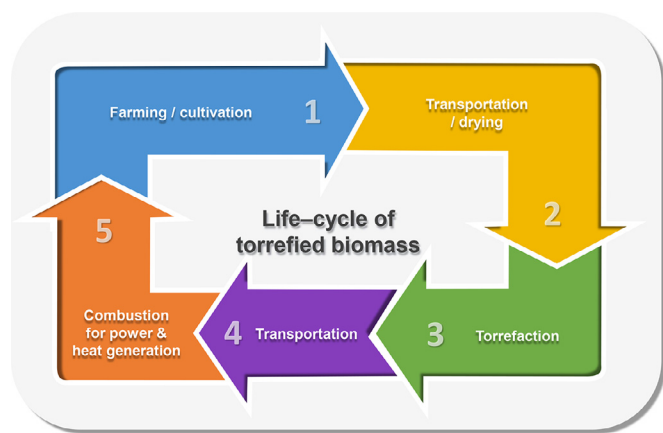
Fig. 14. The life-cycle framework of torrefied biomass.

cycle inventory (LCI) which involves a comprehensive accounting of all material and energy flows of the processes involved in the system of interest. In addition, the flow streams tracked in the LCI include raw material, products, co-products, and emissions. Thirdly, the life cycle impact assessment (LCIA) quantifies the impacts on the flow streams of each process stage. The LCIA provides an impact value to the required flow streams to produce the functional unit. The allocation of impact weights for the product and the co-products is decided in the LCIA stage. Characterization factors are defined to convert the outputs of the LCI to impact categories that represent the environmental burden. Lastly, the interpretation stage allows the systematic evaluation of the results from the LCI and LCIA stages through identification, quantification, and validation. The interpretation stage provides evaluators to establish confidence with the derived results, which is then communicated in a sound and accurate manner. The four stages of the LCA methodology can be redefined interactively by varying the system boundary and by performing a sensitivity analysis.

6.2. State-of-the-art

A bibliometric analysis through Scopus was performed (December 4, 2019) to assess the available articles on the life-cycle assessment of torrefaction. The bibliometric analysis was processed using VosViewer. A search phrase of "life cycle assessment torrefaction" was used limiting the search to articles and review documents yielded 26 scientific papers. Generated from VosViewer, the bibliometric keyword network consists of 26 scientific journals. The most common keywords of these works as shown in the figure are "life cycle", "biomass", "greenhouse gases", "life cycle assessment", and "torrefaction".

Out of the 26 scientific documents, 3 are review documents which are discussed as follows. A review study was performed and compared the environmental impacts of various thermochemical processes, which utilized microalgal and lignocellulosic biomass for bioenergy production [311]. The results have shown torrefaction to have the least global warming potential (GWP) compared with the other thermochemical processes. This was due to the minimal heat requirement of torrefaction compared with other thermochemical processes while significantly enhancing the calorific value of the biomass. A review focusing on the techno-economic and life-cycle analyses was conducted on eight different negative emission technologies (NETs) [312]. Torrefaction was used as a pretreatment technology for biomass combustion to generate power. Power generation through the combustion of torrefied biomass has resulted in the lowest GWP compared with the other NETs. However, it also

had the highest energy and carbon abatement costs. Thus, their work presented the trade-offs between the various NETs. In addition, torrefaction using lignocellulosic biomass to produce torrefied biomass has resulted in a high technology readiness level which indicated a high large-scale adoption. An evaluation of the potential influence of the introduction of sustainability criteria for pelletized biomass (including torrefied biomass) on the European Union and its market was administered [313]. The assessment was focused on the reduction of greenhouse gas emission of biomass pellets consumed in Sweden. Various wood pellet value chains which included torrefied biomass were assessed. The results have shown that torrefied biomass pellets had a slightly higher GWP compared to conventional biomass. However, the GWP impact of transporting the pellets to the consumers have been offsetted by the improved heating value of the torrefied biomass pellets. To date, no studies have reviewed and compared various LCAs of various torrefied bioenergy products based on the bibliometric analysis of the scientific papers found in the Scopus search. The study presents the various assumptions used in these studies and their environmental impacts.

