Abstract

Background: Microalgae have been experimented as a potential feedstock for biofuel generation in current era owing to its rich energy content, inflated growth rate, inexpensive culture approaches, the notable capacity of CO₂ fixation, and O₂ addition to the environment. Currently, research is ongoing towards the advancement of microalgal-biofuel technologies. The nano-additive application has been appeared as a prominent innovation to meet this phenomenon.

Main text: The main objective of this study was to delineate the synergistic impact of microalgal biofuel integrated with nano-additive applications. Numerous nano-additives such as nano-fibres, nano-particles, nano-tubes, nano-sheets, nano-droplets, and other nano-structures’ applications have been reviewed in this study to facilitate microalgae growth to biofuel utilization. The present paper was intended to comprehensively review the nano-particles preparing techniques for microalgae cultivation and harvesting, biofuel extraction, and application of microalgal-biofuel nano-particles blends. Prospects of solid nano-additives and nano-fluid applications in the future on microalgae production, microalgae biomass conversion to biofuels as well as enhancement of biofuel combustion for revolutionary advancement in biofuel technology have been demonstrated elaborately by this review. This study also highlighted the potential biofuels from microalgae, numerous technologies, and conversion processes. Along with that, the study recounted suitability of potential microalgae candidates with an integrated design generating value-added co-products besides biofuel production.

Conclusions: Nano-additive applications at different stages from microalgae culture to end-product utilization presented strong possibility in mercantile approach as well as positive impact on the environment along with valuable co-products generation into the near future.

Keywords: Microalgae, Microalgal biofuel, Nano-additives, Bioenergy, Biodiesel

Background

Biofuel has caught substantial attention worldwide nowadays as an alternative fuel due to its capability to adapt with gasoline for a maximum 85% blend without any engine modification. Subsequently, the suitability of various candidates for biofuel is being continuously quested by the researchers and environmentalists [1–5]. In this recent era, one of the most sophisticated technologies, nano-technology integration with bioenergy application by the nano-energy sector has brought a revolutionary impact on biofuel conversion processes and enhancement of engine performances. Nano-technology is defined as designing a device or material in nano-scale (10⁻⁹ m). To accelerate the biofuel yield and improve the efficiency of biofuel utilization in petrol and diesel, nanotechnology has been initiated via nano-additives such as nano-magnets, nano-crystals, nano-fibres, nano-droplets, and others [6–8]. Figure 1 presents the perspectives of nano-additives on microalgae cultivation to microalgal-biofuel implementation.

On this eve of the quest for suitable biomass for biofuel, the concept of microalgae cultivation appeared to the spotlight for biofuel manufacturing due to several positive perspectives such as (i) they do not clash with human or...
animal food chains, (ii) very rich with carbohydrate, protein, and oil content, (iii) can grow in aqueous media such as wastewater, freshwater, saline water, and assimilate nutrients from brackish water, salt water, or highly polluted water, (iv) demand low water, (v) sustain capability to grow whole year naturally with sunlight presence, (vi) can be cultivated in the waste dump area, sea, ponds, rivers, industrial, and municipal waste drainage, wet bare lands especially in cold regions, (vii) develop sustainable O2 generation system, and (viii) diminish CO2 by up taking it for photosynthesis respiration [9–14]. In addition, microalgae contain very short harvesting life cycle and yield nascent biomass that drives higher productivity of the desired biofuel. Interestingly, microalgae carry a prodigious amount of carbohydrates, protein and lipid, the sole components of biofuel conversion [13, 15–17]. Nano-technology applications have been implemented to biofuel industries, since the existing controversial approaches of traditional microalgae culture-biofuel production contain a number of limitations such as inconsistent industrial-scale microalgae production, high microalgae production and harvesting cost, energy consumption for biofuel production from microalgae, and the increase of greenhouse gas intensity in environmental [18]. Nano-technology applications can be entailed in different stages from microalgae cultivation to microalgae-biofuel application in fuel engines due to durability, recyclability, adsorption efficiency, catalytic performance, stability, crystallinity, economical advantage, high storage capacity, excellent biofuel yield, and environment-friendly characteristics. According to the previous studies, nano-technology application enhanced microalgae cultivation, the maximum yield of numerous microalgae biofuels as well as microalgae-biofuel implications in petrol and diesel engines. Various nano-materials, e.g., nano-fibres, nano-particles, nano-tubes, nano-sheets, and other nano-structures, have been investigated as effective nano-catalysts in direct and indirect approaches in biofuel (e.g., bioethanol, biodiesel, biomethane, and others) yield enhancement [19–22]. For instance, magnetic nano-particles were used as a carrier for enzyme immobilization for bioethanol and biodiesel generation effectively. Owing to high coercivity and powerful paramagnetic characteristics, magnetic nano-particles were also preferred for methanogenesis to produce biomethane [21].

To authors’ best knowledge, no review study has been performed on numerous biofuel productions from microalgae integrated with the nano-additive application so far. The closest review with this study was conducted on the bioenergy production from lignocellulosic biomass (agricultural residues), industrial waste (sludge) as well as algae
(microalgae and macroalgae) with the nano-scale optimization which has merely emphasized on the mechanism of nano-particles, biomass characteristics, and nano-particle application on biomass growth [23]. Compared with that, the current review contextualized the numerous biofuel productions from pure microalgae and optimization with nano-additive application on biomass growth to end-product application. Therefore, the major objectives of this review work are (i) to determine the array of the techniques and methods associated with nano-particles incorporation with microalgae culture as well as microalgal biofuel, (ii) to demonstrate divergent nano-additive applications on microalgae cultivation, biomass conversion to biofuels, and biofuel combustion, (iii) to identify the potential sources of microalgae, especially the carbohydrate, protein, and lipid-enriched microalgae types for biofuel production and determine the possible microalgae biofuels, biomass conversion technologies, and processes to biofuels, and (iv) to assess the future prospects of the process development planning along with integrated design of some other value-added products besides biofuel.

**General perspective of microalgae**

Microalgae are referred as photosynthetically driven single or multi-cellular living being, the habitat of moist environment either on the solid mud or float on various water types, e.g., fresh water, marine water, wastewater with the presence of sunlight, or artificial light. The scientific consensus is that through photosynthesis respiration, they convert CO₂ to O₂ and generate large amounts of cellular energy content embedded with sugar, protein, and lipid [24–27].

Nowadays, industrialization and urbanization threaten the existing ecosystem severely by dumping heavy metal waste containing phosphorus, nitrogen, sulfur and others as well as exhaling high amount CO₂ to the free air. Another knocking threat to the energy sector is rapid depletion of fossil fuel worldwide due to excessive energy uses [28–30]. With this circumstance, microalgae cultivation in the wastewater, unused fresh, and saline water, drainage is considered as suitable scientific solution for green energy due to some favorable aspects such as multi-functionality, genuine conversion competency biologically and flexibility with growth system, wastewater accumulation, CO₂ sequestration, and large amount of carbohydrate–lipid–protein content. To note, carbohydrate–lipid–protein are the main components to generate divergent biofuels (e.g., bio-oil, biodiesel, biobutanol, and others) and biogas (e.g., bio-hydrogen) [31, 32]. The cellular components of microalgae are composed of huge fraction of lipid, protein, and carbohydrates resulting in the driving factors of biofuel

