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Upgrading of micro algal derived bio-fuels in thermochemical liquefaction path and its perspectives: A review

Sundaram Arvindnarayan [a], Kandasamy K. Sivagnana Prabhu [b, *], Sutha Shobana [c], Gopalakrishnan Kumar [d, **], Jeyaprakash Dharmaraja [e]

[a] Department of Mechanical Engineering, Rohini College of Engineering & Technology, Anjugramam, Kanyakumari, Tamil Nadu, India
[b] Department of Mechanical Engineering, R.M.K. Engineering College, R.S.M. Nagar, Kavaraipettai, Tamil Nadu, India
[c] Department of Chemistry and Research Centre, Aditanar College of Arts and Science, Virapandianpatnam, Tiruchendur, Tamil Nadu, India
[d] Center for Materials Cycles and Waste Management Research, National Institute for Environmental Studies, 16-2, Tsukuba, Ibaraki 305-8506, Japan
[e] Division of Chemistry, Faculty of Science and Humanities, Sree Sowdambika College of Engineering, Chettikurichi, Aruppukottai, Tamil Nadu, India

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A B S T R A C T

Micro algae are promising attractive energy carriers. Their biomass productivity is 5–30 times higher than that of first and second generation biomass. Additionally, they utilize CO_2 for their photosynthetic process thereby protects possibly the environment and contributes towards CO_2 remediation at higher rates. Their cultivation can be combined with wastewater and industrial effluents which consequently leads to the bioremediation of inorganic elements more effectively. Among the conversion technologies for the biofuel production from the micro algal biomass, thermochemical conversion is an enduring sustainable alternative path in the view of engineering as this process utilizes all kinds of the biochemical moieties from the micro algal biomass cellular constitution. This article reviews the bio moieties of micro algal biomass, and subsequent use of them in thermochemical liquefaction (TCL) technologies like pyrolysis and hydrothermal liquefaction (HTL) for the extraction of liquid fuels and upgrading of bio-oil processes *via* decarbonylation, decarboxylation (DCO) and hydrogenation for palmitic/oleic using suitable catalysts *viz* activated carbon with noble metals & cost-effective tungsten based catalysts. These two technically feasible processes in an appropriate technical downstream path are dependent on the oil upgrading process. Moreover, a comparative study of pyrolysis and HTL processes has been evaluated towards the challenges and opportunities of a commercial-scale microalgae-to-fuels process in the consideration for mitigating technical, environmental, and logistical concern.

1. Introduction

Sustainable renewable fuels are getting substantial concentration, particularly biodiesel, which is accepted for its environmental reimbursement (Bucker et al., 2011; Mohebali and Ball, 2016). Sustainable renewable energy development deals with issues which relate climate change, energy security and the ever increasing demand for fuel sources. Currently, geopolitical and environmental implications of petroleum availability, supply, and utilization have been in question and not sustainable (Yeh et al., 2013; Striebich et al., 2014; Ururahy Soriano et al., 2015). The dwindling of fossil fuel resources explores cost-effectively and eco-friendly green assets since hazardous accumulation of greenhouse gas emissions can be approachable by traditional technologies for the production of biodiesel fuel, which is a form of solar energy by means of oil crops (Chisti, 2007; Meher et al., 2006). Currently, the oil crops have been significantly replaced by algal biomass in view of the facts that they can be grown even in the wastewater environments and are an obvious substitute for petro-derived liquid fuels in addition to the algal biomass commercialization includes copious environmental and cost-effective reimbursement (Grayburn et al., 2013). The production of alternate sustainable fuels for effective utilization of bio resources can be achieved in an eco-friendly green environmental mode in the world. The consumption of biodiesel results in the diminution of SO_x and greenhouse gas emissions since it forms fairly lesser quantities of carbon

* Corresponding author.
** Corresponding author.
E-mail addresses: kksprmk@gmail.com (K.K. Sivagnana Prabhu), gopalakrishnanchml@gmail.com, kumar.gopal@nies.go.jp (G. Kumar).

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and sulphur based gases on comparison with conventional fossil fuels (Chuah et al., 2016). Moreover, the Clean Development The mechanism (CDM) of the Kyoto Protocol provides Annex-I (industrialized) countries with an incentive to invest in emission reduction projects in non-Annex-I (developing) countries to accomplish a decline in emissions of CO_2 cost-effectively which in turn encourage sustainable development in the host country (Purohit, 2009). In this aspect microalga is considered as third generation fuel feedstock due to its photosynthetic efficiency, growth rate, area-specific yield and higher tolerance level of carbon dioxide (Zhao et al., 2013). In addition, the most intrusion of a wide marketplace of micro algal products *viz* pigments, fertilizers and food supplements for both the animals and humans is due to low cell densities and moderate growth rates of microalgae (Cuellar-Bermudez et al., 2015; Koller et al., 2012).

