Chapter 14
Recent Patents on Biofuels from Microalgae

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Abstract To reduce greenhouse gas emissions and to prevent their devastative impacts of human health and the environment, bioenergy carriers have been at center of attention to supply global energy demand. Microalgae as solar energy-driven factories could efficiently convert carbon dioxide to a variety of hydrocarbons that can be used as biofuels. With the aim of realizing the current status of algal biofuels, respective patents were surveyed in this chapter using various databases, i.e., World Intellectual Property Organization, United States Patent and Trademark Office, and European Patent Office database. Information derived from the aforementioned databases was categorized into three: upstream, mainstream, and downstream strategies. The upstream strategies included patents on selection of algal strain and genetic engineering approaches while the mainstream strategies reviewed and discussed innovations pertaining to improving algal cultivation systems, production media and nutrients supply, and CO_2 supply. Finally, in the downstream strategies section, the inventions aimed at enhancing harvesting and dewatering of microalgae cells and lipid extraction were presented.

Keywords Patent mining · Innovation · Microalgae · Biofuels
Biodiesel

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1 Introduction

It is advisable that innovations presenting promising commercial applications be patent-protected. Going through the patent filing process, it is important to ensure that the set of claims drafted cover all the patentable concepts included in an application. Since this might not be technically feasible in some cases, more than a single patent application might be required to cover all commercial aspects of a given invention. A great deal of patent applications in the area of biofuels production is filed on a daily basis, but only a few are accompanied with a concert commercialization agenda, resulting in considerable investment problems. In line with that, reviews of the recent patent publications in the field could be of great assistance to the inventors and patent examiners in biofuels-related domain. It should be noted that business interests might undergo substantial changes over the course of time, affecting the commercial value of a certain patent as well.

Having reviewed the patent publications filed since 70s, a large number of patents could be found focusing on various aspects of biofuels production from microalgae, e.g., strain selection, process efficiency, and process management. This is mainly ascribed to the unique features of microalgae, i.e., being a non-agricultural crop (triggering no food vs. fuel conflict), possibility of cultivation in various aquatic environments (freshwater, saline water, and wastewater), as well as huge biomass production and high lipid content.

Most recent patent applications concerning microalgal fuels are focused on improving the cellular metabolic flux of the organisms or on improving/optimizing the algal biofuel production processes (Thompson 2013). As an example, the distribution of patents for two candidate microalgae for biodiesel production is presented in Table 1 (de la Jara et al. 2016).

It should be noted that this chapter is not advocating or determining the patentability of any technologies related to microalgal fuel but rather striving to shed light on the latest development in the field in the form of patent applications. More specifically, patent applications are reviewed and discussed under upstream, mainstream, and downstream strategies.

Table 1 Distribution of patents for two candidate microalgae for biodiesel production (adopted from de la Jara et al. 2016)

Patent application details	Microalgae	
	Chlorella sp.	*Dunaliella* sp.
Year of first publication	1964	1978
Year of first publication in energy area	1977	2008
Evolution of published patents	2011	Steady state
Application category (in order of development *vs.* time)	Production methodology, food, energy	Culture media, food, energy

2 Microalgae as Biofuel Feedstock

The introduction of commercially viable microalgal feedstock for biofuels production is among the most important bottlenecks of the whole process and therefore, numerous published patents exist in this regards. Algal biomass could undergo any of the following main pathways to be converted into biofuels: (1) extraction and transesterification of triglycerides to produce biodiesel; (2) fermentation of carbohydrates to produce bioalcohols (e.g., bioethanol and biobutanol); (3) anaerobic digestion to produce biogas (biomethane); and (4) gasification or other thermochemical conversions of the biomass (Craggs et al. 2011). The details of processes and systems to convert algal biomass for production of biofuels are the subject of the patents such as US7977076B2, US2012/0329099, US2012/0288917, US2012/0283496, WO2009158028A2, CN102120938A, US8308949, US8211308. In all these inventions, it has been stressed that microalgae cultivation in an aquatic environment could harness sunlight energy in the form of carbohydrates by photosynthesis. This is environmentally important as the combustion of petroleum-derived energy carriers interferes with the carbon pool, i.e., the energy of sunlight stored in the past, leading to an increased level of atmospheric carbon while algal biofuels capture these released carbon atoms on a current basis.