| Microalgae name          | Type             | Description in brief                                                                 |
|--------------------------|------------------|--------------------------------------------------------------------------------------|
| *Chlamydomonas reinhardtii* | Chlorophyta      | Genetically modified by sex-cross, contains high amount of carbohydrate, lipid and protein in cell wall |
| *Chlorella* sp.          | Chlorophyta      | Unicellular green microalgae, source availability of tropical water with enough solar light |
| *Spirulina platensis*    | Chlorophyta      | Spiral-shaped multi-cellular microalgae (with no true nucleus), fresh water habitant, contains lipopolysaccharides and peptidoglycan (carbohydrate components) in cell wall as well as cyanophycean and starch are the main carbohydrate storage products |
| *Chlorella vulgaris*     | Chlorophyta      | Spherial shaped, single cellular (with nucleus) microalgae, grows in both fresh and marine water with adequate sunlight, contains cellulose and hemicelluloses (carbohydrate components) in cell wall and starch is the main carbohydrate storage product |
| *Botryococcus braunii*   | Chlorophyta      | Green microalgae, shape type pyramidal, source availability of tropical and oligotrophic freshwater such as lakes, ponds, estuaries |
| *Ostreococcus tauri*     | Chlorophyta      | Eukaryote and unicellular                                                             |
| *Phaeodactylum tricornutum* | Phaeodactylum | Salt water diatoms                                                                   |
| *Nannochloropsis* sp.*   | Heterokont       | Grown in both saline and fresh water, genetically modified and paralleled recombinant microalgae type |
| *Symbiodinium* sp.*      | Fungia repanda   | Source availability in sea water, advanced eukaryotic, dinoflagellates                 |
| Phytoplanktons            | Either prokaryotic or eukaryotic | Usually autotrophic, source availability at saline and tropical water sources such as lakes, ponds with sufficient solar energy |
| *Cyanobacterial Mats*    | Prokaryotic      | Easily grown in saline water                                                          |
| *Saccharina japonica*    | Brown type of microalgae | Grown at sea and coastal water sources                                               |
| *Chlorococum* sp. and  *Spirogyra* sp.* | Cyanobacteria/blue-green algae | Shape type spiral, source availability in usually moist environment, marine and fresh water sources, grown randomly in tropical areas where sunlight is available sufficiently |
production. Table 1 presents some well-known potential microalgae candidates for biofuels. These species were extensively researched in the laboratory and large-scale applications so far. Type and description of these species have been tabulated to present a detailed view of selected species, suitable growth conditions (such as water type and region for cultivation), availability, and cellular specifications. Table 2 represents prime microalgae cellular component composition of several well-known microalgae species for biofuel production [24, 33, 34].

**Biofuels from microalgae**

Numerous biofuels, e.g., bioethanol, biodiesel, biooil, biomethane, bio-hydrogen, and others, have been extracted from microalgae [46, 47]. Nano-particles’ incorporation with microalgae cultivation (e.g., cell suspension, cell separation, and cell harvesting), biofuel conversion technologies, and biofuel application have amplified the overall yield in every stage [22]. According to the previous studies, a very small amount of colloidal hydrous iron(III) oxide particles boosted almost 100% microalgae cell suspension; magnetic particles incorporated with aluminum sulfate were very effective for cell separation from the mixed culture of *Anabaena* and *Aphanizomenon* microalgae species; silver nano-particles application on *Chlamydomonas reinhardtii* and *Cyanotothe 51142* microalgae harvesting increased 30% higher biomass productivity; and calcium-oxide nano-particles escalated the large-scale biodiesel conversion yield up to 91% via catalytic transesterification [18, 22, 48]. This study summarized the overall microalgae cultivation integrated with nano-particles until biofuel production in Fig. 2. Different biofuels from microalgae and conversion processes are diagrammed in Table 3.

**Preparing techniques of nano-additives for microalgae biofuel**

Magnetic nano-particle (NP) powder has been enumerated to the microalgae cell suspension in the photobioreactor cultivation process to flocculate cells for uniform distribution of nutrients and light all over the reactor. Immunomagnetic detection and modification of microalgae cell by NPs are another well-practiced method for cell suspension enhancement. Nano-liquid has been injected to the cell culture for microalgae harvesting and bio-separation through this technique. Silver nano-materials have also been implemented on the photobioreactor surface coating for higher light accessibility [22]. Along with microalgae culture and harvesting, sphere nano-particles have been enacted during hydrolysis, lipid extraction, transesterification, and biofuel purification from microalgae via irradiation and ultra-sonication methods and much higher biofuel yield have been obtained. Another established method of nano-materials application includes enzymatic nano-catalyst, lipase carrier. The reactant diffusion rate enhancement by the NPs to the active side of lipase has been determined by Eq. 1 [55]:

\[
R_{df} \propto \frac{1}{D^2},
\]

where \(R_{df}\) = diffusion rate to the active sides of lipase and \(D\) = diffusion path diameter of reactant to the access of lipase active side.

NPs for biofuel doping can be formulated by either physical or chemical methods. For instance, plasma-arc, sol–gel method has been presented as chemical method and ball mill process (agitation rate: 450 rpm) was presented as a physical method for NPs’ preparation in the previous studies [56–58]. Subsequently, NPs

**Table 2 Approximate carbohydrate–protein–lipid–ash content composition of suitable microalgae species (dry weight) for biofuel production [32, 43–45]**

| Type of microalgae       | Total sugars (%) | Protein (%) | Lipids (%) | Others (including ash content) % |
|--------------------------|------------------|-------------|------------|----------------------------------|
| *Chlamydomonas reinhardtii* | 48               | 17          | 21         | 14                               |
| *Chlorella* sp.          | 56               | 22          | 19         | 3                                |
| *Spirogyra* sp.         | 20               | 55          | 16         | 9                                |
| *Porphyridium cruentum*  | 35               | 50          | 11         | 4                                |
| *Spirulina platensis*    | 60               | 12          | 8          | 20                               |
| *Dunaliella salina*      | 57               | 32          | 6          | 5                                |
| *Bellerochea* sp.        | 3                | 24          | 15         | 3                                |
| *Chaetoceros* sp.        | 2                | 18          | 18         | 3                                |
| *Rhodomonas* sp.         | 9                | 74          | 15         | 2                                |
| *Scenedesmus* sp.        | 18               | 56          | 12         | –                                |
were doped with microalgal biofuel (e.g., microalgae oil, biodiesel, bioethanol, and others) with different doses (e.g., 25 ppm, 50 ppm, 100 ppm, and others) via ultrasonication processing by the presence of magnetic stirrer and implemented on compression ignition (CI), direct ignition (DI) engines without any engine modification. NPs are dispersed in a base fuel and smoothen potential agglomerate into nano-scale due to its’ larger surface area and surface energy [58–61]. The ultra-sonication method was conducted with various parameters such as frequency (e.g., 20 kHz, 40 kHz, and 45 kHz), power (e.g., 120 W and 220 W), and time (30 min and 60 min) [60, 62, 63]. Cationic surfactants, e.g., tetra methyl ammonium hydroxide, cetyl trimethyl amonium bromide, have been incorporated on the nano-particle surface for a negative-charge envelope formation.

