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# Perspectives and advances of microalgal biodiesel production with supercritical fluid technology

Cite this: DOI: 10.1039/xoxxoooooox

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Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

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Biodiesel, as a sustainable and clean energy source, has been greatly attracting interests to compete against the serious challenges like energy crisis and environment pollution. Microalgae are currently promoted as the most potential biodiesel feedstock with the advantages of high lipid content and productivity. This paper provides an overview on selection of microalgal strain, supercritical carbon dioxide ($SCCO_2$) extraction of microalgal lipids and the advances of microalgae oils' transesterification for producing biodiesel with supercritical alcohols. In particular, a two-step process of microalgal biodiesel production using supercritical technology and the following $SCCO_2$ extraction are generalized in this study. Considering the commercialization of microalgal biodiesel in the future, the cost of microalgal biodiesel published in recent literature is analysed. Furthermore, the feasible strategies for improvement are proposed. The overall economic efficiency of microalgal biodiesel industry can be improved by the multi-effect co-production coupling technology.

## 1. Introduction

Recently, as crude oil prices increase, limited resources of fossil oil, and the environmental consequences of exhaust gases from petroleum-fuelled engines, alternative renewable fuels research has been attracting global attention. Biodiesel, produced from renewable resources, has been found to be the most potential one as the diesel oil substitute due to its great molecular similarities to paraffinic diesel fuel compounds.[1] This fuel is renewable, biodegradable, nontoxic, and generates lower-emissions in comparison to petroleum-based diesel.[2] According to the Mid- and Long-term Development Plan for Renewable Energy in China, the consumption of biodiesel in China will reach 2.0 million tons in 2020.[3] Usage of biodiesel will allow a balance to be sought between agriculture, economic development and the environment.

It has been found that feedstock alone represents more than 75% of the overall biodiesel production cost. Therefore, selecting the appropriate feedstock is of significance to lower the production cost.[4] The four main categories of raw materials for biodiesel are edible vegetable oil, non-edible vegetable oil, waste or recycled oil and animal fats.[5] Edible vegetable oils that include soybeans, palm oil, sunflower, safflower, rapeseed, coconut and peanut are considered as the first generation of biodiesel feedstock because they were the first crops used for biodiesel production.[6, 7]

Last decade, the majority of biodiesel production over the world used edible vegetable oils, such as in Germany, USA, Malaysia and Brazil.[8-10] However, the dramatically increasing prices of these oils raised food versus fuel crisis, leading us turn attention to non-edible oils which are more efficient and economic. Above all, the usage of non-edible oils eliminated the competition between food and fuels, revitalizing the long-term development of biodiesel production industry. Waste or recycled oil and animal fats have been reported as the second generation feedstock like non-edible oils in literature.[11-16] While, the industrialized application of these feedstocks are still facing up with some challenges like the pre-treatment of the high amount of saturated fatty acids and the collection of decentralized waste oils. Microalgae, which hold great potential for carbon neutral biofuels production, are regarded as the third generation sustainable feedstock for biodiesel production because of the merits of high lipid content and high photosynthetic efficiency.[17]

Brentner *et al.*[18] divided the algal biodiesel pathways for sustainable full-scale production into five distinct process steps: (1) microalgae cultivation, (2) harvesting and/or dewatering, (3) lipid extraction, (4) conversion (transesterification) into biodiesel, and (5) by-product management. The latter three steps can be performed using corresponding supercritical fluid technology. Microalgae lipids and high-value by-products can be extracted by $SCCO_2$ as the primary solvent due to its low toxicity, low flammability, and lack of reactivity. Its moderate critical pressure (72.9 bar) allows for a modest compression cost, while its low critical temperature (31.1 °C) enables successful extraction of thermally sensitive lipid fractions without degradation.[19]

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Transesterification is the most widely-used method to produce biodiesel, in which the triglycerides presented in different types of oils react with an alcohol to produce alkyl esters and glycerol.[20] The conventional transesterification reaction often proceeds with acid, alkali, or enzyme catalyst.[21-25] Whereas, in the catalytic process, free fatty acids (FFAs) and water always have negative effects like soap formation and catalyst consummation, reducing the effectiveness of the catalyst and resulting in a low conversion.[26] To overcome these problems, Saka and Kusdiana[1] studied the transesterification of the rapeseed oils with supercritical methanol and found that this new process shortened reaction time and simplified purification procedure. The transesterification of microalgae oils via supercritical alcohols has been eagerly concerned by researchers, entrepreneurs, and governments in many countries. After many investigations on transesterification of various oils in supercritical alcohols, it has been proven to be the most promising method for biodiesel production.[27] Among the commonly used lower alcohols, methanol is the most suitable one for the transesterification from the previous thermodynamic analysis.[28]

The whole process involves genetic, biological, agricultural and chemical engineering. From a view of chemical engineering, how to improve the conversion technology of microalgae oils to biodiesel and reduce the total cost is important to the development of biodiesel industry.

This review focuses on microalgae strain selection, microalgae lipids extraction in $SCCO_2$ and advances of the transesterification reaction with microalgae oils in supercritical alcohols for biodiesel production. Herein, the microalgal biodiesel production and separation process using SCF technology are summed up in this study. Besides that, the economic analysis regarding with the producing cost of microalgal biodiesel is conducted to evaluate the viability of biodiesel production with microalgae. The multi-effect co-production coupling technology is also stated to connect high value-added functional ingredients in microalgae. Finally, the strategies of using microalgae oils for biodiesel production are proposed.

## 2. Selection of microalgal strain

Microalgae are recognized as one of the oldest living micro-organisms on earth.[29] They grow at an exceptional fast rate: 100 times faster than terrestrial plants and double their biomass in less than one day.[30] Many species of microalgae are known for their high content of lipids in the cells, the average fatty acid contents of the algal oils are 36% oleic (18:1), 15% palmitic (16:0), 11% stearic (18:0), 8.4% iso-17:0, and 7.4% linoleic (18:2).[31] They can be used for biodiesel production; some microalgae are able to accumulate a lot of hydrocarbon which can be made into gasoline or diesel, and some of them can produce hydrogen in some case. With the advantages of easy cultivation, fast growth, high biomass production and enrichment of lipids and hydrocarbon, microalgae oils are novel and important bio-energy resources. Fig. 1 summarizes the potential conversional pathways of using microalgae to produce bio-fuels, hydrogen, hydrocarbon and lipids.

Selection of adequate microalgal strains is the basis of the development of algae-based biodiesel industry. At the present time, microalgae used as the feedstock for biodiesel production has been studied extensively at laboratory-scale due to the high lipid content of certain strains. Besides the lipid content, biomass and lipid productivity seemed to be the other two adequate criteria for evaluating the potential of various microalgae species for producing biodiesel. Table 1 presents the experimental values of the three criteria of 25 strains from the main groups of microalgae in different cultivating conditions. Compared with the specific data of each strain, *Botryococcus braunii* is a green microalga that produces hydrocarbons up to 75% of its dry biomass and its lipid

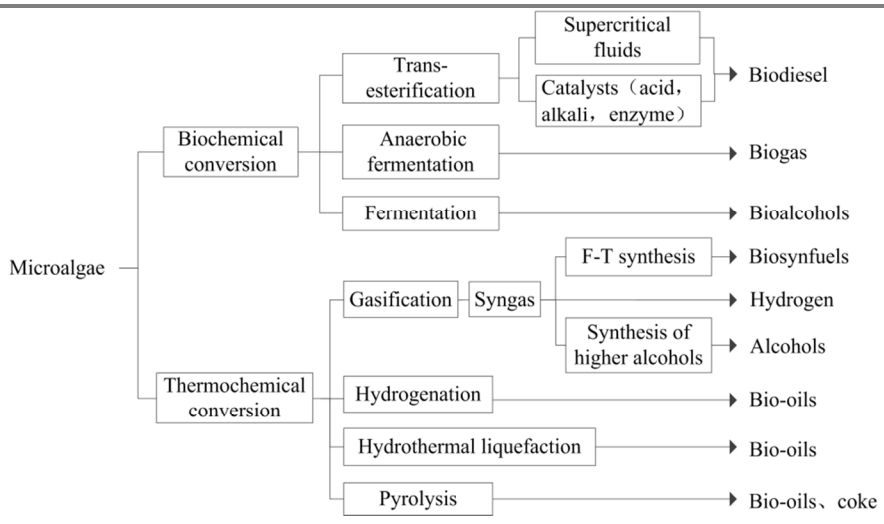


**Fig.1** Potential energy conversion processes from microalgae



 

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**Table 1** Lipid content, biomass productivity and lipid productivity of selected microalgal strains used for biodiesel production.

