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Supercritical CO_2 Extraction of Lipid from Microalgae for Biodiesel Production - A Comprehensive Review

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Abstract

The lipid extraction from microalgae by supercritical CO_2 solution is one of the finest techniques for biodiesel production. The supercritical CO_2 technique is characterized by its considerable yields with the optimization of temperature and pressure, production can be increased. There are many research papers focusing on production of biodiesel using supercritical CO_2 extraction of biodiesel from microalgae. This paper is a review which deals with the effect of operating conditions of $SCCO_2$ with fatty acid composition economic analysis of the supercritical CO_2 extraction and wet microalgae through in-situ-transesterification for producing biodiesel. The critical analysis presented in this paper depicted that the operating parameters used for supercritical CO_2 has significant influence on fatty acid profiles available in the biodiesel produced.

Keywords: Biofuels; fatty acid; supercritical CO_2; economic analysis

Introduction

Global dependence on conventional fuels like diesel and petrol is unsustainable for longer usage [1,2]. For making sustainable, the availability of resources as an alternatives to conventional fuels are vigorously required in the world wide [3,4]. The liquid biofuels like biodiesel, ethanol derived from biomass resources are quite promising alternate fuels for conventional fuels [5]. The triglycerides or oil content in the plants and vegetables, microalgae and many waste organic products can be used for biodiesel production which may be either edible, non edible. The biodiesel produced from edible oils are first generation and causes food versus energy competition whereas the from non edible oils (second generation) causes land versus energy competition [6,7]. The third generation biofuels derived from microalgae and macroalgae and aquatic weeds with higher lipid contents and biomass yield has considered as promising one which avoids the problems first and second generation biofuels [8,9]. Generally, microalgae can produce neutral lipids which of consists mainly triglycerides accumulated as droplets form in the cytoplasm, and polar lipids like phospholipids, which normally stored in cellular membrane [10]. The production of biodiesel from algae and aquatic weeds involves different steps like harvesting, processing of biomass, and extraction of lipid and production of biodiesel [11]. Among these the extraction of lipid from algae is energy consuming. The recovery of lipids from microalgae biomass is a major challenge for the economic production of microalgal biodiesel [12]. Already conventional methods of lipid extraction using n-hexane, ethanol and chloroform are employed and having problems like toxicity, environmental problems, flammability, lipid degradation in higher temperature. Also additional separation process is necessary to take away the lipid out of the solvent [13]. At present the synthesis of biodiesel is very expensive process and doesnot produce a profitable market even its highest producing country USA [14].

Supercritical fluids are green solvent which are used for extracting lipid from microalgae [15,16] with inflammable and non-toxic nature with chemical inertness compared to organic solvents [17]. Moreover, unlike organic solvent extraction, lipid extracts do not contain any solvent residues. Therefore, energy consumption associated with product purification is negligible. The supercritical CO_2 extraction having the advantages such as quick extraction, low toxicity, and easy revival of a solvent free product by depressurizing the system, there is no deprivation of thermally labile compounds due to the low critical temperature of CO_2 at 32°C. Also, the tunable selectivity by changing the extraction pressure and temperature with phospholipid free extraction. Another major advantage is to use wet algae biomass directly for the lipid extraction [18].

Supercritical CO_2 Extraction

Supercritical fluid extraction (SFE) is a substitute to solvent based method of lipid extraction uses high soluble supercritical fluids, lesser gumminess, higher diffusivity, adaptable selectivity and lower surface tension [19]. The supercritical extraction technique considered as effective extraction of lipid from microalgae, mainly for extended chain unsaturated fatty acids [12]. Marika Tossavainen et al. [20] investigated the composition of Euglena gracilis lipid extracts and extraction residues from pilot scale supercritical CO_2 extraction. They used extraction temperature as low as 30°C and 50°C for avoiding degradation of lipid extracted by maintaining a pressure of 300 bar for 2 hour duration. They compared the composition of Euglena gracilis extracts with the accelerated solvent extraction. They reported that saturated fatty acids and tocopherols were efficiently extracted with SFE-CO_2 with most of the polyunsaturated fatty acids remaining in the extraction residue. Also they found that the proteins, amino acids and polyunsaturated fatty acids were not degraded in SFE-CO_2, indicating that they could be further utilized. Also, CO_2 as a solvent is known to be non-polar with favorable properties for the extraction of neutral lipids [21]. Mohammad Soleimani khorramdashti et al. [22] extracted oil from Dunaliella tertiolecta using supercritical CO_2 solution and analysed the fatty acid composition using gas chromatograph with flame ionization detector. They concluded that the best temperature and pressure were 40°C, 370 bar respectively. Marika Tossavainen et al. [20] reported more efficient extraction of saturated fatty acids content of 15 with residues at 30°C whereas 14.2 mg/g dry weight with 50°C reaction time. Ahmad Jafari et al. [23] used single-step conversion of wet Nannochloropsis oculata microalgae, impregnated with 15 cc ethanol per 1 g dry microalgal, to produce biodiesel achieved using supercritical carbon dioxide (CO_2).