**Fig. 2** Process flow diagram of carbon capture, water treatment and biofuels production from microalgae incorporated with nano-particles [18, 25, 49–54]
| Biofuel | Conversion processes | Some potential nano-additives for biofuel yield enhancement | References |
|---------|----------------------|----------------------------------------------------------|------------|
| Bioethanol, biobutanol, biomethanol, bioacetone | Simultaneous saccharification and fermentation (SSF) Separate hydrolysis and fermentation (SHF) Simultaneous saccharification and co-fermentation (SSCF) Separate hydrolysis and co-fermentation (SHCF) Dark fermentation Photo fermentation Anaerobic fermentation Acetone–butanol–ethanol (ABE) fermentation Consolidated bioprocessing | Fe$_2$O$_3$, CeO$_2$-CNT and others | [42, 49, 85–89] |
| Biodiesel | Lipid hydrolysis and chemical, physical, enzymatic transesterification Interestenfication Acidolysis Alcoholysis associated with glycerolysis Folch method (use of chloroform–methanol) Bligh and dyer method (use of chloroform–methanol) Modified method of the Folch/Bligh and dyer methods (use of methyl-tert-butyl-ether) Superior solvent extraction method (use of chloroform) Direct or in situ supercritical transesterification Post-transesterification Wet extraction method Deep eutectic solvent (DES) method | ZrO$_2$, TiO$_2$, Al$_2$O$_3$, CeO$_2$, SiO$_2$, Fe$_2$O$_3$, CaO-NPs and others | [46, 77, 78, 90–100] |
| Syngas | Gasification Pyrolysis Direct combustion Bio-electrochemical fuel cells Supercritical water gasification (SCWG) Hydrothermal gasification | TiO$_2$, CeO$_2$ and others | [88, 101–105] |
| Bio-electricity | Bio-electrochemical system contain anode, cathode and electrode Direct combustion | Fe$_2$O$_3$, CeO$_2$-CNT, CaO-NPs and others | [106–108] |
| Biomethane | Anaerobic digestion Catalytic hydrothermal gasification | SiO$_2$, nano-particles of platinum (Pt), nickel (Ni), cobalt (Co), iron (Fe) and others | [46, 109–112] |
| Bio-hydrogen | Solid-state anaerobic digestion Biophotolysis Photobiological hydrogen production Dark fermentation Photo fermentation Solid-state fermentation Suspended fermentation | TiO$_2$, CeO$_2$ and others | [113–118] |
| Bio-oil and bio-char | Hydrothermal (thermochemical) liquefaction Pyrolysis Expeller press Bead beating Ultrasound assisted extraction method Microwave extraction method Electroporation/electropereamabilization Slow pyrolysis Fast pyrolysis Torrefaction Hydrothermal carbonization Hydrothermal liquefaction Ion exchange Wet impregnation Catalytic hydrolypyrolysis Hydrogenation Hydrodeoxygenation | CeO$_2$-CNT, SiO$_2$-MgO nanohybrids and others | [46, 90, 119–127] |
| Microalgae and other biofuel | Sources for biofuel extraction | Nano-particles (NPs) | Dosage | Combinations of biofuel and nano-particle blends | Application output | References |
|-----------------------------|--------------------------------|----------------------|--------|-----------------------------------------------|-------------------|-----------|
| Biodiesel Caulerpa racemosa | TiO$_2$                        | 50 ppm               | 100 ppm| B2050 ppm B20100 ppm                         | Reduction of hydrocarbon (HC), carbon-monoxide (CO) Nitrogen oxide (NO$_x$) emission increase | [59]       |
| Biodiesel Madhuca longifolia | ZrO$_2$                        | 100 ppm              | 200 ppm| BD100T100 ppm BD100T200 ppm                  | Reduction of 5.8% unburned HC, 9.3% CO, 2.7% smoke and 6.6% NO$_x$ emission | [128]     |
| Biodiesel blended with diesel Jatropha curcas | Al$_2$O$_3$ CeO$_2$ | 30 ppm | 30 ppm | B20A30C30 ppm                                | 12% improved brake thermal efficiency Reduction of 30% NO$_x$, 60% CO, 44% HC and 38% smoke | [61]       |
| Biodiesel Jatropha curcas | Al$_2$O$_3$ CeO$_2$ | 30 ppm | 30 ppm | B100A30C30 ppm                                | Improved brake thermal efficiency Reduction of NO$_x$, CO, HC and smoke | [61]       |
| Biodiesel Botryococcus braunii | TiO$_2$ SiO$_2$ | 50 ppm | 100 ppm | B20TiO$_2$SiO$_2$50 ppm B20TiO$_2$SiO$_2$100 ppm | Increased calorific value Decrease in brake-specific fuel consumption (BSFC) Improved brake thermal efficiency (BTE) Reduction of ignition delay time Improved brake thermal efficiency Improvement of combustion characteristics Minimum CO, HC Maximum NO$_x$, CO$_2$ | [60]       |
| Biodiesel Pongamia pinnata | Rh$_2$O$_3$ | 100 nm | 100 nm | B100Rh$_2$O$_3$5 ppm | Reduces CO, 37% NO$_x$, 45% unburnt HC Improvement of thermal efficiency | [58]       |
| Biodiesel Glycine max | Co$_3$O$_4$ | 100 mg/l 38–70 nm | 100 Co$_3$O$_4$ | 1.03% better engine performance than usual biodiesel combustion Reduction of smoke and 7.46% NO$_x$ emission | | [56]       |
| Biodiesel Glycine max | Al–Mg | 100 mg/l 38–70 nm | 100 Al–Mg | Better engine performance than usual biodiesel combustion Reduction of smoke and 16.33% NO$_x$ emission | | [56]       |
| Biodiesel Jatropha curcas | Al$_2$O$_3$ Al$_2$O$_3$ Carbon nano-tube (CNT) Al$_2$O$_3$ CNT | 25 ppm 50 ppm | BA$_2$O$_3$ ppm BA$_2$O$_3$ ppm BCNT25 ppm BCNT50 ppm BA$_2$O$_3$CNT 25 ppm | Considerable enhancement of brake thermal efficiency Marginal reduction of harmful emissions Improved heat transfer rate Short ignition delay effect Enhancement of heat conduction properties and surface area/volume ratio | | [129]     |
| Biodiesel Azadirachta indica | Ag$_2$O | 5 ppm | 10 ppm | B100Ag$_2$O 5 ppm | Decrease of 12.22% CO, 10.89% HC, 4.24% NO$_x$ and 6.61% smoke Enhancement of brake thermal efficiency with reduction in brake-specific fuel consumption | [63]       |
to resist NPs’ sedimentation [56, 64]. After biofuel-NPs’ doping, the NP-blended biofuel was preserved under the static condition to stabilize for fuel purpose [59]. Several potential NPs–microalgae-biofuel blends are tabulated in Table 4. The morphology and crystalline phases after NP-doping were analysed through a scanning electron microscope and X-ray diffraction, respectively [61]. *Botryococcus braunii* oil was doped with almost 50 nm sized titanium dioxide (TiO2) and silicon dioxide (SiO2) incorporated with biodiesel (B20) of different doses for enhanced fuel efficiency in CI engine [60]. *Caulerpa racemosa* green algae biodiesel (B20) was doped with 50 nm sized zirconium dioxide (ZrO2) by the different doses for CI engine [59].

**Future applications of nano-additives for microalgae-biofuel**

Nano-additive application on microalgae-biofuel enhancement has been categorized into several stages from raw material production to end-product implications. The stages are:

(i) nano-additives for microalgae cultivation;

