A state-of-the-art review on dual purpose seaweeds utilization for wastewater treatment and crude bio-oil production

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ABSTRACT

Due to the negative environmental impacts of fossil fuels and the increasing global energy demands, biofuels are receiving increasing attention as the best short-term substitute for petroleum. Recently, thermochemical conversion of seaweeds is in industrial focus to obtain high-value products with more potential applications than the conventional raw material. Beside biofuel production and due to their autotrophic growth, seaweeds are receiving a great attention in the field of bioremediation. Thus, pyrolysis of seaweeds is a promising approach for renewable bio-oil production with positive environmental impacts. However, a pretreatment drying step is required to improve the conversion process of the biomass. Application of electro-osmotic dewatering as well as on-site mechanical dewatering methods prior to the drying process were reported as useful techniques to reduce the energy requirements. On the other hand, the bio-oil produced from pyrolysis of seaweeds usually has high contents of oxygen-, nitrogen- and sulphur-containing compounds, which should be as minimum as possible to enhance the bio-oil stability and reduce NO_x and SO_x emissions. The present review introduces a suggested route combining a number of technologies that create an economically-feasible process for conversion of seaweeds to high-grade crude bio-oil through pyrolysis. In addition, the paper sheds light on the environmental impacts and economic feasibility of the crude bio-oil production from seaweeds. The current status and challenges related to pyrolysis, as well as future perspectives for enhanced conversion and upgraded bio-oil production, are discussed.

1. Introduction

The growing industrialization and human population during the recent decades resulted in potential increase in the global energy demands. The current petroleum consumption rate is estimated by about 10^5 times faster than the nature can create [1]. If this energy consumption rate continues, it is predicted that the world will face an energy crisis due to exhaustion of the worldwide fossil oil reserves in shorter than 3 decades [2]. In addition, dependence on fossil oil as a main energy source contributes to excessive CO_2 emission [3], with about 20% of the worldwide CO_2 emissions from transportation sector only [4]. Taking this sector as an example, the total new-vehicle annual sales in 2013 were 84 million, which is expected to increase to 127 million by 2035, bringing the total global vehicle number to 2 billion

[5]. CO_2 is the main contributor for the global warming, which is the *'talk of the town'* all over the world as a great threat to mankind and the planet. In addition to the significant changes in weather patterns, global warming results in potential increase in the sea level and consequently flooding of lowlands and islands. Therefore, continuous reliance on petroleum is now widely documented to be unsustainable. Replacement of fossil-based energy with green renewable resources has received much attention globally from research sectors as well as governments and industry. Amongst, different biofuels have been discussed as a biomass-derived fuels which are renewable, sustainable, and eco-friendly alternatives to petroleum. Together with other renewable energy sources, biofuels have the potential to completely replace the current conventional energy sources, reinforcing energy security to reduce the emissions of the greenhouse gases (GHGs).

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Photoautotrophic microorganisms are considered as a promising candidate for unceasing energy appetite. Recently, more interest has been devoted to the third-generation biofuel feedstocks, representing algae, because first-generation edible feedstocks are under serious controversy due to the competition with human food [6]. In addition, conversion of second-generation biofuel feedstocks, such as lignocellulosic wastes, is limited due to the elevated cost of lignin degradation [7]. Therefore, algae-based biofuels progressed wildly in the last decades as one of the most important renewable energy research directions for countering these issues. Algae, including micro- and macroalgae/seaweeds, are photoautotrophic organisms with high photosynthetic efficiency of 6–8%, which reported to be much higher than that of terrestrial plants (1.8–2.2%) [8]. In addition, algae are very efficient in utilizing the nutrients from wastewater [9] or seawater [10], and they don't need arable land to grow [11]. Algal biomass can be converted into different forms of bioenergy such as crude bio-oil, biogas, bio-ethanol and biodiesel through different routes including thermochemical conversion, anaerobic digestion, fermentation and lipid transesterification, respectively (Table 1).

Seaweeds have been explored as a biofuel feedstock, which needs further research to fully explore their potential for crude bio-oil production. Due to the low lipid content of seaweeds in comparison to microalgae, they are widely discussed as a high potential feedstock for crude bio-oil production through different methods of thermochemical conversion. Comparing to terrestrial plants, the annual biomass productivity of seaweeds is much higher, and at the same time is much easier to maintain and harvest compared to microalgae [19]. According to a Life Cycle Assessment (LCA) carried by Aitken et al. [34], seaweeds can generate a net energy of 11.0 GJ ton^{-1} of dry weight (dw) compared to 9.5 GJ ton^{-1} dw of microalgae. However, applications of seaweeds for crude bio-oil production are at infancy stage and need economically-efficient technological solutions [35,36]. So far, there is limited review papers to evaluate seaweeds conversion into crude bio-oil, especially, via pyrolysis of seaweeds cultivated in wastewater effluents for dual propose of energy production and phycoremediation. Therefore, the objective of this review is to discuss and provide up-to-date knowledge on seaweeds utilization for dual purpose of crude bio-oil production and wastewater treatment. The recent progress in advanced pyrolysis methods of seaweeds including catalytic pyrolysis, co-pyrolysis, and catalytic co-pyrolysis for production of upgraded bio-oil was discussed. In addition, this work sheds light on the economic feasibility and environmental impacts of using seaweeds as a crude bio-oil feedstock.

2. Macroalgae/seaweeds

In a simple term, macroalgae are multicellular photosynthetic plant-like organisms that grow mainly in the seas and oceans. They play an important role as a valuable food to the seawater aquarium by providing a basic-chain food source for herbivorous animals. In addition, they work as a natural filter to aquarium system by reduction of total nitrogen and total phosphate levels and releasing oxygen. Based on their pigmentation variations, Kraan [37] categorized different seaweeds into three main phyla; Rhodophyta (red algae), Phaeophyta (brown algae) and Chlorophyta (green algae). Generally, Rhodophyta is the most species-rich macroalgal phylum containing about 6000 known species, followed by Chlorophyta and Phaeophyta with about 4500 and 2000 identified species, respectively [38]. Chlorophytes grow almost in all types of aquatic environments. However, Rhodophytes grow mostly in inter-tropical zones, while Phaeophytes grow mainly in temperate to cold water bodies [39]. Currently, seaweeds are cultivated for human food production, bio-fertilizers and hydrocolloids. China, Japan, Korea and Philippines account for about 72% of the global annual production of macroalgae [40]. Over 23×10^6 tons dry biomass of macroalgae were produced during 2012 from aquaculture, which worthed over US$ 6 billion [41]. In recent years, macroalgal farming has been expanded fast

Table 1
The most common biomass conversion routes showing the pros and cons of each method.

Conversion method	Description	Advantage	Disadvantage	Refs.
Fermentation	A microbial-assisted process for conversion of sugars into bioethanol	Low energy consumption / High economy / Mild reaction conditions	Long reaction time / Difficult byproducts recycling	[12–14]
Anaerobic digestion	A microbial-assisted process for conversion of organic compounds into biogas	Low energy consumption / Mild reaction conditions / High economic feasibility	Long reaction time / Generation of large amounts of digestate / Usually requires a pretreatment step	[15,16]
Transesterification	A chemical process for biodiesel production from lipids rich in glycerides, mainly triacylglycerides (TAGs).	Fast process / Can be applied for a wide-range of feedstocks	Compete with human food / Has negative environmental impacts	[17–19]
Esterification	A chemical process for biodiesel production from lipids rich in free fatty acids such as waste cooking oil.	Fast process / Cost-effective and available feedstocks	Followed by transesterification which increases the production cost / Has negative environmental impacts	[17,20]
Pyrolysis	A thermal conversion process which is carried out at high temperature and oxygen-free environment. The products include bio-oil, non-condensable gas, and biochar.	Fast conversion rate / No additional pressure is required / High energy products yield / No solvent is required	High energy consumption / Poor thermal stability / High biofuel acidity / Requires pretreatment for biomass drying	[21–25]
Liquefaction	A thermal conversion process which is carried out in the presence of solvents, high temperature and high pressure. The main energy products are bio-oil, non-condensable gas and biochar	Fast conversion rate / High energy products yield / No need for the drying step	High energy and solvent consumption / Poor thermal stability / High biofuel nitrogen content / Huge amount of liquid byproducts	[26–30]
Gasification	A thermal conversion process that converts biomass into syngas under high temperature	Fast conversion rate / High energy products yield / No need for the pretreatment	Severe air pollution / High energy consumption / Low calorific value of the produced syngas	[31–33]

in different regions of the world from Southeastern Asia down to East Africa and South America due to the efforts to reduce the over-exploitation of natural resources and encouraged expanded seaweeds applications [42].

3. Chemical composition of macroalgae

There is a significant difference in the chemical composition of macroalgae comparing to the terrestrial plants and microalgae [40]. Table 2 shows a comparison between macroalgae and microalgae with regard to main chemical components and advantages/disadvantages of each group. In addition, Table 3 shows the main composition of some seaweeds in comparison to typical lignocellulosic biomass such as sawdust and rice husk. The main advantages of seaweeds over micro-algae include the lower production cost due to ease harvest, and the well-established industrial infrastructure. Moreover, unique components such as carrageenan, laminarin, alginate, agar, mannitol, fucoidin, and fucose [38] make macroalgae different from lignocellulosic biomasses and even microalgae. Furthermore, the absence or low lignin content of macroalgae, as low as 0.03 g kg^{-1} dw [38,43,44], offers ease processing and degradation without the costly pretreatment required in case of lignocelluloses [7].