| Microalgal group | Strain | Lipid content /% dw | Biomass productivity /mg·L$^{-1}$·d$^{-1}$ | Lipid productivity /mg·L$^{-1}$·d$^{-1}$ | Ref. |
|---|---|---|---|---|---|
| Ankistrodesmus | *A. falcatus* | 17 | 340 | 54-58 | 32 |
| | *A. fusiformis* | 19-23 | 240 | 43-56 | 32 |
| Botryococcus | *B. braunii* | 25-75 | 27-250 | 4-124 | 32-35 |
| | *B. terribilis* | 49 | 200 | 95-102 | 32 |
| Chlorella | *Ch. emersonii* | 19-34 | 36-290 | 54 | 36, 37 |
| | *Ch. minutissima* | 50-57 | 320-400 | 48-70 | 38 |
| | *Ch. protothecoides* | 18 | 250 | 45 | 37 |
| | *Ch. saccharophila* | 28 | 220 | 60 | 38 |
| | *Ch. salina* | 11 | 170 | 18 | 37 |
| | *Ch. sorokiniana* | 19 | 230 | 45 | 39 |
| | *Ch. sp.* | 19 | 230 | 42 | 39 |
| | *Ch. vulgaris* | 5-58 | 104-482 | 0.5-127 | 33, 36, 37, 39-41 |
| Dunaliella | *D. salina* | 24 | 150 | 37 | 37 |
| | *D. sp.* | 20-24 | 120 | 26 | 37 |
| Nannochloropsis | *N. oculata* | 11-65 | 30-380 | 41-65 | 42, 43 |
| | *N. sp.* | 22-31 | 170-210 | 38-61 | 39 |
| Pavlova | *P. salina* | 31 | 160 | 49 | 39 |
| | *P. lutheri* | 36 | 140 | 50 | 39 |
| Scenedesmus | *S. acutus* | 13-28 | 74 | 13 | 44 |
| | *S. obliquus* | 22-60 | 250-626 | 41-140 | 34, 45 |
| | *S. obtusus* | 18-26 | 179-193 | 36-43 | 46 |
| | *S. rubescens* | 15 | 298 | 50 | 38 |
| | *S. pectinatus* | 23 | 119 | 27 | 46 |
| | *S. quadricauda* | 18 | 190 | 35 | 39 |
| | *S. sp.* | 19-21 | 210-260 | 41-54 | 39 |

productivity is relatively higher than those of most other strains. More than half of the mentioned studies focused on the strains of chlorella and scenedesmus groups. *Chlorella vulgaris* and *Scenedesmus obliquus* are the most appropriate strains for producing biodiesel. The lipid productivity increases around 130 mg·L$^{-1}$·d$^{-1}$ and an average biomass productivity of 550 mg·L$^{-1}$·d$^{-1}$. For other strains, such as *Nannochloropsis oculata,* although the maximum neutral lipid content can achieve 65%, the lipid productivity is much lower than 100 mg·L$^{-1}$·d$^{-1}$, which is unacceptable for industrial cultivation. As microalgal strains are used to produce triacylglycerols,[47] species selection of microalgal for biodiesel production should give priority to the lipid productivity and the lipid content.[48]

## 3. $SCCO_2$ extraction of microalgal lipids

Before the production of microalgal biodiesel, efficient lipid extraction from microalgae is significant to make preparation for the following transesterification.

The two main kinds of extracting methods are chemical solvents extraction and supercritical fluids extraction (SFE).[49] The fundamental difference between SFE and traditional organic solvent lipid extraction method for lipid extraction from microalgae is no requirement of catalyst via SFE.[50] In addition, the chemical solvent method has some drawbacks like inherent toxicity, poor selectivity, difficult separation of the contaminants as well as solvents from the desired product, energy consuming and pollutant.[51] SFE has several advantages of offering mild operating conditions, negligible environmental impact, higher selectivity, shorter extraction time, favourable mass transfer and production of a solvent-free extract.[51, 52 53]

$SCCO_2$ extraction currently gains considerable attention as the promising green technology method, which can possibly replace the conventional organic solvent lipid extraction method.[54] $SCCO_2$ has high solvation ability and no toxicity. Intermediate diffusion/viscosity properties lead to favourable mass transfer equilibrium and this process produces solvent-free crude lipids.[55] Solvent extraction using hexane was found to be remarkably less efficient than $SCCO_2$ extraction, which achieved a comparable lipid yield.[56]

The methods and results of recent studies investigating $SCCO_2$ extraction of microalgal lipids are summarized in Table 2. The corresponding significant discussions are presented as well.

## 4. Uncatalyzed Microalgal Biodiesel Production

The viscosities of vegetable oils and microalgal oils are usually higher than those of diesel oils.[57] Hence, they cannot be applied to engines directly. The transesterification of microalgal oils will dramatically reduce the original viscosity and increase the fluidity. It is apparent that the transesterification of microalgae oils for biodiesel produced with different kinds of catalysts (like acid, alkali and enzyme catalysts) or SCFs is being investigated as an alternative.

Huang *et al.*[58] summarized the advantages and disadvantages of three types of catalytic transesterification. The conventional catalysis process can obtain high conversion of biodiesel with a cheap and well-controlled reaction condition, which is appropriate for large scale production. However, the later disposal process is always complex due to the existence of acid or base catalyst. The enzymatic catalysis process holds the moderate reaction condition with a small amount of alcohol and has no pollution to the environment. Nonetheless, the enzymes are easy to be poisoned and are restricted to conbvert short-chain fatty acids.

However, direct (or in-situ) transesterification with supercritical methanol has advantages of the minimal usage of solvents, easy separation of products, and reduced reaction time.[59] Another positive effect of SCF technology is that the alcohol is not only a reactant but also an acid catalyst.

**Table 2** Methods and results summary of recent studies investigating $SCCO_2$ extraction of microalgal lipids.

| Microalgal species | T (°C) | P (bar) | Flow rate (g $min^{-1}$) | Duration (min) | Optimum conditions and discussion | Optimum lipid yield (dwt. %) | Ref. |
|---|---|---|---|---|---|---|---|
| *Scenedesmus sp.* | 35-65 | 200-500 | 1.38-4.02 | - | 500 bar, 53 °C and 1.9 g $min^{-1}$ | 7.41 | 60 |
| *Chlorococcum sp.* | 60, 80 | 300 | - | 80 | (i) Decreasing temperature and increasing pressure resulted in increased lipid yields;<br>(ii) The rate of lipid extraction decreased with experimental time. | 7.1 | 54 |
| *Scenedesmus dimorphus* | 50-100 | 100-500 | 3.33 | 60 | 414 bar and 100 ºC | 9 | 61 |
| *Pavlova sp.* | 60 | 306 | - | 360 | The SFE method is effective and provides higher selectivity for triglyceride extraction. | 10.4-17.9 | 62 |
| *Crypthecodinium cohnii* | 40 and 50 | 200, 250 and 300 | - | 180 | 300 bar and 50 °C<br>(i) At constant pressure, temperature increase has the effect of decreasing the density of the supercritical fluid and thus its solvation capacity;<br>(ii) Increasing the temperature increases the vapour pressure of the solutes, thus increasing their solubility in the supercritical solvent. | 9 | 63 |
| *Nannochloropsis sp.* | 40, 55 | 400, 550, 700 | 170 | 360 | (i) At constant T, lipid extraction rate increased with P;<br>(ii) At constant P, lipid extraction rate slightly increased with T. | 25.0 | 64 |
| *Spirulina maxima* | 20-70 | 15-180 | 1.998 | - | 150 bar and 50 °C<br>(i) Both the temperature and the pressure affected the extraction rate;<br>(ii) The effect of temperature prevailed over that of pressure. | 16.2 | 65 |

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Furthermore, the SCF method requires no pre-treatment of microalgae because impurities in the feedstocks do not affect the reaction significantly. The three types of reactions (transesterification, hydrolysis of triglycerides, and alkyl esterification of fatty acids) occur simultaneously.[66]

As the advantages mentioned above, the catalyst-free biodiesel synthesis process using SCF technology is expected to replace catalytic production methods, especially for microalgae which contains a proportion of water and FFAs. Bello *et al.*[17] technically compared two transesterification processes of biodiesel production from microalgae (*Chlorella protothecoides*). The energy efficiency of the supercritical transesterification process was reported as 52.85% with most energy (75.55%) used in the separation step. The alkali-catalytic process had 49.67% energy efficiency with 35.25% used in the product purification step. The analysis data suggested that the supercritical transesterification method has higher energy efficiency and slightly lower the unit price of biodiesel in comparison to the alkali-catalytic process.