### Table 4 (continued)

| Microalgal and other biofuel | Sources for biofuel extraction | Nano-particles (NPs) | Dosage | Combinations of biofuel and nano-particle blends | Application output | References |
|-----------------------------|--------------------------------|----------------------|--------|------------------------------------------------|-------------------|------------|
| Biodiesel                   | Azadirachta indica            | Ag2O                 | 10 ppm | B100Ag2O                                       | Reduction of 16.47% CO, 14.21% HC, 6.66% NOx, and 8.34% smoke | [63]        |
|                             |                                |                      |        | 10 ppm                                         | Significant improvement of brake thermal efficiency with reduction in brake-specific fuel consumption |            |
| Biodiesel                   | *Jatropha curcas*              | Co3O4                | –      | B10Co3O4, B20Co3O4, B100 Co3O4                | Reduction of the ignition delay | [57]        |
|                             |                                |                      |        |                                                | Improvement of combustion by its’ catalytic effect |            |
|                             |                                |                      |        |                                                | Burning of the carbon deposits |            |
|                             |                                |                      |        |                                                | Reduction of black smoke |            |
| Biodiesel–bioethanol        | Vegetable oil–alcohol         | Fe2O3                | 150 ppm| B8 Fe2O3, 150 ppm                              | 1% increase in thermal efficiency | [57]        |
|                             |                                |                      |        |                                                | 60% reduction of emission characteristics, reduction of NOx, CO, HC and smoke |            |
|                             |                                |                      |        |                                                | Burning of the carbon deposits |            |
|                             |                                |                      |        |                                                | Reduction of black smoke |            |
|                             |                                |                      |        |                                                | Presence of secondary atomization, disruption of primary droplet |            |
|                             |                                |                      |        |                                                | Complete combustion |            |
| Biodiesel                   | Azadirachta indica            | CaCO3 nano-fluids   | 3 mg/l | B100CaCO3                                      | Reduction of 4.08% specific fuel consumption reduction | [130]       |
|                             |                                |                      | 5 mg/l |                                                | 3.9% increase of brake thermal efficiency |            |
|                             |                                |                      |        |                                                | 8.57% higher mechanical efficiency |            |
|                             |                                |                      |        |                                                | Reduction of NOx and HC emission |            |
| Biodiesel                   | *Linum usitatissimum*          | CuO                  | 80 ppm | B20CuO                                         | Significant increase in thermal efficiency | [62]        |
|                             |                                |                      | 40 μmol/L |                                                | 3–4% increase of brake thermal efficiency |            |
|                             |                                |                      | 80 μmol/L |                                                | 25% reduction of CO |            |
|                             |                                |                      | 120 μmol/L |                                                | Reduction of NOx and HC emission |            |
| Biodiesel–castoroi–diesel–bioethanol | Vegetable oil–*Ricinus communis* oil | CeO2-CNT | 25 ppm | –                                              | Reduction of HC, CO, CO2, smoke and NOx | [84]        |
|                             | Vegetable oil–alcohol          |                      | 50 ppm |                                                | Increase of calorific value and brake thermal efficiency |            |
|                             |                                |                      | 100 ppm|                                                | |            |
| Biodiesel                   | FeCl3                           |                      | 20 μmol/l | BFeCl3                                         | Reduction of HC, CO, CO2, smoke and NOx | [84]        |
|                             |                                |                      |        |                                                | Increase of calorific value and brake thermal efficiency |            |
(ii) nano-additives for microalgae biomass conversion to biofuels;
(iii) nano-additives for microalgae-biofuel applications.

Nano-additives for microalgae cultivation

Improvement of the microalgae biomass productivity with the minimum area requirement is considered as the main purpose of nano-additive application in the microalgae culture. Nano-technology is being applied for enzyme immobilization, since nano-structures broaden the immobilization surface area causing high loading power of enzymes and stability of immobilized enzymes. Enzyme immobilization can be performed in different approaches such as electrospun nanofibers, covalently attached enzymes into nano-fibres, and enzyme aggregate coatings on nanofibers. The enzyme immobilization was investigated on various carbon nano-particles, e.g., graphene oxide (GO), multi-walled carbon nano-tubes (MWNTs), oxidized-MWNTs (O-MWNTs), and fullerene (C60). Among these nano-structures, O-MWNTs yielded the highest, and C60 yielded the lowest [21, 22]. Nano-particles’ (NPs’) application was implemented on several microalgae species harvesting and yielded outstanding in each phase of the application. Application of nano-particles on microalgae harvesting claimed 20–30% microalgae production cost in large-scale application [22]. Table 5 presents the harvesting efficiency of several microalgae species cultivated with various nano-particles. Nano-particles also boosted the light conversion efficiency in photobioreactor (PBR) during the microalgae culture period. It is also worth mentioning that PBR is run by artificial light sources consuming additional energy and cost. However, during biomass growth, light sources do not reach in culture broth inadequately due to self-shading and biofilm formation on the PBR surface.

To achieve desired illumination properties and photo-conversion efficiency in the PBR, various light-emitting diodes (LEDs) equipped with nano-materials fabrication are being implemented recently. Gallium aluminium arsenide (GAA)-fabricated LEDs have been experimented on laboratory scale algae culture so far. It was evident that the application of optical fibres in algal culture saves much energy, additional light cost, and increase efficiency [18]. Another latest development of nano-particle, integration of metallic nano-particles (MNP) with localized surface plasmon resonance (LSPR) amplifies the light scattering at certain wavelength [65]. An experimental study revealed that silver nano-particles’ (Ag-NPs’) suspension in plasmonic mini-PBRs backscatter blue light strongly. The blue light increased the photosynthetic efficiency significantly for green microalgae, *Chlamydomonas reinhardtii*, and blue-green microalgae, *Cyanothece* 51142, and 30% higher microalgae biomass have been obtained [48]. Nano-particles addition in microalgae cultivation can also improve the yield of the CO₂ absorption from the atmosphere and CO₂ sequestration that can boost the biomass growth. For instance, nano-bubbles in microalgae culture remained stable for a longer time. Nano-bubbles also floated algae biomass into the culture, ensured high mass transfer efficiency, and improved biomass density by sufficient accumulation of CO₂, O₂ stripping, and minor buoyancy. Moreover, nano-bubbles suspended the biomass around airlift-loop bioreactor (ALB) and required less energy than micro-bubbles. Uniform nonporous membrane of ALB was also capable of producing 100 nm sized bubbles for this purpose [18, 66, 67]. The previous studies also delineated that nano-additives played a significant role in flocculation and separation process before biofuel production besides microalgae harvesting [22].

### Table 5  Harvesting efficiency of various microalgae species with the addition of nano-particles

| Microalgae species | Nano-particles                                                                 | Harvesting efficiency (%) | References |
|--------------------|--------------------------------------------------------------------------------|---------------------------|------------|
| Chlorella ellipsoidea | Modified Chu 13, doses 380 mg/g                                                | 90                        | [22]       |
| Chlorella ellipsoidea | Fe₃O₄ nano-particles functionally coated with polyethylenimine (PEI)           | 97                        | [22]       |
| Chlorella ellipsoidea | Iron oxide and cationic polyacrylamide (CPAM), doses 120 mg/l                 | > 95                      | [131]      |
| Batryococcus braunii | Modified Chu 13, doses 20 mg/g                                                 | 100                       | [22]       |
| Batryococcus braunii | Iron oxide and CPAM, doses 15 mg/l                                            | > 95                      | [131]      |
| Marine Nannochloropsis sp. | Magnetic Fe₃O₄ nano-particles, doses 99 mg/g                                  | 95                        | [22]       |
| Chlorella sp. | Surface-functionalized iron-oxide nano-particles (SF-IONPs) with PDA (polydimethylammonium chloride) | 99                        | [22]       |
| Chlorella sp. | Chitosan/magnetic nano-particles (CS-MNPs)                                    | 97                        | [132]      |
| Chlorella sp. KR-1 | Naked Fe₃O₄ magnetic particles                                                | 90                        | [22]       |
Nano-additives for microalgae biomass conversion to biofuels
Among microalgae biofuel, biodiesel has been appeared as the most popular and commercial biofuel in the mobile fuel market. For the case of biodiesel production, applications of acidic and basic nano-catalyst spheres can substitute the chemical compounds such as sodium methoxide by reacting with the free fatty acids and oils. Additional advantages of these nano-catalysts are recyclability and positive economical impact. Moreover, reactions can take place with low temperature and pressure as well as this approach reduces the contaminant release to the environment borne by sodium methoxide [6]. An industrial biodiesel study demonstrated that commercial CaO-NPs presented 91% biodiesel conversion efficiency during scaled-up catalytic transesterification [18]. Experimental study of microalgae cultivation with spherical nano-particles composed with sand (silica) and calcium compounds revealed that microalgae cellular growth increased drastically without harming harvesting as well as biofuel production from vegetable oil. The best way to address this issue was described as one of the major driving factors for commercial biofuel, biofuel production cost dropped effectively [6–8, 68]. The experimental study mentioned that mesoporous silica nano-catalyst, Ti-loaded SBA-15 presented ten times higher free fatty acids (FFA) and water tolerance level than any other catalysts for biodiesel production from vegetable oil as well as this nano-catalyst performed three times better than other effective nano-catalysts titanium silicalite-1 (TS-1) and titanium dioxide silicate (TiO$_2$-S) [69].