Brown macroalgae are olive-greenish to dark brownish in color due to the abundance of the yellow-brown pigment fucoxanthin, which masks the chlorophyll's green color. This group of macroalgae includes the largest kelp (*Laminaria* sp.), which may reach 100 m in lengths at a growth rate as high as 50 cm day^{-1} [59]. Kelps can be harvested from temperate and polar regions at depths below the low tide level, and are farmed extensively in China, Japan, and South Korea as food products [62]. Phaeophytes composition includes up to 55% of dry weight laminarin and mannitol. Laminarin is a carbohydrate that can be hydrolyzed into glucose by laminarase (endo-1,3(4)-b-glucanase) [62]. Mannitol is a sugar alcohol that can be dehydrogenated into fructose, for further bioconversion into bioethanol [63]. In addition, phaeophytes contain cellulose and alginate, which are important structural polysaccharides providing mechanical strength to the cell wall.

Rhodophytes have a characteristic pink or red color due to the presence of phycocyanin and phycoerythrin, which allow light capture and growth at relatively deep water. Therefore, red algae can be found in the subtidal and intertidal zones of the sea at 40 m water depths or, occasionally, as deep as 250 m [64]. Their composition varies according to the species but, generally, consist of cellulose, galactan, and glucan. The cell wall of red seaweeds contains two kinds of long-chain polysaccharides, namely agar and carrageenan, which are valued for gel-forming abilities and are used economically for thickening foods such as ice cream, yogurt, and pudding [65].

Due to their need for high light intensity, most of green macroalgae live at the shallowest water columns close to the surface. They are common in estuaries and bays where freshwater is mixed with salt water. Mostly, their composition includes cellulose and pectin as the main structural polysaccharide in the cell wall, in addition to starch as a food reserve [66]. However, the ash content and biochemical composition have wide seasonal variations due to the changes of environmental conditions. For instance, *Ulva* sp. recorded the highest carbohydrates value in June (61 dw%), while showed a gradual decline from 49 to 41 dw% during July to September, respectively [67]. Similarly, *Ulva intestinalis* showed the highest protein content of 27.7 dw% in winter, which reached to the lowest value of 6.7 dw% in spring [68]. Moreover, the wide seasonal variation in water characteristics leads to significant variations in seasonal areal biomass yields of seaweeds. In

Table 2
Comparing the main biochemical composition, advantages and disadvantages of seaweeds with those of microalgae.

Algal species	Group	Proteins (dw%)	Carbohydrates (dw%)	Lipids (dw%)	Advantages	Disadvantages	Refs.
Seaweeds							
Hypnea valentiae	Rhodophyta	11.8–12.6	11.8–13.0	9.6–11.6	Wide distribution in natural ecosystems	Nuisance of the coastal areas	[24]
Acanthophora spicifera	Rhodophyta	12.0–13.2	11.6–13.2	10.0–12.0	Don't require agricultural land Easy to harvest	Lower growth rate than microalgae	[24]
Laurencia papillosa	Rhodophyta	11.8–12.9	12.0–13.3	8.9–10.8	High carbohydrate content	Contain high metal ions that	[24]
Ulva lactuca	Chlorophyta	11.4–12.6	11.6–13.2	9.6–11.4	A well-established industrial	are not desirable for bio-oil	[45]
Caulerpa racemosa	Chlorophyta	11.8–12.5	16.0	9.0–10.5	applications (e.g. agar, carrageenan,	production	[46]
Halimeda macroloba	Chlorophyta	5.4	32.6	9.9	alginate, and colloids production)	Low lipid content	[47]
Valoniopsis pachynema	Chlorophyta	8.8	31.5	9.1		Relatively lower CO_2 fixation rate	[48]
Ulva reticulata	Chlorophyta	12.8	16.9	8.5			[48]
Enteromorpha compressa	Chlorophyta	7.3	24.8	11.5			[49]
Caulerpa cupressoides	Chlorophyta	7.4	51.8	11.0			[50]
Dictyopteris australis	Phaeophyta	1.3	33.1	9.7			[51]
Stoechospermum marginatum	Phaeophyta	3.9	33.6	10.9			[51]
Lyengaria stellata	Phaeophyta	2.8	32.0	11.7			[24]
Stypopodium schimperi	Phaeophyta	1.9	29.8	8.9			[24]
Turbinaria turbinata	Phaeophyta	0.2–2.9	20.5–33.9	8.0–13.8			[52]
Microalgae							
Chlorella vulgaris	Chlorophyta	52.0–56.4	17.3–19.2	12.4–15.7	Higher growth rate and biomass	Difficult to harvest	[53]
Chlorella sp.	Chlorophyta	34.0–42.7	9.4–15.5	2.5–7.0	production	High energy consumption for	[51]
Dunaliella tertiolecta	Chlorophyta	61.3	21.7	2.9	Controllable cultivation conditions	processing	[54]
Chlamydomonas reinhardtii	Chlorophyta	61.7	3.3	12.19	Higher lipid content Higher CO_2 fixation rateUsed in m	Can be easily contaminated with undesired microbes	[55]
Chlamydomonas debaryana	Chlorophyta	59.4	10.1	19.90	any industrial applications as food supplement	High cultivation cost	[55]
Nannochloropsis sp.	Ochrophyta	40.8	19.2	30.00	Higher efficiency of waste removal		[56]
Nannochloropsis oculata	Ochrophyta	24.0	6.9	14.46			[56]
Spirulina platensis	Cyanophyta	48.4–65.2	12.0–30.2	10.30–13.30			[57]
Schizochytrium limacinum	Heterokontophyta	51.0	24.0	14.00			[58]

Table 3

Proximate chemical composition of some representative macroalgae in comparison to lignocellulosic feedstocks.

Parameter	Macroalgae				Lignocelluloses	
	Laminaria japonica	*Sargassum fulvellum*	*Gelidium amansii*	*Ulva lactuca*	Sawdust	Rice husk
Group	Phaeophyta	Phaeophyta	Rhodophyta	Chlorophyta	Lignocellulosic wastes	
Ash (dw%)	31.5	46.0	8.6	18.9	5.9	15.4
Carbohydrates (dw%)	51.9	39.6	77.2	54.3	57.1	27.1
Lignin	0	0	0	0	28.7	46.6
Lipids (dw%)	1.8	1.4	1.1	6.2	–	1.2
Proteins (dw%)	14.8	13.0	13.1	20.6	0.7	2.9
Carbohydrate composition	Laminarin, mannitol, alginate, fucoidan, cellulose		Agar, carrageenan, cellulose	Starch, cellulose	Cellulose, hemicellulose	
References	[59]	[59]	[59]	[59]	[60]	[61]

addition, there is an interspecies variation within the same season and growth area. In a recent screening study, *Ulva intestinalis* showed the highest annual biomass yield of 61.5 g m^{-2} year^{-1}, while *Ectocarpus siliculosus* showed the lowest yield of 1.3 g m^{-2} year^{-1} [68]. Therefore, seaweed selection and the optimum harvest time for seaweeds should be determined based on the growth cycle, season and the desired end products.

4. Algal wastewater treatment

Aquaculture farms and industrial effluents in many coastal areas around the world result in profound pollution and environmental degradation, which is considered as a serious problem in many countries. Treatment of the discharged water at the source is the most effective way to reduce pollution, however, most of factories and aquaculture farms do not have such *in-situ* treatment systems. In general, wastes originated from different sources can be classified into two main groups; biological wastes and non-biological wastes. The biological wastes are biodegradable and include those originated primarily from living resources, such as most of aquaculture wastes. Non-biological wastes include the recalcitrant pollutants such as chemical additives and heavy metals which are not easy to be degraded. Physical, chemical and biological treatment methods are the three available techniques to treat wastewater. Amongst, biological methods are the most advantageous in terms of low cost, simple operation and eco-friendly. Seaweeds can be used for biological removal of nitrogen and phosphorus in wastewater. They can take up nitrate and ammonia, which are the prevalent nitrogen compounds in domestic/urban sewage, agricultural and industrial water effluents. Devi and Gowri [69] reported a removal efficiency of 87.2% nitrate, 87.2% nitrite, 84.1% phosphate and 82.5% ammonia by *Enteromorpha flexuosa* from aquaculture farm discharge water after 20 days of cultivation. They also cultivated *Gracilaria verrucosa* and reported higher removal efficiency of 91.4%, 94.5%, 100%, and 99.3%, respectively. In addition, dissolved oxygen increased from 4.2 to 5.1 mg L^{-1} and from 3.3 to 5.1 mg L^{-1} with *E. flexuosa* and *G. verrucose*, respectively. Interestingly, the growth of both seaweeds increased by 35.5% and 40.5%, respectively, using wastewater.

For recalcitrant pollutants and heavy metals removal from industrial wastewater, different technologies have been developed. Heavy metals can be precipitated into their hydroxide derivatives by addition of sodium hydroxide or lime (calcium hydroxide). This method is relatively cheap and can be used to remove bulk of heavy-metal ions. However, it cannot be used if a final clarification is required, and also have negative environmental concerns [70]. Metals can be removed from a solution using electrolysis in solid metallic form, with the advantages of no produced sludges and avoiding usage of extra chemical reagents. However, this method strongly depends on the energy price, and the final treatment cost depends on the amount of electricity consumed. Other methods, such as osmosis and reverse osmosis, membrane processes, dialysis, and electrodialysis, were recommended but they are tending to be used in very specialized applications [70].

