Recent Advances in Production of Biofuel and Commodity Chemicals from Algal Biomass

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1 Introduction

Rapid development of technocratic society and sustainability of conventional fossil fuel sources are antipodal to each other. During past few decades, we have witnessed dramatic increase in the consumption of fossil fuels, causing several socio-economic changes across the world. Interestingly, conventional fossil fuel reserves are limited, thereby leading to the possibility of energy crisis in near future. Thus, recent focus of research has been shifted towards development of sustainable and renewable sources of energy. Albeit, solar, wind, hydrothermal, and tidal energy sources may be an alternative to upcoming energy crisis, biomass as a source of renewable, and sustainable energy is more interesting due to its ability to produce both chemicals and fuel (Alam et al. 2015; Ahmad et al. 2016). On the contrary, not all the biomass sources can be considered as a sustainable source. For example, first generation biofuel biomass sources such as sugarcane, sunflower, corn, and soybean have conflicts with the food usage which limits their applicability for further consideration (Bardhan et al. 2015), whereas second generation biofuel sources have shown promising results and are used to produce a wide range of biofuel such as bio oil, biochar, biofuel, and hydrogen (Tinwala et al. 2015; Kumar and Pant 2015; Saikia et al. 2015; Pant and Mohanty 2014). However, majority of the products obtained either oxygenates which require further upgradation or other form of fuel which may require modification in existing engine system. For example, bio-hydrogen can be directly produced from biomass derived ethanol (Mondal et al. 2016). On the contrary, application of hydrogen based vehicle is yet to be adopted at large scale. In addition, promotion of lignocellulosic biomass may promote deforestation and depletion of resources as it takes several years for a tree to grow. Noteworthy that energy density of bio oil (10.6 GJ/m^3) obtained from conversion of lignocellulosic biomass is unsubstantial as compared to energy content of the regular gasoline and diesel (35.7 and 39.7 GJ/m^3, respectively). Furthermore, most of the biofuel contains oxygen, therefore used as a fuel additive instead of being directly used as a fuel. Consequently, it necessitates the production of biofuel having comparable properties with gasoline and diesel.

Interestingly, energy density of biodiesel (35.6 GJ/m^3) obtained from algal biomass is found to be comparable with conventional diesel. Moreover, application of algal biomass for biofuel production can be helpful in curbing environmental and aquatic pollution (Chisti 2007). For example, Eduardo et al. have reported an integrated process for the production of biofuel from algal biomass that can be attached to power plants to consume flue gases (Santillan-Jimenez et al. 2016). Although further integration of this technology is possible which we believe that yet to be explored. To be noted that power plants generate huge amount of wastewater and flue gases. Therefore, we hypothesize that algal biomass cultivation may serve as an efficient method to tackle wastewater treatment and flue gas emission simultaneously. However, this approach is yet to be established. Interestingly, unlike lignocellulosic biomass, algal biomass is divided into several categories on the basis of their properties and pigmentation. Filamentous and phytoplankton are

two most abundant varieties of algae which are further classified into four distinct categories, namely golden algae, blue-green algae, green algae, and diatoms. However, two broad major categories of algal biomass are macroalgae and microalgae. Macroalgae based on their pigmentation are further classified into three major categories, namely green seaweed, red seaweed, and brown seaweed. Similarly, microalgae is classified by a variety of methods. Some of them are based on the microalgae cellular structure, pigmentation, and life cycle (Demirbas 2010). Albeit there are several categories of algae, all are capable of utilizing greenhouse gases and sunlight to produce energy and chemicals. However, since oil content of microalgae is relatively higher as compared to macroalgae, thus recent research interest is more inclined towards microalgae. Microalgae is a unicellular microorganism that can survive under both the freshwater and saline water. Diatom algae belongs to the family of phytoplakton and represents largest producers of world's total biomass.

Consequently, a paradigm shift in the biofuel research has been witnessed after consideration of algae as sustainable feedstock for biofuel production (Ullah et al. 2014). The possible reason could be attributed high oil yield with respect to per acre of cultivation land (1200–10,000 gallons per acre of land cultivation land, Table 1, entry 1). It is evident from Table 1 that none of the feedstock are even near to algae in terms of overall oil yield from equal area of land of cultivation. To be noted that free fatty acid content of cottonseed oil, rapeseed oil, and jatropha oil makes them an interesting feedstock for production of oxygen linear chain fuel range hydrocarbons via various routes. However, low oil yield per acre of land remains a challenge.

On the contrary, it is possible to further enhance oil yield by cultivating genetically modified microalgae. In general, algal biomass is extracted using a suitable solvent followed by further processing to yield free fatty acids. Obtained fatty acids are generally converted into FAME via similar process implied for vegetable oil transesterification. The second most common route is hydrodeoxygenation, where free fatty acids (FFA) obtained from algal biomass are hydrogenated to yield oxygen free fuel range hydrocarbons. In particular, long chain hydrocarbons such as diesel and aviation fuel hold great economic and environmental value. Albeit the differences in per acre oil yield for different substrates, the chemical composition of algal biomass based feedstock does not vary significantly. However, the final yield and conversion may vary. This is due to the

Table 1 Oil yield of different crops per acre of cultivated land

Entry no.	Crop	Oil yield (gallons/acre)
1.	Algae	1200–10,000
2.	Cotton	35
3.	Soybean	48
4.	Sunflower	102
5.	Rapeseed/Canola	127
6.	Jatropha	202

fact that FFA are mainly saturated, hence the possibility of C—C cleavage at carbonyl carbon is expected to be higher as compared to unsaturated feedstock where C—C cleavage is also expected in between carbon chain. Moreover, difference in degree of saturation and unsaturation may lead to completely different reaction pathway under varying process conditions. For example, degree of unsaturation of fatty acids may lead to formation of oligomers and aromatics, thus resulting into low selectivity of the linear chain products. Alternatively, it may lead to strong C—C cleavage to produce more coke, thereby a high catalyst deactivation. However, noteworthy that carbon chain length of the feedstock does not alter the overall reaction rate even when experimental conditions such as temperature and solvents are changed. For further study on effect of feed type over conversion and selectivity, review by Hermida et al. can be referred (Hermida et al. 2015).

Nevertheless, several reports on fuel range hydrocarbons production (mainly diesel and aviation grade) from algae and their techno-economic feasibility are available, indicating a new window of possibilities in this area (Ford et al. 2013; Hengst et al. 2015; Bala and Chidambaram 2016; Zhao et al. 2015; Wang 2016; Singh et al. 2016). With respect to techno-economic feasibility analysis between different methods for FFA conversion, study by Netlson et al. is worth reading (Natelson et al. 2015). It is estimated that jet fuel break-even cost could be as low as $0.80/kg which is significantly lower than DOE reported price for jet fuel ($1.0/kg). It is also predicted that under worst case scenario, the maximum cost could go up to $1.04/kg which is not much higher than the DOE projected price. However author's study was based on fatty acids obtained from camelina oil which has similar composition of free fatty acids obtained from algal biomass.