A patent analysis by using a major generic keyword, i.e., “microalgae biodiesel” in the title, abstract or full text, led to 49 hits in the Worldwide EN database (https://www.epo.org). The related patents were also mined in the USPTO Patent Full-Text and Image Database (http://www.uspto.gov/) from 1976 to 2017, and 107 hits were found. While using the free trial version of Matheo Patent software, the number of patents found using the same keyword was only one since the year 2011. However, by using “microalgae” as keyword, more than 2048 US patents describing microalgae potential applications were found since the year 1979. These patents are mostly focused on limited applications such as introduction of novel cultivation conditions (e.g., SU678065, SU663723, and SU686686), or for water treatment (e.g., SU701570). After a lag phase between 1960s and 1990s, the publication of patents related to the general term “microalgae” experienced a slight increase. Interestingly, the introduction of the industrial applications of microalgal biotechnology led to an exponential growth in the number of patents following the year 2007.

Apart from the liquid biofuels produced from microalgae such as bioethanol and biodiesel, production of other bioenergy carriers such as biohydrogen and biomethane from this feedstock is also of substantial interest. Researchers have also developed genetically modified algae to produce specific biofuel precursors. In the subsequent sections, some examples of algal potentials in bioenergy production are presented. Contrary to the algae-related applications published in last decades (usually disclosing methods that were interesting, but not necessarily commercial), in the past 6 years, both aspects of novelty and commercial viability have been considered while some patents have also taken environmental considerations (e.g., life cycle assessments) into account.

2.1 Biodiesel

"How do scientists make biodiesel from microalgae?" The answer lies in the ability of microalgae to synthesize huge amounts of free fatty acids and accumulate them in storage form of lipids, i.e., triglycerides (TAGs), in their cells. These lipids are then used as feedstocks for biodiesel production. The lipid bodies are extracted and the TAGs would be converted to the corresponding methyl/ethyl esters through a reaction called transesterification. The term "biodiesel" has been considerably more frequently cited in patent databases than bioalcohol or hydrogen (de la Jara et al. 2016). Further details on converting algal oil to biodiesel, from extraction to catalytic conversion, have been provided in the following patents: US7977076B2, US4341038, US8475543B2, US20110136189, and US20160053191A1.

2.2 Bioalcohols

Some microalgae contain carbohydrates (generally not cellulose) that can be used as feedstock for alcoholic fermentation. It should be highlighted that bioalcohols production process from microalgae is very simplified owing to the fact that microalgae cells do not require lignin and hemicelluloses for their structural support and therefore, no chemical and enzymatic pretreatment step would be required to extract sugars. Nevertheless, a simple and economically justified physical pretreatment process such as extrusion and mechanical shear is still required to break down the cell wall to release the fermentable sugars for subsequent conversion into bioalcohols such as bioethanol (John et al. 2011). In spite of all the aforementioned favorable features, fermentative fuels produced from algae are still faced by some challenges such as low fermentable carbohydrate content of algae biomass compared with other starchy crops such as maize. Some nutritional limitations such as nitrogen starvation and genetic manipulation have been considered in the published patents as promising solutions to overcome this shortcoming. Suitable starting materials, methods of fermentation, involved strains and enzymes as well as general processes and systems to produce and isolate alcohols from microalgal feedstock have been the subject of numerous patents such as US patent applications 5578472A, 7135308B1, 7507554, and 9260730.

2.3 Biohydrogen

Hydrogen is promoted by many because of possessing the potential to be a clean sustainable energy carrier. Photoautotrophic H_2 producing green algae, including *Chlamydomonas reinhardtii*, has been shown to metabolize H_2 under anoxic conditions. In the photosynthetic system, H_2 can be produced through hydrogenase-catalyzed reduction of protons by the electrons generated from photosynthetic oxidation of water. Sunlight acts as generator to supply the required energy to continue this stepwise reaction (Lee 2010). In spite of the numerous research efforts put into improving algal H_2 production, the limited rate of this reaction has so far made H_2 production commercially impractical.