Patil *et al.* [67-70] performed a series of transesterification to convert wet or dry algae biomass to biodiesel using supercritical methanol or ethanol. The latest integrated approach has been proposed to convert dry algae (*Nannochloropsis* sauna) into FAEEs via non-catalytic transesterification under microwave-mediated supercritical ethanol (MW-SCE) conditions.[70] Lipids extraction from algal biomass and transesterification of them simultaneously proceed to convert into biodiesel in a relatively short reaction time. It reduced energy consumption versus traditional processes by simplifying separation and purification steps. High conversion rates are available when the extractive-transesterification of algal biomass is performed in sub-critical or supercritical conditions. It was demonstrated that the direct transesterification with SCFs provides an energy-efficient and economical route for algal biodiesel production.

Cao *et al.*[71] studied the biodiesel prepared with large-scale aquaculture microalgae and also analysed the oil quality. The results indicated that the output rate of the biodiesel prepared with *Chlorella* was evidently higher than that of other types of algae. The supercritical reaction condition almost doubled the output rate of biodiesel and the oil quality had nearly the same carbon/hydrogen mass ratio, density and calorific value with No.0 diesel.

Interestingly, Tsigie *et al.*[72] developed a direct process for biodiesel production from wet *Chlorella vulgaris* biomass (80% moisture content) using subcritical water as catalyst. The yield of FAMEs achieved 89.71% at the ratio of wet biomass to methanol 1/4 (g/mL), 175 °C and 4 h. The yield is 0.29 g FAMEs per g dry biomass. This is considerably higher than the yield of 0.20 g FAMEs per g dry biomass obtained when the neutral lipid of *Chlorella vulgaris* biomass was extracted and converted into FAMEs.

Compared with the direct transesterification in a single step, the two-step process suggested by Kusdiana and Saka has more advantages.[73] The first step is hydrolysis of triglyceride in subcritical water to produce FFAs. The second step is the subsequent alkyl esterification of the FFAs in supercritical alcohol to produce biodiesel. The rate of alkyl esterification is higher than that of transesterification. Besides, the alkyl esterification ensures that all FFAs in microalgae, whether present originally or products of hydrolysis, are completely transformed into FAMEs.[74] Furthermore, it can be accomplished at lower temperatures and pressures, which might reduce the cost of production and the ratio of alcohol to oil.[75] Before the second step, the only by-product glycerol from the ester formation step is already removed. Therefore, the two-step process is cleaner than the direct transesterification one.[76]

Levine *et al.*[77] developed a catalyst-free, two-step technique for biodiesel production from lipid-rich, wet algal biomass. In the first step, wet algal biomass (ca.80% moisture) reacts in subcritical water to hydrolyze intracellular lipids and conglomerate cells into an easily filterable solid at 250 °C for 15 to 60 min. It retains the lipids, and produces a sterile, nutrient-rich aqueous phase. In the second step, the wet fatty acid-rich solids undergo supercritical in situ transesterification (SC-IST/E) with ethanol to produce biodiesel in the form of fatty acid ethyl esters (FAEEs). On the basis of lipid in the hydrolysis solids, longer time, higher temperature, and more ethanol increase crude biodiesel that range from 56-100% and FAEE yields 34-66%. A considerable benefit of the process described herein is the ability of hydrolysis to create two sterile products: relatively low moisture (<50% water), FA-rich solid and a nutrient-rich aqueous phase. They both may be amenable to a variety of downstream processes. In the subsequent work, Levine *et al.*[78] focused on the production of biodiesel from wet, lipid-rich algal biomass using a two-step process that involves hydrothermal carbonization (HTC) and supercritical in situ transesterification (SC-IST). SC-IST has superiority of the reduced costs since it does not require catalysts and generally has higher tolerance for feedstocks that contains water and FFAs. Reaction temperatures above 275 °C resulted in substantial thermal decomposition of unsaturated FAEE, thereby reducing yields. At 275 °C, time and ethanol facilitate the FAEE yield while increasing reaction water content and pressure reduced yields. The results indicated that overall FAEE yields from partially dried hydrochars obtained 89% with 20:1 EtOH/FA molar ratio at 275 °C for 180 min. This work demonstrates that nearly all lipids within algal hydrochars

are available to be converted into biodiesel through SC-IST with only a small excess of alcohol and water tolerance, partly saving cost.

Savage et al. [79] proposed a method to produce biodiesel from a wet biomass that includes water and biomass solids. The method minimizes biodiesel synthesis time and minimizes prevalence of heteroatoms in the biodiesel by trans-esterifying the hydrolyzed lipid component to form biodiesel.

Research on transesterification of microalgae with SCFs has begun in recent years. There are still many topics need to be explored. Because the reaction conditions for esterification are more moderate than those for transesterification with supercritical methanol. This new process is especially suitable for the low price materials (*i.e.* microalgae oil, waste oil and oil by-products) with high water or FFAs contents, the two step process combining hydrolysis and esterification is considered as a more promising technology for microalgal biodiesel production.

We conclude the production of microalgal biodiesel by two-step SCF process and the following downstream step in Fig. 2. In the first step, the disrupted microalgae by high-pressure slush pump react in subcritical water to release the intracellular lipids and hydrolyze them into fatty acids with the by-product glycerol. The fatty acids rise to the top of the gravity clarifier to prepare for the next reaction step. The water dissolved the glycerol is in the middle and the cell debris settles to the bottom can be discharged from the gravity clarifier. In the second step, the fatty acids are preheated and esterified with supercritical methanol to produce FAMEs. Then, after the products are washed with hot water, the unreacted methanol is rectified from the top of the rectification column and then recycled for the reaction step. The upper lipid phase materials containing FAMEs and other oil soluble fractions are mixed with the $SCCO_2$ to transfer into the extraction column. After the further step of fractionation with $SCCO_2$, the FAMEs are collected from the top of the column through valve 40 and the high value by-product pigments are removed out from the bottom through valve 43. Three parts of the microalgae production process with corresponding SCFs are efficient and environment friendly, which need no more separation steps and reserve the high value-added components in maximum.

## 5. Economics of microalgal biodiesel production

Although many challenges remain in microalgal biodiesel production, a growing number of researchers committed to believe that the rewards would eventually outweigh the risks. Research on the microalgal biodiesel production dates back to the energy crisis in 1970s.[80] Every year, more than $7.5 \times 10^6$ tons of algae are harvested representing a world market of US$ $6 \times 10^9$ per year. The main bottleneck for the production of biodiesel from microalgae is the economic viability for development and establishment of this technology at industrial level.[52] The main two factors contributing to the cost of biodiesel are algal productivity and processing technology. So research should focus on various aspects of algal biology which have the greatest impact upon growth rate and lipid biosynthesis.[81]

Recently, there are many studies on the economics of algal production in open ponds (OP), photo bioreactor (PBR) systems and some evaluation of hybrid systems combining the use of both OP and PBR systems. Detailed economic analysis on the costs for the production of microalgal biodiesel has also been reported. Table 3 summarizes the comparison between the costs for microalgal biodiesel production by OP, PBR and Hybrid systems on the basis of the published data in recent years. Assumed that the density of microalgal biodiesel is 0.85 $g \cdot cm^{-3}$. The calculated cost data from Table 3 indicate that the total cost of lipid production in the OP systems is lower than that of in the PBR systems. If the price of crude oil rises to $80/barrel as predicted, then microalgal oil costing $87/barrel is possible to economically substitute for crude petroleum.[82] Therefore, since the oil price has been recently around US $100/barrel, microalgal oil can in theory already be produced economically.

However, studies on industrial feasibility vary enormously with the precise parameters. Richardson *et al.*[83] used a multi-year, Monte Carlo financial feasibility model to estimate the costs of production and chance of economic success for large-scale algal biofuel facilities in the US Southwest. Average total costs of production for lipids were $12.73/gal and $31.61/gal for OP and PBRs, respectively. The values are higher than those ones reported by Davis *et al.*[84] This is due to fully accounting for financial costs and risk including high amounts of capital expenses, which are generally excluded from techno-economic studies. It is noted that algae production is technically feasible, but it is not yet economically feasible.

Additionally, Rios *et al.*[85] used computational tools to model different scenarios of the harvesting, oil extraction and transesterification of microalgal biodiesel. The analysis indicated that the OP cultivation technology has encountered the bottleneck of the development biological and engineering production, conversely the PBR systems are more appropriate to improve the production rates and lipid content from the single selected strain with no contamination.

Sawaengsak *et al.* [86] evaluated the economic feasibility of microalgal biodiesel production with high-value by-products in both OP and PBRs in Thailand. The life cycle cost showed that although the $\omega$-3 fatty acid production gained higher revenue, the capital and operating cost need to be reduced by more than 50% to make the systems beneficial. Further research is necessary to find the improvement for the system to be profitable.