In contrast, high production cost of algae could be a challenge for implementation of FFA derived fuel range hydrocarbons production technologies. However, it has a promising environmental sustainability due to fact that algae cultivation requires carbon dioxide, thus reducing environmental load in an efficient way (Kiran et al. 2014). Moreover, since algae are non-edible, therefore such processes will not make any effect food supply chain. Furthermore, it is possible to FFA yield from algae by cultivating genetically modified algae that in result will lead to higher oil yield per acre. In addition, industrial and domestic waste could be utilized for production of algae. Furthermore, algal biomass production can also serve as an efficient method for consumption of carbon dioxide from flue gases of power plants. These perspectives make algae an interesting and promising feedstock that needs to be explored for their conversion into fuel range hydrocarbons. A general comparison of different generation's feedstock for biofuel production is given (Table 2) followed by various conversion technologies for algal biomass in subsequent section. However, emerging routes such as decarbonylation and decarboxylation have been focused thereafter.

In general, several processes have been developed for production of biofuel from algal biomass. However, for ease of discussion we have divided all the processes

Table 2 1st, 2nd, and 3rd Generation feedstock for biofuel production, advantages, and disadvantages (Pant and Mohanty 2014)

	1st Generation	2nd Generation	3rd Generation
Feedstock	Sugar, starch crops, vegetable oils, soybean, animal fat, straw, etc.	Wood, agri waste, MSW, animal manure, pulp, sludge, grass	Algal biomass
Product	Biodiesel, sugar alcohol, ethanol	Hydro-treating oil, bio oil, FT oil, etc.	Algae oil, fatty acids, esters, lubricants
Advantages	Economic and environment friendly	Non-competing with food, better conversion techniques	High oil content and lipid content
Disadvantages	Limited feedstock, low blending	Lignin content, high oxygenates	Slow growth, difficult extraction

into three major categories, namely thermal, catalytic, and biological routes. All of these processes are well known and reported in literature. The operating conditions and other parameters within these three routes itself vary, thereby resulting into different products and by-products. In Fig. 1, we have summarized the major processes, products, and their advantages as well as disadvantages for algal biomass conversion. Thereafter, a detailed discussion is followed in subsequent sections for explaining further sub-categorization of each route.

2 Thermal Routes for Biofuel Production from Algal Biomass

Albeit various technologies have been developed for production of biofuel from algal biomass, thermal (or thermochemical) route is most preferred and established process for biofuel production at large scale. Possibly, this process is preferred due to the fact that no major pretreatment (except drying) of feedstock is required. The major thermal routes reported in this regard are combustion, gasification, pyrolysis, and liquefaction. In general, all these processes require elevated temperature, thus requires advanced instrumentation. Interestingly, both macroalgae (such as Enteromorpha prolifera, Ulva lactuca L, and others) and microalgae (such as *Chlorella vulgaris*, Spirulina sp., and others) can be processed via thermal routes, thus making it an important process for further considerations (Raheem et al. 2015). A typical diagram showing major thermal routes for algal biomass conversion and products is given below (Fig. 2).
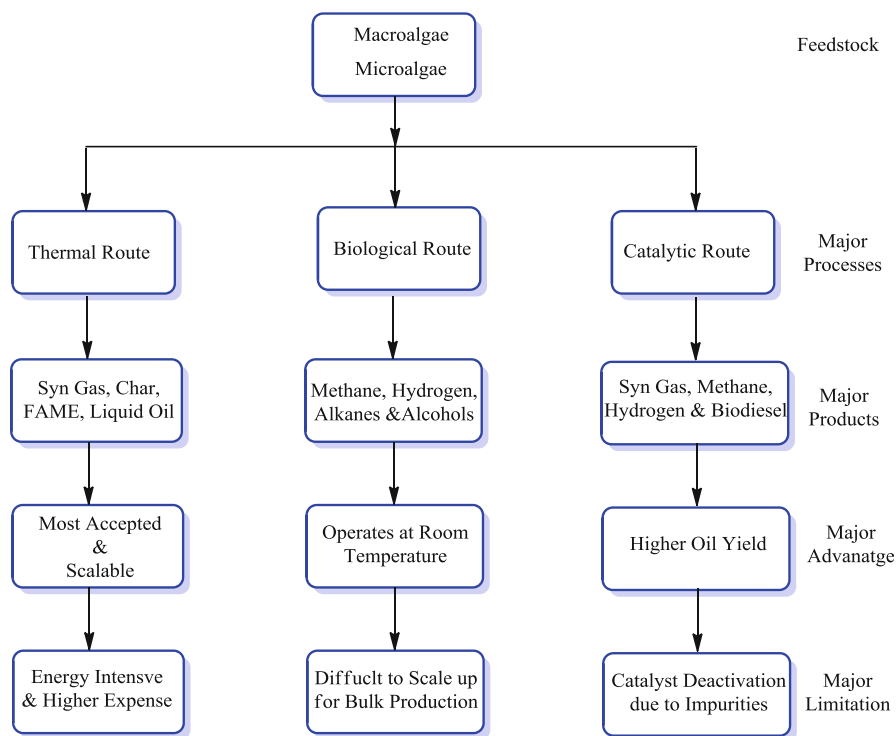
Fig. 1 Major processes for algal biomass conversion, products, advantages, and limitations

2.1   Combustion of Algal Biomass

Direct combustion is a well-known widely accepted process employed for the conversion of second generation biofuel feedstock, e.g., lignocellulosic biomass. Indeed, it is among the most sought-after processes for industrial scale up. Interestingly, the direct combustion process has found crucial applications in the production of energy from algal biomass (Brennan and Owende 2010). In a typical direct combustion process, the algal biomass is charged into combustion chamber with continuous supply of air for complete. The combustion chamber is usually a steam turbine, boiler, or furnace operating at very high temperature range ($>800°C$) that converts stored chemical energy of algal biomass into heat energy. This heat energy in the form of gases is utilized for preheating, steam generation, or power generation. However, it is crucial to recover the produced heat instantly after generation to avoid the heat loss. Noteworthy that the direct combustion process can be applied at any scale, i.e., for production of energy from domestic application to large and commercial applications (100–300 MW).

However, water content of algal biomass is a major constraint for the successful implementation of the direct combustion process. Thus, it necessitates
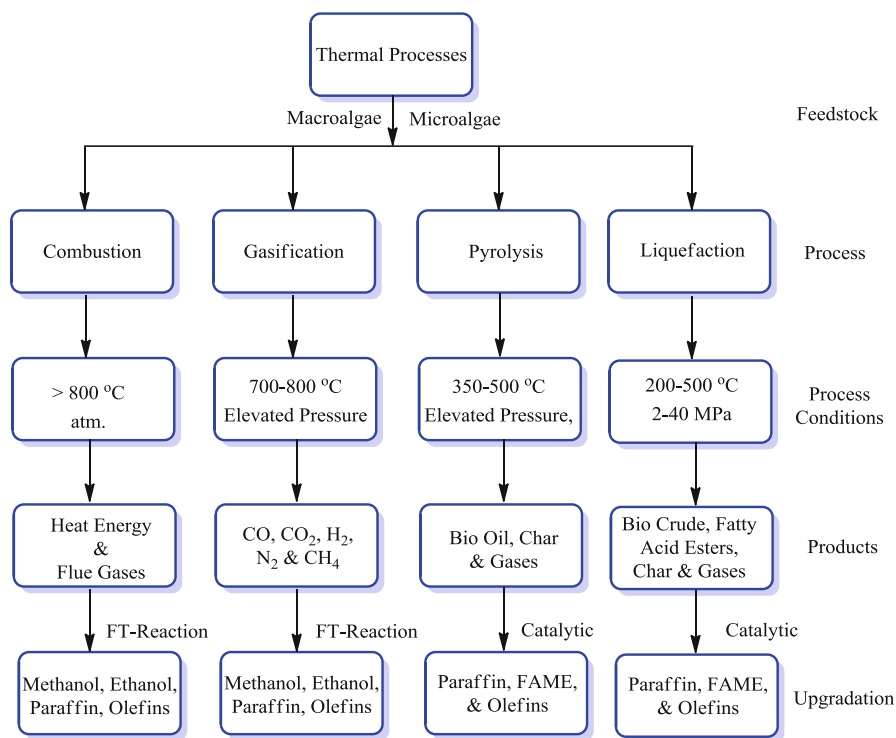
Fig. 2 Thermal routes for biofuel production from algal biomass

