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ALGAE AS A POTENTIAL FEEDSTOCK FOR PRODUCTION OF BIODIESEL

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Abstract - *In the present study, the efficiency of biodiesel production from microalgae spirogyra oblonga and cladophora vagabunda were studied using alkali based transesterification process. The solvent extraction method was used to extract oil and quantitative yield was compared for both algae. The yield of extracted oil was found to be more in cladophora sp. than spirogyra sp. The reaction affecting parameters such as operating temperature and reaction time were studied for two different catalysts. The yield of biodiesel produced from cladophora vagabunda was 94%. The operating parameters were temperature 65^{0}C, reaction time 90 minutes and oil: methanol ratio of 1:10. KOH (0.7 wt %) was used as a catalyst for this process. The biodiesel obtained from both the species has properties comparable to conventional fuels. Cladophora vagabunda and spirogyra oblonga showed high ability to produce a good quality biodiesel.*

Key Words: **Algae, biodiesel, solvent extraction, transesterification.**

1. Introduction

The world's energy needs currently are strongly dependant on fossil fuels like petroleum, coal, natural gas. The energy crisis is becoming the most grown-up global problem for human civilization and its development [1]. Since the energy demand of more than 80% is fulfilled by fossil fuels [2]. The current fluctuating global oil prices and limited fossil fuel resources have induced an interest of researchers and consultancies worldwide to find prominent renewable energy solutions for transportation fuel and other energy needs [3]. Bio-energy has great potential to fulfill the energy needs as a renewable energy for human society. Biodiesel, biogas, bioethanol, biohydrogen are the main forms of biofuels. Biodiesel renders a promising alternative to petroleum fuels because it can be easily blended with them without much modification in the design of diesel engine [3, 4, 5]. Biodiesel comprises monoalkyl esters derived from either animal fats or vegetable oils such as soybean oil, corn oil, rapeseed oil, canola oil, palm oil, castor oil, etc. Biodiesel or methyl ester is the renewable, biodegradable and non-toxic fuel and therefore it is a clean source of energy which has the potential to replace fossil fuels [6].

The transesterification process is used to produce biodiesel from crop oils in which triglycerides are present. Reaction with methanol results in the formation of methyl ester or biodiesel. The biodiesel produced from the sunflower oil, palm oil, rapeseed oil, canola oil, etc (edible oil) is called first-generation biofuel and biodiesel produced from oils of jatropha, cassava, miscanthaus (non-edible) is called second-generation biofuel [7]. Both first and second generation biofuels entail a high demand for land to cultivate these plants which may affect cultivation of food crops with an uncertainty of the availability of food. The food prices may go higher if the farmlands are used to produce biofuels. The third-generation biofuels can solve this problem. The biofuels produced from microalgae, seaweeds, microbes are called third-generation biofuels. Alage have been recognized as potentially exploitable biomass feedstock to produce third-generation biofuels [8]. It can grow on non-arable lands and captures carbon dioxide. Microalgae have the same mechanism of photosynthesis to that of higher plants [9, 10]. Microalgae have unicellular or simple multicellular structure which helps them to grow very abruptly and live in very harsh conditions [11]. About 50000 plus microalgal species exist in nature. Among them, only 30000 are studied and examined yet [12]. Microalgae have many potential advantages over traditional agricultural oil crops. Hydrodictyon reticulum, Spirogyra orientalis, Chlorella vulgaris, Microcystis aruginosa, Cosmarium nitudulum, Mougetia parvula algae have oil percentage (w/w) between 16.5 to 23.80 on dry matter basis with pH range 6.0 to 7.0, density range 0.856 to 0.890g cm^{-3} and viscosity range 3.94 to 4.11 mm^2 sec^{-1} [13]. Oedogonium species has a better yield of oil than spirogyra using sodium hydroxide (NaOH) as a catalyst [14]. 45g of algal oil was extracted from 100 g dry biomass of chlorella emersoni and 35g from 100g dry biomass of rizoclonium using sodium methoxide ($NaOCH_3$) as a catalyst [15]. Comparison of cladophora species with oedogonium and spirogyra shows that oedogonium produces a higher quantity of biodiesel than cladophora and spirogyra. Oedogonium has the highest yield of oil at 3.98g from 15g dry biomass [16]. The biodiesel from chlorella vulgaris gives the best result about 95 % and 92 % for R. hieroglyphicum using transesterification process. Palmitic(C16:0), Stearic (C18:0), Oleic (C18:1), Linoleic (C18:2) and Linolenic (C18:3) are the most common fatty acids of microalgae. Optimum balance of unsaturated and saturated fatty acid methyl ester should give a good biodiesel quality [17].