The various LCA studies on torrefaction are summarized in Table S9. Most of the studies focused on lignocellulosic biomass, except for a study [314] which evaluated the environmental impact of torrefied microalgal biomass. The LCA study on the torrefied microalgal biomass was later on extended by a review work [311] to compare with other lignocellulosic biomass processed with other thermochemical processes such as gasification, hydrothermal liquefaction, and pyrolysis. Few studies have focused on the torrefaction of microalgal biomass, thus presenting opportunities for future LCA evaluation. The majority of the studies shown in Table S10 have produced torrefied biomass which was used as a solid fuel for combustion to generate electricity or processed heat. Most of these studies have employed a cradle-to-gate system boundary and have considered performing a sensitivity analysis, however, ignoring the allocation and uncertainty analysis.

The supply-chain of torrefied biomass is shown in Fig. 15. From the forest, the forest residues and chippings are transported to the torrefaction facility for drying and torrefaction. Once the biomass has been dried and torrefied, the torrefied biomass is stored and transported to the industrial plant or power plant for combustion to generate either electricity or process heat. As shown in Fig. 15, each stage results in CO_2 emissions. Through photosynthesis, the CO_2 emissions are absorbed by the forest providing CO_2 uptake and a negative emission effect in the supply-chain of torrefied biomass. The LCA framework of the torrefied biomass is shown based on the majority of the studies reviewed as shown in Table S9.

6.3. Greenhouse gas emissions

The functional unit and the resulting greenhouse gas emission impact of the studies can be found in Appendix materials. The majority of the studies have utilized energy as a basis for the functional unit of the LCA work such as electricity produced and energy content of the torrefied biomass. With the disparity of the functional units for each study, it remained a challenge to compare the different studies conducted on various biomass feedstocks. This includes the different assumptions employed, supply-chain considered, and torrefaction technologies and settings utilized for each study. The LCA review [311] attempted to compare the global warming potential (GWP) impact of the numerous LCA studies on torrefied biomass with other bioenergy products of thermochemical processes. The GWP index represents the equivalent impact of a certain greenhouse gas to that of CO_2, allowing the comparison of the greenhouse effect [315]. The results of the impact on torrefied biomass yielded a GWP impact which ranged
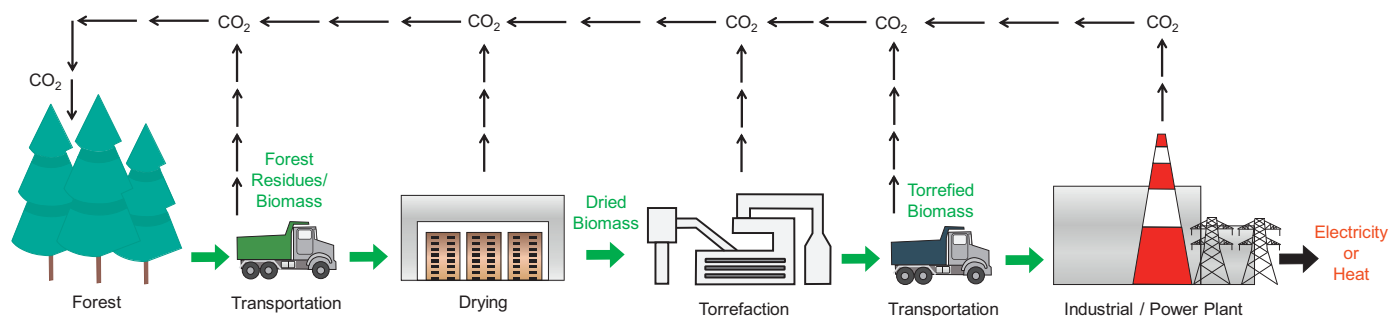
Fig. 15. The supply-chain of torrefied biomass.

from ∼0 kg$_{CO2}$/MJ$_{energy}$ to ∼0.03 kg$_{CO2}$/MJ$_{energy}$ with a means GWP of ∼0.008 kg$_{CO2}$/MJ$_{energy}$. When compared with the GWP impact of other thermochemical processes, the GWP range and mean values of torrefied biomass is relatively lower. Despite the positive emission impact of torrefied biomass, a negative emission impact for torrefied biomass can be achieved through the excess electricity generated during the biofuel conversion process, mainly attributing to the elevated heating value of the gas produced [316]. Moreover, carbon uptake of plants through photosynthesis can sufficiently compensate for the emission impact during the combustion of torrefied biomass. Moreover, the valuation of the co-products of torrefaction through the biorefinery on circular bioeconomy can enhance the environmental performance and economic viability of the torrefied biomass [317]. However, further studies on torrefaction specifically focusing on its potential as a negative emission technology (NET) needs to be further evaluated in future works [318].