2.4 Biogas (Biomethane)

Following lipid (oil) extraction or ethanol fermentation, the remaining algal biomass could also be anaerobically digested to produce biogas. If upgraded, i.e., by increasing the methane content of the gas stream, biogas can be used directly for heating or for electricity generation. Conversion of wet algal biomass to biomethane along with a liquid fertilizer (anaerobic digestate) is an advisable strategy to harness the majority of the remained energy and nitrogen contained in the algal biomass after oil and/or carbohydrates extraction (Scott et al. 2010). Biogas obtained from microalgae was found 7–13% more enriched in terms of its methane content in comparison with the biogas obtained from maize (Sialve et al. 2009), but the production was still limited by the relatively high N content of biomass or in another word, the ammonia inhibition effect. An average yield of approximately 0.30 m^3 (0.20 kg) CH_4/kg algal biomass (energy value equivalent to 1 L of petrol (34 MJ) for each cubic meter of biogas) was reported by Craggs et al. (2011).

2.5 Biomass to Liquid (BTL) Fuel

Biomass to liquid (BTL) is an integrated process aimed at fuel by thermal conversion of biomass. More specifically, the biomass gasified through biosyngas production systems is converted into liquid fuels through different processes such as Fischer–Tropsch (Medina et al. 2010). Carbon monoxide and hydrogen can be produced from gasification of any biomass such as algal feedstock. Methanol for instance can then be produced through direct reaction between these gases. US Patents 20090321349, 8163041B1 as well as WO2012109720A1 and WO2014057102A1 present further details on the catalysts and methods involved in the conversion of syngas to liquid fuels.

3 Microalgal Biofuels-Related Patents

Based on a logical order, the microalgal biofuels-related patents could be categorized into three major groups, i.e., patents concerning upstream, mainstream, and downstream strategies. The patents presented were selected from the Matheo patent database software which contains more than 80 million patents.

3.1 Upstream Strategies

It is usually easier to optimize existing biofuel technologies rather than exploring newly emerged capacities. Accordingly, to overcome the existing shortcomings of algal biofuels production, selection of more productive strains to boost productivity is considered as the first approach. As the subsequent approaches, reprogramming of algal metabolism either by modifying growth conditions or by genetic engineering tools could be considered.

3.1.1 Selection of Algal Strain

Selection of appropriate algal strains is a prerequisite to successful and economically viable algae-based biofuel industry. In fact, proper strain selection results in better breeding, engineering, and adaptation of strains to reach the most desirable phenotypes. This is because each microalgal genus may need specific requirements for growth and cultivation conditions, harvesting equipment, downstream processes as well as extraction protocols due to cell different physiology or morphology. Therefore, development of non-species specific and common devices can be helpful in achieving a more successful algal-based bioenergy market. Numerous patents are focused on specific genera of *Chlorella*, *Spirulina*, *Dunaliella*, *Haematococcus, Synechocystis, Microcystis, Desmodesmus,* and *Chlamydomonas*. US20140302569A1, US20090211150A1, and WO2008083352A1 are just a few examples. Among algal species, *Chlorella* sp. is of largest interest in this field, probably due to its high growth rate and comparatively lower production costs. For instance, the more economical the produced lipid, the more competitive the produced biodiesel would be. The first patent related to this species in the EPO database dates back the year 1977, but the number of records increased to 36 in the year 2016 (de la Jara et al. 2016).

Further search in Espacenet showed that considering only quantitative growth parameters would not be sufficient for an efficient biodiesel production and high intracellular lipid content would also act as a key criterion for selection of candidate microalgae strains for biodiesel production. On such a basis, *Isochrysis galbana* was introduced as a productive strain by the patent ES2088366A1. Furthermore, strains of *Characium polymorphum* and *Ankistrodesmus braunii* were also studied as oil-rich microalgae which can be used as feedstock for biofuel production by the US patent 20130157344A.

It should be mentioned that the selection of species for scaling-up an algal biofuel production system would also depend on fatty acid (FA) composition and lipid productivity. In line with that, Weiss in a US patent 20080220486A1 claimed that the strains of *Skeletonema costatum* and *Nannochloropsis* sp. could be considered as prone oleaginous microalgal strains; according to their FA profile and growth rate (20 g/m^2/d) under certain conditions.