2. Material and methodology

2.1 Algae Sampling and Identification

The algae cladophora vagabunda were collected from the prawn farm of aquaculture sites at Ansure village in Ratnagiri district of Maharashtra, India. The algae spirogyra oblonga were collected from Institute of environment education and research, Bharati Vidyapeeth University, Pune. The algal

species were identified using standard methods under high-resolution microscopes. The microscopic image of cladaphora vagabunda is shown in figure 1.

Fig. 1: Microscopic image of Cladaphora Vagabunda

The algae collected from the site were washed and squeezed to drain all water. Then, the algae were cut into small pieces and dried in sunshade for 48 hours followed by heating in an oven at 40^{0}C until the moisture was removed and weight was observed for constant value. The dried pieces of algae were ground with blender as much as possible to turn it in powder form. Lipid content was determined by gravimetric quantification method. The flow diagram of biodiesel production from algae is shown in figure 2.

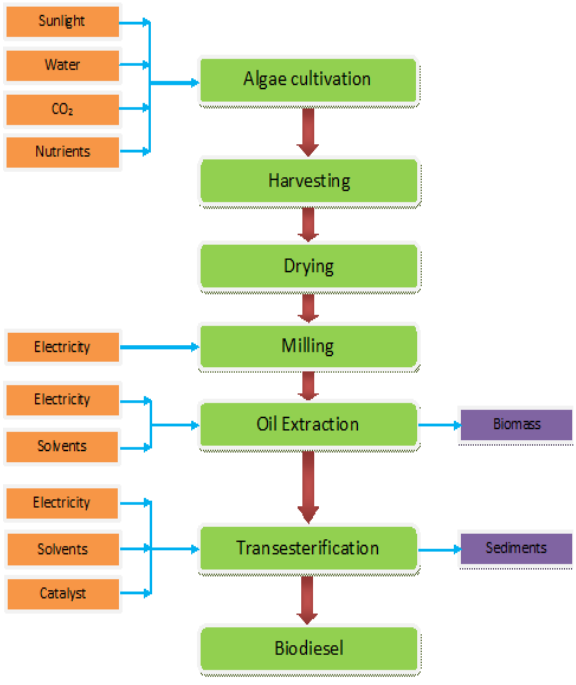

Fig. 2: The flow diagram of biodiesel production process from algae

2.2 Extraction of Oil

Solvent extraction was carried out to extract the oil from the algae. The solvent used was recycled to reduce the processing cost. Two methods were followed for extraction of oil as discussed below.

1. Chloroform : methanol (2:1 v/v) method:

A dried algal species of known weight (200 g dry weight) was taken and mixed with chloroform: methanol (2000 ml 2:1 v/v) extraction solvent mixture for 20 minutes with the help of agitator. Mixture of chloroform: methanol (1000 ml 1:1 v/v) was added after 10 minutes. Extraction of the filter was done and the algal residue was washed three times with 500 ml chloroform. The resultant solution was separated from the solvent by simple distillation.

2. Hexane: ether (1:1 v/v) method

A dried algal species of known weight (500 g dry weight) was taken and mixed with hexane: ether (5000 ml 1:1 v/v) extraction solvent mixture and kept for 24 hrs, followed by filtration of the solution.

2.3 Determination of FFA in Oil

Extracted algal oil was checked out for FFA content because high content of FFA decreases the catalytic activity by formation of soap in biodiesel synthesis.

2.4 Biodiesel Synthesis

The single stage alkali based catalyst transesterification process was followed for biodiesel production from extracted algal oil. The extracted algal oil was heated up to 65^{0}C to remove the solvent mixture from solution. The mixture of methanol and catalyst (0.7 wt %) was stirred for 10 min and added to the reactor containing algal oil. The reaction mixture was stirred at 110 rpm. Alkali catalyzed transesterification reaction was carried out at different temperature 50^{0}C, 55^{0}C, 60^{0}C, 65^{0}C, 70^{0}C, 75^{0}C with constant time of 1 hour using catalyst KOH. The process was also carried out at different agitation period of 60, 90 and 120 minutes with constant temperature of 65^{0}C under atmospheric pressure for KOH catalyst. The same procedure was followed for sodium methoxide catalyst. The experimental setup used for the transesterification reaction is shown in figure 3.