the pretreatment of feedstock which essentially includes several steps such as drying, chopping, and grinding, thereby leading to increased energy demand. Consequently, increased energy and equipment costs imparts a negative impact on the overall economics of the process. On the contrary, dry algal biomass enhances the efficiency of CHP power plants up to 40%, thus resulting into overall reduction of power cost. Moreover, application of algal biomass in coal based power plants helps to curb greenhouse gases emission and air pollution (Lane et al. 2014). Therefore, a more detailed and elaborative techno-economic feasibility study is required in this area to calculate the optimum scenario for the application of algal biomass into power plant. Alternatively, a blend of algal biomass and coal can be considered for further studies. Moreover, the gaseous products obtained from such processes may be recovered to produce value added chemicals or feedstock for the growth of algae.

2.2 Gasification of Algal Biomass

Gasification is similar process to combustion where algal biomass is partially oxidized via controlled combustion. In contrast, major focus of gasification process is to produce a mixture of combustible gases that can be stored for a period of time which is, so far, unlikely with direct combustion process. In a typical process, algal

biomass is charged into combustion chamber and controlled quantity of oxygen. Simultaneously, water in the form of steam is also supplied. The overall process operates at a temperature range of 700–900°C and produces a mixture of gases consisting of CO, CO_2, H_2, and methane gas (Azadi et al. 2014). It is reported that gasification process proceeds via Fischer–Tropsch reaction which is well-developed and commercially applied technology. Interestingly, Fischer–Tropsch reaction can be used to upgrade the obtained gases into methanol, long chain paraffin, olefins, and other fuel range hydrocarbons. Indeed, syngas obtained from gasification of algal biomass has significant potential to produce an array of chemicals when used a feedstock.

Recent interest in development of technologies for algal biomass gasification is primarily focused towards the production of value added chemicals. For example, methanol is one such valuable chemical that can be produced from the algal biomass derived syngas. Alternatively, a more direct process could be to use the algae itself instead of using syngas because both the processes essentially undergo FT synthesis reaction. However, the major limitation of this process is formation of tar which may suppress the overall yield of the desired product, thus leading to reduced economic advantage. In addition, the presence of tar or undesired impurities may result into suppressing the overall activity of the catalyst during catalytic conversion or upgradation of the algal biomass derived intermediates into useful products. This limitation may be eliminated via designing a suitable reactor configuration (Nikoo and Mahinpey 2008). For example, a combination of FT reactor and reformer can be suggested by NREL in this regard (National Renewable Energy Laboratory 2010).

2.3 Pyrolysis of Algal Biomass

Although, direct combustion and gasification holds a promising future, intensive energy requirement and high cost of reactor setup may be a constraint for such processes for biofuel production from algal biomass. Consequently, low temperature processes have been developed and widely implied for the algal biomass into biofuel. One such interesting and promising process is pyrolysis of algal biomass (Zhang et al. 2007). Pyrolysis of algal biomass is carried out a relatively lower temperature as compared to the gasification and direct combustion process. In addition, products of this process are obtained in all the three phases, i.e., solid, liquid, and gas. The liquid product obtained is essentially bio oil whereas, gaseous products are mostly combustible gases that can be used to meet energy demands of the process and to produce value added chemicals. On the contrary, the solid product properties are comparable to char, thereby finding application as solid fuel source.

Interestingly, pyrolysis of algal biomass is further divided into three sub-categories, i.e., (1) flash pyrolysis, (2) intermediate pyrolysis, and (3) slow pyrolysis. To be noted that all pyrolysis processes applied for the conversion of

lignocellulosic biomass can be applied for the algal biomass as well (Maddi et al. 2011). However, flash pyrolysis has advantage in terms that it is extremely fast, thereby leading to a reduced time for processing of the feedstock. The flash pyrolysis is usually carried out at a temperature range of 350–500°C where algal biomass is brought in contact with heat for a fraction of minutes usually for 2–3 s. In general, feedstock for flash pyrolysis is required to be fine and chopped into smaller particles. Thus, algal biomass has better prospects as compared to lignocellulosic biomass for utilization in flash pyrolysis. The major products obtained through this process are liquid fuel, usually bio oil that can further be upgraded into fuel range hydrocarbons via various catalytic routes. In addition, solid and gaseous products are also obtained that have equal fuel value. However, bio oil yield obtained from flash pyrolysis of algal biomass (e.g., seaweed) is relatively lower as compared to the bio oil yield obtained from flash pyrolysis of lignocellulosic biomass (Yanik et al. 2013). On the contrary, char yield is found to be higher than that of the lignocellulosic biomass. The bio oil yield may improve by utilizing suitable species of algae. To be noted that bio oil yield from pyrolysis of algal biomass depends on several factors such as pyrolysis temperature, flash time, heating rate, and feed composition. Therefore, it is deduced that selecting a suitable algal feedstock and optimizing process parameters may help to improve the bio oil yield further. For example, Budarin et al. have reported the conversion of algal biomass at a very low temperature (130°C) when experiments were performed under microwave irradiation (Budarin et al. 2011). Nevertheless, intermediate and slow pyrolysis processes can be applied for a higher gaseous and solid products yield.

2.4 Liquefaction of Algal Biomass

Thermochemical liquefaction of algal biomass is another interesting process which holds a major advantage. It does not require drying of feedstock which is unlikely the case with pyrolysis (Guo et al. 2015). Indeed, thermochemical liquefaction process can directly be applied for conversion of wet algal biomass into value added products and chemicals. Moreover, it is low temperature process usually operates at a temperature range less than 350°C, thereby leading reduced energy consumptions. On the contrary, this process operates at elevated pressure (10–25 MPa) that may incur additional energy cost (Yang et al. 2016). Furthermore, setting up a reactor may be expensive for liquefaction process due to its complex instrumentation requirements. In a typical liquefaction process, algal biomass is broken down into small molecular fragments using water in bulk quantity under subcritical conditions. Interestingly, this technique is driven from the natural process of formation of fossil fuels which essentially works on the principle of subcritical methods. Consequently, liquefaction yields a viscous crude oil like product called "bio crude." At present, liquefaction technologies have been applied to recover up to 70% bio crude yield based on dry weight of the algal biomass. The average heating value of bio crude obtained from this processes is in the range of 30–60 MJ/kg which is

comparable to the calorific value of conventional petroleum oil. However, this area is yet to be explored in detail.