Microalgae can boom in a range of habitats where light and water are available including ocean, lake, soils, ice, rivers, *etc.* and they make obviously a great biodiversity of about 200,000 and several millions of species. Depending on their pigmentation, biological structure, life cycle and metabolism they can be divided into different divisions and classes (Natrah et al., 2007) and during photosynthesis, they convert solar energy into chemical energy in the form of carbohydrates, oils, and proteins. The stored energy can be converted to biodiesel. Microalgae can produce different types of biofuels which are principally the liquid oil by thermal liquefaction (Koberg et al., 2011), biomethane by anaerobic digestion (Sialve et al., 2009), biohydrogen by photobiological process (Kapdan and Kargi, 2006), bioethanol by fermentation (Yu et al., 2011). Even if industrial scale biofuels from microalgae remain at an early stage, they remain a sustainable solution as a transportation fuel. The conventional technique of conversion of microalgal biomass into biofuels involves lipid extraction for the production of biodiesel through transesterification which utilizes only algal lipids while the thermo chemical methods involves conversion of entire algal cell including proteins, carbohydrates and lipid into fuel oil (Mata et al., 2010). Indeed, the conversion of low lipid microalgae into biofuel is a promising area of research (Roberts et al., 2013; Oh et al., 2010; Duffy et al., 2009) since, their proteins and carbohydrates contain C, H, N and other elemental variants effectively utilized for thermo chemical conversion of microalgae biomass.

Pyrolysis is the conversion of biomass to bio-oil is one of the potential sustainable techniques (Lim et al., 2016). The microalgal biomass is over functionalized and removal of functionalities like O—/N—/S— groups are required. In this review, we have discussed the oil extraction techniques through thermo chemical path into liquid fuels from low lipid content microalgae (Schenk et al., 2008; Meher et al., 2006). Several reviews have discussed high lipid microalgae extraction to biodiesel *via* lipid extraction and transesterification process (Arvindnarayan et al., 2016, 2015; Ahmad et al., 2011). Thus, the algal biomass can be considered as an emerging resource for the biofuel production (Satheeja Santhi et al., 2014; Zhen et al., 2016). In this view, this article focuses mainly on the bio-moieties in microalgae, thermochemical conversion technologies like pyrolysis & hydrothermal liquefaction (HTL) with/without catalysts for the extraction of liquid fuels upgrading of bio-oil & residual organic moieties and challenges and opportunities of a commercial-scale microalgae-to-fuels process along with its perspectives.

2. Bio-moieties in micro algal biomass and their bio-oil conversion

Micro algal biomass consists of a complex structuralism which includes biopolymers, lipids and proteins (Table 1), which have been considered to be an attractive feedstock/precursors for bio-oil production (Chen et al., 2015). The bio-moieties present in microalgae and conversion of microalgae biomass to bio-oil can be illustrated as follows, on the other hand in the conversion process for the liquid fuel production, the detachment of hetero functionalities like O/N/S from the biomass are carried out and so fewer aromatic structuralism & their derivatives were found in the bio-oil.

Table 1
Composition of biomoieties (wt%)in dry micro algal biomass.

Species	Proteins	Carbohydrates	Lipids
Anabaena cylindrica	43–56	25–30	4.0–7.0
Aphanizomenon flos-aquae	62	23	3.0
Chlamydomonas rheinhardii	48	17	21
Chlorella protothecoides	53	11	15
Chlorella pyrenoidosa	71.3	22	0.1
Chlorella sp.	30	15–17	9.0–13
Chlorella vulgaris	42–58	12–17	14–22
Chlorococcum littorale	38	23	16
Cladophora sp.	25	25	6.0
Desmodesmus sp.	38–44	13–20	10–14
Dunaliella bioculata	49	4.0	8.0
Dunaliella salina	57	32	6.0
Dunaliellatertiolecta	64	21	15
Euglena gracilis	39–61	14–18	14–20
Lyngbya sp.	30	13	1.0
Microcystis aeruginosa	31	12	13
Nannochloropsis oculata	42.6	6.0	24
Nannochloropsissalina	37	33	12
Nannochloropsissp.	52	12	28
Nannochloropsis oculata	57	8.0	32
Nannochloropsis oculata	39	20	17
Porphyridium cruentum	28–39	40–57	9.0–14
Prymnesium parvum	28–45	25–33	22–38
Scenedesmus dimorphus	8–18	21–52	21–52
Scenedesmus obliquus	50–56	10–17	12–14
Scenedesmus quadricauda	47	–	2.0
Spirogyra sp.	6.0–20	33–64	11–21
Spirulina maxima	60–71	13–16	6.0–7.0
Spirulina platensis	46–63	8.0–14	4.0–9.0
Streptomyces platensis	48	30	13
Synechoccus sp.	63	15	11
Tetraselmis maculate	52	15	3.0

Modified Ref. (Chen et al., 2015).

2.1. Bio-moieties in microalgae

Micro algal organisms consists the bio-moieties of C, H, O & N elements in the form of carbohydrates, lipids and proteins which can be converted into bio-fuels (Garcia Alba et al., 2012; Chen et al., 2015). Due to their photosynthetic efficiency, there is an accumulation of about 5–23 wt% biopolymers especially glucose monomers obtainable from plastid/cell wall starch reserved functionalities specifically carbohydrate homopolymers consists of *D*-glucopyranose structural units through β-glycosidic/α-glycosidic linkages (Chen et al., 2013, 2015). The saturated/polyunsaturated fatty acids construct 14–20 carbons which can account for 7–23 wt % lipids structuralism in the form of triacylglycerides (TAG) (Ho et al., 2011). In addition, 6–52 wt% of proteins in the form of amino acids are the major source of nitrogen in micro algal organisms (Silva et al., 2013).

2.2. Conversion of microalgae biomass to bio-oil

The complex structuralism of micro algal biomass effectively necessitate energy effectable defunctionalization processes *viz* deoxygenation of carbohydrates, decarbonylation of residual lipids and deamination of proteins for hydrocarboned bio-fuels productivity, on one hand such reactions are more challenging when