Moreover, Ti-loaded Santa Barbara Amorphous-15 (SBA-15) nano-catalyst application reduced the chemical (alkaline catalyst, NaOH) cost of transesterification process for biodiesel production by recycling the nano-catalyst as well as this process is more environment-friendly [6, 69]. On the other hand, sulfate incorporated Ti-SBA-15 also performed as biocatalyst to convert vegetable oil to 100% esterified bio-lubricant. In consequences, this nano-particle can be expected to produce bio-lubricant from bio-oil of microalgae [70]. Other study showed that Niobia (N$_2$O$_5$) incorporated with SBA-15 application on biodiesel production from biomass through esterification presented a significant scenario for microalgae-biodiesel yield [71]. Another study delineated that the enzyme extracted from Pseudomonas cepacia conjugates with the nano-particles such as polyacrylonitrile (PAN) nanofibre, Fe$_3$O$_4$ and nanoporous gold; silica nano-particles with lipase enzyme from Rhizopus miehei; ferric silica and magnetic nano-particles with lipase from Burkholderia sp., polyacrylonitrile nano-fibre bound with lipase from Thermomyces lanuginosa has performed very effectively to produce biodiesel from various bio-oil by the transesterification process [7]. Furthermore, nanomagnetic biocatalyst of KF/CaO–Fe$_3$O$_4$, Li(lithium)-doped CaO, Fe$_3$O$_4$–CaO, sulfate (SO$_4$$^-_2$) incorporated Zn (zirconium), sodium titanate and carbon-based nano-tubes and nano-particles reached up to 95% or above biodiesel yield from diverse types of biomass and biodegradable waste [7, 72]. Besides enhancement of biodiesel-yield efficiency, a type of NP, zeolite (an alumina silicate mineral), has been used as commercial absorbent during the transesterification process. Zeolites absorbed the undesirable moisture content (4–6%) and produced pure glycerine as co-product besides biodiesel. Mesoporous nano-particles also presented a vital capability for continuous microalgal-biofuel generation from biomass without cell lysis. Zeolites also removed lipids from the microalgae cell membrane [18, 73]. Table 6 presented the applications of nano-additives for biodiesel-yield enhancements during microalgae to biofuel conversion, suitable conversion processes, and efficiencies.

Nano-particles were efficiently capable to perform as immobilizing beds for valuable enzymes due to their large surface area-to-volume ratio. This capability of NPs broke down the long chains of complex sugar of microalgae, vegetable oil to 100% esterified bio-lubricant. In consequences, this nano-particle can be expected to produce bio-lubricant from bio-oil of microalgae [70]. Other study showed that Niobia (N$_2$O$_5$) incorporated with SBA-15 application on biodiesel production from biomass through esterification presented a significant scenario for microalgae-biodiesel yield [71]. Another study delineated that the enzyme extracted from Pseudomonas cepacia conjugates with the nano-particles such as polyacrylonitrile (PAN) nanofibre, Fe$_3$O$_4$ and nanoporous gold; silica nano-particles with lipase enzyme from Rhizopus miehei; ferric silica and magnetic nano-particles with lipase from Burkholderia sp., polyacrylonitrile nano-fibre bound with lipase from Thermomyces lanuginosa has performed very effectively to produce biodiesel from various bio-oil by the transesterification process [7]. Furthermore, nanomagnetic biocatalyst of KF/CaO–Fe$_3$O$_4$, Li(lithium)-doped CaO, Fe$_3$O$_4$–CaO, sulfate (SO$_4$$^-_2$) incorporated Zn (zirconium), sodium titanate and carbon-based nano-tubes and nano-particles reached up to 95% or above biodiesel yield from diverse types of biomass and biodegradable waste [7, 72]. Besides enhancement of biodiesel-yield efficiency, a type of NP, zeolite (an alumina silicate mineral), has been used as commercial absorbent during the transesterification process. Zeolites absorbed the undesirable moisture content (4–6%) and produced pure glycerine as co-product besides biodiesel. Mesoporous nano-particles also presented a vital capability for continuous microalgal-biofuel generation from biomass without cell lysis. Zeolites also removed lipids from the microalgae cell membrane [18, 73]. Table 6 presented the applications of nano-additives for biodiesel-yield enhancements during microalgae to biofuel conversion, suitable conversion processes, and efficiencies.

Table 6: Applications of nano-additives for biodiesel-yield enhancements during microalgae to biofuel conversion, suitable conversion processes, and efficiencies

| Nano-additives                                      | Conversion processes         | Conversion efficiency | References |
|-----------------------------------------------------|------------------------------|-----------------------|------------|
| Calcium oxide nano-particles’ blends (CaO-NPs)       | Catalytic transesterification| 91%                   | [18]       |
| Mesoporous silica nano-catalyst, Ti-loaded SBA-15    | Transesterification          | 10 times higher yield | [6, 69]    |
| Niobia (N$_2$O$_5$) incorporated with SBA-15         | Esterification               | Significant increase  | [71]       |
| PAN nanofibre, Fe$_3$O$_4$ and nanoporous gold incorporation, silica nano-particles, ferric silica and magnetic nano-particles incorporation, polyacrylonitrile nano fibre transesterification process | Transesterification          | Effective rise in biodiesel productivity | [7] |
| KF/CaO–Fe$_3$O$_4$, Li(lithium)-doped CaO, Fe$_3$O$_4$–CaO, sulfate (SO$_4$$^-_2$) incorporated Zn (zirconium), sodium titanate and carbon-based nano-tubes and nano-particles | Transesterification | $\geq$ 95% | [7, 72] |
converted it to simple sugar, and consequently turned into bioethanol via the fermentation process. Due to the large surface area, the interaction between the surface of the nano-particles and fuel surrounded by them achieved adequate stability to overcome density variations. Nano-particles prepared by carbon nano-tubes doped with iron-oxide nano-particles presented excellent biocatalytic efficiency in a bioreactor, recyclable option enzyme applications, less capital cost as well as better enzyme loading for this purpose [6, 7, 74]. A catalytic study mentioned that mesoporous niobium oxide (N₃O₃) application on complex sugar (sucrose) possessed both Lewis acid (LA) and Bronsted acid (BA) sites to convert fructose to 5-hydroxymethylfurfural (HMF) with the highest yield so far. The synergistic catalytic effect from a large amount of both LA and BA acid site quantities and surface areas played a positive impact on the reaction rate with a few times faster conversions [75]. Functionalised multiwall carbon-nano-tube (MWCNT) immobilization presented more than 55% initial activity of microalgal hydrolysis for Candida Antarctica. Nano-catalysts such as cobalt–molybdenum fabricated with Si/Al have been experimented on Botryococcus braunii and presented stable hydrocarbons. Another nano-catalyst, mobilen composition of matter No. 41 (MCM-41), mesoporous material effectively reduced oxygenated fractions of bio-oil through catalytic pyrolysis [18].