Interestingly, algal biomass can be processed by a more recent and robust process called supercritical processing (Bi et al. 2015). The supercritical processing of algal biomass is considered as most efficient of process for the production of biofuel. Unlike, other conventional processes, bio oil produced through supercritical process is simultaneously upgraded into fuel range hydrocarbons. Moreover, product obtained through this process meets the criteria of conventional biodiesel. The major advantage of this process relatively lowers operating temperature as compared to thermochemical liquefaction process. Furthermore, no solvent residues are left over in this process. In a typical supercritical processing unit, algal biomass is charged with a suitable solvent, possibly an alcohol, for extraction of bio oil at elevated pressures. Post this, the produced bio oil undergoes transesterification reaction to produce esters of fatty acids. These fatty acid esters can be utilized as fuel additive to various diesel engines. Noteworthy that bio crude obtained from normal liquefaction process is very complex in process and consists of a wide range of products of different functional groups (Homsy 2012). In contrast, the products obtained from supercritical processing majorly consist of esters as functional group, thus making it easy to determine suitability with the existing fuel (Patel and Hellgardt 2016).

Similarly, supercritical processing of algal biomass when carried out in the presence of water as a solvent produces hydrogen, syngas, and natural gas. Possibly due to its gaseous product composition, supercritical processing is often confused with gasification. However, supercritical processing of algal biomass to produce gaseous products is entirely different from the gasification process. Based on operating conditions and type of feed used, the composition of resulting gas can be optimized. For example, Duman et al. have reported the production of hydrogen rich gas via steam reforming of algal biomass (Duman et al. 2014). Interestingly, up to 100% tar reduction was observed during this process which gives it a cutting edge over other technologies.

3 Catalytic Routes for Biofuel Production from Algal Biomass

Albeit conventional thermal processes are widely accepted and most techniques for production of biofuel from algal biomass, energy consumption needs to be minimized to improve the sustainability of the process. Thus, efforts have been made to develop alternative processes that consumes less energy. In this regard, catalyst supported techniques have emerged as promising method capable of reducing energy consumption significantly, thereby leading to a reduction in overall cost of the process. Worth noticing that more than 90% of industrial chemical processing units utilizes catalysts for production of a wide range of fuel and chemicals.

Interestingly, based on final product obtained, catalytic routes for production of biofuel from algal biomass can be dived into two major sub-categories, i.e., (1) catalytic processes producing gaseous products and (2) the catalytic processes producing liquid fuels. However, the overall process remains similar except the catalyst which is changed to obtain enhanced selectively of desired product.

3.1 Catalytic Process for Production of Gaseous Production from Algal Biomass

Supercritical processing is the primary process applied for the production of gaseous biofuel from algal biomass. As stated earlier, the supercritical process is often referred as gasification. However, gasification is an entirely different process. Interestingly, supercritical processing is also referred as thermal liquefaction which is true to some extent. However, catalytic supercritical processing process for algal biomass conversion is a separate process. Unlike, thermal liquefaction supercritical processing which does not require any catalysts and operates at slightly elevated temperatures, catalytic supercritical processing operates at a relatively lower temperature and thus, consumes less energy. A wide range of catalysts has been reported in this regard that helps to lower the requirement of higher temperature and acts as reforming catalysts simultaneously. For example, Stucki et al. have reported 60–70% heat energy from algal biomass in the form of methane using a ruthenium based catalyst (Stucki et al. 2009). On the contrary, heat energy can be recovered in the form of a relatively cleaner form, i.e., hydrogen by replacing ruthenium catalyst with a nickel based catalyst (Onwudili et al. 2013). Majority of the catalyst employed in this process belongs to the family of transition metals. However, other operating conditions remain similar to that of uncatalyzed supercritical processing.

3.2 Catalytic Process for Production of Liquid Products (Biodiesel) from Algal Biomass

For sustainability of biofuel producing technologies, it is of utmost importance to have their compatibility with existing engines and infrastructure. In this regard, biodiesel produced through transesterification of algal biomass holds an important portfolio. Worthy to note that biodiesel can directly be applied into existing engines and fuel supply chain management system which is unlikely the case with other fuels. This is probably due to the fact that the biodiesel has similar properties and molecular structure with respect to regular diesel. Indeed, biodiesel can replace a significant portion of conventional fuel used in transportation industry (Chisti 2008). This process becomes further important due to similarity in carbon chain

length of the algal biomass esterified biodiesel and regular diesel. Consequently, majority of the algal biomass oil extraction processes are provided with a second stage catalytic reactor for the conversion of bio oil and fatty acid esters. Important to note that transesterification of algal biomass may be carried out either with an acid catalyst or a basic catalyst. Moreover, it is possible to process the wet biomass via this process, which makes it an interesting choice.

In general, the transesterification of algal biomass is done in two steps. Firstly, bio oil from the algal biomass is extracted using various technologies such as supercritical processing. Thereafter, catalytic esterification of obtained bio oil is followed. However, one pot processes for in-situ transesterification of algal biomass have emerged and almost replaced the typical two-step process. Interestingly, this process converts both the free fatty acids and triglycerides into biodiesel. Moreover, it enhances the biodiesel yield by suppressing process losses which are frequent in two-step process, especially during transportation of the fuel. More importantly, this process can be carried out using a variety of homogeneous, heterogeneous catalyst, ionic liquids, and enzymes, thus making it a popular choice in interdisciplinary areas of research (Park et al. 2015). For example, Haas et al. have reported 90% fatty acid methyl ester when experiments were performed at 65°C for 2 h in the presence of sulfuric acid catalyst and methanol (Haas and Wagner 2011). Worth noticing that methanol used here has dual role, i.e., it extracts the oil from algal biomass and esterify it simultaneously (Park et al. 2015). However, the foresaid reaction is reversible in nature; therefore, excess methanol is required to prevent conversion of formed product into reactants. In addition, sulfuric acid is also required in excess due to the fact that huge amount of water present in algal biomass may compete with the protons formed. Thus, further research in this area is required to minimize the methanol and acid requirement. In addition, there is possibility to apply microwave and ultrasound heating methods which may help in improving the overall yield of the process.

4 Biological Routes for Biofuel Production from Algal Biomass

In general, biological routes for production of any chemical and fuel are most preferred and environment friendly route. One possible reason could be the elimination of high temperature requirement. Most of the biological processes operate at room temperature and do not require complex instrumentation system. Moreover, scale up of biological processes is easy as compared to thermal and catalytic routes. To be noted that biological processes consume most of the algal biomass, thereby resulting into maximum utilization of the feed. Interestingly, biological routes do not essentially require pretreatment and cultivated algal biomass can be used as feedstock without any further processing (drying, etc.). Moreover, products

obtained such as methane, hydrogen, alcohols, and alkanes through biological routes are ready to use without further upgradation.
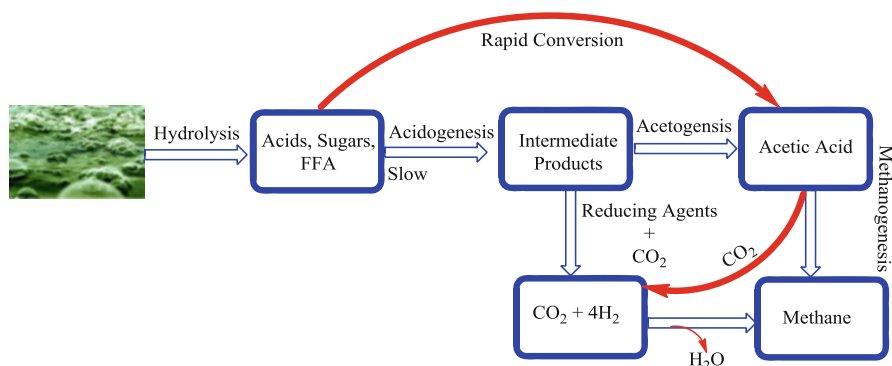
4.1 Production of Methane via Anaerobic Digestion of Algal Biomass