Xiong et al. [71] reported advanced oxidation processes (AOPs) as one of effective technologies for waste removal, but their application is limited for large-scale applications due to the required high maintenance and operational costs. Moreover, some byproducts with toxicity comparable to or greater than that of the initial compounds might be generated due to the incomplete mineralization of some chemicals during AOPs [72]. Purified oxidative enzymes, such as laccase, have been utilized to remediate recalcitrant pollutants. This technique is disadvantageous due to the low activities, high cost, and selectivity. Moreover, the elevated cost and limitations of the enzymatic reaction environment restrict the large-scales utilization of enzymes [73]. Application of adsorption processes for the removal of impurities from liquid or gaseous media are versatile and relatively simple. So far, some industrial important adsorbers such as silica gel, activated carbon, and alumina, have been developed with a porous surface structure which provides high surface area. However, the removal efficiency of the applied adsorber is significantly affected by the background organic compounds [74]. Alternatively, biosorption is a kind of adsorption techniques which overcome the aforementioned disadvantages and, therefore, received increasing consideration over the last few years. It is a process by which soluble substances in a solution can be collected on a suitable interface of a living cell or organism. It is also used to describe the passive or physicochemical attachment of the substance to a biomass, thus excluding the metabolic or active-uptake processes.

Using bacteria and fungi for bioremediation has been widely investigated and is receiving a great attention nowadays. However, those microorganisms grow heterotrophically and require additional carbon sources for sufficient growth. Particularly, utilization of fungi in large-scale is limited because of the mycelial structure and slow catabolic kinetics [75]. Due to the autotrophic growth of algae, they are receiving a great attention in the field of bioremediation. Algal cell walls contain many polymers including cellulose, hemicellulose, pectin, and arabinogalactan proteins. The dominant functional groups including phosphoryl, carboxyl, and amines provide the algal cell walls with a negative charge, which activates the attraction of contaminants carrying cationic groups into the algal surface enhancing the biosorption process. Algal cells absorb the organic pollutants together with other growth nutrients into the cell through bioaccumulation. Latinwo et al. [76] evaluated the potential of collected green seaweeds to remove heavy metals from textile wastewater within 10–90 min. Results showed maximum removal efficiency for Fe, Ca, Mg, K, Ag and Cr by 87.5%, 99.9%, 59.7%, 57.2%, 100% and 86.8%, respectively, after 60 min. Ungureanu et al. [77] studied the biosorbents efficiency of *Sargassum muticum* and *Ascophyllum nodosum* for antimony (Sb(III)). Biosorption of Sb(III) by *S. muticum* was found to be a fast process with maximum biosorption capacities of 2.1 and 4.0 mg g^{-1} at pH 2 and 7, respectively.

Navarro et al. [78] studied the biosorption of phenol by the marine seaweeds *Lessonia nigrescens* and *Macrocystis integrifolia*. Results showed the maximum adsorption efficiency of 35% at pH 10 using *Macrocystis integrifolia* due to a purely polar adsorption mechanism rather than an electrostatic adsorption. The study suggested that phenol was adsorbed onto the surface of seaweeds by formation of hydrogen bonds with the hydroxyl groups of the polysaccharides, such as alginates, that form the algal biomass structure. Using brown, green, and red seaweeds biomass for benzene and toluene biosorption, as two of the most soluble aromatic

hydrocarbons, was recently studied [79]. Results showed that phaeophytes have the highest removal efficiency for toluene and benzene (28 and 112 mg g^{-1}, respectively). The biosorption mechanism was attributed to hydrophobic interaction mainly with lipids and, to a lesser degree, with proteins and carbohydrates by nonspecific Van der Waals interactions. In addition, micropollutants bioaccumulation by algae was confirmed as an important route for removal of trimethoprim, sulfamethoxazole, and triclosan [80]. Another advantage of biosorption is the intracellular biodegradation which is considered as the most effective method by which living algal cells can eliminate the chemical pollutants from the surrounding environment [71]. In that context, approximately 30–80% of recalcitrant chemicals such as carbamazepine, ibuprofen, tris(2-chloroethyl)phosphate, and caffeine in wastewater were degraded within the algal cells [81–83]. Thus, biosorbents activity of seaweeds could be considered as a potential alternative to diminish the toxic effect of different pollutants in the aquatic ecosystems, which provides a promising approach for integrated energy production.

5. Thermal conversion of seaweeds

The process of biomass conversion aims to generate energy by converting biological materials to condensed energy product such as biogas, biodiesel, bioethanol, or crude bio-oil. Among different biomass conversion methods, thermal conversion has recently gained a great attention because it is much faster than biological processes, such as anaerobic digestion or fermentation. Due to low lipids content of seaweeds, thermochemical conversion may be more suitable than biochemical techniques such as lipid transesterification [84]. Kan et al. [85] concluded that thermochemical processes can convert not only lipids, but also other organic components such as proteins and carbohydrates into liquid and gaseous fuels. Therefore, thermal conversion of nuisance wild macroalgae for bioenergy production is a promising approach for renewable fuel production and environmental improvement. In addition, thermal decomposition can be used for energy production from some wastes that are biologically undegradable, such as plastic [86]. Thermal conversion processes mainly include pyrolysis, hydrothermal liquefaction, and gasification, in addition to direct combustion for heat generation (Fig. 1). Although all these methods have the same basic mechanism where heat is used to covert biomass into usable energy compounds, the amount of air supply and the energy output are quite different. For example, direct combustion needs excessive oxygen to produce energy in the form of heat, while pyrolysis takes place in the absence of air to produce mainly crude bio-oil [87]. Among different methods, pyrolysis is receiving more attention due to the wide range of

feedstocks, higher conversion efficiency and desirable end products with high yield of liquid bio-oil [88–90]. However, a pretreatment step is required to improve the conversion of residual biomass to bioenergy.

5.1. Pretreatment

For pyrolysis, macroalgal biomass must be dried to maintain a stable and efficient conversion process as well as oxygen-free conditions. Approximately, 0.7 MJ kg^{-1} is the energy required for macroalgal biomass drying with a moisture content of 88%, which was reported to be higher than the corresponding lower heating value (LHV) of the dried seaweeds [91]. In addition, storage of high moisture-contained biomass for long time results in biomass deterioration and energy loss [92]. Therefore, dewatering of wet seaweeds to 20–30% allows lower energy consumption during drying and prevents the spoilage of the biomass [93]. Application of electro-osmotic dewatering of seaweeds (Fig. 2A) before drying was reported as a useful technique to reduce the energy requirements of the drying process [94]. In addition, on-site mechanical dewatering methods; e.g. pressing and centrifugation; reduce the energy cost required for biomass transportation. Mobile compressors have already been used for on-site seaweed dewatering (Fig. 2B). After dewatering, fuel-fired ovens may be used for drying and torrefaction of the biomass, however, the cost of the overall process increases greatly with undesired emissions. Alternatively, sun drying is the most commonly eco-friendly used method since it depends on the solar radiation and, therefore, reduces the drying energy costs. However, it is weather dependent and requires large areas as only around 100 g d^{-1} m^{-2} of the dried biomass can be produced [95]. Consequently, the
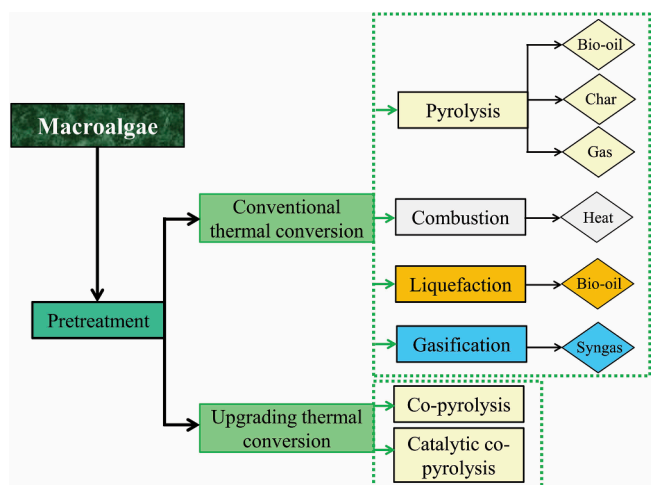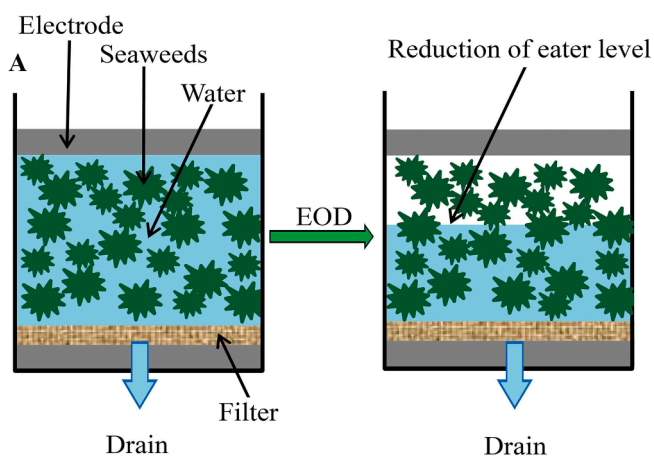
Fig. 2. Concept of electro-osmotic dewatering (EOD, A), and on-site mechanical dewatering of seaweeds at Qingdao, Shandong Province, east coast of China (B).

Fig. 1. Different thermochemical conversion routes of macroalgal biomass.

feasibility of *seaweeds-to-fuels* relies on finding a more cost-effective and controllable dewatering/drying method.