Torres *et al.* [87] found that it is significant to formulate realistic scenarios regarding the biomass composition (*i.e.* ash free, dry weight) due to the final product are very sensitive to the lipid content. Economic profitability of microalgal biodiesel still need be improved. Walker's study found the reliable evidence that, if all of the inputs are taken into account, the net energy gain of liquid biofuels is either very modest or non-existent. Therefore, it leads to little or no sparing of carbon dioxide emissions.[88] Energy ratios which range from 3.3 to 7.5 are



 

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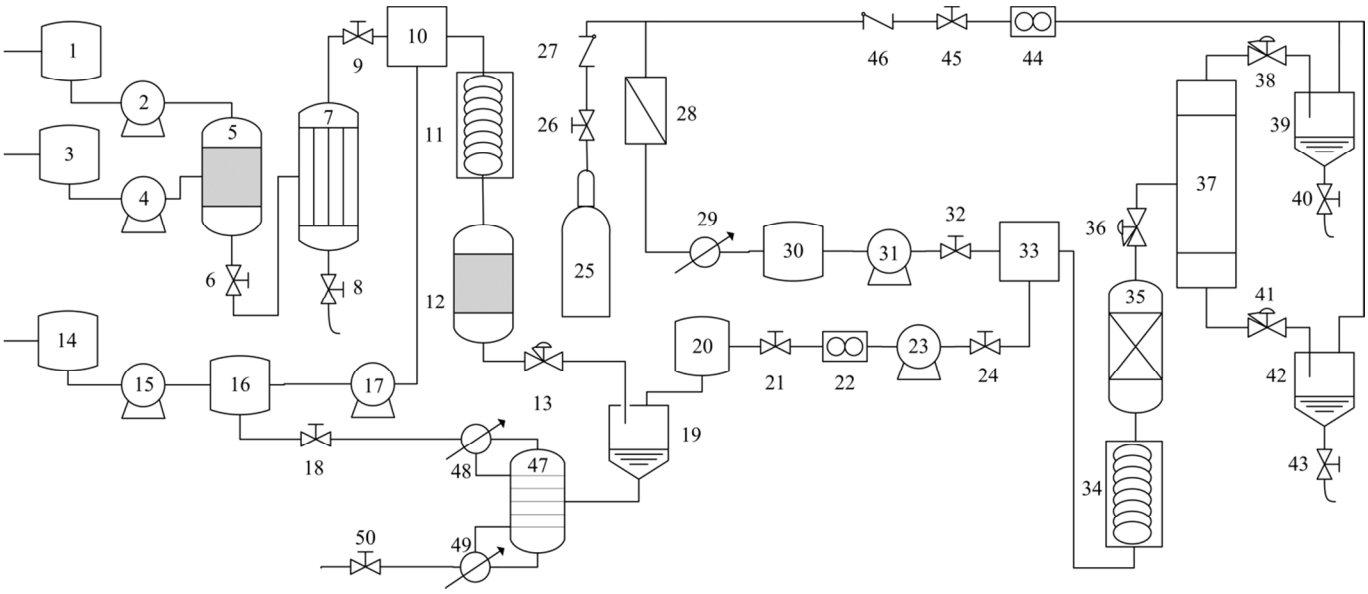


1-microalgae; 2-high-pressure slush pump; 3-fresh water; 4,15,17,23,31-delivery pump; 5-subcritical water reactor; 6,8,9,18,21,24,26,32,40,43,45,50-line valve; 7-gravity clarifier; 10,33-mixer; 11,34-pre-heater; 12-supercritical methanol reactor; 13,36,38,41-back-pressure regulator; 14-methanol; 16-methanol recovery tank; 19-water washing; 20-crude biodiesel and other oil soluble fractions; 22,44-flowmeter; 25-$CO_2$ gas cylinder; 27,46-check valve; 28-filter; 29,48-cooler; 30-$CO_2$ storage tank; 35-extraction column; 37-fractionation column; 39,42-separator; 47- rectification column; 49- reboiler.

**Fig.2** Global scheme of the microalgal biodiesel production by supercritical fluid technology

dependent on various parameters such as areal biomass productivity, biogas yield resulting, harvesting and extraction processes, algal cell oil yields, waste-water treatment, and fertilizer/nutrient recycling.[89]

It is still too early to conclude that microalgae biodiesel production has achieved the ultimate goal and is already economically feasible. Further investigations need to be performed to optimize the current technologies in order to overcome the limitation of microalgal biodiesel industrialization. Some strategies are addressed here for some inspiration of microalgal biodiesel.

## 6. Feasibility strategy of microalgal biodiesel

From the comparative analysis of microalgal production, to reduce the total cost of this project, research should focus on increase of the microalgae lipid content, production and downstream processes, even with combining the exploitation of high value by-products. Some strategies are provided as follows.

1) Sewage drained from municipal, agricultural and industrial activities potentially provide cost-effective and sustainable means of algal growth for biofuels. In addition, it is also potential for combining sewage treatment by algae, such as nutrient removal with biofuel production. Studies also have shown that microalgae could grow and efficiently remove nutrients from primary settled sewage.[90] Cai z. [91] developed an economical method for microalgae cultivation and biodiesel refinement to treats polluted water efficiently. It reduces emission of $CO_2$ and enables clean production of biodiesel by efficiently using sewage, waste gas, dregs, waste heat, and crude glycerin by-product.

2) The transesterification reaction of microalgae with SCFs is more viable because it can lower greenhouse gases emissions and simplify separation step without any catalysts. Contrarily, the alkali-catalysed process requires slightly higher production cost because of numerous unit operations and processing steps.[17] Especially, the two-step process that combines hydrolysis and esterification may become a promising alternative for producing biodiesel due to its milder reaction conditions and the same tolerance as the direct transesterification for microalgal oil with high FFAs and water.

3) An integration of the conversion of microalgal oils to biodiesel along with the extraction of high value functional ingredients can reduce the total cost of the microalgae biodiesel production industry. Currently, many industries are devoted to the cultivation of microalgae for different purposes, *e.g.* some

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**Table 3** Comparison between the costs for microalgal biodiesel production according to the published data in recent years

| | Lipids content /% dw | Productivity[a] /( $g \cdot m^{-2} \cdot d^{-1}$) | Lipids production cost /$/gal | Cost of Biodiesel ($/ton) | | | Ref. |
|---|---|---|---|---|---|---|---|
| | | | | OP | PBR | Hybrid | |
| Benemann and Oswald (1996) | 50 | 30 | - | 541-671 | - | - | 92 |
| | 50 | 60 | - | 376-400 | - | | |
| Chisti (2007) | 30 | N/A | - | 3294 | 3776 | - | 82 |
| | 30-70 | 35 | - | 8024-16471 | - | - | |
| | 30-70 | 1.535 (kg $m^{-3}$ $day^{-1}$) | - | - | 6600-13176 | - | |
| Huntley and Redalje (2007) | 40 | 18.5 | - | - | - | 280 | 93 |
| | 40 | 60 | - | - | - | 910 | |
| Pienkos (2008) | 25 | 20 | - | 718 | - | - | 94 |
| | 50 | 40 | - | 1082 | - | - | |
| | 60 | 60 | - | 3259 | | - | |
| Pienkos & Darzins (2009) | 15 | 10 | 25 | 7500 | - | - | 95 |
| | 25 | 25 | 7. 5 | 2250 | - | - | |
| | 50 | 50 | 2. 5 | 750 | - | - | |
| Davis *et al* (2011) | 25 | 25 | 8. 52 | 3058 | - | - | 84 |
| | - | 1.25 (kg $m^{-3}$ $day^{-1}$) | 18. 10 | - | 6380 | - | |
| Sun *et al.* (2011) | 25-60 (OP) | 20-60 | 2. 4-10. 6 | - | - | - | 96 |
| | 35-60 (OP) | 35-58 | 9. 7-38. 7 | - | - | - | |
| | 16-47 (Hybrid) | 25-40 | 0. 9-31. 8 | - | - | - | |
| Amer *et al*. (2011) | 50 | 24 | 24.1 | 4176 | | | 97 |
| Delrue *et al.* (2012) | 20-50 | 20-30 | 10.2 | 3412 | | | 98 |
| | 20-50 | N/A | 17.7 | | 5706 | | |
| | 20-50 | - | 16.9 | | | 5482 | |
| Sawaengsak *et al.* (2014) | 25 | 25 | - | 2500 | | | 86 |
| | 25 | 1.25 (kg $m^{-3}$ $day^{-1}$) | - | | 8235 | | |

[a]Productivity is on an areal basis ( $g \cdot m^{-2} \cdot day^{-1}$) for open ponds and a volumetric basis ($kg \cdot m^{-3} \cdot day^{-1}$) for PBRs

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industries produce microalgae biomass as a final product, others take biomass to obtain high value by-products such as proteins, Vitamins or Carotenoids.[52] The co-production of some high value fraction and their marketing are also significant. Even though 50% oil content in algae species, the additional 50% of the biomass remains. This biomass fraction contains valuable proteins for livestock, poultry and fish feed additives valued from $ 800 up to $ 2500/tonne.[99] When the microalgae are used for the production of high value chemicals with the by-product biomass, the overall process is expected to be economical feasible.[100-102] Some high-value by-products extracted from microalgae are presented in Table 4.