With the results of the available studies in the literature on the LCA of torrefaction, the GHG emission impact of torrefaction is relatively low when compared with other technologies. However, its potential for NET can be enhanced through an LCA study specifically accounting for the carbon uptake of plants in its growing stage and considering the excess electricity generated from the co-product gas.

6.4. Net energy analysis

A net energy analysis is an assessment methodology to account for the energy expenditures and quantify the energy gains of an energy product [319] such as torrefied biomass. In most cases, life-cycle energy analysis is employed to assess the energy content of biofuels [320]. The net energy gain is the surplus energy from a conversion process which accounts for the energy expenditure and the gross energy wherein a higher value is desired [321].

Previous works employed net energy analysis to assess the net energy gain of torrefied biomass. The non-oxidative torrefaction of groundnut shells was performed in an industrial burner and reactor chamber which resulted in a net energy gain of 17.15 to 22.53 MJ kg^{-1} [322]. The pretreated cotton stalk through torrefaction was assessed using an energetic performance, and the analysis revealed that the torrefied cotton stalk had a higher net energy efficiency by 60% [323]. Torrefaction of corn stover was performed to assess the net energy balance of the generated solid carbonaceous product, which yielded 92.2% of the energy input [324]. The net energy potential was evaluated to estimate the energy demand for the production of refuse-derived fuel torrefaction in a waste-to-carbon framework [325]. The life-cycle net energy balance for microalgal biomass was quantified at 6.48 MJ MJ^{-1} for the gas generated from torrefaction [326]. Various types of biomass were evaluated to quantify the net energy ratio of the mixture of torrefied biomass and coal ranging from 0.37 to 0.42 [327]. The energy output of tor-

refied rice straw and torrefied fountain grass were quantified to evaluate the implication of torrefaction as a biomass pretreatment process [328]. Life-cycle energy analysis was performed to compare various conversion processes, including torrefaction for the production of rice-straw bioenergy where the results yielded an energy return on investment ratio of 4.13 to 8.86 and a net energy ratio ranging from 3.13 to 7.86 [329]. Using an integrated approach with net energy analysis, the tradeoff between environmental and energy performance of torrefied biomass was evaluated, and it was found that torrefaction was a good stand-alone system that could generate bioenergy while achieving negative emissions [330].

The net energy analysis enabled the quantification of the energy content of various biomass materials through torrefaction. The results revealed that by using torrefaction as a pre-treatment process for biomass gasification, it maximizes the potential of the biomass to produce bioenergy [326,329]. Furthermore, integrating net energy analysis with the life-cycle assessment [326,329] and techno-economic analysis [330] provides a multi-criteria assessment tool for torrefaction of biomass which can outline underlying tradeoffs between energy content, environmental impact, and costs.

7. Challenges and perspectives

In recent years, torrefaction is a fast-developed technology to produce solid biofuel (biochar) or sustainable materials for several applications. For the utilization of solid fuels such as coal, biomass, and biochar, self-heating is a serious problem due to the safety concern of producers and users [331,332]. The self-heating phenomenon in the course of fuel storage occurs when the exothermic reactions like oxidation reactions become pronounced. Self-heating starts at a low temperature and gradually increases under the heat released by the reactions. A significantly rising temperature can be found when the heat release rate is faster than the heat dissipation rate in a torrefied biomass stockpile [333]. Self-heating will be followed by self-ignition and then combustion which may even give rise to a firing. Self-heating of torrefied wood is initiated with oxidation below 100°C, and the lower limit of the initiation temperature is between 85 and 90°C [334]. Evangelista [333] examined self-heating and self-ignition of torrefied beech chips in contact with oxygen and found that oxygen adsorption on the wood surface was enhanced by torrefaction severity. This implied that the increase of self-heating and self-ignition propensity increased with increasing torrefaction severity. To reduce the self-heating, finding operating conditions with a feasible cooling process is a crucial issue for torrefaction industrial plants. Detailed self-heating mechanism during torrefied biomass storage is a potential issue for further research.