In addition to the high water content, macroalgae have significantly higher amounts of inorganic compounds, mainly metal ions such as K, Na, Mg and Ca, than lignocellulosic biomasses, causing fouling problems during thermal processing such as ash fouling and agglomeration in fluidized-bed reactor [96–98]. Generally, metal ions will also be attached on carbon surface rather than be evaporated during thermal conversion [99]. Therefore, removal of these inorganic elements improves the conversion process and upgrades the produced bio-oil [98,100,101]. In addition, Choi et al. [102] concluded that removal of macroalgae-specific organic components including alginate, laminarin, and mannitol is required in order to increase and upgrade the conversion products. In that regard, using seaweed residues after extraction of valuable industrial compounds provides a cost-effective enhanced energy recovery from wastes. Consequently, different pre-treatments using acid, water or $CaCl_2$ have been studied to remove the undesired inorganic and organic components from seaweeds.

Ross et al. [97] carried out the pretreatments of seaweeds *Fucus vesiculosus*, *Laminaria hyperborea* and *Macrocystis pyrifera* by water and weak acids. They found that Mg, K and Na in all studied algae were reduced by 30–40% after water pretreatment, with insignificant changes in Ca content. However, acid pretreatment resulted in significant reduction in all metal ions by over 90%. Ly et al. [101] reported that inorganic content of *Cladophora socialis* decreases significantly from 19.3 to 9.2 dw% after acid washing. In addition, the removal rates of Ca, Mg, P, Al, K, and Na were 90.5, 92.7, 74.3, 97.6, 97.6, and 97.9%, respectively. Hu et al. [50] confirmed that H_2SO_4 was more effective on the removal of metal ions than other tested acids and water. In addition to removal of inorganic compounds, acid pretreatment showed significant removal of organic components from biomass [50,103,104]. However, washing with water recorded a relatively slight reduction in some organic compounds, with insignificant changes in fucoidan, laminarin and alginic acid contents of seaweeds biomass [97]. Furthermore, Bae et al. [105] confirmed that acid pretreatment significantly reduces the ash content during pyrolysis of *Undaria pinnatifida*, which enhanced the bio-oil yield by 15%. Pretreatment using $CaCl_2$ was also utilized to soften the macroalgal cellular structures for extraction of the valuable fucoidan [106,107]. Due to softening the cellular structures and the efficient removal of catalytic minerals, $CaCl_2$ pretreatments increased the fatty acids ratio and reduced sugar derivatives in the produced heavy oil; with reduction of anhydrous dimers of mannitol and sorbitol in the light oil [102]. Recently, pyrolysis products of *Enteromorpha clathrata* washed with 7% phosphoric acid, sulfuric acid, and hydrochloric acid were studied [98]. Results showed that washing significantly increased the yield of bio-oil in favor of biochar, with higher aliphatic hydrocarbons contents in the bio-oil. Thus, washing of seaweeds as a pretreatment plays a key role to enhance the bio-oil yield and significantly influences its characteristics. Not only the bio-oil quality was improved as a result of pretreatment, but also the characteristics of the biochar as a solid fuel source were improved. For example, the biochar produced from acid-pretreated *Saccharina japonica* showed relatively higher carbon content and higher heating value (HHV) with lower ash content [102]. Although other chemicals were used successfully for the pretreatment, e.g. ethanol, it is not suitable for large commercial scale due to the high processing cost.

5.2. Pyrolysis

Among different thermal conversion processes, pyrolysis is considered as the most efficient method with highest fuel-to-feed ratios [88]. It is a highly complex process that involves many thermochemical reactions and physical transformations, which has been widely investigated using thermogravimetric analysis (TGA) under both non-isothermal and isothermal conditions [108–110]. It occurs usually at 400–700 °C in the absence of oxygen resulting in three final products;

bio-oil, biochar and non-condensable gas consisted mainly of H_2 and CO_2 [111,112] as shown in Table 4. The liquid bio-oil obtained from pyrolysis is easier to be stored and transported in comparison to syngas produced by gasification or heat produced by direct combustion. In addition, the gas produced from pyrolysis showed net calorific value of 10–20 MJ Nm^{-3}, which is higher than the syngas produced from gasification and combustion (4–15 MJ Nm^{-3}), which is attributed to anaerobic conditions during pyrolysis. Moreover, less dioxin and trace heavy metals emissions are produced in the gas stream of pyrolysis because it can be achieved at lower temperatures compared to combustion and gasification [113]. Nevertheless, the crude bio-oil from pyrolysis is typically inappropriate for direct use in engines because of its high viscosity and low pH, which might result in severe engine deposition and corrosion [114]. In addition to bio-oil uses, biochar and gas have high economic value. Moreno-Piraján et al. [115] recorded the high adsorption capacity of biochar produced from cow bone residues for the heavy metals Cu^{2+} and Pb^{2+}. Mullen et al. [116] also reported the effective use of biochar for metal removal from wastewater, with adsorption efficiency up to 50 and 80% for Cu^{2+} and Pb^{2+}, respectively. In addition, biochar can be used for soil improvement [117], as renewable solid fuel [118,119] or for enhanced energy recovery from biomass [120,121]. Concerning the produced non-condensable gases, they can be re-circulated to the process and thus serve as an additional heating source [122,123].

Recently, there is a growing interest in bio-oil and renewable carbonaceous materials production from seaweeds [98,132–134]. Pyrolysis, however, requires relatively dry materials as discussed in section 8.1, and, therefore, it is only feasible after extraction of high-value products from macroalgae. Thermochemical behavior of various dry marine macroalgae differs greatly, not only from the terrestrial biomasses, but also between each other [135,136]. Different kinetic parameters of pyrolysis process can be calculated from the characteristic parameters obtained by differential thermogravimetric (DTG) and thermogravimetric (TG) curves during TGA analysis. Li et al. [137] investigated pyrolysis of the brown macroalga *Sargassum pallidum* using TGA and recorded average activation energy of 203.5 and 202.9 kJ mol^{-1} using Kissinger-Akahira-Sunose and Flynn-Wall-Ozawa methods, respectively. Recently, Ali and Bahadar [110] used four iso-conversional kinetic methods to study the degradation kinetics of *Sargassum* sp. and found an exponential increase in the apparent activation energy of pyrolysis from 35 to 640 kJ mol^{-1} by increasing the thermal degradation from 10% to 90%.

Generally, there are three main stages of seaweed thermal decomposition; dehydration (stage I), devolatilization (stage II) and decomposition of carbonaceous solids (stage III) [138,139]. Fig. 3 represents a comparison of the thermal degradation stages of different seaweeds at different decomposition temperatures with the profile peak of weight loss. The first thermal degradation stage occurs within a temperature range up to 200 °C. It involves a relatively small weight loss, which is attributed to the evaporation/removal of moisture and decomposition of light volatile compounds. Further, a greater mass loss can be recorded within the temperature range of 200–550 °C as a result of devolatilization of carbohydrates, proteins and lipids (the second stage). The third stage involves a slow weight loss that usually continues, in most cases, up to 600 °C due to gradual loss of volatile metals and decomposition of carbonates at low rates. Thus, the maximum weight loss stage of the pyrolysis profile of seaweeds occurs during the second stage of decomposition.

Apart from thermal treatments of macroalgae by TGA, identification of the main chemical compounds of the bio-oils from different macroalgae has been grossly investigated [46,140,141]. Fig. 4 represents a comparison of elemental compositions of bio-oil produced from pyrolysis of different seaweeds. Generally, seaweed bio-oil mainly contains carbon (45.3–68.4%) and oxygen (12.9–43.6%). However, hydrogen and nitrogen represent relatively much lower proportions, with very little or absence of sulfur.

Table 4

Yields and characteristics of pyrolysis products from different macroalgae.

Seaweeds	Product yield (%dw)			BTP	Characteristics of bio-oil					References
	Bio-oil	Biochar	Gas		HHV	Flash point (°C)	M	D	pH	
Enteromorpha clathrata	41.20	41.50	17.3	500	12.01	NA	NA	NA	NA	[124]
Sargassum natans	33.70	47.90	18.4	500	8.68	NA	NA	NA	NA	[124]
Saccharina japonica	48.40	32.30	NA	450	28.70	84.0	1.49	NA	5.7	[125]
Saccharina japonica	44.99	34.20	20.81	350	24.80	NA	6.90	NA	4.68	[101]
Ulva lactuca	65.00	20.00	NA	550	25.70	NA	26.60	0.98	4.3	[126]
Undaria pinnatifida	39.50	60.30	30.0	500	23.33	NA	NA	NA	NA	[105]
Laminaria japonica	37.50	54.20	34.0	500	33.57	NA	NA	NA	NA	[105]
Porphyra tenera	47.40	60.00	22.0	500	29.74	NA	NA	NA	NA	[105]
Algal seaweed meal	35.60	30.80	33.7	550	26.21	NA	NA	NA	NA	[127]
Cladophora glomerata	39.00	40.00	22.0	500	17.19	NA	NA	NA	NA	[128]
Posidonia oceanica	52.40	22.80	24.8	500	26.10	NA	12.68	1.25	4.05	[129]
Laminaria digitata	32.00	34.00	32.0	500	23.08	NA	4.60	NA	NA	[130]
Fucus serratus	37.00	42.00	23.0	500	32.46	NA	1.20	NA	NA	[130]
Laminaria japonica	35.4	29.0	NA	500	29.60	NA	70.7	NA	6.9	[131]
Macroalgae mix	37.00	37.00	30.0	500	26.40	NA	3.70	NA	NA	[130]