## 7. Conclusion

As the world energy consumption is increasing steadily with the rapid promotion of global economics, the contradiction between diminishing fossil fuel supplies and increasing demand will further deteriorates. The rise of crude oil prices brings new opportunities for the development of renewable energy sources, especially, biodiesel. The transesterification for microalgae conversion into biodiesel with SCFs is regarded as the most promising process for industrial application. Although economic analysis of microalgae production indicates that the present technologies still have drawbacks, feasible strategies are illuminated here by using SCF technology. Following these developments, commercial production of microalgal biodiesel, simultaneously associated with $CO_2$ emission reduction, waste water treatment and high-valuable products' extraction, will become competitive in comparison with other conventional sources of energy in the foreseeable future.

**Table 4** Some high value by-products extracted from microalgae

| Product group | Product | Examples (producer) | Applications | Ref. |
|---|---|---|---|---|
| Carotenoids | Astaxanthin | *Haematococcus pluvialis* | Pigments, cosmetics, pro-vitamins, pigmentation | 103 |
| | Canthaxanthin | *Chlorella vulgaris* | | 104 |
| | Violaxanthin | *Chlorella ellipsoidea* | | 105 |
| | *β*-carotene | *Dunaliella salina* | | 104 |
| | *Lutein* | *Chlorella pyrenoidosa* | | 106 |
| Polyunsaturated fatty acids (PUFAs) | *γ*-linolenic acid (GLA) | *Arthrospira maxima* | Food additive, nutraceutics pharmaceuticals | 104 |
| | Eicosapentaenoic acid (EPA) | *Nannochloropsis oculata* | | 107 |
| | *Arachidonic acid (AA)* | *Nannochloropsis oculata* | | 107 |
| | Docosahexaenoic acid (DHA) | *Nannochloropsis oculata* | | 108 |
| Vitamins | Pro-vitamin A | *Dunaliella salina* | Food, health, Nutrition | 104 |
| | *α*-tocopherol (Vitamin E) | *Spirulina platensis* | | *109* |
| Proteins | Phycobiliproteins | *Nostoc sp* | Food, cosmetics, medicine | 110 |

## Acknowledgements

The authors would like to acknowledge the following financial supports: National Natural Science Foundation of China (No.21376186), the Ministry of Education (Doctoral Special Research Foundation No. 20110201110032), China and the Fundamental Research Funds for the Central Universities (New Teacher Research Support Plan No. 08141002, International Cooperation Project No. 2011jdhz37 and Integrated Cross Project xjj2014136 in Xi'an Jiaotong University), Natural Science Basic Research Plan in Shaanxi Province of China (No. 2012JM2010), and the Ministry of Human Resources and Social Security of China (Sci. & Tech. Project for Overseas Scholars, No. 19900001).

## References

1. S. Saka and D. Kusdiana, *Fuel*, 2001, **80**, 225-231.
2. A. Srivastava and R. Prasad, *Renewable Sustainable Energy Rev.*, 2000, **4**, 111-133.
3. Y.-G. Li, L. Xu, Y.-M. Huang, F. Wang, C. Guo and C.-Z. Liu, *Appl. Energ.*, 2011, **88**, 3432-3437.
4. A. E. Atabani, A. S. Silitonga, I. A. Badruddin, T. M. I. Mahlia, H. H. Masjuki and S. Mekhilef, *Renewable Sustainable Energy Rev.*, 2012, **16**, 2070-2093.
5. N. N. a. N. Yusuf, S. K. Kamarudin and Z. Yaakub, *Energ. Conv. Manage.*, 2011, **52**, 2741-2751.
6. A. L. Ahmad, N. H. M. Yasin, C. J. C. Derek and J. K. Lim, *Renewable Sustainable Energy Rev.*, 2011, **15**, 584-593.
7. S. N. Naik, V. V. Goud, P. K. Rout and A. K. Dalai, *Renewable Sustainable Energy Rev.*, 2010, **14**, 578-597.
8. M. Balat, *Energy Sources, Part B*, 2009, **4**, 48-58.
9. S. Mekhilef, S. Siga and R. Saidur, *Renewable Sustainable Energy Rev.*, 2011, **15**, 1937-1949.
10. U. Biermann, U. Bornscheuer, M. A. R. Meier, J. O. Metzger and H. J. Schafer, *Angew. Chem., Int. Ed.*, 2011, **50**, 3854-3871.
11. J. Dufour and D. Iribarren, *Renewable Energy*, 2012, **38**, 155-162.
12. M. G. Kulkarni and A. K. Dalai, *Ind. Eng. Chem. Res.*, 2006, **45**, 2901-2913.
13. Z. Yaakob, M. Mohammad, M. Alherbawi, Z. Alam and K. Sopian, *Renewable Sustainable Energy Rev.*, 2013, **18**, 184-193.
14. L. Canoira, M. Rodriguez-Gamero, E. Querol, R. Alcantara, M. Lapuerta and F. Oliva, *Ind. Eng. Chem. Res.*, 2008, **47**, 7997-8004.
15. J. M. Encinar, N. Sanchez, G. Martinez and L. Garcia, *Bioresour. Technol.*, 2011, **102**, 10907-10914.
16. F. R. Ma, L. D. Clements and M. A. Hanna, *Ind. Eng. Chem. Res.*, 1998, **37**, 3768-3771.
17. B. Z. Bello, E. Nwokoagbara and M. Wang, in *22 European Symposium on Computer Aided Process Engineering*, eds. I. D. L. Bogle and M. Fairweather, Elsevier Science Publishers, London, Editon edn., 2012, vol. 30, pp. 132-136.
18. L. B. Brentner, M. J. Eckelman and J. B. Zimmerman, *Environ. Sci. Technol.*, 2011, **45**, 7060-7067.
19. L. T. Taylor, *Supercritical Fluid Extraction*, John Wileys & Sons, Inc., New York, 1996.
20. A. Demirbas, *Energy Convers. Manage.*, 2009, **50**, 14-34.
21. R. Jothiramalingam and M. K. Wang, *Ind. Eng. Chem. Res.*, 2009, **48**, 6162-6172.
22. B. Wang, S. Li, S. Tian, R. Feng and Y. Meng, *Fuel*, 2013, **104**, 698-703.
23. H. Wu, J. Zhang, Q. Wei, J. Zheng and J. Zhang, *Fuel Process. Technol.*, 2013, **109**, 13-18.
24. L. Fjerbaek, K. V. Christensen and B. Norddahl, *Biotechnol. Bioeng.*, 2009, **102**, 1298-1315.
25. M. K. Lam, M. T. Lee and A. R. Mohamed, *Biotechnol. Adv.*, 2010, **28**, 500-518.
26. K. Komers, J. Machek and R. Stloukal, *Eur. J. Lipid Sci. Technol.*, 2001, **103**, 359-362.
27. A. Demirbas, *Progr. Energy Combust. Sci.*, 2005, **31**, 466-487.
28. D. Zeng, R. Li, T. Jin and T. Fang, *Ind. Eng. Chem. Res.*, 2014.
29. D. Song, L. Hou and D. Shi, *Chinese J Biotechnol*, 2008, **24**, 341-348.
30. M. R. Tredici, *Biofuels*, 2010, **1**, 143-162.
31. M. F. Demirbas, *Energy Educ. Sci. Technol., Part A,* 2010, **25**, 31-43.
32. I. A. Nascimento, S. S. I. Marques, I. T. D. Cabanelas, S. A. Pereira, J. I. Druzian, C. O. Souza, D. V. Vich, G. C. Carvalho and M. A. Nascimento, *BioEnergy Res.*, 2012, **6**, 1-13.
33. C. Yoo, S. Y. Jun, J. Y. Lee, C. Y. Ahn and H. M. Oh, *Bioresour. Technol.*, 2010, **101 Suppl 1**, S71-74.
34. A. Abomohra, M. Wagner, M. El-Sheekh and D. Hanelt, *J. Appl. Phycol.*, 2013, **25**, 931-936.
35. Y. T. Huang, H. T. Lee and C. W. Lai, *J. Nanosci. Nanotechnol.*, 2013, **13**, 2117-2121.
36. A. H. Scragg, A. M. Illman, A. Carden and S. W. Shales, *Biomass Bioenergy*, 2002, **23**, 67-73.
37. A. F. Talebi, S. K. Mohtashami, M. Tabatabaei, M. Tohidfar, A. Bagheri, M. Zeinalabedini, H. H. Mirzaei, M. Mirzajanzadeh, S. M. Shafaroudi and S. Bakhtiari, *Algal Res.*, 2013, **2**, 258-267.
38. N. Hempel, I. Petrick and F. Behrendt, *J. Appl. Phycol.*, 2012, **24**, 1407-1418.
39. L. Rodolfi, G. Chini Zittelli, N. Bassi, G. Padovani, N. Biondi, G. Bonini and M. R. Tredici, *Biotechnol. Bioeng.*, 2009, **102**, 100-112.
40. S. S. I. Marques, I. A. Nascimento, P. F. de Almeida and F. A. Chinalia, *Appl. Biochem. Biotechnol.*, 2013, **171**, 1933-1943.
41. E. C. Francisco, D. B. Neves, E. Jacob-Lopes and T. T. Franco, *J. Chem. Technol. Biotechnol.*, 2010, **85**, 395-403.
42. N. Gu, Q. Lin, G. Li, Y. H. Tan, L. M. Huang and J. D. Lin, *Eng. Life Sci.*, 2012, **12**, 631-637.