The quality parameters of biodiesel (i.e., Cetane number, heat of combustion, cold flow properties, oxidative stability, and viscosity) depend on the characteristics of individual FA alkyl esters and are determined by the structural features of the FAs such as chain length, number and the situation of double bonds, and chain branching) (Ramos et al. 2009; Talebi et al. 2013a, b). The type of the produced FAs by algal cells is greatly influenced by genetic characteristics and also by the environmental conditions during cultivation. In general, intrinsic tolerance to higher temperatures and higher CO_2 concentrations could lead to a high biomass growth rate with a huge quantity of lipids. Overall, super microalgal strains could be either isolated or mutated. There are patents which try to introduce methods to mutate and maintain "old" strains to obtain "prone and powerful" ones, e.g., JP10248553A, US20130236951A1, US7935515B2, and CN101412965A. Other publications such as JP8257356A, JP10248553A, and TW291493B highlight the use of thermophilic microalgae when hot flue gases are employed.

3.1.2 Genetic Engineering Approaches

To obtain superior microalgae strains capable of swift cell growth, efficient photosynthesis, enhanced inorganic carbon fixation, as well as producing improved type and quality of fuel genetic engineering approaches have been exploited. Thanks to the developments made in sequencing tools since early 2000s, substantial advances in genetic manipulation of single-celled photosynthetic microalgal model organisms such as *C. reinhardtii* and *Chlorella vulgaris* have been achieved (Talebi et al. 2013a, b).

In general, genetically modified microalgae could be efficiently used for biofuel production, CO_2 sequestration, as well as other bioremediation goals. For instance, the patent US20170191094A1 claimed that the recombinant algae strains harboring at least one of the following exogenous genes were able to produce greater amounts of lipids under nitrogen starvation conditions [acyl-CoA synthetase, acyl-CoA reductase, acetyl-CoA carboxylase, acyl-ACP thioesterase, phosphatidic acid phosphatase, or diacylglycerol 0-acyltransferase (DGAT)]. Moreover, the quality of biodiesel can be also improved by engineering the cells toward the accumulation of lipids with a more desired FAs profiles. Among the strategies considered to engineer FA biosynthesis toward more compatible lipid profiles are the overexpression of FAs enzymes and their up-regulation by transcription factors as well as increasing the availability of precursor molecules (acetyl-CoA) and reducing power (NADPH). Moreover, down-regulation of FA catabolism by inhibiting β-oxidation, or lipase hydrolysis is also among the other available strategies (see patents US8951777B2, WO2011026008A1, WO2013034648A1, and US9593351B2). Microalgae can also be modified to express different enzymes that influence the production of long-chain FAs (e.g., patent WO2010019813A2). Also related to fatty acid synthesis is the polyketide synthase enzyme (PKS), whose impacts on the production of poly unsaturated FAs are discussed in the US patent 20070244192A1. Altering the saturation degree through the introduction or regulation of desaturases, and optimization of FA chain length with thioesterases are among various biomimetic approaches proposed to enhance the quality and yield of the produced biodiesel from microalgae (Talebi et al. 2013a, b).

Apart from enhancing metabolic lipid synthesis, other targets of genetical modification of microalgae concern improving light utilization, enhancing photosynthetic efficiency, as well as modifying carbon assimilation and trophic conversion pathways. For example, methods for enhancing cell growth of microalgae by transgenic expression of a bicarbonate transporter, carbonic anhydrase, and light-driven proton pump were introduced by the US patents 2014/0120623 and US20170211086A1.

Light penetration characteristic (also known as chlorophyll engineering) is a new interesting area being explored by related patents such as the US patent 20090023180A1 presenting methods to increase the efficiency of light utilization of photosynthetic microorganisms.

In conclusion, it worth quoting that although the aim of the upstream strategies is not to cover all topics involved in algal biofuels production, it is important to highlights that potential achievements made in this category could play key roles in overcoming the economic challenges faced by industries dealing with large-scale microalgal biofuels production. Microalgae can be selected or modified to express different valuable byproducts. On the other hand, the nutritional requirements, compatibility to available facilities, tolerance to biotic and abiotic stress could also be engineered through proper upstream processes, since the possibilities of both selection (genetic diversity) and genetic engineering seem infinite.