Nano-catalysts can synthesize biomethane produced from microalgae from wastewater into pure hydrogen and carbon content. In a further step, this methane can produce biogas through anaerobic digestion. Biogas could be used as raw material of bio-fuelled electricity generation further. The elemental carbon can also be utilized as pure nano-graphite for the applications on batteries, aerospace, automobiles, and others [6]. The latest development conducted by quantum sphere on marine microalgae species evinced biogasification from wet microalgae biomass by metal nano-catalysts [18]. Besides that, nano-particles such as TiO₂, CeO₂ were manifested to improve 10–11% of the biogas yield from wastewater treatment. Therefore, these nano-particles can be projected further for the biomethane production from microalgae grown in wastewater [7]. Apart from that, nano-substances with SiO₂, nano-particles of platinum (Pt), nickel (Ni), cobalt (Co), and iron (Fe) can increase methane production from biomass up to 70%. Nano-fly ash and nano-bottom ash were proved to increase biomethane yield up to 3.5 times more. Nano-metal oxides, e.g., MgO, CaO, and SrO, nano-materials such as silica, single-walled nano-tubes of carbon-based materials, nano-clay, and nano-zero valence metal applications in biodiesel, bio-hydrogen, and biomethane production from microalgae and other biomass presented outstanding yield. These nano-particles can be projected for large-scale microalgal-biofuel production in the future to obtain revolutionary yield [7, 8]. In addition, nano-hybrid catalysts are being commercialized as emulsion stabilizers in industrial applications. For instance, quaternary ammonium salts have been documented as an emulsifying surfactant for separation, extraction, isolation, and purification of biofuels. Carbon nano-tubes with silica fusion, SiO₂–MgO nano-hybrids have been performed as stabilizers on bio-oil in water emulsion due to its inherent hydrophobicity and resulted in full conversion in different emulsion phases [18].

**NANO-ADDITIONS FOR MICROALGAE-BIOFUEL APPLICATIONS**

Solid nano-particles, nano-fluids, or nano-droplets with biofuel and fossil fuel were proved to improve the fuel lubricity, cetane number, burning rate, chemical reaction, catalytic performance, fire/flash point, heat and mass transfer efficiency and water co-solvency as well as decrease delay period [76, 77]. That resulted in more complete and cleaner combustion of microalgal biofuel mixed with fossil fuel in compression ignition (CI), spark ignition (SI), and direct ignition (DI) engines. In line with that, nano-technology applications showed the capability of amplifying microalgal-biofuel combustion efficiency and reduced soot, NOₓ, smoke, HC, CO₂ and CO emission to the environment up to 72% [6, 76, 78]. Application of solid nano-additives such as alumina (Al₂O₃), CERIA, carbon nano-tubes (CNT), Co₃O₄, ZrO₂, La₂O₃, CeO₂, SiO₂, Ni₃O₄, TiO₂, ZnO, Fe₂O₃, CuO, CeₓZr(1−x)O₂, and amide-doped MWCNTs-CeO₂ boosted the engine power, torque, and brake thermal performance of biodiesel (extracted from microalgae and other biomass) in CI and DI engines up to 11% [59, 76, 79, 80]. The experimental study of nano-particles on DI engines demonstrated that nano-particles blended with biodiesel as well as diesel–biodiesel mixture performed outstanding. The effectiveness was higher compared to usual catalysts [61, 81]. Another study presented that nano-particles of CeO₂ incorporated with an emulsion of biofuel with sol–gel combustion technology performed excellent monocylinder 4 stroke direct CI and DI engines without any hardware modification. Nano-particles addition with biofuels escalated the fuel calorific value, fastened evaporation rate, improved brake-specific fuel consumptions and thermal efficiency, reduced greenhouse gases (GHGs) such as CO, NOₓ, and smoke, and unburned HCs. Chemical reactions between CeO₂ and GHGs gases are presented in Rc. 2, Rc. 3, and Rc. 4 [82]:

\[
(2y + x)CeO₂ + H_xC_y \rightarrow \left[\frac{2y + x}{2}\right]Ce_2O_3 + \frac{x}{2}H_2O + \frac{y}{2}CO_2
\]

(2)
2CeO₂ + CO → Ce₂O₃ + CO₂

Ce₂O₃ + NO → 2CeO₂ + ½N₂.

In contrast, liquid nano-additive, nano-Al-droplet application (nano-suspension) on biofuel mixture has been manifested more efficient than even micro-suspension. Liquid nano-additives also presented outstanding performance by achieving better suspension than n-decane-based fuels. Nano-Al suspension with ethanol was strong enough for a longer period than other particles, because ethanol tended to form a gel around the nano-particles due to higher viscosity [74]. Nano-droplets coated a monolayer on the mechanical parts of the engine touched with liquid fuel and improved fuel efficiency [18]. In addition, NPs such as nano-Al, Al₂O₃, CuO, MgO, MnO, and ZnO incorporated with water–diesel–biodiesel (E10) emulsion and bioethanol performed remarkably. Among these NPs, Al₂O₃ performed the best because of mandate disabling, consistent torque boosting, higher heat of combustion, super-high DTG max value, tiniest size of water droplets, the minimum value of brake-specific fuel consumption, and lowest values of Soot, NOₓ, CO, and HC [19, 83].

Challenges and future prospects

Although nano-additive applications played significant role in microalgae cultivation, harvesting, conversion to biofuel and biofuel applications to enhance the efficiency, yet some challenges remained before the implementation of nano-additives for the mercantile approach. Most of the nano-additives from experimental research were not well-characterized in terms of particle size, shape, and size distribution as well as clustering [84]. Before large-scale application, well characterization of nanoparticles and nano-fluids must be studied comprehensively. Appropriate nano-additive selection, preparation methods, and time for the selected application should be emphasized for optimum productivity. The effect of nano-catalyst implementation for microalgae-biofuel combustion quality, engine performance, and gas emission should be well studied and well-understood before implementation. In line with that, the availability of appropriate nano-additives with large amount might be a challenge for mass application though for laboratory scale, nano-additives are adequately available. Another constraint is cost-effectiveness of nano-catalysts for an industrial application which may hinder the commercial perspective, since many nano-catalysts are quite expensive.

Along with the potential microalgae determination and biofuel generation, integration of a plant design of value-added co-products will be the predominant advantage of the overall project with the economical aspect. This review encouraged biofuel research and development (R&D) sector worldwide to convert their unused, abandoned and wastewater sources, wet, and barren lands into microalgae farm as an eminent source of biofuel production. However, it should be highlighted that based on the existing research experiments, microalgae fuel production still stands at initial stage due to downward economic profile worldwide. Nano-additive applications on microalgae biofuel are yet confined into laboratory and pilot scale which can be counted as a significant limitation. Hence, it is strongly recommended to figure out large-scale process development with nano-additive applications for enhancement of microagal growth, biofuel transformation processes, and fuel utilization in CI and DI engines. Nano-additive applications at different stages from microalgae culture to end-product utilization have a strong possibility to gain economical feasibility. Therefore, the detailed techno-economic analysis must be commanded to determine whether NP applications on microalgae biofuel are economically favorable or not, since economical issue is one of the most effective factors behind large-scale plant setup. Besides, these applications also have positive impact on the environment with value-added co-product generation into near further. Since the nano-additive utilization manifested itself environment-friendly, still a comprehensive life cycle assessment should be conducted to present the environmental positivities transparently. Besides all these factors, public safety, impact on flora and fauna, and the possibility of bio-hazards are also needed to be analysed extensively before commercialization.