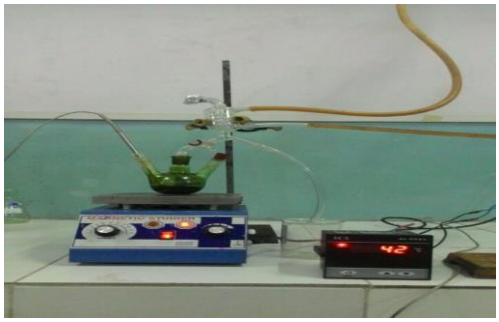

Fig. 3: The experimental setup for transesterification process

After completing the reaction, the solution was allowed to settle. The upper layer of biodiesel and lower layer of glycerin, pigments, etc were formed clearly after 16 hours.

The biodiesel was separated from the lower layer i.e. glycerin by gravity with the help of separating funnel. The biodiesel phase is further purified into biodiesel by cleansing with warm distilled water. Biodiesel was subjected to the drying operation to remove moisture with the help of dryer and the quantity of biodiesel produced was measured. The pH of biodiesel was recorded and stored for moreover analysis.

3. Results and discussion

3.1 Drying of Algae

The dry weight of algae cladophora was 2000 gm after drying operation from fresh weight (wet wt.) of 6250 gm and the dry weight of algae spirogyra oblonga was 2070 gm from fresh weight (wet wt.) of 7390 gm after drying as shown in table 1.

Table 1: Measurement of conversion of fresh wt to dry wt. of algal biomass with % conversion

Algae Species	Fresh wt./wet wt.	Dry Wt.	% conversion
Cladophora vagabunda	6250 (g)	2000(g)	32(%)
Spirogyra oblonga	7390 (g)	2072(g)	28.03(%)

Dry Wt. percentage of biomass was greater in cladophora vagabunda than in spirogyra oblonga species.

3.2 Lipid Percentage Calculation

The lipid percentage value in algal species was evaluated as 16.20% in cladophora and 14.25% in spirogyra on a dry weight basis.

3.3 Algal Oil Yield

The algal oil extracted from algal species cladophora and spirogyra was measured and compared for both chloroform: methanol (2:1 v/v) and hexane: ether (1:1 v/v) solvent extraction method as shown in table 2 and table 3 below

Table 2: Measurement of oil extracted from cladophora and spirogyra species using chloroform: methanol (2:1 v/v) method

Algae Species (1000 g dry wt.)	Extracted algal oil	Biomass
Cladophora vagabunda	167.7 g	465.5 g
Spirogyra oblonga	154.3 g	472.4 g

Table 3: Measurement of oil extracted from cladophora and spirogyra species using hexane: ether (1:1 v/v) method

Algae Species (1000 g dry wt.)	Extracted algal oil	Biomass
Cladophora vagabunda	162.2 g	479.4 g
Spirogyra oblonga	147.9 g	485.0 g

167.7 g of algal oil and 465.5 g of biomass were produced from 1000 g (dry wt.) of cladophora species and 154.3 g of algal oil and 472.4 g of biomass was produced from 1000 g (dry wt.) of spirogyra species by chloroform: methanol (2:1 v/v) method. While a 1000 g (dry wt.) of cladophora produced 162.2 g of algal oil and 479.4 g of biomass. A 1000 g of spirogyra produced 147.9 g of algal oil and 485 g of biomass by hexane: ether (1:1 v/v) method. Extracted oil was found greater in cladophora than spirogyra. The biomass after oil extraction was higher in spirogyra than cladophora algae.

3.4 Free Fatty Acid (FFA) Calculation

The FFA percentage value in algal species was found to be 2.016% in cladophora and 2.604% in spirogyra on a dry weight basis.

3.5 Effect of Catalyst Concentration on Algal Methyl Ester

The effect of catalyst concentration (potassium hydroxide and sodium methoxide) on yield of methyl ester was studied for cladophora and spirogyra algal oil with 0.5, 0.7 and 1 wt % at 60^0C and oil: methanol ratio of 1:10. Biodiesel yield was low at lesser catalyst loading due to incomplete reaction and then increased as the catalyst loading was increased. The maximum methyl ester yield was found at 0.7 wt% of potassium hydroxide and sodium methoxide as a catalyst.