Anaerobic digestion process is primarily applied for production of methane from macroalgae. Interestingly, it is considered to be one of the most efficient processes which eliminates several intermediate steps required during conventional processing of the algal biomass. Moreover, application of anaerobic digestion based technologies may escalate the biofuel production rate. Furthermore, the anaerobic digestion process occurs naturally in digester and does require any special arrangement. In contrast, methane obtained in the form of biogas is a potential greenhouse gas, thereby necessitates the special arrangement to trap the gases. The gaseous product obtained through anaerobic digestion consists of methane and CO_2 in major quantity (Bruhn et al. 2011). CO_2 from methane can be separated using suitable techniques such as gas scrubber, thus resulting into natural gas like composition. Albeit several reactions take place during the anaerobic digestion process, the major reactions which can be considered as limiting factor are hydrolysis, acetogenesis, and methanogenesis (Alaswad et al. 2015).

Interestingly, hydrolysis itself proceeds via two steps, i.e., hydrolysis and acidogenesis. Firstly, algal biomass breaks down into smaller fragment of molecules. These smaller and defragmented molecules are primarily amino acids, fatty acids, and sugars. Thereafter, defragmented molecules are partially consumed by methanogenesis microorganisms and partially convert into intermediate products via acetogenesis step. Primarily, acetates and acetic acids are obtained by the later process. Thereafter, acids are consumed by methanogenic microorganisms to yield methane and energy. To be noted that acetic acids can directly undergo decarboxylation reaction to yield CO_2 and methane whereas hydrogen is generated by the microorganisms. CO_2 and hydrogen further react together to yield methane, thus eliminating the possible danger of global warming. Interestingly, the hydrogen is generated in-situ because of the production of several reducing agent type intermediates during acetogenetic step. There is no clear agreement on the reaction mechanism so far. However, the overall process for the production of methane from algal biomass is given in Fig. 3.

4.2 Hydrogen Production via Biological Routes

Hydrogen is the cleanest fuel that has potential to solve all environmental problems. Primarily hydrogen is produced from conventional sources of fossil fuels via energy

Fig. 3 Anaerobic digestion of algal biomass to produce methane

intensive processes such as reforming of natural gas, gasification of coal, and water electrolysis. Therefore, biological methods for hydrogen production may be an alternative option for sustainability of biorenewable fuel. Indeed, biological routes for hydrogen production may be an ideal process for hydrogen production in terms of energy consumption when compared with conventional processes. Biological processes, in general, do not require elevated temperatures and pressures which give it a winning edge over coal gasification, steam reforming, and water electrolysis. It is interesting to note that algae initially was used a source to produce oxygen. However, Professor Melis and his colleagues from National Renewable Energy (NREL), in 1999, observed that algae could be a promising resource for hydrogen production (Ullah et al. 2014). In general, biological routes for hydrogen production from algal biomass can be broadly classified into two major categories, i.e., (1) fermentation and (2) photosynthetic (Burgess et al. 2011). Interestingly, fermentation is further divided into two categories, namely (a) photo-fermentation and (b) dark fermentation whereas photosynthetic method is categorized as (c) direct biophotolysis and (d) indirect biophotolysis.

However, the yield of hydrogen is primarily dependent upon the type of enzyme used. The three major enzymes which are widely applied for the production of hydrogen from algal biomass are Fe-hydrogenase, NiFe-hydrogenase, and nitrogenase. The nitrogenase is mainly used in fermentation, especially in photo-fermentation. The fermentation route for hydrogen production essentially requires hydrolysis of the algal biomass as first step which is very similar to the methane production process (Xia et al. 2015). Absence of the sunlight, water, and oxygen is essential for dark fermentation process. Once the polysaccharides are broken down into monomeric form, e.g., acid and alcohols, the acidogenic bacteria such as anaerobes cause glucose to undergo glycolysis reaction that finally yields pyruvate and NADH. Thereafter, these intermediates via series of oxidation and reduction steps produce hydrogen. The major advantage of this process is that it does not require sunlight or oxygen to proceed. On the contrary, photo-fermentation essentially requires sunlight in order to produce hydrogen. The entire photo-fermentation

process is almost similar to anaerobic digestion of algal biomass for methane production. This process holds merit over dark fermentation in terms of removal of pollutants and industrial waste. On the contrary, pretreatment of industrial effluents may lead to the requirement of additional processing units.

Interestingly, photosynthetic processes for hydrogen production have attracted the attention of research community for its photosynthesis properties. In this process, hydrogenase is used as major microorganism responsible for the hydrogen production (Rumpel et al. 2014). The direct biophotolysis dissociates the molecular water into hydrogen and oxygen. The chlorophyll content of cyanobacteria or green algae helps in photosynthesis. The photons from the sunlight absorbed by the pigments result into the generation of strong anti-oxidants that split water molecule into oxygen, free proton, and free electron. The electrons generated via this process reduce intermediates products which are utilized by hydrogenase or nitrogenase to yield hydrogen. However, major disadvantage of this process is that hydrogenase activity may reduce if generated oxygen is not removed immediately. On possible reason could be high sensitivity of hydrogenase towards oxygen. On the contrary, the major advantage of indirect biophotocatalysis is the immediate separation of hydrogen and oxygen. The whole process takes place in two steps. Firstly, water molecules split into electron, proton, and oxygen which is a similar process like direct biophotolysis. However, splitting of water is followed by CO_2 fixation to produce more carbohydrates. Thereafter, the formed carbohydrate undergoes a series of reactions to finally yield hydrogen as a source of clean fuel. Interestingly, recent reports suggest that hydrogen can be produced under aerobic conditions from algal biomass (Hwang et al. 2014). However, this area is still under research and would be interesting to further progress.

4.3 Alcohols Production via Biological Routes

Next to hydrogen, alcohols especially bioethanol and biobutanol have potential to play a crucial role in the biofuel industry. Indeed, bioethanol production has been considered among top 12 chemicals suggested by United States Department of Energy for future considerations. Moreover, bioethanol held the major portfolio in the list of first generation fuel. Sugar cane is widely used for the production of bioethanol via different routes. However, possible conflict with food industry ruled out the possibility of commercialization of such technologies. Post this, second generation biofuel production technologies emerged as an alternative to the first generation biofuel production technologies. Thus, bioethanol production from lignocellulosic biomass was emphasized (Balat 2011). However, to best of our knowledge no commercial process is reported for the production of bioethanol from lignocellulosic biomass. One of the possible reasons could be the lignin content of the lignocellulosic biomass which acts as a binder and prevents cellulose and hemicellulose from taking part in further reactions. Moreover, it is difficult to convert lignin into useful products at mild process conditions, thereby resulting

into huge amount of residual waste. Therefore, it is of utmost importance to develop alternative feedstock for the production of bioethanol with low lignin content. In this regard, algal biomass is found to having minimum lignin content, thus making it a suitable feedstock for the production of bioethanol and alcohols via various biological routes (Dawoud et al. 2007).