Conclusions

Microalgae utilization for biofuel production is undoubtedly desirable all over the world. Though this approach is energy-efficient and environment-friendly, experts are still looking for an innovation that can boost the microalgae-biofuel yield from primary stage to end product as well as shift the whole process towards a cost-effective fuel solution. Hence, this review was emphasized on the synergistic effect of nano-additive-enhanced microalgal biofuel for mercantile approach and fuel-yield extension. Application of various forms of nano-additives in different phases on microalgae growth to biofuel demonstrated an excellent outcome that may project revolutionary improvement of commercial microalgae biofuel. However, the sustainability analysis of stepwise production rounds for microalgae biofuel still presented a bare need of further research and innovative concepts. These concepts may determine the most appropriate nano-additive for the desired type of biofuel in the context of
economical aspect. Since nano-additive application on microalgae is quite new research concept, policy making and implementation of nano-additives will remain as the most vital issues for commercial output especially in developing countries. Therefore, managerial insights are needed to be emphasized further on proper policy, socio-economic impact, advantages and limitations for the overall system to attract the government and non-government fuel industries.

**Highlights**

- Enhancement of microalgae cultivation and harvesting by nano-bubbles and nano-particles application.
- Identification of suitable microalgae species, possible biofuels from microalgae, latest conversion technologies, processes, and required equipments.
- Excellent microalgal-biofuel yield by nano-droplet and nano-additives.
- Complete and cleaner combustion in fuel engines by nano-emulsion and nano-stabilizers.

**Abbreviations**

AEB: acetone–butanol–ethanol; Ag-NPs: silver nano-particles; AgO: silver oxide; ALB: airlift-loop bioreactor; Al2O3: alumina/alumina; Al-droplet: aluminum droplet; BA: brass; C60: fullerene; CaCO3: calcium carbonate; CeO2/CERIA: cerium oxide; CaO: calcium oxide; CaO-NPs: calcium oxide nanoparticles blends; CI: compression ignition; CO2: carbon-dioxide; CO: carbon mono oxide; CoO: cobalt oxide; CNT: carbon nano-tubes; CuO: copper oxide; Ce/ZrO2: cerium–zirconium oxide; CS-MNPs: chitosan/magnetic nano-particles; D: direct ignition; DES: deep eutectic solvent; DTGmax: maximum derivative thermogravimetry; FF: free fatty acids; Fe2O3: ferric oxide; FeCl3: ferric chloride; GAA: gallium aluminium arsenide; GHGs: greenhouse gases; G: graphene oxide; HCL: hydrochloric acid; HMF: 5-hydroxymethyl furfural; LA: Lewis acid; La2O3: lanthanum oxide; LEDs: light-emitting diodes; LSPRs: localized surface plasmon resonance; MWCNTs: multiwall carbon nanotubes; MCM-41: Mobil composition of matter No 41; MgO: magnesium oxide; MnO: manganese oxide; MNPs: metal nano-particles; N2O5: niobia/niobium oxide; NiO: nickel oxide; NOx: nitrogen oxides; O-MWNTs: oxidized MWNTs; PAN: polycrylonitrile; PBR: photobioreactor; PDA: polydimethylsiloxane; R&D: research and development; RhOx: rhodium oxide; SBA-15: santa barbara amorphous-15; SCWG: supercritical water gasification; SF-IONPs: surface-functionalized iron-oxide nano-particles; Si: spark ignition; SiO2: silicon dioxide; SSC-MNPs: simultaneous saccharification and co-fermentation; SHCF: separate hydrolysis and co-fermentation; SHF: separate hydrolysis and fermentation;SSF: simultaneous saccharification and fermentation; SrO: strontium oxide; TiO2: titanium dioxide; TiO2-S: titanium dioxide silicate; Zeolite: aluminosilicate mineral; ZnO: zinc-oxide; ZrO2: zirconium dioxide.

**Authors’ contributions**

The authors solely prepared this review article. All authors read and approved the final manuscript.