3.2 *Mainstream Strategies*

Different patents exist with an aim to improve the production of biomass and/or biocompounds. It is worth highlighting that economically produced algal biomass is an essential part of successful large-scale algal fuels industries. This clearly explains major efforts put into this category. Photobioreactor (PBR) designs for cultivating microalgae might be the most important challenge, but there are other mainstream bottlenecks as well, such as controlling systems. While harvesting systems, extraction and conversion of microalgal biomass to various biofuel are the subjects of downstream strategies considered when an ideal large-scale model plant producing algal biofuels is discussed.

3.2.1 Improving Algal Cultivation Systems

As mentioned earlier, sustainable large-scale cultivation of microalgae is a prerequisite for successful production of algal biofuels such as algal biodiesel. To identify the most relevant activities carried out in the development of microalgal cultivation, patents issued pertaining to this topic are summarized in this subcategory. There are three main alternatives for cultivating photoautotrophic algae: (1) open systems such as the routinely used raceway pond systems, (2) closed systems involving PBRs, and (3) hybrid production systems which are combinations of the other two systems. Among these systems, open ponds like raceway pond systems are the most common design employed for large-scale applications (Pulz 2001). A typical raceway pond comprises a closed oval channel, open to the air, and mixed with a paddle wheel to circulate the water and prevent sedimentation. These ponds are usually shallow; i.e., ~0.25–0.4 m deep, to facilitate light penetration and prevent self-shading by algal cells. Limited light penetration through the algal broth would decrease the photosynthesis and consequently the biomass production. Some genetic manipulations aimed at remodeling photosynthesis apparatus to enhance this trait were discussed in Sect. 3.1.2. High rate algal ponds (HRAPs) are shallow, open raceway ponds. HRAPs have been originally used for the treatment of municipal, industrial, and agricultural wastewaters; however, the algal biomass produced from these systems could be converted through various pathways to biofuels.

A semi-closed ocean system enriched by iron was introduced by the US patent 2014/0113331 leading to atmospheric CO_2 sequestration, reduced ocean acidity, as well as efficient cultivation and harvesting of a high deal of algal biomass. Although open systems in general look promising for commercial applications, their several shortcomings led to a widespread search for alternative algal cultivation systems. In light of that, tubular PBRs were introduced through which problems like susceptibility to contamination (as seen in open pond systems), large water consumption, low CO_2 absorption efficiency, the presence of dark zones (or in another word, low light penetration efficiency), and the resultant low photosynthesis efficiency were overcome. The issue of surface–volume ratio, light, $CO_{2,}$ and nutrients supply as well as the development of tools to control temperature and pH have been extensively studied and have been the subject of numerous patents such as US20090211150A1, US5104803A, US20090291485A1, US2010000571A1, US20090029445A1, and US9605238B2.

Different configurations of tubular PBRs (i.e., horizontal, helical, and flat panels) have also been introduced in a number of patents (e.g., US20100248333A1 and US20080311649A1). Moreover, airlift reactors in which bubbles are used as bubble-columns to mix the media were later introduced (US20110113682A1) to overcome the problems associated with the large surface–volume ratio observed in tubular PBRs. However, bubble-columns and airlift reactors require high gas flows to ensure an efficient circulation would be taking place between the light and dark zones. This could further impose a shearing force on the growing algal cells. A novel PBRs design elaborated in the patent US20150275161A1 eliminated the need for sparging and compressors for suspending cells and mixing carbon dioxide through the introduction of attendant mixing by subtending wave motion. The novel system resulted in reduced initial investment required as well as the elimination of the above-mentioned sharing force. Another example of novel PBRs is discussed in WO2015056267A1.

In conclusion, PBR systems allow for better control of the algal cell growth but are also accompanied with higher energy demands and, therefore, are more costly than open systems to operate (US20090011492A1). On the other hand, areal productivity of airlift PBRs is higher than that of the tubular PBRs, but their volumetric productivity is around half of what achieved using tubular PBRs (Tabernero et al. 2013). More detailed information on cultivating microalgae using PBRs could be found in patents such as US20090130704A, US20140356931A1, WO2015050775A1, US9045724B2, and US8003379B2.