As mentioned earlier, torrefaction has been applied in gasification, small-scale combustion, and co-firing in pulverized coal-fired power plants, resulting from the property upgrade of torrefied biomass [297,305]. However, the persistent organic pollu-

tants (POPs) such as polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) during torrefaction at the temperature range of 200-350°C may be formed [335]. It was reported that POPs formation occurs mainly via heterogeneous reactions in two possible ways: a precursor pathway and de novo synthesis from a carbonaceous matrix [336,337]. Gao [335] evaluated the formation of PCDDs and PCDFs during torrefaction from various biomass materials such as stem wood, bark, wood from a discarded telephone pole, cassava stems, and particle board. Their examinations suggested that PCDDs formed partly originated from new formation and partly physical transformation from volatilization, as well as re-condensation of PCDDs present in the feedstock. Meanwhile, the net formation of PCDFs was lower than that of PCDDs, except for the telephone pole sample. The results also indicated that the highly chlorinated congeners tend to be retained in biochar, whereas the less chlorinated ones were predominantly volatilized into the gas phase during torrefaction. When biomass undergoes torrefaction, the improved physical-chemical properties make the produced biochar more appropriate for energy conversion [338] and as an alternative fuel to coal [101]. On the other hand, the torrefaction process increases the ash content in final products, and this limits the applications of combustion and gasification from torrefied biomass [339]. This arises from the fact that the ash-related problems such as alkali-induced slagging, silicate melt-induced slagging, and corrosion occurring in biomass-fired furnaces, will be encountered [340].

To overcome the emissions and ash-related issues, washing pretreatment could be a promising route to reduce pollutant emissions during torrefaction and remove ash in torrefied biomass. It was reported that the pretreatment by washing could remove the problematic chemical species such as K, Na, Ca, Mg, Fe, Cl, S, and P from biomass [341,342]. The hot water washing can enhance the removal efficiency of these compounds. The removal of S and Cl decreases acid gaseous products and results in reducing corrosion in boilers and environmental impacts [341]. Abelha et al. [342] evaluated combustion improvements of upgraded biomass by washing and showed that approximately 90% of Cl and up to 60-80% of K could be removed by washing. The experimental combustion work showed that NO_x emissions were decreased after upgrading, and high-temperature chlorine corrosion could be effectively mitigated. The biochar with higher ash content also presents the potential to be used as construction materials, low-cost adsorbents, and agricultural soil ameliorant [145,340]. When biochar is used for soil amendment, carbon sequestration can be implemented, thereby achieving negative carbon emissions [343]. The use of biochar as a soil amendment is commonly proposed to improve soil water retention, especially in dry climate areas suffering from water scarcity [344]. Heikkinen et al. [344] pointed out that the biochars obtained from slow pyrolysis and torrefaction increased the soil volumetric water content at field capacity. Moreover, future work should also consider the environmental impact of torrefied preservative-treated wood as it contains heavy metals that are harmful to human health and the environment [345]. However, it was found that torrefied biomass and biochar are good adsorbent alternatives for the removal of acid gases [346] and should be further explored in future studies.

The problem induced by tar, one of the by-products formed from biomass torrefaction, is also an important challenge that needs to be solved, especially in industrial systems. The main product from biomass torrefaction is biochar, however, tar and liquid products account for around 10-40 wt%, depending on feedstocks and torrefaction severity [138,347]. This implies, that 2,000-8,000 ton year^{-1} of tar could be produced for the torrefaction industry with a production capacity of 20,000 ton year^{-1}. The produced tar causes difficulty in the pipeline, reactor, and facility management.

Form this viewpoint, the new process or tar application concepts should be developed for the post-treatment of tar.