 

43. J. C. Quinn, T. Yates, N. Douglas, K. Weyer, J. Butler, T. H. Bradley and P. J. Lammers, *Bioresour. Technol.*, 2012, **117**, 164-171.
44. M. S. de Alva, V. M. Luna-Pabello, E. Cadena and E. Ortiz, *Bioresour. Technol.*, 2013, **146**, 744-748.
45. S. H. Ho, C. Y. Chen and J. S. Chang, *Bioresour. Technol.*, 2012, **113**, 244-252.
46. L. Xia, H. M. Ge, X. P. Zhou, D. L. Zhang and C. X. Hu, *Bioresour. Technol.*, 2013, **144**, 261-267.
47. Q. Hu, M. Sommerfeld, E. Jarvis, M. Ghirardi, M. Posewitz, M. Seibert and A. Darzins, *Plant J.*, 2008, **54**, 621-639.
48. R. Huerlimann, R. De Nys and K. Heimann, *Biotechnol. Bioeng.*, 2010, **107**, 245-257.
49. V. Makareviciene, V. Skorupskaite and V. Andruleviciute, *Rev. Environ. Sci. Bio/Technol.*, 2013, **12**, 119-130.
50. I. Rawat, R. Ranjith Kumar, T. Mutanda and F. Bux, *Appl. Energ.*, 2013, **103**, 444-467.
51. A. Santana, S. Jesus, M. A. Larrayoz and R. M. Filho, *Procedia Eng.*, 2012, **42**, 1755-1761.
52. A. M. Aguirre, A. Bassi and P. Saxena, *Crit. Rev. Biotechnol.*, 2013, **33**, 293-308.
53. M. Perrut, in *Proceedings of 5th Italian Conference on Supercritical Fluids and Their Applications.* , Garda (Verona), Italy, Editon edn., 1999, vol. 13-16, pp. 1-8.
54. R. Halim, M. K. Danquah and P. A. Webley, *Biotechnol. Adv.*, 2012, **30**, 709-732.
55. N. Pragya, K. K. Pandey and P. K. Sahoo, *Renewable Sustainable Energy Rev.*, 2013, **24**, 159-171.
56. R. Halim, B. Gladman, M. K. Danquah and P. A. Webley, *Bioresour. Technol.*, 2011, **102**, 178-185.
57. J. Fuls, C. S. Hawkins and F. J. C. Hugo, *J. Agric. Eng. Res.*, 1984, **30**, 29-35.
58. G. H. Huang, F. Chen, D. Wei, X. W. Zhang and G. Chen, *Appl. Energ.*, 2010, **87**, 38-46.
59. J. Kim, G. Yoo, H. Lee, J. Lim, K. Kim, C. W. Kim, M. S. Park and J. W. Yang, *Biotechnol. Adv.*, 2013, **31**, 862-876.
60. H. Taher, S. Al-Zuhair, A. H. Al-Marzouqi, Y. Haik, M. Farid and S. Tariq, *J. Supercrit. Fluids*, 2014, **86**, 57-66.
61. L. Soh and J. Zimmerman, *Green Chem.*, 2011, **13**, 1422-1429.
62. C. H. Cheng, T. B. Du, H. C. Pi, S. M. Jang, Y. H. Lin and H. T. Lee, *Bioresour. Technol.*, 2011, **102**, 10151-10153.
63. R. M. Couto, P. C. Simoes, A. Reis, T. L. Da Silva, V. H. Martins and Y. Sanchez-Vicente, *Eng. Life Sci.*, 2010, **10**, 158-164.
64. G. Andrich, U. Nesti, F. Venturi, A. Zinnai and R. Fiorentini, *Eur. J. Lipid Sci. Technol.*, 2005, **107**, 381-386.
65. A. P. R. Canela, P. T. Rosa, M. O. Marques and M. A. A. Meireles, *Ind. Eng. Chem. Res.*, 2002, **41**, 3012-3018.
66. D. Kusdiana and S. Saka, *Bioresour. Technol.*, 2004, **91**, 289-295.
67. P. D. Patil, V. G. Gude, A. Mannarswamy, S. Deng, P. Cooke, S. Munson-McGee, I. Rhodes, P. Lammers and N. Nirmalakhandan, *Bioresour. Technol.*, 2011, **102**, 118-122.
68. P. D. Patil, V. G. Gude, A. Mannarswamy, P. Cooke, N. Nirmalakhandan, P. Lammers and S. Deng, *Fuel*, 2012, **97**, 822-831.
69. P. D. Patil, H. Reddy, T. Muppaneni, T. Schaub, F. O. Holguin, P. Cooke, P. Lammers, N. Nirmalakhandan, Y. Li, X. Lu and S. Deng, *Bioresour. Technol.*, 2013, **139**, 308-315.
70. P. D. Patil, H. Reddy, T. Muppaneni, S. Ponnusamy, P. Cooke, T. Schuab and S. Deng, *J. Supercrit. Fluid.*, 2013, **79**, 67-72.
71. N. Cao, Y. Wang, C. Du, G. Zhang and K. Li, *Trans. Chin. Soc. Agric. Mach.*, 2013, **44**, 125-127.
72. Y. A. Tsigie, L. H. Huynh, S. Ismadji, A. M. Engida and Y.-H. Ju, *Chem. Eng. J.*, 2012, **213**, 104-108.
73. D. Kusdiana and S. Saka, *Appl. Biochem. Biotechnol.*, 2004, **113**, 781-791.
74. Y. Warabi, D. Kusdiana and S. Saka, *Bioresour. Technol.*, 2004, **91**, 283-287.
75. T. Pinnarat and P. E. Savage, *Ind. Eng. Chem. Res.*, 2008, **47**, 6801-6808.
76. S. Saka, D. Kusdiana and E. Minami, *J. Sci. Ind. Res.*, 2006, **65**, 530-530.
77. R. B. Levine, T. Pinnarat and P. E. Savage, *Energ Fuel*, 2010, **24**, 5235-5243.
78. R. B. Levine, A. Bollas and P. E. Savage, *Bioresour. Technol.*, 2013, **136**, 556-564.
79. P. E. Savage, R. Levine and T. Pinnarat, *US Pat.,* 20120079760A1, 2012.
80. J. Sheehan, T. Dunahay, J. Benemann and P. Roessler, *Look Back at the U.S. Department of Energy's Aquatic Species Program:Biodiesel from Algae*, 1998.
81. P. T. Pienkos and A. Darzins, *Biofuels, Bioprod. Biorefin.*, 2009, **3**, 431-440.
82. Y. Chisti, *Biotechnol. Adv.*, 2007, **25**, 294-306.
83. J. W. Richardson, M. D. Johnson and J. L. Outlaw, *Algal Res.*, 2012, **1**, 93-100.
84. R. Davis, A. Aden and P. T. Pienkos, *Appl. Energ.*, 2011, **88**, 3524-3531.
85. S. D. Rios, C. M. Torres, C. Torras, J. Salvado, J. M. Mateo-Sanz and L. Jimenez, *Bioresour. Technol.*, 2013, **136**, 617-625.
86. W. Sawaengsak, T. Silalertruksa, A. Bangviwat and S. H. Gheewala, *Energy Sustainable Dev.*, 2014, **18**, 67-74.
87. C. M. Torres, S. D. Rios, C. Torras, J. Salvado, J. M. Mateo-Sanz and L. Jimenez, *Bioresour. Technol.*, 2013, **147**, 7-16.
88. D. A. Walker, *J. Appl. Phycol.*, 2009, **21**, 509-517.
89. Y. Chisti, *Trends Biotechnol.*, 2008, **26**, 351–352.
90. J. K. Pittman, A. P. Dean and O. Osundeko, *Bioresour. Technol.*, 2011, **102**, 17-25.
91. Z. W. Cai, *CHN Pat.* CN101368193, 2009.
92. J. R. Benemann and W. J. Oswald, in *Final Report to the Department of Energy Pittsburgh Energy Technology Center*, Editon edn., 1996.
93. M. E. Huntley and D. G. Redalje, *Mitigation and adaptation strategies for global change*, 2007, **12**, 573 - 608.