3.2.2 Production Media and Nutrients Supply

As mentioned earlier, by using PBRs, growth-limiting factors such as light, CO_2, nutrients supply, and temperature can be easily controlled. Numerous patents like US20110092726A, US20110107664A1, US20130023044A1, and US20110294196A1 are concerned about efficient nutrient supply. More specifically, their aim is the development of nutrient media to increase biomass production and boost accumulation of valuable compounds. Introduction of novel sources of essential minerals and CO_2 to enhance the economic aspects of the systems has also been among the objectives of such patents.

Historically, biochemical engineering, e.g., nutrients management (such as nitrogen and phosphor starvation), precursor addition as well as design of growth and/or environmental conditions (like salinity, acidity, and photon flux) in microalgae have been used as primary forward tools to enhance desired metabolic productivity (Courchesne et al. 2009). Exploring the respective regulatory mechanisms was the subject of the following patents: GB2501101A, US9295206B2, and WO2015088127A1.

As it was previously mentioned, the environmental conditions as well as provided nutrients could directly affect the FA profile of oleaginous microalgae. Heterotrophic culture system is an example of ways to increase FA concentration in microalgae. Within the heterotrophic culture, the microalgal cells consume an organic source (e.g., glucose, glycerol) instead of CO_2. In spite of increased cost and reduced environmental benefits, several advantages such as an increase in growth speed and lipid concentration are expected. This has been the subject of numerous investigations such as the patents WO9107498A1, US20090209014A1, US5130242A, and US20060094089A1.

Although the mechanisms of wastewater tolerance in microalgal community are yet to be discovered, strains which are naturally adapted and are capable of efficiently growing in wastewaters/effluents are regarded as successful strains to achieve economical biofuel production. This is ascribed to the fact that nutrient-rich municipal, agricultural, and industrial wastewaters could provide an economically sustainable means of cultivation for different strains of microalgae. In addition, such systems offer the advantage of combining wastewater treatment (i.e., heavy metal and nutrients removal) with biofuels production systems (Pittman et al. 2011). Such combination can potentially reduce unit cost energy by 20–25% in addition to eliminating the cost of nutrients and freshwater supply (Craggs et al. 2011). It has been reported that algal cells can efficiently remove contaminating nitrogen (N) and phosphorus (P) nutrients as well as toxic metal pollutants from wastewaters (de-Bashan and Bashan 2010; Ruiz-Marin et al. 2010). The claims of multiple patents, e.g., US20110247977A1, FR3023548A1, WO2014076327A1, GB2484530A, and GB2509710A, are focused biofuel production systems coupled with wastewater remediation. Nevertheless, to achieve desired levels of wastewater treatment with algal systems, maximizing autotrophic production and discovering physiological characteristics of algal cell are of primary importance and has been the subject of the following patent: US2010267122, CN101368193A, US20090294354A1, and US8101080B2.

To benefit all the advantageous features of coupled systems, some sustainable systems such as HRAPs have already been developed (see ES2563852T3). HRAP system in comparison with the conventional wastewater treatment methods requires lower capital and operating costs and needs no intensive advanced technology to operate compared with the conventional mechanical treatment technologies (Craggs et al. 2012). Eight comprehensive patents could be found by searching the term “HRAPs” in the PGPUB production database since the year 2001; for example, the patents US20160122705A1 and US20100252498A1 discuss simultaneous methods for HRAP-based wastewater treatment and algal production in detail.

3.2.3 CO_2 Supply

Most microalgae strains have been evolved to mitigate the environmental impacts. This capability of microalgae strains to remove pollutants was first introduced in the 1970s and twenty years later patents such as JP4075537A, JP314777A, and US5011604A strived to describe the details of removing pollutants from power stations with microalgae. To facilitate the utilization of ambient CO_2, microalgae possess a CO_2-concentrating mechanism (CCM) (Ndimba et al. 2013). Nevertheless, direct CO_2 addition to medium has still been shown to significantly enhance algal productivity. This can be simply achieved through control of pH inhibition, reducing phosphate precipitation and nitrogen loss (mainly by reduced ammonia volatilization), as well as by increasing nutrient assimilation into algal biomass (Park and Craggs 2011).