Like hydrogen production, fermentation (heterotrophic) is the major route for production of bioethanol and other alcohols from the algal biomass such as seaweed, *Chlorella vulgaris*, and *Chlamydomonas perigranulata*. To be noted that these species of algal biomass contains higher amount of starch as compared to other species, thus fits into the criteria to qualify as a suitable feedstock for production bioethanol and biobutanol. However, sugars obtained from starch may breakdown into other products, thereby resulting into low alcohol yield and higher by-products formation. For example, some of the sugars obtained from seaweed are difficult to digest by certain enzymes such as *Saccharomyces cerevisiae*, thus limiting the further prospects of the process (Milledge et al. 2014). Interestingly, initial steps in overall process for production of alcohols from algal biomass are similar to biological routes for methane production. Firstly, algal biomass feed is prepared and charged into a digester or fermenter in the presence of suitable enzymes (acid catalyst for catalytic hydrolysis) to breakdown polysaccharides into reducing sugars (Dawoud et al. 2007). Albeit up to 20% of algal biomass can be hydrolyzed into reducing sugars or monosaccharides, acid hydrolysis is preferred due to its capability to enhance hydrolysis yield up to 50% of the dry total dry weight. Thereafter, hydrolyzed feedstock undergoes fermentation step which is a well-known and commercially available process. However, traces of acid remaining in the feedstock may lead to more problematic situation and result into inhibition of microorganisms responsible for hydrolysis. In general, all kinds of algae (green, red, and brown) can be used to produce alcohols, however, brown algae is preferred due to its higher carbohydrate content.

Recently, application of photobioreactors has been reported for the simultaneous production of algal biomass and alcohols altogether. These reactors contain cyanobacteria capable of producing alcohols while protecting itself from harsh conditions such as salinity of water and temperature. Thus, this process makes an integrated technology for alcohol production from algal biomass by linking photosynthesis and sugar production at one place. Noteworthy that these processes are not a way to produce alcohols but primarily to reduce greenhouse gases such as carbon dioxide. For example, it is reported that photobioreactor technology utilizes 90% of the system carbon dioxide to produce algae, sugars, and bioethanol (National Renewable Energy Laboratory 2010). To be noted that 60–70 L of bioethanol is produced from one ton of CO_2, making it a suitable choice for future considerations. Moreover, the bioethanol yield per acre of land can be up to 10,000 gallons. Thus it would be interesting to see, photobioreactor based technologies for alcohol production from algal biomass.

In contrast, ethanol as fuel faces several difficulties, thus limited to blending purposes. In this regard, biobutanol is an emerging fuel which has potential to replace bioethanol in near future. Worth noticing that biobutanol has relatively

lower vapor pressure and high energy density as compared to bioethanol. In addition, some bacterial species used for biobutanol production digest cellulose along with starch and sugars, thereby leading to possibility of enhanced alcohol production. The production of biobutanol from algal biomass follows a similar process to that bioethanol production. However, biobutanol yield is significantly lower than the bioethanol yield, thereby limiting the commercial prospects. The possible reason could be inability of the bacterial species to convert sugars and starch into long chain alcohols. However, we anticipate that biobutanol production will emerge as a potential replacement for bioethanol production in near future.

4.4   Production of Alkanes via Biological Routes

Albeit algal biomass derived alcohols holds a promising future, majority of fuel produced either needs modifications in existing engines design before application or cannot be used as a standalone fuel. One reason could be their compositional difference when compared with fuel obtained from conventional fossil reserves. Noteworthy that conventional fossil fuels are mainly linear chain alkanes whereas biofuel obtained from algal biomass are composed of oxygenates. Therefore, recent interest in the area of algal biomass derived biofuel is directed towards the development of alkane like hydrocarbons (Klähn et al. 2014; Peramuna et al. 2015). Interestingly, algal biomass for alkane production can be cultivated in closed reactor which may not necessarily require sunlight. In these reactors, sugars obtained from various biorenewable sources such as lignocellulosic biomass are fed to the algae. Depending upon the strain of the algae, the composition and range of alkane produced may vary (Chang et al. 2013). However, further upgradation techniques can be implied to enhance the properties of the obtained alkanes.

Unlike alcohols production, photosynthesis reaction needs to be suppressed, thereby leading to enhanced metabolic activities responsible for production of alkanes. Therefore, alkane production fermentation is generally favored in the dark condition, resulting into a higher yield as compared to photobioreactors. Additionally, the sugar fed to algae enhances its growth rate enabling higher algae cultivation in less area. One reason could be the readily available feedstock in concentrated form. This is in contrast to the photosynthesis procedure which takes longer time to generate food from sunlight, thereby slowing growth of the algae. Moreover, conventional photobioreactors require large infrastructure to produce the same amount of algae that can be produced in dark room for alkane production. This is due to the fact that energy required for algae growth is given in concentrated form and faster growth rate, thus higher production in reduced time.

Interestingly, sugar obtained from lignocellulosic biomass can be utilized for the production of biofuel in the presence of a suitable microorganism. However, majority of the fuel obtained from lignocellulosic biomass are cyclic oxygenates such as furans, lactones, pyrones, and esters that may not qualify the criteria of oxygen free alkane obtained from the biomass. On the contrary, it is possible to

produce linear chain alkanes from the lignocellulosic biomass via a similar process applied for algal biomass conversion. But the cyclic oxygenates produced as a by-product in this case may create operational issues, thus limiting economic viability. For example, separation of oxygenates and alkanes may contribute significantly in overall cost of the product. In addition, these cyclic oxygenates may inhibit the activity of the microorganism due to their toxic nature, thereby reducing overall alkane yield. On the contrary, alkanes produced from algae may not necessarily require separation (Chang et al. 2013).

5 Emerging Routes for Production of Commodity Chemicals from Algal Biomass

Development of alternative methods and technologies other than conventional methods for biofuel production leads to efficient utilization of biorenewable resources. The most promising route in this regard is decarboxylation–decarbonylation (DCO) leading to production of high value commodity monomer olefins and fuel grade hydrocarbons. Specially, the present stage when biofuel sustainability and feasibility is under question due to several environmental and economic reasons (Michel 2012). The progressive removal of oxygen via DCO may be considered as a promising route which seems more feasible in terms of overall economic of biofuel production technologies. Indeed, it is found to be most effective route for efficient utilization of third generation feedstock such as algae and free fatty acids obtained from algae. In addition, DCO route is equally effective for deoxygenation of carboxylic acids obtained from any source as well as non-edible vegetable oils consisting of mainly free fatty acids. Moreover, on integration with existing technologies for biomass processing, it is possible to convert organic acids obtained from various sources into fuel and value added products (Fig. 4). Furthermore, obtained chemicals can be further processed to produce a wide range of chemicals such as polymers, plasticizers, aldehydes, detergents, wax, and lubricants. Indeed, exploration of this area could lead to a new window of opportunity towards attaining goals of sustainability.