NA Not available; BTP Optimum temperature (°C) for maximum production; HHV Higher heating value of bio-oil (MJ kg^{-1}); D Density at 40 °C (g cm^{-3}); M Moisture content (%).
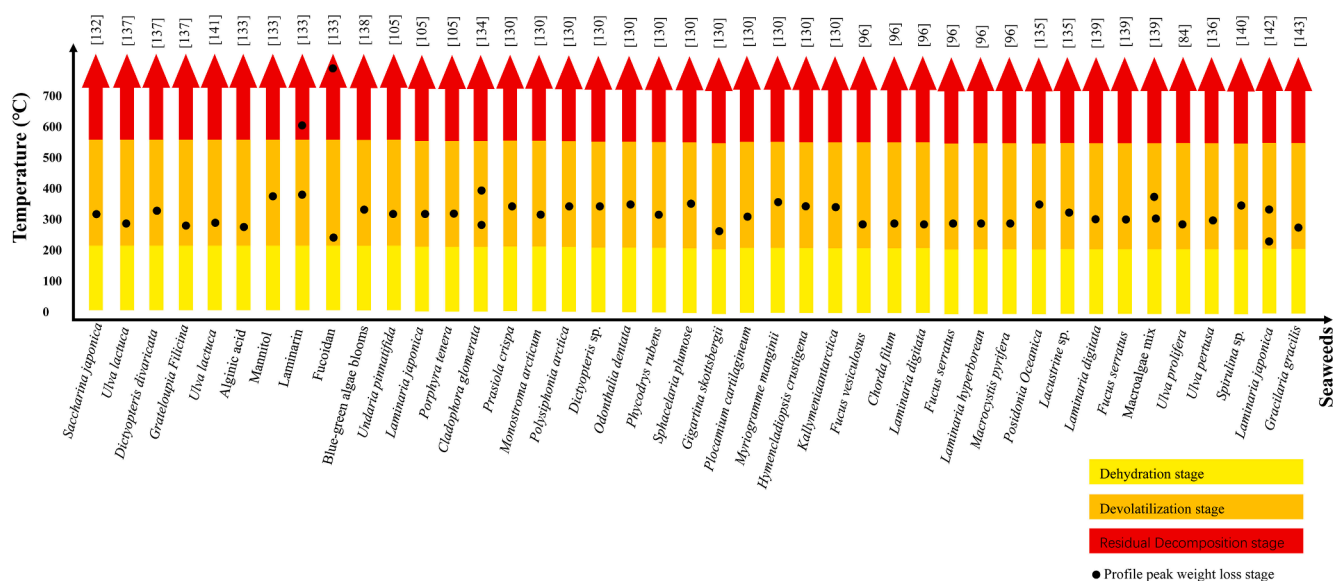
Fig. 3. Comparison of the main stages of thermal degradation of different seaweeds using TGA/DTG pyrolysis.

In addition, the yield and characteristics of pyrolysis outputs vary in different macroalgae. Bio-oil yield of seaweeds ranges from 32 to 65 dw %; the yield of biochar is between 20 and 60 dw%; while that of the gaseous product is within the range of 17 to 34 dw% (Table 4). However, bio-oil from different seaweeds recorded relatively HHV (up to 33.57 MJ kg^{-1}) compared to that of lignocellulosic biomasses, which is more desirable from energy aspect. The main recorded chemical compounds in different seaweed bio-oils have been studied by many researchers. Table S1 (Supplementary data) shows a survey for the main chemical compounds in pyrolytic bio-oils of various seaweeds. The major chemical compounds in the bio-oils are similar to some extent, which might be attributed to the interspecies chemical composition similarities of macroalgae. The main components of bio-oils are hydrocarbons, aldehydes, ketones, alcohols, carboxylic acids, phenols, and their derivatives, with minor proportions of heterocyclic compounds such as pyridines, furans, and pyrans (Table S1, Supplementary data).

Several studies have compared the macroalgal pyrolysis with that of lignocellulosic biomasses. Trinh et al. [126] compared energy recovery and different products from pyrolysis of macroalgae, lignin, wood and straw. Macroalgae produced 65 dw% bio-oil with 76% bio-oil energy recovery, while lignin yielded 47 dw% bio-oil with 45% bio-oil energy

recovery. The HHV of wood, straw, lignin, and algae bio-oils were 24.0, 23.7, 29.7, and 25.7 MJ kg^{-1} dry weight, respectively. As a general statement, lignocellulosic biomasses require higher pyrolysis temperatures than macroalgae, likely due to the cellulose, hemicellulose, and lignin components [139,142]. Contrary to lignocellulosic biomasses such as husks, straws and sawdust, seaweeds have lower thermal stability and, therefore, they volatize at lower temperatures. In a previous study, Kebelmann et al. [138] pyrolyzed psychrophilic macroalgae collected from the Arctic region and recorded that the maximum decomposition rate of *Prasiola crispa* was within the temperature range of 220–320 °C, which was lower than that of lignocellulosic biomasses. Wang et al. [143] recorded the release of volatiles during pyrolysis of seaweeds earlier than that of lignocelluloses. In addition, seaweeds pyrolysis was exothermic resulting in heat, meaning that less net energy input is required [143]. Ross et al. [96] compared the thermal degradation behavior of five brown seaweeds with that of terrestrial plants. Results showed a lower proportion of phenolic compounds in macroalgae. As shown in Table S1, seaweed pyrolysis showed almost the absence of some phenolic fragments common in lignocellulosic bio-oil such as methoxyphenols. Absence of such phenolic fragments is attributed to the absence of lignin in seaweeds [96,144]. This is also
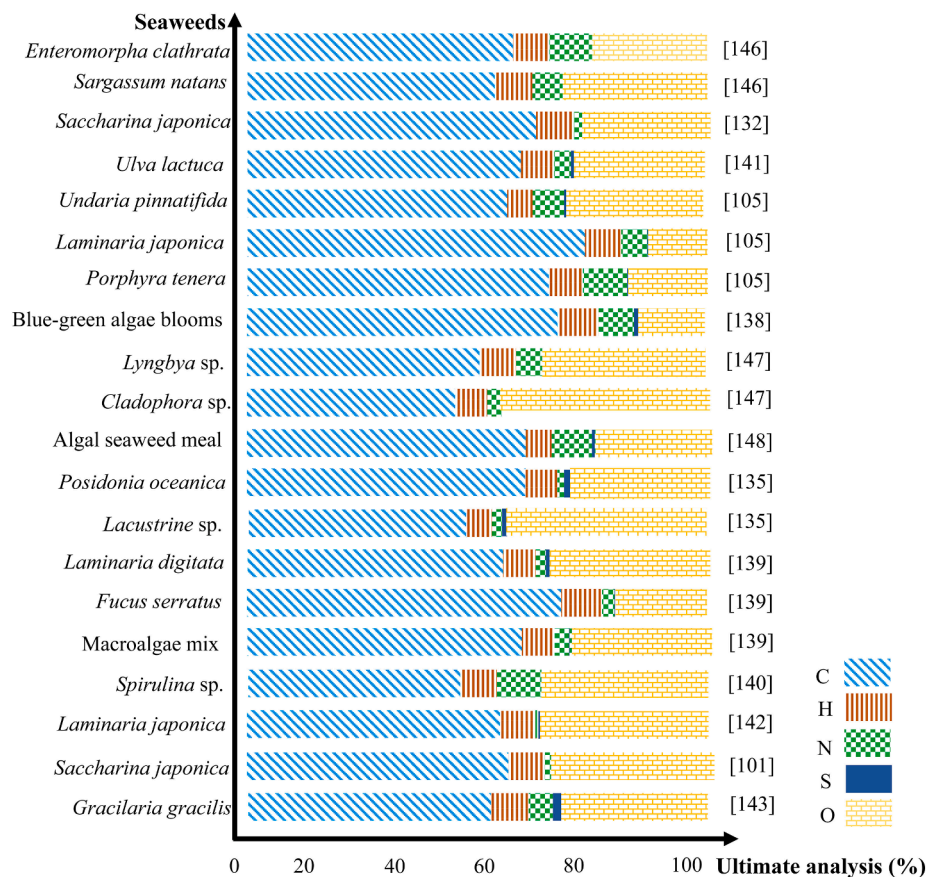
Fig. 4. Elemental compositions of bio-oil produced from pyrolysis of different seaweeds.

advantageous for higher bio-oil quality, because the presence of such   phenolic compounds results in a difficulty during deoxygenation process

Table 5
Recent progress on advanced pyrolysis methods of seaweeds (catalytic pyrolysis, co-pyrolysis, and catalytic co-pyrolysis).