Effect of Supercritical CO_2 Lipid Extraction Conditions Fatty Acid Composition

The large variation in the FAME yields, is attributed to the varying SC-CO_2 operational parameters, which was also reported by other researchers [24,25]. A study reported by Mariam Alhattab et al. [26] used supercritical CO_2 (SC–CO_2) extraction and studied the effect of fatty acid composition with extraction condition. They used four extraction parameters such as biomass moisture content, reaction temperature, reaction pressure and reaction time in response surface methodology study.

A study reported by Diego A. Esquivel-Hernández et al.[27] considered the effect of conditions of SFE on fatty acid composition. They reported a highest fatty acid content of 32.11 ± 0.12 mg/g) using co-solvent concentration of 11 g/min, pressure 450 bar, static extraction 15 min, dynamic extraction 25 min, temperature 60°C, dispersant 35.

Christelle Crampon et al. [28] used 10g per batch of Nannochloropsis oculata for studying the influence of pretreatments and water content on the extraction kinetics. They compared the fatty acid composition of SFE lipid with Bligh and Dyer method extracted lipid using GC-MS FAME analysis. They reported similar composition of fatty acid methyl esters using SFE conditions of 333K with operating pressures of 50MPa and 85MPa.

Phase behavior of solutes in supercritical fluids can be modified by the addition of small amounts of co-solvents. The addition of a co-solvent may increase solubility selectively or non-selectively. This solubility enhancement results from an increase in solvent density and/or intermolecular interactions and can be used to improve the feasibility of a process by improving solvent loading and/or selectivity.

A study reported by Ozlem Guclu-Ustundag and Feral Temelli [29] analysed the solubility behavior of ternary systems of lipids, co-solvents and supercritical carbon dioxide and processing aspects.

A. Paula R. F. Canela et al. [30] studied the supercritical fluid extraction of fatty acids and carotenoids from the microalgae Spirulina maxima with CO_2. They studied the effect of pressure and temperature on the yield and chemical composition of the extracts under temperatures of 20-70°C and pressure of 15-180 bar. They reported that temperature and pressure affected the extraction rate of fatty acids and at 100 bar and 45°C, the extracts were rich in essential fatty acids.

Sara Obeid et al. [31] considered different operating parameters for SC-CO_2 such as co-solvent, pressure and time on freeze dried Chlorella vulgaris and Nannochloropsis oculata. They used solid phase extraction technique for assessing the yield of extracted neutral lipids, glycolipids and phospholipids. The effect of extraction pressure on the lipid yield of Nannochloropsis oculata is studied and reported an increase in the lipid yield of 20% with a pressure varied from 250 bar to 750 bar.

Also, they observed with increase in solubility of neutral lipid with increase in pressure. The composition of lipid extracted from Nannochloropsis oculata with different extraction pressures of 450 bar and 750 bar indicated similar quality of lipid extracted. Hanifa Taher et al. [25] reported that with an increasing extraction temperature from 35 to 50◦C increased the extraction yield, whereas a decrease in the yield was observed at higher temperatures. This is mainly due to the competing effects of CO_2 solvation and lipid volatility on the solubility.