5.1 Decarbonylation–Decarboxylation of Algal Biomass Derived Fatty Acids

In general, DCO route involves removal of carbonyl group from free fatty acids, thus resulting into production of CO, CO_2, and H_2O as by-product besides alkane and alkenes. However, in case of product specific technologies such as for production of high value linear alpha olefins, decarbonylation is favored due to selective C─C bond scission whereas in case of decarboxylation to produce fuel range
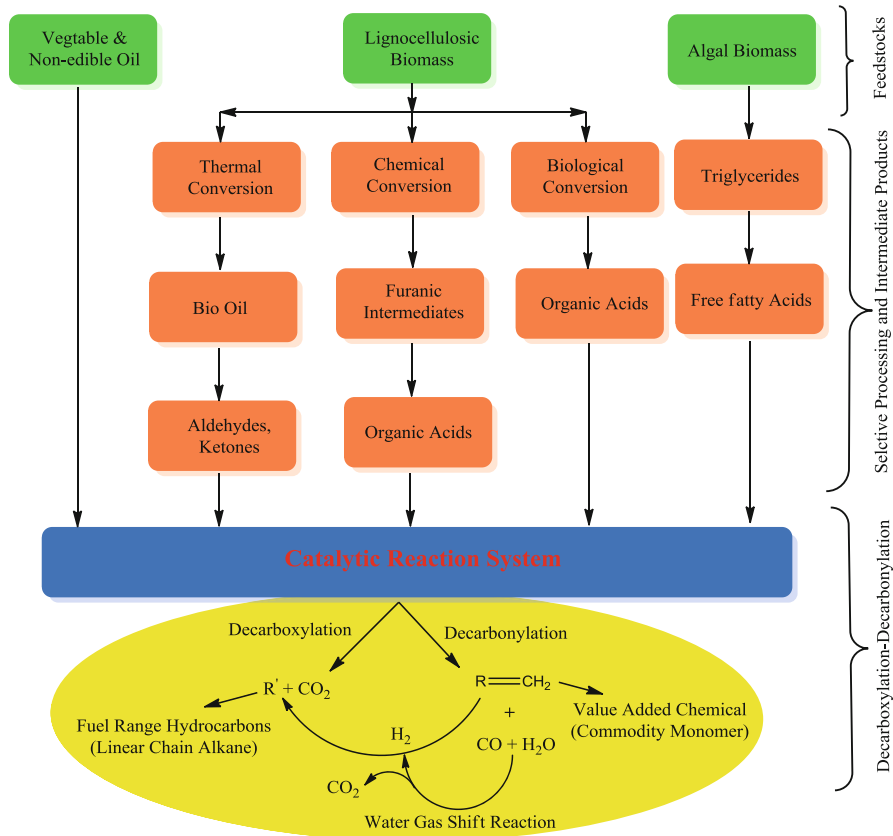
Fig. 4 Integrated approach for production of fuels and value added chemicals via DCO route from various algal biomass and other feedstocks

hydrocarbons such as linear chain alkane, additional hydrogen is required (Van Der Klis et al. 2015). Therefore, reaction mechanism which is considered to be one of the major factors responsible for determining final product selectivity is explored and correlated with operating process parameters and catalyst properties. Thermodynamic study suggests that both decarbonylation and decarboxylation are favored simultaneously at elevated temperatures above 300°C (Immer et al. 2010). Therefore, role of operating parameters is crucial. Albeit DCO route has been reviewed in past by some of prominent research groups (Santillan-Jimenez and Crocker 2012; Dawes et al. 2015; Gosselink et al. 2013), a detailed discussion towards advantages of oxygen free fuel range hydrocarbons production from algal biomass has not been reported. To be noted that oxygen free fuel range hydrocarbons obtained from biomass sources are also called as jet fuel or green diesel due to its structural analogy with fossil derived diesel. However, we expect that production of linear

alpha olefins (monomeric compounds) would be an emerging area of research due to its high value and capability to produce a wide range of commodity chemicals.

5.2 Catalytic Production of Linear Chain Hydrocarbons from Algal Biomass

At present, majority of transportation system uses linear chain hydrocarbons which is in contrast to the oxygen containing biofuel obtained from algal biomass. Possibly, due to this compositional difference bulk of biofuel ends up as a fuel additive rather than being directly used as a fuel. Interestingly, triglycerides obtained from algal biomass can be processed via different techniques such as hydrodeoxygenation to yield fuel range hydrocarbons. For example, hydrotreatment of triglycerides produces C_{13}―C_{20} hydrocarbons which have identical properties and composition to regular diesel. In addition, further processing steps such as catalytic cracking, reforming, and hydrocracking can be applied to upgrade the obtained hydrocarbons into jet fuel. In a typical hydrodeoxygenation process, unsaturated carbon chain of triglycerides obtained from algal biomass is saturated with hydrogen which helps to break the long chain carbon into smaller chain followed by oxygen removal via decarboxylation, decarbonylation, or simple deoxygenation reaction (Carlson et al. 2010). In general, hydrodeoxygenation is carried out at high temperature and high pressure in the presence of a suitable catalyst. The liquid product primarily consists of diesel range hydrocarbons whereas gaseous product contains CO, CO_2, methane, and propane. In general, linear chain fuel range hydrocarbons production from algal biomass is a two-step process. Firstly, triglycerides and bio oil are extracted from the algae via different thermal methods. Thereafter, catalytic hydrodeoxygenation reaction is done using a suitable noble metal or transition metal derived catalyst. On the contrary, recent reports suggest that this hydrodeoxygenation reaction can be performed using other catalysts such as zeolites as well (Wang et al. 2014).

Moreover, some interesting and less complex processes for fuel range hydrocarbons production from algal biomass or its derivatives have been reported in past few years. For example, Bala et al. have reported the production of C_{10}―C_{14} hydrocarbons from algal oil at 400°C temperature and 400 psi pressure in the presence of ceria supported zeolite (Bala and Chidambaram 2016). Consequently, the 98% algal oil conversion and 85% selectivity towards desired product were obtained. Moreover, the product obtained can be directly implied as an aviation or jet fuel. However, noteworthy that this process requires algal biomass with high lipid content because lipids primarily contain fatty acid esters and free fatty acids which become a feedstock for hydrodeoxygenation. Hydrodeoxygenation in general is not explored much as standalone and one pot process for fuel range hydrocarbons production from algal biomass. However, it is an important and emerging process that has potential to be scaled up further, possibly due to its

integration with existing technologies. For example, pyrolysis and liquefaction can be equipped with a hydrodeoxygenation unit to convert produced algal oil into fuel range hydrocarbons simultaneously. Alternatively, one pot hydrodeoxygenation process for production of fuel range hydrocarbons directly from algal biomass may be explored in near future.

5.3 Catalytic Process for Production of Aromatics from Algal Biomass

In general, majority of the processes employed for biofuel production from algal biomass either produced oxygenates or diesel range fuel. However, since gasoline range fuel essentially consists of low molecular weight hydrocarbons and aromatics, therefore it is essential to produce aromatics and light hydrocarbons from the algal biomass. Besides their application in gasoline and other fuel, aromatics are considered as important class of petrochemicals used to produce an array of chemicals. Thus, efforts have been made to produce oxygen free aromatics such as benzene, toluene, and xylene (BTX) from algal biomass to meet the growing petrochemicals demand. In addition, several other value added chemicals may be obtained simultaneously with production of biofuel.