Seaweeds/components	Co-feeding element of high C & H contents	Pyrolysis system, conditions, and applied catalyst	Results	Refs.
Enteromorpha prolifera (EP)	Rice husk (RH)	Fixed-bed reactor, 400–600 °C; 5–25 °C min^{-1}; N$_2$ gas; 100 mL min^{-1}	Results revealed positive synergy existed between EP and RH which increased the oil yields and improved the oil quality.	[139]
Enteromorpha clathrata polysaccharides and *Sargassum fusiform* polysaccharides	Cellulose	TGA instrument coupled with GC/MS; N$_2$ gas; 100 L min^{-1}	Results also revealed the existence of synergy & the simulation results were consistent with the experimental results.	[149]
Enteromorpha clathrata polysaccharides and *Sargassum fusiform* polysaccharides	Cellulose	Stainless steel fixed bed reactor; 550 °C; ZSM-5 catalyst; N$_2$ gas; 0.8 L min^{-1}	Results showed an increase in oil yields due to ZSM-5 and a great reduce in acids and N-containing compounds in the oil, while furans and ketones were greatly increased.	[150]
Laminaria japonica	Polypropylene	Batch-type fixed-bed reactor; TGA instrument; Py-GC/MS; N$_2$ gas; 50 mL min^{-1}; 500 °C; Catalysts used are: HZSM-5, HBETA and HY	Results revealed a sharp decrease in the oil water content and improvement in oil quality due to increased mono-aromatic hydrocarbons in the oil.	[151]
Enteromorpha clathrata	Rice husk (RH)	Fixed bed reactor; 190, 320 and 550 °C; N$_2$ gas; 200 mL min^{-1}	Results showed positive synergistic effects, and a release of N- substances was inhibited by addition of RH at low temperature (<190 °C) range.	[147]
Laminaria japonica	Polypropylene	U-type quartz fixed-bed reactor; TGA instrument; Py-GC/MS; N$_2$ gas; 50 mL min^{-1}; 500 °C; Catalysts used are: HZSM-5, mesoporous MFI, Pt/mesoporous MFI, & mesoporous Al-SBA-16.	Result showed a decrease in oxygenates, acids, and wax components, and increase in hydrocarbons (aromatics and light).	[148]
Ulva lactuca	–	Quartz tubular reactor; N$_2$ gas; 100 mL min^{-1}; 460 °C; HZSM-5 catalyst	Results indicated a huge amount of aromatic hydrocarbons and high denitrogenation effect for amides, amines and nitriles, however, with a great amount of coke.	[152]
Laminaria japonica	–	Py-GC/MS analyzer; Catalysts used are: nanoporous Al-MCM-48 and hierarchical Meso-MFI zeolite	Meso-MFI exhibited a higher activity in deoxygenation and aromatization than Al-MCM-48, producing higher yields of aromatics, gases and phenolics owing to the strong acidic sites.	[153]

which requires further bio-oil upgrading.

5.3. Upgraded bio-oil

Algae, most especially seaweeds, have been acknowledged by many researchers as a promising future energy source due to the high photosynthetic efficiency and biomass productivity [2,18,110,136,145,146]. However, bio-oil produced from pyrolysis of seaweeds often exhibits severe instability as a result of high oxygen contents. In addition, nitrogen-containing compounds and sulphur should be as minimum as possible to reduce the NO_x and SO_x emissions. Thus, it requires either direct catalytic reforming or upgrading via co-pyrolysis, with or without catalysts, to improve the bio-oil stability and emission performance [25,147,148]. Many studies have been carried out on catalytic pyrolysis of lignocelluloses and other organic wastes, indicating that application of a suitable catalyst improves the heating value and lowers the oxygen and nitrogen contents of the bio-oils. However, studies on catalytic pyrolysis of seaweeds are still very limited compared to those of terrestrial biomass and wastes, while investigations on co-pyrolysis of seaweeds are very few in literature. It is thus imperative to focus more research attention on the advanced pyrolysis methods of seaweeds via application of different catalysts or by employment of several upgrading methods such as catalytic co-pyrolysis in order to properly evaluate the pyrolysis of seaweeds as a potentials and effective energy source. This section of the article, therefore, represents a holistic summary of the recent progress in advanced pyrolysis methods of seaweeds (catalytic pyrolysis, co-pyrolysis, and catalytic co-pyrolysis), and optimization of the co-pyrolysis parameters/conditions towards enhanced bio-oil production. Table 5 summarizes the recent progress on the most commonly advanced pyrolysis methods of seaweeds.

5.3.1. Catalytic pyrolysis of seaweeds

Generally, biomass catalytic pyrolysis involves the application of a suitable catalyst during thermochemical decomposition process, which is irreversible reaction. The products of biomass catalytic pyrolysis often differ owing to the utilized catalyst type (e.g., zeolites, solid phosphoric acid, metal loaded catalysts, etc.). The microporous zeolites, e.g., HZSM-5 among other types of catalysts, are active for production of hydrocarbons [154–156]. However, the transformation pyrolyzates of large molecular sizes from biomass pyrolysis over microporous zeolites is limited due to the difficulty with which the pyrolysis products of large particles could diffuse into the microporous zeolites' small pores. Alternatively, mesoporous catalysts, e.g., SBA-15 and MCM-41, can be used for active conversion of pyrolyzates of large molecules [157–159]. Besides, deoxygenation reactions take place during catalytic pyrolysis and result in a significant decrease in the bio-oil oxygen content, with an increased heating value and removal of acids. However, the bio-oil from catalytic pyrolysis of biomass, including that of algae, contains considerable amounts of coke and low oxygenates, but with improved miscibility, most especially, with the petroleum-derived liquid fuels.

Research results revealed that lignocelluloses have been widely employed as catalytic pyrolysis feedstock compared to macroalgae, which are currently receiving a considerable attention as a new feedstock for crude bio-oil production. For example, Lorenzetti et al. [152] performed catalytic pyrolysis of seaweeds over HZSM-5 catalyst. They observed a huge proportion of aromatic hydrocarbons and high denitrogenation effect for amides, amines and nitriles, however, with a great amount of coke. Lee et al. [153] also carried out catalytic pyrolysis of the seaweed *Laminaria japonica* over a nanoporous Al-MCM-48 and hierarchical Meso-MFI zeolite (Meso-MFI) via direct Py-GC/MS to examine the impact of different catalysts on the products distribution and chemical compositions of the produced bio-oil. Results showed that Meso-MFI exhibits higher activity in aromatization and deoxygenation compared to Al-MCM-48, resulting in higher yields of aromatics, gases and phenolics due to the strong acidic sites which accelerate the cracking of pyrolysis oil molecules. The production of large amount of coke has been

identified by several researchers as a major challenge to the catalytic pyrolysis. Thus, the quest for a lasting solution to this problem has recently paved way for the employment of other biomass thermal conversion methods such as co-pyrolysis with different feedstocks.

5.3.2. Co-pyrolysis of seaweeds

Recent progress in pyrolysis of seaweeds focused on application or development of advanced pyrolysis technologies, known as co-pyrolysis and catalytic co-pyrolysis, with optimization of the co-pyrolysis parameters/conditions for enhanced bio-oil production. Co-pyrolysis refers to the pyrolysis of two or more feedstocks to enhance the products yield and quality via a synergistic effect of different intermediates during the reaction [21,47,160,161]. Thus, ideal co-pyrolysis of seaweeds involves pyrolysis with a feedstock which contains a lot of hydrogen and carbon such as plastics, tires or rubbers. Co-pyrolysis of biomass with plastic materials significantly enhance the hydrogen and carbon contents of the produced bio-oil, resulting in improved fuel quality at higher bio-oil yields [111,152,162,163]. Likewise, comprehensive reviews on the different aspects of pyrolysis technology of different biomass feedstocks and polymers have been presented by many researchers. Zhang et al. [164] carried out a comprehensive review on pyrolysis technology of polymers with lignocellulosic biomass, particularly. However, their focus was on the catalytic co-pyrolysis chemistry. Uzoejinwa et al. [111] recently provided a holistic and comprehensive review on the recent advances, findings and perspectives of seaweeds co-pyrolysis technology with different plastic wastes for enhanced bio-oil production. However, this section of the present article specifically represents the current advances in research and development in co-pyrolysis of seaweeds or their components and various feedstock materials containing relatively high carbon and hydrogen contents, with or without catalysts.

Detailed information on co-pyrolysis of seaweeds with other feedstock materials containing lots of carbon and hydrogen towards enhanced biofuels production is currently not readily available in literature. For the first time, Lee et al. [151] investigated the pyrolysis and co-pyrolysis of the brown seaweed *Laminaria japonica* and polypropylene over a mesoporous material Al-SBA-15 using a fixed-bed reactor and Py-GC/MS (Table 5). Results showed that co-pyrolysis of *Laminaria japonica* with polypropylene results in significant reduction in the water content of the bio-oil and improves the bio-oil quality as the mono-aromatic hydrocarbons increased owing to catalytic co-pyrolysis. Recently, Uzoejinwa et al. [139] investigated the co-pyrolysis of seaweeds with lignocellulosic biomass and optimized the production of the pyrolysis products. Authors confirmed a positive interactive synergetic effect between lignocellulosic biomass (rice husk) and seaweeds (*Enteromorpha prolifera*) during co-pyrolysis, which resulted in significant increase in the bio-oil yield and concurrently improved the products quality. Wang et al. [149] also studied the co-pyrolysis mechanism of seaweed polysaccharides and cellulose through macroscopic analysis and molecular simulations to investigate the synergistic effects. The study confirmed the existence of synergy during co-pyrolysis, and the simulation results were found to be consistent with the experimental results. According to Brebu et al. [165], synergetic formation of aromatic hydrocarbons is the main target of co-pyrolysis. Generally, synergistic effect represents the interactions that exist between two or more elements which results in a total effect that is higher than the integral sum of the effects from the individual feeding elements, which usually improves the quantity and quality of the produced bio-oil, or might also worsen the characteristics of the resultant products [139]. Kim et al. [148] carried out the co-pyrolysis of *Laminaria japonica* and polypropylene using fixed-bed reactor and Py-GC/MS over different catalysts. They observed the reduction of acids, oxygenates, and wax contents of components via catalytic upgrading, while hydrocarbons content was considerably increased, enhancing the quality and economic value of the bio-oil. Likewise, Xu et al. [147] studied the synergistic mechanism during co-pyrolysis of seaweeds and rice husk through char/coke characteristics investigation. Their results confirmed

synergistic effects of co-pyrolysis which resulted in significant inhibition in the released nitrogenous substances at lower temperature (<190 °C). Catalytic co-pyrolysis of seaweeds polysaccharides with cellulose over ZSM-5 did not only increase the yields of bio-oil, but also significantly reduced the acids and nitrogen-containing compounds, while furans and ketones were considerably increased, suggesting the catalytic co-pyrolysis as a better method over co-pyrolysis [150]. Thus, the use of a suitable catalyst in the co-pyrolysis of seaweeds is one of the most recent areas of interest, where much attention is currently focused on high quality bio-oil production.