Concerning the challenges of commercialization in biomass torrefaction, the major commercial challenges of torrefaction are financing, market maturity, and availability of the products. The economic analysis shows that torrefied biomass is not yet competitive to wood pellets, mainly because of the additional investment for the torrefaction reactor. The raw material price is the most influencing factor in the overall economics of the torrefaction. Most torrefaction developers are small companies with a limited financial base. Convincing investors to finance the necessary R&D and up-scaling effort is a real challenge. One or more torrefaction concepts will emerge out of a large variety of technologies and initiatives. Therefore, torrefaction suppliers require enough development power to optimize and scale-up their torrefaction concepts. Attaining product standardization is also needed to make the market more transparent and reliable. The study of Wilén et al. [348] suggested that an integrated concept may offer potential benefits to meet the required cost level.

8. Conclusions

Relevant fundamentals of torrefaction have been elaborated, and the reaction phenomena during torrefaction have been exhaustively illustrated. The influences of some important operating parameters such as temperature, duration, particle size, carrier gas, catalyst, etc., on torrefaction outcome have been described, while the torrefaction indexes have also been introduced to characterize torrefaction performance.

Torrefied biomass has been applied in co-combustion and co-gasification for the productions of heat, electricity, and syngas. Recently, torrefied biomass has also been researched for different applications such as soil amendment and adsorbents for pollutant removal to achieve carbon sequestration, and even the development of negative CO_2 emission technologies. In the overview of the torrefaction systems, there is still no optimal pretreatment, reactor, or post-treatment. It is quite dependent on the type of feedstock, the application of the products, and the consideration of costs. Besides, several technologies are required to be promoted to achieve higher thermal efficiency, higher productivity, homogeneous products, and better temperature control. The development of a continuous system is also an important part. Furthermore, economic analysis is also necessary to be taken into account to evaluate the integrated torrefaction process for commercialization purposes. It has been recognized that non-oxidative torrefaction presents a promising result in terms of biochar quality, however, may also present investment challenges. Thus, the development of oxidative torrefaction may command future research and development work to enable the cost-effective production of biochar.

Torrefaction provides an environmental-friendly biomass pretreatment for bioenergy production by improving its heating value while resulting in a relatively lower greenhouse gas emissions compared with other pretreatments and thermochemical processes. It is considered as a negative emission technology by the carbon uptake of biomass considering the life-cycle of torrefied biomass. Future studies may focus on the LCA of different microalgae species to produce torrefied biomass. Various allocation and uncertainty analyses can also be performed in conducting future LCA studies on torrefaction. Moreover, impact assessment of heavy metal contaminants in the torrefaction of various biomass feedstocks must be considered in future works to deeply understand the risk involved in human health and the environment. Biochar has also been found to be a good alternative adsorbent for the removal of acid gas which may further be explored in future studies.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Wei-Hsin Chen: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Writing - original draft, Writing - review & editing. **Bo-Jhih Lin:** Data curation, Investigation, Writing - original draft. **Yu-Ying Lin:** Data curation, Investigation, Writing - original draft. **Yen-Shih Chu:** Writing - original draft. **Aristotle T. Ubando:** Data curation, Investigation, Writing - original draft. **Pau Loke Show:** Investigation, Writing - review & editing. **Hwai Chyuan Ong:** Investigation, Writing - review & editing. **Jo-Shu Chang:** Investigation, Writing - review & editing. **Shih-Hsin Ho:** Writing - review & editing. **Alvin B. Culaba:** Writing - review & editing. **Anélie Pétrissans:** Resources, Writing - review & editing. **Mathieu Pétrissans:** Resources, Writing - review & editing.

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Supplementary materials

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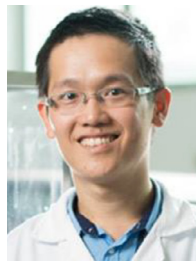
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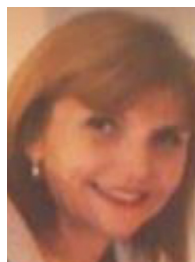
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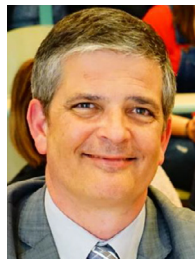
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