94. P. T. Pienkos, National algal biofuels technology roadmap workshop, university of Maryland, Editon edn., 2008.
95. P. T. Pienkos and A. Darzins, *Biofuels Bioproducts & Biorefining-Biofpr.*, 2009, **3**, 431-440.
96. A. Sun, R. Davis, M. Starbuck, A. Ben-Amotz, R. Pate and P. T. Pienkos, *Energy*, 2011, **36**, 5169-5179.
97. L. Amer, B. Adhikari and J. Pellegrino, *Bioresour. Technol.*, 2011, **102**, 9350-9359.
98. F. Delrue, P. A. Setier, C. Sahut, L. Cournac, A. Roubaud, G. Peltier and A. K. Froment, *Bioresour. Technol.*, 2012, **111**, 191-200.
99. J. Singh and S. Gu, *Renewable Sustainable Energy Rev.*, 2010, **14**, 2596-2610.
100. A. J. de Boer and J. van Doorn, Biomass for Energy and Industry, Rimpar, 1998.
101. M. D. Bai, C. H. Cheng, H. M. Wan and Y. H. Lin, *J. Taiwan Inst. Chem. Eng.*, 2011, **42**, 783-786.
102. A. Tabernero, E. M. M. del Valle and M. A. Galan, *Biochem. Eng. J.*, 2012, **63**, 104-115.
103. F. A. Reyes, J. A. Mendiola, E. Ibañez and J. M. del Valle, *J. Supercrit. Fluids*, 2014, **92**, 75-83.
104. R. L. Mendes, B. P. Nobre, M. T. Cardoso, A. P. Pereira and A. F. Palavra, *Inorg. Chim. Acta*, 2003, **356**, 328-334.
105. K. H. Cha, S. Y. Koo and D.-U. Lee, *J. Agric. Food Chem.*, 2008, **56**, 10521-10526.
106. Z. Wu, S. Wu and X. Shi, *J. Food Process Eng.*, 2007, **30**, 174-185.
107. A. T. Soares, D. C. Costa, B. F. Silva, R. G. Lopes, R. B. Derner and N. R. Antoniosi Filho, *BioEnergy Res.*, 2014.
108. S. Pieber, S. Schober and M. Mittelbach, *Biomass Bioenergy*, 2012, **47**, 474-482.
109. J. A. Mendiola, D. García-Martínez, F. J. Rupérez, P. J. Martín-Álvarez, G. Reglero, A. Cifuentes, C. Barbas, E. Ibañez and F. J. Señoráns, *J. Supercrit. Fluids*, 2008, **43**, 484-489.
110. E. M. Johnson, K. Kumar and D. Das, *Bioresour. Technol.*, 2014.



 

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**Figure Captions**

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**Table 1** Lipid content, biomass productivity and lipid productivity of selected microalgal strains used for biodiesel production.

| Microalgal group | Strain | Lipid content /% dw | Biomass productivity /mg·L$^{-1}$·d$^{-1}$ | Lipid productivity /mg·L$^{-1}$·d$^{-1}$ | Ref. |
|---|---|---|---|---|---|
| Ankistrodesmus | *A. falcatus* | 17 | 340 | 54-58 | 32 |
| | *A. fusiformis* | 19-23 | 240 | 43-56 | 32 |
| Botryococcus | *B. braunii* | 25-75 | 27-250 | 4-124 | 32-35 |
| | *B. terribilis* | 49 | 200 | 95-102 | 32 |
| Chlorella | *Ch. emersonii* | 19-34 | 36-290 | 54 | 36, 37 |
| | *Ch. minutissima* | 50-57 | 320-400 | 48-70 | 38 |
| | *Ch. protothecoides* | 18 | 250 | 45 | 37 |
| | *Ch. saccharophila* | 28 | 220 | 60 | 38 |
| | *Ch. salina* | 11 | 170 | 18 | 37 |
| | *Ch. sorokiniana* | 19 | 230 | 45 | 39 |
| | *Ch. sp.* | 19 | 230 | 42 | 39 |
| | *Ch. vulgaris* | 5-58 | 104-482 | 0.5-127 | 33, 36, 37, 39-41 |
| Dunaliella | *D. salina* | 24 | 150 | 37 | 37 |
| | *D. sp.* | 20-24 | 120 | 26 | 37 |
| Nannochloropsis | *N. oculata* | 11-65 | 30-380 | 41-65 | 42, 43 |
| | *N. sp.* | 22-31 | 170-210 | 38-61 | 39 |
| Pavlova | *P. salina* | 31 | 160 | 49 | 39 |
| | *P. lutheri* | 36 | 140 | 50 | 39 |
| Scenedesmus | *S. acutus* | 13-28 | 74 | 13 | 44 |
| | *S. obliquus* | 22-60 | 250-626 | 41-140 | 34, 45 |
| | *S. obtusus* | 18-26 | 179-193 | 36-43 | 46 |
| | *S. rubescens* | 15 | 298 | 50 | 38 |
| | *S. pectinatus* | 23 | 119 | 27 | 46 |
| | *S. quadricauda* | 18 | 190 | 35 | 39 |
| | *S. sp.* | 19-21 | 210-260 | 41-54 | 39 |

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**Table 2** Methods and results summary of recent studies investigating $SCCO_2$ extraction of microalgal lipids.

| Microalgal species | T (°C) | P (bar) | Flow rate (g $min^{-1}$) | Duration (min) | Optimum conditions and discussion | Optimum lipid yield (dwt. %) | Ref. |
|---|---|---|---|---|---|---|---|
| *Scenedesmus sp.* | 35-65 | 200-500 | 1.38-4.02 | - | 500 bar, 53 °C and 1.9 g $min^{-1}$ | 7.41 | 60 |
| *Chlorococcum sp.* | 60, 80 | 300 | - | 80 | (i) Decreasing temperature and increasing pressure resulted in increased lipid yields;<br>(ii) The rate of lipid extraction decreased with experimental time. | 7.1 | 54 |
| *Scenedesmus dimorphus* | 50-100 | 100-500 | 3.33 | 60 | 414 bar and 100 ºC | 9 | 61 |
| *Pavlova sp.* | 60 | 306 | - | 360 | The SFE method is effective and provides higher selectivity for triglyceride extraction. | 10.4-17.9 | 62 |
| *Crypthecodinium cohnii* | 40 and 50 | 200, 250 and 300 | - | 180 | 300 bar and 50 °C<br>(iii) At constant pressure, temperature increase has the effect of decreasing the density of the supercritical fluid and thus its solvation capacity;<br>(iv) Increasing the temperature increases the vapour pressure of the solutes, thus increasing their solubility in the supercritical solvent. | 9 | 63 |
| *Nannochloropsis sp.* | 40, 55 | 400, 550, 700 | 170 | 360 | (i) At constant T, lipid extraction rate increased with P;<br>(ii) At constant P, lipid extraction rate slightly increased with T. | 25.0 | 64 |
| *Spirulina maxima* | 20-70 | 15-180 | 1.998 | - | 150 bar and 50 °C<br>(i) Both the temperature and the pressure affected the extraction rate;<br>(ii) The effect of temperature prevailed over that of pressure. | 16.2 | 65 |