Likewise, optimization of biomass co-pyrolysis parameters/conditions such as reaction temperature, heating rate, residence time, feedstock blending ratio, inert gas flow rate, particle size, and feed-to-catalyst weight ratio is another interesting aspect that is recently gaining increasing attention. For example, Hu et al. [166] investigated the co-pyrolysis of petroleum sludge and waste biomass using a response surface methodology to evaluate the interaction effects of temperature and heating rate on bio-oil and biochar yields. The study revealed a significant interaction between heating rate and sawdust percentage and between the heating rate and temperature on the bio-oil yield. However, several studies on optimization of individual pyrolysis of biomass have been carried out by many researchers [167–169], but for the first time, Uzoejinwa et al. [139] performed an optimization study on the co-pyrolysis of seaweed biomass. They studied the interaction effects of three effective parameters during seaweed co-pyrolysis on the yield of

bio-oil and biochar, then performed a simulation and modeling analysis in order to predict the optimal conditions to maximize the bio-oil yield. The study concluded that the synergistic effect between seaweeds and rice husk during co-pyrolysis resulted in significant increase in the products' yields and improved the co-pyrolysis products' quality. Moreover, co-pyrolysis of seaweeds and lignocellulosic biomasses was reported to improve the biochar properties [23].

6. Environmental impacts and economic feasibility

6.1. Environmental impacts

Environmental issues represent one of the key parameters used to evaluate a process acceptability to drive the next generation of a certain economic opportunity. Seaweeds grown in different kinds of wastewater discharges can provide an advantageous route for water treatment and biodegradation of recalcitrant compounds at comparatively lower cost and reduced ecological risks. While constructing such integrated system, achieving the maximum biodegradation/biosorption rate with the minimum cost is a critical issue for large-scale application. In addition, some concerns can arise about the utilization of seaweeds for human or animal feed due to the high pollutants within the biomass. Therefore, more investigations and efforts are required in order to overcome these concerns. Although using microbial consortium, consisted from micro-algae and bacteria, for biological processes enhanced the process
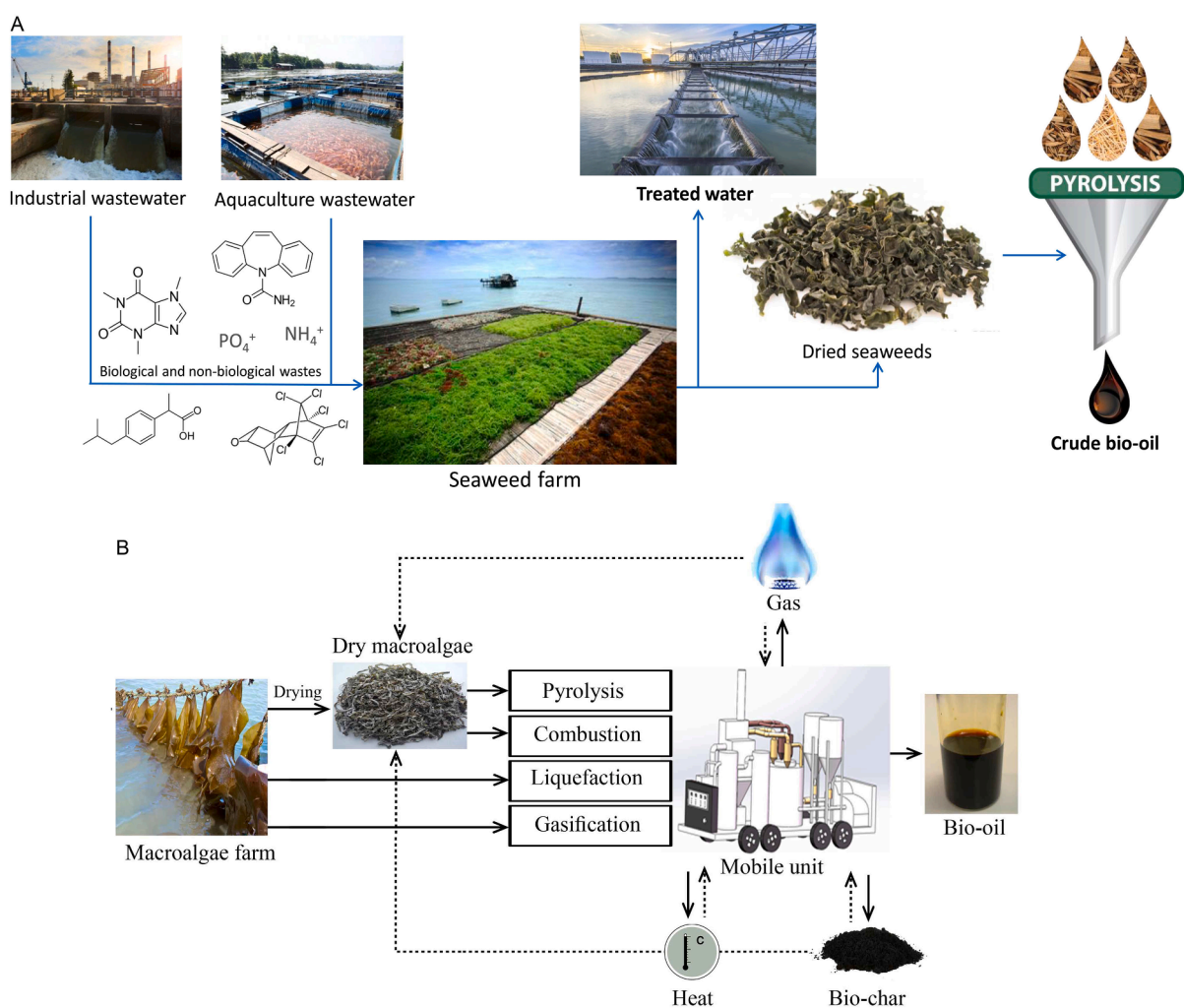
Fig. 5. Integrated concept of seaweeds grown in wastewater for crude bio-oil production and wastewater treatment (A) and pathways of thermochemical conversion of seaweeds to bio-oil using on-site thermal decomposition (B), dotted lines represent heat recovery.

efficiency than the individual system, integration of algal bio-technologies with other current technologies have rarely been studied. Most of the recent studies on application of algae-based technologies are devoted and focused on laboratory-scale using individual methods, and only few studies have been conducted on pilot- or large-scales. Thus, thermal decomposition of seaweeds grown in wastewater for integrated crude bio-oil production and water treatment provides the best route for biomass utilization (Fig. 5A). However, more studies should be conducted to investigate the dual use of seaweeds for efficient removal of recalcitrant compounds and their impact on the produced bio-oil.

Nowadays, CO_2 emissions are discussed as an international political issue, and CO_2-induced global warming is in the everyday news. Due to the high economic cost of CO_2 emissions reductions, biomass-generated fuels are receiving increasing attention as more economically and eco-friendly alternatives to the conventional petroleum fuel [20,170,171]. In addition to bioenergy production, macroalgae have a great potential for CO_2 bioremediation without competing with terrestrial crops for farm land or freshwater [24,172–174]. Previous work has shown that production of one ton of dry seaweeds approximately absorbs 960 kg net CO_2 [175]. Moreover, seaweeds can be grown in seawater without additional nutrients or pesticides [40,176], improving the water quality in which it is grown [177,178]. Therefore, macroalgal biomass represents a promising biofuel feedstock to provide environmentally-feasible alternatives for fossil fuel.

On the other hand, application of commercial macroalgal bioenergy systems expands the usage of algae farming, and thus special attention should be paid to their prospective impacts on coastal and marine environments. Such impacts include nutrient depletion, decrease of biodiversity, possible alteration of natural habitats, change of hydrology, and coral reefs disturbance [59]. Currently, environmental impacts of macroalgae farming might be seen as a minor issue in some cases, and may even have some benefits to increase the populations of invertebrates and fish in the area where seaweeds grow [179]. However, extensive long-term wild-harvesting of seaweeds will affect the environmental sustainability by disturbing the wild life and biodiversity of sea ecology [180]. Environment & Heritage Service statement [181] indicated that the depletion of *Laminaria digitata* in France might be attributed to different factors including over-exploitation. Therefore, sustainable harvest should be considered, using advanced instruments that leave parts of the vegetative organs of seaweeds for re-growth. Overall, a balance must be attained between macroalgal biomass production and the paid environmental cost.

6.2. Economic feasibility

Biorefinery through concurrent production of valuable co-products that have wide industrial, medical, and nutritional applications simultaneously with biofuels has more significant potential towards circular economy. For example, by integrating seaweeds and fish farms, macroalgae can remove nitrogen, phosphorus and heavy metals from the pond [175,177] and oxygenate the water while utilizing the ammonia excreted by fish for algal growth [182]. In general, farming of seaweeds has additional socio-economic benefits, and is a vital industrial route as well as providing employment chances in developing countries. The social and economic dimensions of macroalgae farming were investigated by Valderrama et al. [93] who concluded that the net return to a family of four persons was higher than the international poverty line. However, due to the high labor demand and costly equipment required for cultivation of seaweeds, the economic value of the target product should be considered in order to be sufficient to make it worthwhile. For enhanced capacity of aquaculture to meet the economic feasibility, integration and expansion of macroalgae in marine aquaculture production has been proposed [183,184]. Despite the potential of numerous applications of macroalgal farms, it has not taken off globally due to the high production cost [185]. The manipulation costs, mainly coming from transportation and drying, should also be considered.