Table 1: Comparison of fatty acid content with operating conditions of $SCCO_2$ extraction

Algae	$SCCO_2$ condition	Fatty acid content in %	References
Euglena gracilis	30°C, 300 bar, 2 h	SFA= 73 MUFA= 7.8 PUFA= 10.4 LC-PUFA= 8.8	[20]
Euglena gracilis	50°C, 300 bar, 2 h	SFA= 70.9 MUFA= 8.6 PUFA= 11.9 LC-PUFA= 8.7	[20]
Dunaliella salina teodor	200 bar, 40°C	SFA= 68.95 MUFA= 5.37 PUFA= 7.74	[32]
	285 bar, 40oC	SFA= 70.99 MUFA= 6 PUFA= 8.23	
	370 bar, 40oC	SFA= 74.55 MUFA= 6.7 PUFA= 8.89	
	200 bar, 80°C	SFA= 61.21 MUFA= 5.94 PUFA= 6.71	
	285 bar, 80oC	SFA= 63.21 MUFA= 4.57 PUFA= 6.93	
	370 bar, 80°C	SFA= 66.24 MUFA= 5.49 PUFA= 7.12	
Chlorella vulgaris	200 bar, 40°C	SFA= 65.59 MUFA= 4.42 PUFA= 6.24	[32]
	285 bar, 40°C	SFA= 67.67 MUFA= 5.13 PUFA= 6.76	
	370 bar, 40°C	SFA= 71.34 MUFA= 5.92 PUFA = 7.46	
	200 bar, 80°C	SFA= 57.61 MUFA= 3.13 PUFA = 5.12	
	285 bar, 80°C	SFA= 58.23 MUFA= 3.48 PUFA = 5.36	
	370 bar, 80°C	SFA= 62.69 MUFA= 4.53 PUFA= 5.56	
Nannochloropsis oculata	150 bar, 35°C,	SFA= 59.45 MUFA= 35.34 PUFA= 5.21	[33]

A study reported by Thomas Alan Kwan and Julie Beth Zimmerman [34] used neat SC-CO_2 to fractionate MUFA and PUFA triglycerides from Chlorella sp. and reported with increasing densities of SC-CO_2 in a step wise order as 450, 550 and 750 mg/ml produced 88% SFA whereas MUFA had 60% and PUFA had 80% of fatty acids, repectively. They also proposed step-wise extraction to extract and simultaneous fractionization of non-polar triglycerides.

In-Situ Supercritical Transesterification of Wet Microalgae

In-situ transesterification performs lipid extraction and biodiesel production in a single step, in which microalgae is in direct contact with a solvent in the presence of a suitable catalyst. The acid or base catalyst used in the in-situ transesterification causes both cell wall damage and esterifies the lipid. Robert B. Levine et al. [35] used two step process combined with hydrothermal carbonization and supercritical insitu transesterification This work focuses on the production of biodiesel from wet, lipid-rich algal biomass using atwo-step pro- cess involving hydrothermal carbonization (HTC)and supercritical in-situ transesterification (SC-IST). Algal hydro chars produced by HTC were reacted in supercritical ethanol to determine the effects of reaction temperature, time, ethanol loading, water content, and pressure on the yield of fatty acid ethyl esters (FAEE). Reaction temperatures above 275°C resulted insubstantial thermal decomposition of unsaturated FAEE, thereby reducing yields. At 275°C, time and ethanol loading had a positive impact on FAEE yield while increasing reaction water content and pressure reduced yields. FAEE yields as high as79% with a 5:1 ethanol: fatty acid (EtOH:FA) molar ratio (150min) and 89%with a20:1 EtOH: FA molar ratio (180 min) were achieved. This work demonstrates that nearly all lipids within algal hydrochars can be converted into biodiesel through SC-IST with only a small excess of alcohol.

Cost Analysis

Supercritical fluid extraction (SFE) has proven to be technically and economically feasible, presenting several advantages when compared to traditional extraction methods. However, after three decades of development, of the over 200 commercial plants in the world [36].

The total investment capital is the cost related to the plant construction and is divided into direct costs and indirect costs. The direct costs include all expenses related to the installation of the plant, such as: equipment, installation, instrumentation and control, electrical systems, piping, building and land. The indirect cost involves the cost related to installation of the plant like engineering and supervision, legal fees, construction, contractors fees, start up assistance and contingencies [37].

Conclusions

SC-CO_2 extraction of lipid from microalgae is viable technique by considering the high-added-value compounds are extracted for cosmetic, pharmaceutical, and neutraceutical industrial applications. Pertaining to the potential biofuel application, SC-CO_2 extraction from microalgae seem to be underisable at the industrial scale due to cost effective point of view with the batch-mode operation having the energy-consuming step of drying the microalgae. However, this technique requires further development in order to reduce the cost of lipid extraction with the the usage of dry and wet microalgae.

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