For example, Wanga et al. have reported the production of aromatics and ammonia from the catalytic pyrolysis of algal biomass in the presence of a zeolite based catalyst. Authors have claimed to achieve 24% aromatics yield when experiments were performed using *Chlorella vulgaris* as feedstock at a temperature below 600°C. Interestingly, authors have claimed to recover to 53% nitrogen in the form of ammonia which is unlikely the case with other technologies where nitrogen is often discarded as waste product. Thus, this process has potential to reduce load of oil and gas industry, petrochemical industry, and supply feedstock for fertilizer industry simultaneously. Moreover, this process can further be improved for better utilization of remaining feedstock. For example, Gopakumar et al. have reported up to 25% wt% of carbon algal biomass converted into aromatics (Thangalazhy-Gopakumar et al. 2012). In addition, it is suggest by the authors that ammonia production may be improved by increasing the amount of HZS-5 catalyst applied for the production of aromatics from the algal biomass. However, this area is still under development and we anticipate a major breakthrough in algal biomass conversion technology if the aromatic yield can be improved further.

6 Opportunities and Challenges in Algal Biomass Conversion

In general, algal biomass can be considered as sustainable and promising source of energy and chemicals. It provides several opportunities over other biomass sources in terms of overall recycling of greenhouse gases, thus making it more environment friendly. Indeed, it is photoautotrophic organism capable of utilizing solar energy and carbon dioxide to produce chemicals in a short cultivation cycle (Guo et al. 2015). Thus, enabling efficient utilization of solar energy and reducing environmental load simultaneously. On the contrary, additional oxygen release during growth of algal biomass may serve as a source of oxygen. To be noted that algal biomass is fastest growing plant, which is unlikely to be the case with lignocellulosic biomass. In addition, it can be grown anywhere and does not necessarily require a fertile land, thereby avoiding conflict with food crop production. It can be used as mean to curb water pollution by growing algae in polluted water ponds and seaside, thereby preserving aquatic ecosystem. Similarly, algae cultivation may be considered as a means to restore degraded and contaminated areas. Moreover, oil yield (20,000–80,000 L) per acre of cultivated land which is 7–31 times than the sum of the best oil producing crops such as palm oil (Demirbas and Fatih Demirbas 2011).

Noteworthy that algal biomass can be used to produce a wide range of chemicals and fuel ranging from biodiesel, alcohols, renewable hydrocarbons, biogas, fertilizers, animal feed, surfactant, monomers for plastics to recovery of nutrients such as phosphorous, proteins, and other minerals. Moreover, application of algal biomass derived biofuel (biodiesel) helps to suppress environmental damages by capturing CO_2, SO_x, NO_x, and other toxic elements (Vassilev and Vassileva 2016). Besides biofuel, algal biomass derived fatty esters have found several applications in bio-lubricant industry. Interestingly, bio-lubricant market is estimated to be $40 billion at present which may escalate in future with development of sustainable technologies. Indeed, algal biomass derived fatty acid esters have potential to replace conventional food grade bio-lubricant sources such as vegetable oil. Development of such technologies would have great societal and economic impact.

On the contrary, high production cost of feedstock limits its application as a source of biofuel and commodity chemicals. In general, preparation of algal biomass feedstock for biofuel production typically involves cultivation, harvesting, and drying. Algal biomass feedstock cost is about 5–7 times higher than that lignocellulosic biomass (Huber et al. 2006). Furthermore, capital cost investment for algal biomass based biorefineries is quite high. National Renewable Energy Laboratory (NREL) has conducted techno-economic feasibility study, resource assessment, and life cycle assessment (Davis et al. 2012). On the basis of their assessment, it was suggested that increased production and high lipid content of algal biomass alone cannot make the process economically viable. Therefore, feedstock cost preparation and processing cost must be reduced to sustain such technologies. Interestingly, several methods such as thermal route, catalytic route, and biological routes, as discussed in this chapter, are implied for production of

biofuel. However, low crude oil prices at present situation remains a threat for further progress in this area. Other interesting process for production of diesel like hydrocarbons is hydrodeoxygenation which essentially requires additional hydrogen supply, thus limits the applicability for industrial processes. On the contrary, other techniques such as decarboxylation and decarbonylation are yet to be proven on a relatively larger scale.

Other important criteria for techno-economic viability of any process is the availability of feedstock. Although, algal biomass can be cultivated anywhere, seasonal effects may limit its availability. In addition, excessive cultivation of algal biomass for application in biofuel production may lead to water contamination and acidification, thus resulting into environmental damages. Furthermore, excessive algae cultivation may cause disturbance in the ecosystem which is in contrast to the overall of objectives of promoting biofuel production from algal biomass. Therefore, a more robust and sustainable methodology for algal biomass cultivation is required.

7 Summary and Outlook

Algal biomass is a promising substitute of conventional fossil fuel that has potential to meet enormous energy and chemical demands. Unlike lignocellulosic biomass, algal biomass produces a relatively higher yield of bio oil which makes it an interesting feedstock for biofuel industry. Moreover, several technologies have been established and proven authenticating the feasibility of biofuel production at commercial scale. Algal biomass can be directly used for the power generation in power plants via direct combustion or it can be co-fed with coal in the power plants to improve the overall plant efficiency by 20–40%. Moreover, depending upon the requirement, solid, liquid, or gaseous fuels can be produced. The gaseous products are primarily CO, CO_2, methane, and hydrogen whereas liquid product can be mixture of several oxygenates. On the contrary, solid product is char like material. Interestingly, all the products hold great fuel value and application to meet energy demands. At present, thermal routes such as combustion, gasification, pyrolysis, and liquefaction are predominant for the production of biofuel from algal biomass. However, these processes are energy intensive, thus catalytic routes have been explored. In contrast, biological routes are not energy extensive and can be applied to produce hydrogen, methane, alcohol, and alkanes. The major limitation of biological routes is their inability to produce the chemicals in bulk and huge space requirement for processing. Overall, algal biomass as source of biofuel and commodity chemicals remains an attractive choice due to its better oil yield and energy density as compared to lignocellulosic biomass.

Albeit the oil content and energy density of algal biomass is comparatively high. The oil content per acre of land of algae cultivation can further be enhanced by application of genetic engineering based technologies. It would be interestingly to mix algae DNA with some other species to escalate oil content and reduced cultivation time. It is anticipated that genetically modified crops would cheap and

economic having high oil content and require less cultivation area as compared to existing algal biomass. Alternatively, other emerging technologies such as photobioreactors can be used for continuous and sustainable production of algal biomass. Similarly, it would be interesting to produce long chain monomers from algal biomass derived fatty acids. These monomers may strengthen interdisciplinary research areas especially in biopolymer and polymer industry.

Nevertheless, many interesting and sustainable technologies for algal biomass conversion into biofuel have emerged. For example, hydrodeoxygenation, hydrotreatment, decarboxylation, and deoxygenation technologies have capability to produce oxygen free fuel range hydrocarbons. However, these processes are still under development and demonstrated at lab scale. Further scale up studies and process optimization can be a promising area to work in. Moreover, synthesis of non-transition metal and noble metal based catalysts such as zeolites or metal doped zeolites may find a great interest. Since crude oil prices have gone to a very low level, therefore techno-economic feasibility of such processes needs to be improved. Alternatively, efforts can be made to produce high value commodity chemicals such as linear alpha olefins via decarbonylation route. Decarbonylation may help to sustain the biofuel industry in future even if the crude oil prices are very low.

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