Since exhaust emission gases usually include NOx and SOx, the attractive idea of biorefining urban air harboring NOx and SOx originated from automobile emissions was first discussed in the year 1998 by the patent US6083740A based on the fact that gaseous pollutants such as CO_2, NOx, and SOx can be used as nutrients for microalgae. In the case of CO_2 supply from power stations, the pretreatment steps such as desulfurization and setting CO_2 concentration as well as transportation to an algal cultivation system should be taken into account (see US20080220486A1).

Many researchers such as Chisti (2008) and Lardon et al. (2009) have emphasized that to minimize operational costs in full-scale applications, carbon dioxide should be supplied by waste gaseous emissions such as flue gas from fossil fuel burning power plants. Providing CO_2 in form of micronized bubbles could improve mass transfer and consequently the CO_2 diffusion in the system (see CN101555455A). Moreover, the US patent 5659977A elaborated on a closed system for carbon sequestration in which CO_2 from the exhaust gas would be introduced as nutrient to the microalgae production plant. It should be mentioned that the electrical energy obtained from the algal biomass could be used to produce artificial illumination and/or drive pumps, motors, and control unit in the microalgae production plant. Having achieved this, such a system could be operated like a sustainable biorefinery platform. Another cyclic system consisting of several integrated processes is discussed in the patent US8510985B2 advocating a method for simultaneous production of energy and some byproducts coupled with pollutant sequestration.

The issue of CO_2 supplementation into algal growth chamber involves different aspects which should be taken into serious consideration, from susceptibility of microalgae strains to certain CO_2 concentrations to the impacts of different sources of CO_2 and nutrients pollution which could be potentially caused by emissions of power stations. These have been the subject of patents like US20130217082A1, WO2010010554A1, US8262776B2, and US20080220486A1.

In brief, sustainable production of biofuels from microalgae still requires technological innovations and highly optimized cultivation systems, and without a positive energy and carbon balance, microalgae cultivation presents a mixed picture.

3.3 Downstream Strategies

The issue of transformation of biomass into biofuels is a very wide topic and more than 28,000 scientific papers and 3000 international patents have been published to describe this issue during the last decade only (Faba et al. 2015). Therefore, given the diversity of the subjects, this section is only focused on different methods used to obtain liquid biofuels (more specifically biodiesel) from algal biomass. While solid fuels or other types of energy are generally obtained from the entire algal biomass as feedstock, biodiesel production requires specific processes to transform a certain fraction of algal biomass, i.e., FAs.

Extensive downstream processing, like biomass harvesting and drying, lipid extraction and fuel processing are regarded as major hurdles in algal biofuel commercialization. These steps (especially harvesting and extraction) usually take up more than half of the input energy required for algal biodiesel production. Since the final cost of the marketable produced lipid (regardless of their use in the health or energy market) is determined during these steps, downstream category has a strong impact on the other categories as well as final productivity. In addition to that, downstream processes (especially extraction and transesterification) determine the quality of the obtained biodiesel. In better words, the higher the biochemical quality of the lipid is, the more competitive the final product will be. Therefore, optimization of the steps involved is critical and has been the focus of many patent applications.

3.3.1 Harvesting and Dewatering of Microalgae Cells

The harvesting process involves two sets of operations, i.e., bulk harvesting and concentrating the resultant slurry (Brennan and Owende 2010). Recently published patents such as US6000551 and US7022509B2 are focused on a promising and sustainable way as bulk harvesting alternative, i.e., gas flotation or adsorptive bubble separation process. This method not only removes the need for flocculants application, but it is also capable of lysing algal cells concurrent to gathering. In addition, inventors have also developed a number of hydrophobic chemical treatments for harvesting algal cells from broth. More specifically, by adding a hydrophobic liquid/flocculent with lower salinity, the microalgae suspension forms a top phase comprising the hydrophobic liquid and at least a portion of the microalgal cells and a bottom phase comprising the aqueous solution (see the patents US20110165662A1 and US4958460A).