**Funding**

The authors would also like to acknowledge University of Technology Sydney for seed fund with (Org Unit 321740) and Account Number (2232397) for supporting this research.
63. Devarajan Y, Munuswamy DB, Mahalingam A. Influence of nano-additive on performance and emission characteristics of a diesel engine running on neat neem oil biodiesel. Environ Sci Pollut Res Int. 2018;25:26167–72.
64. Ranaware AA, Satpute ST. Correlation between effects of cerium oxide nanoparticles and ferrofluid on the performance and emission characteristics of a CI engine. IOSR J Mech Eng. 2012;2:78–95.
65. Steele JM, Grady NK, Nordlander P, Halas NJ. Plasmon hybridization in complex nanostructures. In: Brongersma ML, Kik PG, editors. Surface plasmon nanophotonics. Dordrecht: Springer; 2007. p. 183–96.
66. Zimmerman WB, Tesař V, Bandulasena H. Towards energy efficient nanoparticle additives in diesel engine. Int J Innov Res Sci Eng Technol. 2013;2:14–19.
67. Silitonga AS, Atabani AE, Mahlia TMI, Masjuki HH, Badruddin IA, Mekhilef S. Evaluation of the engine performance and exhaust emissions of bio-diesel engines fueled with biodiesel blends. Environ Sci Pollut Res Int. 2018;25:15307–25.
68. Kothari S, Patel P, Sahu A, Jaiswal D. Thermodynamic analysis of supercritical water pyrolysis of microalgae for high syngas production. Bioresour Technol. 2017;239:378–86.
69. Hu Z, Ma X, Li L, Wu J. The catalytic pyrolysis of microalgae to produce synthesis gas. Energy Source Part A. 2017;39:1167–75.
70. Wang S, Zhu J, Dai L, Zhao X, Liu D, Du W. A novel process on lipid extraction of microalgae for biodiesel production. Energy. 2016;115:963–8.
71. Mohamedzadeh Shirazi H, Karimia Sabiet J, Ghotbi B. Biodiesel production from Spirulina microalgae feedstock using direct transesterification near supercritical methanol condition. Bioresour Technol. 2017;239:378–86.
72. Chen S-Y, Mochizuki T, Abe Y, Toba M, Yoshimura Y. Ti-incorporated SBA-15 mesoporous silica as an efficient and robust Lewis solid acid catalyst for the production of high-quality biodiesel fuels. Appl Catal B Environ. 2014;148:149–154.
73. Sharma RV, Dalai AK. Synthesis of bio-lubricant from epoxy canola oil using sulfated Ti-SBA-15 catalyst. Appl Catal B Environ. 2013;142:143–604–14.
74. Silva A, Wilson K, Lee AF, dos Santos VC, Cons Bacilla AC, Mantovani KM, et al. Nb2O5/SBA-15 catalyzed poxanolic acid esterification. Appl Catal B Environ. 2017;205:498–504.
75. Liu G, Liao Y, Wu Y, Ma X. Synthesis gas production from microalgae gasification in the presence of Fe2O3 oxygen carrier and CaO additive. Appl Energy. 2018;121:955–65.
76. Liu X, Piao X, Wang Y, Zhu S, He H. Calcium methoxide as a solid base catalyst for the transesterification of soybean oil to biodiesel with methanol. Fuel. 2008;87:1076–82.
77. Gan Y, Qiao L. Combustion characteristics of fuel droplets with addition of nano and micron-sized aluminum particles. Combust Flame. 2011;158:354–68.
78. Kreiis HT, Nakagawa K, Peng Y-K, Koito Y, Zheng J, Tsang SCE. Niobium oxides: correlation of acidity with structure and catalytic performance in sucrose conversion to 5-hydroxymethylfurfural. J Catal. 2016;338:329–39.
79. Sinha VK, Sharrin. A review approach on exhaust emission reduction by nano and micron-sized aluminum particles. Combust Flame. 2011;16:350–6.
80. Karthikeyan S. Environmental effects of nano additive Co3O4 in grape seed oil biofuel fuelled in CI engine. Res J Chem Environ. 2014;18:14–8.
81. Ramanware AA, Satpute ST. Correlation between effects of cerium oxide nanoparticles and ferrofluid on the performance and emission characteristics of a CI engine. IOSR J Mech Eng. 2012;2:78–95.
82. Dhinesh B, Annamalai M. A study on performance, combustion and emission behaviour of diesel engine powered by novel nano nirium oleander biofuel. J Clean Prod. 2018;196:74–83.
83. Jones M, Li CH, Afjee A, Peterson G. Experimental study of combustion characteristics of nanoscale metal and metal oxide additives in biofuel (ethanol). Nano Res Lett. 2011;16:246.
84. Sharma T, Sairam K, Gopinath A, Kumareshan G, Velraj E. Effect of dispersion of various nanoadditives on the performance and emission characteristics of a CI engine fuelled with diesel, biodiesel and blends—a review. Renew Sust Energ Rev. 2015;49:563–73.
85. Kamirski W, Tomczak E, Góra A. Biobutanol—production and purification methods. Ecol Chem Eng. 2011;18:31–7.
86. Phwan CK, Ong HC, Chen WH, Ling TC, Ng EP, Show PL. Overview: comparison of pretreatment technologies and fermentation processes of bioethanol from microalgae. Energy Convers Manag. 2018;173:81–94.
87. Shokirkar H, Ebrahim S, Zaman M. Bioethanol production from acidic and enzymatic hydrolysates of mixed microalgae culture. Fuel. 2017;200:380–6.
88. Tsukahara K, Sawayama S. Liquid fuel production using microalgae. Jpn Petrol Inst. 2005;48:251–9.
89. Hossain N, Zaini J, Jall R, Mahlia TM. The efficacy of the period of saccharification on oil palm (Elaeis guineensis) trunk sap hydrolysis. Int J Technol. 2018;9:652–62.
90. Ranjith Kumar R, Hanumantha Rao P, Arumugam M. Lipid extraction methods from microalgae: a comprehensive review. Front Energy Res. 2015;2:1–9.
91. Feltex MMC, de Oliveira D, Ninois JL, de Oliveira JV. An overview of enzyme-catalyzed reactions and alternative feedstock for biodiesel production. New York: Federal University of Santa Catarina; Brazil: Intech; 2011.
92. Wang S, Zhu J, Dai L, Zhao X, Liu D, Du W. A novel process on lipid extraction of microalgae for biodiesel production. Energy. 2016;115:963–8.
93. Rahman MA, Aziz MA, Al-khalidi RA, Sabik N, Islam M. Biodiesel production from microalgae Spirulina maxima by two step process: optimization of process variable. J Radiat Res Appl Sci. 2017;10:140–7.
94. Mohamadzadeh Shirazi H, Karimia Sabiet J, Ghotbi B. Biodiesel production from Spirulina microalgae feedstock using direct transesterification near supercritical methanol condition. Bioresour Technol. 2017;239:378–86.
95. Cheng J, Qiu Y, Huang R, Yang W, Zhou J, Chen K. Biodiesel production from wet microalgae by using graphene oxide as solid acid catalyst. Bioresour Technol. 2016;221:344–9.
96. Kings AJ, Raj RE, Miriam LRM, Viswanathan MA. Cultivation, extraction and optimization of biodiesel production from potential microalgae Euglena sanguinolenta using eco-friendly natural catalyst. Energy Convers Manag. 2017;141:224–35.
97. Pan Y, Alam MA, Wang Z, Huang D, Hu K, Chen H, et al. One-step production of biodiesel from wet and unbroken microalgae biomass using deep eutectic solvent. Bioresour Technol. 2017;238:157–63.
98. Ehimen EA, Sun ZF, Carrington CG, Birch EJ, Eaton-Rye JJ. Anaerobic digestion of microalgae residues resulting from the biodiesel production process. Appl Energy. 2011;88:3454–63.
99. Razon LF, Tan RR. Net energy analysis of the production of biodiesel and biogas from the microalgae: haematococcus pluvialis and nanochloropsis. Appl Energy. 2011;88:3507–14.
100. Silitonga AS, Masjuki HH, Ong HC, Sebayang A, Sharma D, Kusumo F, et al. Evaluation of the engine performance and exhaust emissions of biodiesel–bioethanol–diesel blends using kernel-based extreme learning machine. Energy. 2018;159:1075–87.
101. Damanik N, Ong HC, Tong CW, Mahlia TMI, Silitonga AS. A review on the engine performance and exhaust emission characteristics of diesel engines fuelled with biodiesel blends. Environ Sci Pollut Res Int. 2018;25:15307–25.
108. Costa C, Hadiyanto A. Bioelectricity production from microalgae-microbial fuel cell technology (MMFC). MATEC Web Conf. 2018;156:2–4.

109. Stucki S, Vogel F, Ludwig C, Haiduc AG, Brandenberger M. Catalytic gasification of algae in supercritical water for biofuel production and carbon capture. Energy Environ Sci. 2009;2:S35.

110. Liu C-H, Chang C-Y, Liao Q, Zhu X, Liao C-F, Chang J-S. Biohydrogen production by a novel integration of dark fermentation and mixotrophic microalgal cultivation. Int J Hydrog Energy. 2013;38:15807–14.

111. Molino A, Nanna F, Ding Y, Bikson M, Braccio G. Biomethane production by anaerobic digestion of organic waste. Fuel. 2013;103:1003–9.

112. Gruber-Brunhumer MR, Jerney J, Zohar E, Nussbaumer M, Hieber P. Associated effects of storage and mechanical pre-treatments of microalgal biomass on biomethane yields in anaerobic digestion. Biomass Bioenergy. 2016;93:259–68.

113. Visceral. Biophotolysis: green hydrogen fuel production. Daily Kos. 2008. http://www.dailykos.com/story/2008/6/27/543096/-.

114. Carrillo-Reyes J, Buitron G. Biohydrogen and methane production via a two-step process using an acid pretreated native microalgal consortium. Bioresour Technol. 2016;221:324–30.

115. Tapia-Venegas E, Ramirez-Morales JE, Silva-Illanes F, Toledo-Alarcon J, Paillet F, Escudie R. Biohydrogen production by dark fermentation: scaling-up and technologies integration for a sustainable system. Rev Environ Sci Biotechnol. 2015;14:761–85.

116. Rashid N, Rehman MSU, Memon S, Rahman ZU, Lee K, Han JI. Current status, barriers and developments on algal biochar production and characterization. Bioresour Technol. 2017;246:2–11.

117. Chaiwong K, Kiatsiriroat T, Vorayos N, Thararox C. Study of bio-oil and bio-char production from algae by slow pyrolysis. Biomass Bioenergy. 2013;56:600–6.

118. Huang Y, Chen Y, Xie J, Liu H, Yin X, Wu C. Bio-oil production from hydrothermal liquefaction of high-protein high-ash microalgae including wild Cyanobacteria sp. and cultivated Bacillariophyta sp. Fuel. 2016;183:9–19.

119. Zainan NH, Sivatsa SC, Li F, Bhattacharya S. Quality of bio-oil from catalytic pyrolysis of microalgae Chlorella vulgaris. Fuel. 2018;223:12–9.

120. Chang Z, Duan P, Xu Y. Catalytic hydropyrolysis of microalgae: influence of operating variables on the formation and composition of bio-oil. Biore- sour Technol. 2015;184:349–54.

121. Shamsul NS, Kamardin SK, Rahman NA. Conversion of bio-oil to bio gasoline via pyrolysis and hydrothermal: a review. Renew Sust Energ Rev. 2017;80:538–49.