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**Table 3** Comparison between the costs for microalgal biodiesel production according to the published data in recent years

| | Lipids content /% dw | Productivity[a] /( g $m^{-2}\cdot d^{-1}$) | Lipids production cost /$/gal | Cost of Biodiesel ($/ton) | | | Ref. |
|---|---|---|---|---|---|---|---|
| | | | | OP | PBR | Hybrid | |
| Benemann and Oswald (1996) | 50 | 30 | - | 541-671 | - | - | 92 |
| | 50 | 60 | - | 376-400 | - | | |
| Chisti (2007) | 30 | N/A | - | 3294 | 3776 | - | 82 |
| | 30-70 | 35 | - | 8024-16471 | - | - | |
| | 30-70 | 1.535 (kg $m^{-3}$ $day^{-1}$) | - | - | 6600-13176 | - | |
| Huntley and Redalje (2007) | 40 | 18.5 | - | - | - | 280 | 93 |
| | 40 | 60 | - | - | - | 910 | |
| Pienkos (2008) | 25 | 20 | - | 718 | - | - | 94 |
| | 50 | 40 | - | 1082 | - | - | |
| | 60 | 60 | - | 3259 | | - | |
| Pienkos & Darzins (2009) | 15 | 10 | 25 | 7500 | - | - | 95 |
| | 25 | 25 | 7. 5 | 2250 | - | - | |
| | 50 | 50 | 2. 5 | 750 | - | - | |
| Davis *et al* (2011) | 25 | 25 | 8. 52 | 3058 | - | - | 84 |
| | - | 1.25 (kg $m^{-3}$ $day^{-1}$) | 18. 10 | - | 6380 | - | |
| Sun *et al.* (2011) | 25-60 (OP) | 20-60 | 2. 4-10. 6 | - | - | - | 96 |
| | 35-60 (OP) | 35-58 | 9. 7-38. 7 | - | - | - | |
| | 16-47 (Hybrid) | 25-40 | 0. 9-31. 8 | - | - | - | |
| Amer *et al*. (2011) | 50 | 24 | 24.1 | 4176 | | | 97 |
| Delrue *et al.* (2012) | 20-50 | 20-30 | 10.2 | 3412 | | | 98 |
| | 20-50 | N/A | 17.7 | | 5706 | | |
| | 20-50 | - | 16.9 | | | 5482 | |
| Sawaengsak *et al.* (2014) | 25 | 25 | - | 2500 | | | 86 |
| | 25 | 1.25 (kg $m^{-3}$ $day^{-1}$) | - | | 8235 | | |

[a]Productivity is on an areal basis ( g $m^{-2}$ $day^{-1}$) for open ponds and a volumetric basis (kg $m^{-3}$ $day^{-1}$) for PBRs

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**Table 4** Some high value by-products extracted from microalgae

| Product group | Product | Examples (producer) | Applications | Ref. |
|---|---|---|---|---|
| Carotenoids | Astaxanthin | *Haematococcus pluvialis* | Pigments, cosmetics, pro-vitamins, pigmentation | 103 |
| | Canthaxanthin | *Chlorella vulgaris* | | 104 |
| | Violaxanthin | *Chlorella ellipsoidea* | | 105 |
| | *β*-carotene | *Dunaliella salina* | | 104 |
| | *Lutein* | *Chlorella pyrenoidosa* | | 106 |
| Polyunsaturated fatty acids (PUFAs) | *γ*-linolenic acid (GLA) | *Arthrospira maxima* | Food additive, nutraceutics pharmaceuticals | 104 |
| | Eicosapentaenoic acid (EPA) | *Nannochloropsis oculata* | | 107 |
| | *Arachidonic acid (AA)* | *Nannochloropsis oculata* | | 107 |
| | Docosahexaenoic acid (DHA) | *Nannochloropsis oculata* | | 108 |
| Vitamins | Pro-vitamin A | *Dunaliella salina* | Food, health, Nutrition | 104 |
| | *α*-tocopherol (Vitamin E) | *Spirulina platensis* | | *109* |
| Proteins | Phycobiliproteins | *Nostoc sp* | Food, cosmetics, medicine | 110 |

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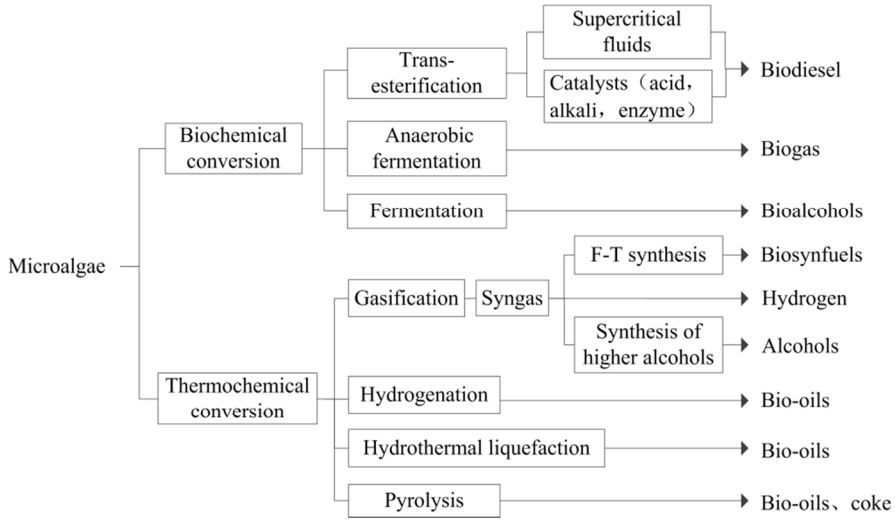


**Fig.1** Potential energy conversion processes from microalgae

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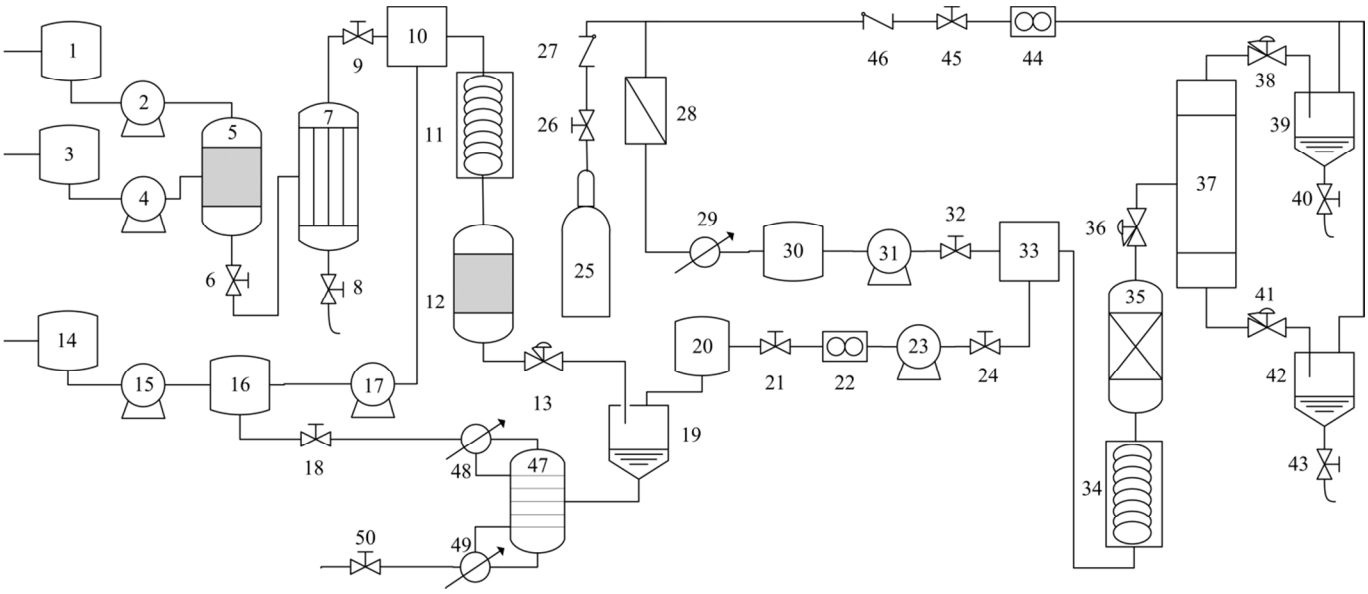


1-microalgae; 2-high-pressure slush pump; 3-fresh water; 4,15,17,23,31-delivery pump; 5-subcritical water reactor; 6,8,9,18,21,24,26,32,40,43,45,50-line valve; 7-gravity clarifier; 10,33-mixer; 11,34-pre-heater; 12-supercritical methanol reactor; 13,36,38,41-back-pressure regulator; 14-methanol; 16-methanol recovery tank; 19-water washing; 20-crude biodiesel and other oil soluble fractions; 22,44-flowmeter; 25-$CO_2$ gas cylinder; 27,46-check valve; 28-filter; 29,48-cooler; 30-$CO_2$ storage tank; 35-extraction column; 37-fractionation column; 39,42-separator; 47- rectification column; 49- reboiler.

**Fig.2** Global scheme of the microalgal biodiesel production by supercritical fluid technology