Based on the microalgae size or density, several methods for dewatering of concentrated algal suspension are available. Conventional processes like filtration, gravity, mesh lining centrifugal sedimentation, chemical coagulation and flocculation, use of adsorbents, magnetic separators as well as ultrasonic aggregation have been explained in the patents US4554390A, US20090317886A1, US20090134091A1, US8399239B2, US8399239B2, US8772004B2, and EP2747890A1.

3.3.2 Lipid Extraction

Once an algal biomass is dewatered and dried, only then high-value products could be extracted. Various methods for algal lipid extraction have been developed among which oil press machine, organic solvent extraction, supercritical fluid, subcritical water, and electrochemical extraction methods have seen significant technological advances over the course of recent years. In general, to achieve a desired extraction productivity, some important consideration should be taken, e.g., optimization of pretreatment steps, type and amounts of selected solvents, etc., which have been the aim of several patent applications (see patents US20150252285A1, US20120083617, US20120238732A1, and US20140243540). It should be noted that the fuel properties of biodiesel are significantly influenced by the extraction method used.

Overall, extracting algal oil from the microalgae cells could be achieved through biological or non-biological cell wall rupturing methods. More specifically, the lysis can be performed with vapor (see the patent US2009081742A1), solvents (such as methylene chloride as elaborated upon in the patent US4554390A), mechanical means (such as flotation processes as elaborated upon in the patents US7022509B2 and US6000551), pulsed electric field (US20110107655A1 and US20040224397), electromagnetic radiation (US2009087900A1 and WO2009142765A2), pulsing ultrasonic waves (US20120125763, US8043496B1, and US20100151540A1), or even through genetic manipulation (autolysis as elaborated upon in the patent US20170022436A1 and US20160130627). In addition, the procedure may use at least one enzymatic (such as a cellulose, protease or glycoproteinase) or physico-chemical treatments to disrupt the cells (WO2010039030A1 and US20120238732A1), followed by repetitive steps to separate different cell compounds which finally leads to extract the oil. No-solvent cell lysis or single step extraction protocol is always promising since the extracted oil can be released from wet microalgae, directly entering the subsequent steps. More information on this methodology can be found in the patents US20120040428A1, US20160265011, and US20110107655A1.

Compared with conventional and mechanical means of oil extraction, in which cells into should be transformed into dried granules and different solvents are used, alternative methods have been developed with an aim to further save time and financial resources (see the patents US2012065416 and US2011225878). For example, FAs can be simultaneously extracted and saponified from dry biomass using ethanol and hydroxide sodium in an argon atmosphere at 75–90 °C (ES2289898A1). Even wet microalgae biomass can be extracted directly (US2009227678A1 and US5928696A). A US patent publication 2014/0113363 entitled "process of producing oil from algae using biological rupturing" introduced an oil extraction bioreactor operatively connected to algae growth reservoirs. In this system, for biologically rupturing algal oil vesicles, a structured enzyme system such as a cellulosome was claimed. Different patents, i.e., US8450111B2 and US20110076748A1, claimed that utilizing a single hydrophilic ionic liquid was effective for a one-step process for the lysis of microalgae cell walls and separation of the lipids contained for use in biodiesel production.

Overall, diverse strategies have been put forth claiming success in oil extraction from diverse set of dried and/or wet algal materials. To draw a distinction, patents US20130210093 and WO2010039030A1 made a comparison among the methods described in the other patents, from routine solvent extraction to supercritical fluid extraction and a modified Bligh and Dyer method. The findings reported showed that more long-chain omega-3 FAs could be obtained using a solvent miscible with water in comparison with the supercritical fluids extraction and hexane extractions.

4 Conclusions

In this chapter, patents published since 70s on biofuels production from microalgae were reviewed and discussed in order to shed light on the state of the art of algal fuel production. Overall, a significant number of patents could be found on various aspects of biofuels production from microalgae with a sensible increase in their number since 70s probably due to the general awareness regarding the depletion of conventional energy resources and the environmental problems associated with the widespread utilization of fossil-oriented energy carriers. The published patents presented herein were classified into three main categories, i.e., upstream, mainstream, and downstream strategies. The upstream strategies were focused on algal strain selection and genetic modification for enhancing the quality and quantity of biomass produced. The mainstream strategies concerned improving cultivation systems and conditions, while downstream strategies dealt with improving harvesting, dewatering, and lipid extraction.

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