In order to reduce the transportation and drying costs, a mobile thermal decomposition unit can be built on-site with energy recycling (Fig. 5B). Heat recovery can be achieved via combustion of gases and biochar for biomass drying and thermal decomposition. In addition, the exothermal heat during pyrolysis can also be used to realize an energy self-balancing system in the large-scale plant. For such system, organic Rankine cycle will have a vital role as a simple, high reliable, and efficient route to convert low-grade waste heat to power [89,186]. In that context, Brigljević et al. [187] studied the economic feasibility of a large-scale poly-generation pyrolysis process of 4×10^5 tons year^{-1} of the dry brown seaweed *Saccharina japonica* as a feedstock to produce diesel-range hydrocarbons, power and heat with heat recycling through Rankine cycle. The sensitivity analysis parameters included internal economic parameters (fixed capital investment, internal rate of return, and income tax rate) and external economic parameters (the prices of seaweed, natural gas, power, acid, and hydrogen). The hydrogen price was considered as the selling price (Case 1) and the purchase price (Case 2). Comparison of four net present values (NPV) for both cases showed a similar increasing trend. However, Case 1 showed higher trend than Case 2, which was attributed to the higher capital investment in Case 1 (Fig. 6A). It was further confirmed by calculating the average return on investment (ROI) against NPV trends. At the same NPV value, results showed a notable higher ROI in Case 1 than Case 2 (Fig. 6B). Despite the low CO_2 emissions in the 2 studied cases, the study estimated higher CO_2 emissions in Case 1 than Case 2 (0.043 and 0.007 kg of CO_2 per kg of dry seaweed, respectively), which provide a beneficial environmental potential as CO_2 emissions are reduced by 7- to 45-fold compared to that produced from conventional crude oil (Fig. 6C). However, the estimated minimum product selling prices for Case 1 and Case 2 were US\$ 2.821 L^{-1} and US\$ 2.847 L^{-1}, respectively, which are higher than the current global average of diesel prices (US\$ 1.060 L^{-1}) (Fig. 6C). Therefore, integration of seaweeds energy production with other industrial applications could enhance the process economy. For instance, seaweed aquaculture in combination with offshore wind energy production was suggested to reduce the costs of both offshore wind energy generation and seaweeds biomass production [188,189].

7. Future perspectives

Despite the positive environmental impacts and potential of seaweeds to produced crude bio-oil, the economic feasibility provided in the present study confirmed that the process is not economically feasible yet. The main challenge is to reduce the overall production cost and enhance the process economy. In addition, biofuel production from seaweeds encounters many technical challenges such as variation in seaweed growth and chemical composition depending on the season and geographical location [68,190]. Moreover, there is an urgent need to evaluate the impact of wild-harvesting on the marine ecosystems [191]. Therefore, developing advanced cultivation techniques is important in order to fulfil the specific characteristics of a certain algal species. Although some recent studies provided positive estimations on the cost of seaweed production for value-added products, much lower production cost must be achieved in case of biofuel. For that regard, combination of seaweed production, fish aquarium, phycoremediation, and offshore wind energy generation is expected to have synergetic interaction which turns the seaweed production into a profitable business. In addition, the economic feasibility of biofuel production from seaweeds can be further improved using an integrated biorefinery approach for simultaneous production of high-value products and biofuel, which enables the circular economy. Nowadays, the market for bioproducts from seaweeds is diverse, with a huge amount of residual biomass left behind. According to Tedesco and Daniels [191], 83–90% of the total seaweed-based industry are used as food, while the remaining 10–17% are used for bioproducts extraction, which produces huge amounts of biomass residues suitable for biofuel production.

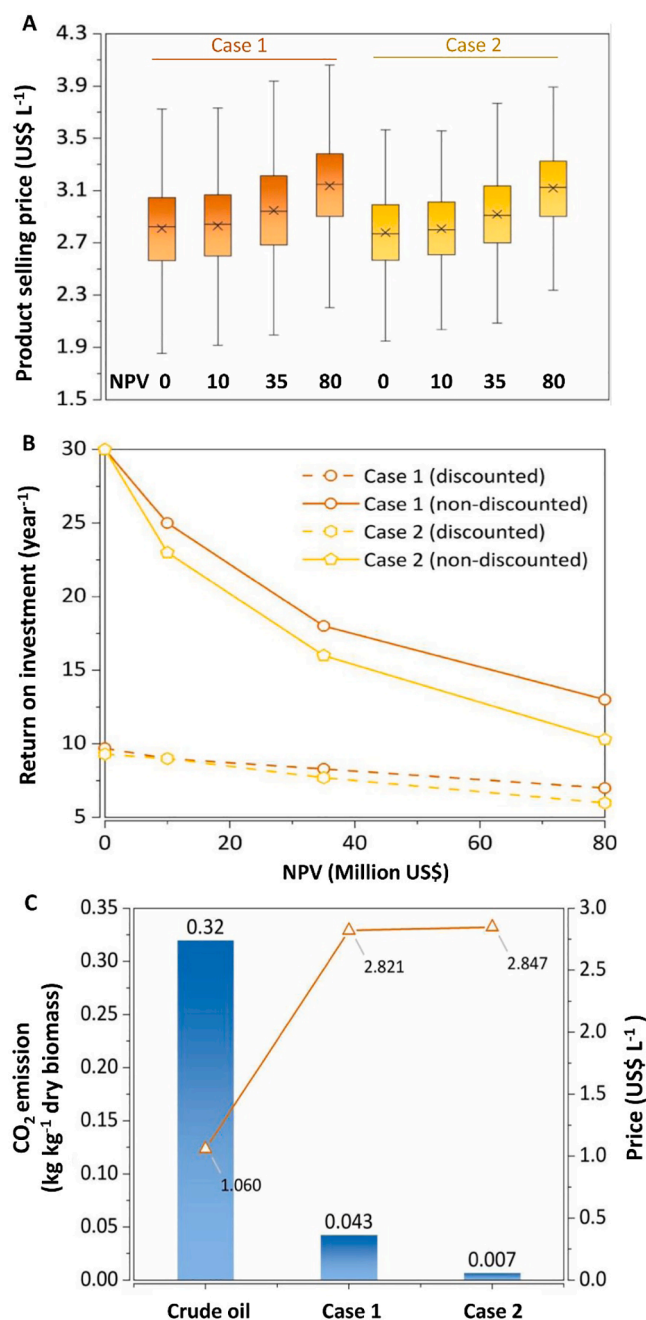Developing advanced conversion technologies is also important in

Fig. 6. A) Product selling price ranges at different net present values (NPV) of US$ 0–80 mil (from left to right) at Case 1 and Case 2. B) Annual return on investment at different NPV for Case 1 and Case 2. C) CO_2 emissions (columns) and fuel price (line) of crude oil compared to biofuel produced from the two scenarios. Figures adopted from Ref. [187] after obtaining the required copyright permission from Elsevier.

order to enhance energy recovery from seaweeds. In that context, microwave pyrolysis was recently discussed as a promising technique for biomass conversion [162,192–194]. In addition, co-pyrolysis of seaweeds with high H and C feedstocks, such as waste plastic, could improve the yield and characteristics of the bio-oil [21,111,195]. Moreover, co-pyrolysis of seaweeds with cost-effective feedstocks such as fat, oil, and grease (FOG) could enhance the process economy. In general, developing the better economic models is essential to estimate how the cost of the integrated process varies with the characteristics of the final products, and the relative cost of the different crude bio-oil production routes versus algae-integrated technologies. Thus, more

studies should be conducted on the economic feasibility of pilot-scale conversion plants in order to provide a clear evaluation for the industrial applicability.

8. Conclusions

Crude bio-oil production from seaweeds could provide dual benefits of efficient biomass feedstock and save the environment from detrimental effects. Although many studies reported the efficiency of seaweeds for bio-oil production, large-scale production at low cost is the main challenge for that purpose. Combining algal farming, wastewater treatment, fish aquarium, wind power generation, synthesis of novel bioproducts and biofuel production is a promising strategy of biorefinery towards circular economy that might reduce the overall cost. In addition, lower production cost can be achieved by developing new innovative technologies that reduce the cost at each processing step including; farm design, harvesting, pretreatment, transportation, feedstock selection, and conversion process. At the same time, environmental impacts of algal large-scale cultivation and/or extensive wild-harvesting need to be carefully considered. Overall, a balance must be attained between macroalgal bioenergy production, biofuel cost, and the environmental impacts.

CRediT authorship contribution statement

Shuang Wang: Conceptualization, Methodology, Funding acquisition. **Shuang Zhao:** Methodology, Writing - original draft. **Benjamin Bernard Uzoejinwa:** Methodology, Writing - original draft. **Anqing Zheng:** Methodology, Writing - original draft. **Qingyuan Wang:** Writing - review & editing, Funding acquisition. **Jin Huang:** Writing - review & editing. **Abd El-Fatah Abomohra:** Conceptualization, Writing - review & editing, Funding acquisition.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.enconman.2020.113253.

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