3.6 Effect of Temperature on Algal Methyl Ester

The effect of operating temperature was observed at 50^0C, 55^0C, 60^0C, 65^0C, 70^0C, 75^0C by keeping other parameters constant such as time 1hour, catalyst KOH (0.7 wt%) and oil to methanol ratio (1:10) as shown in figure 4.

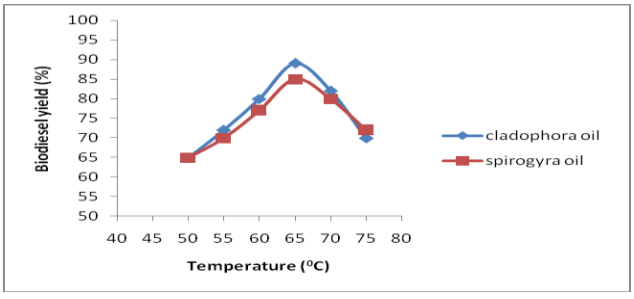

Fig. 4: Effect of temperature on biodiesel yield for constant time 1 hour, catalyst KOH

The same procedure was followed for catalyst $NaOCH_3$ and it was found that yield of methyl ester was higher at 65^{0}C which is the boiling point of methanol for both algal oils as shown in figure 5.

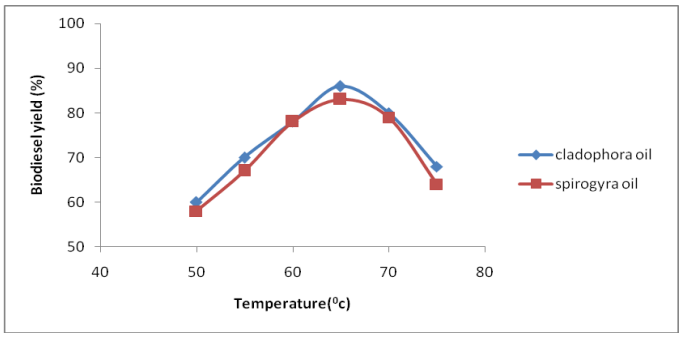

Fig. 5: Effect of temperature on biodiesel yield for constant time 1hr, catalyst $NaOCH_3$

3.6 Effect of Time on Algal Methyl Ester

The effect of reaction time on yield of biodiesel was observed for 60 min, 90 min, and 120 min as shown in table 6 and table 7. The other parameters were kept constant such as temperature 65^{0}C, catalyst KOH/$NaOCH_3$ (0.7 wt %) and oil to methanol ratio (1:10). The temperature 65^{0}C was selected as biodiesel yield was highest at 65 ^{0}C.

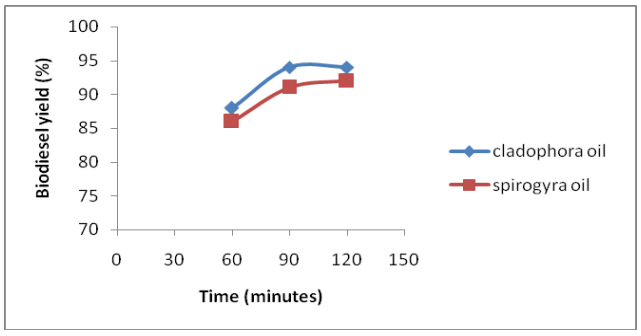

Fig. 6: Effect of reaction time on biodiesel yield for constant temp. 65^{0}C, catalyst KOH

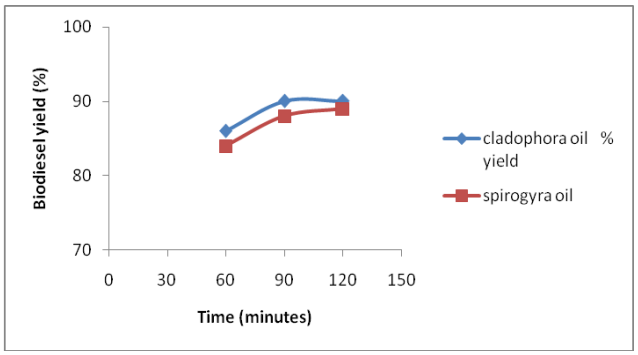

Fig. 7: Effect of reaction time on biodiesel yield for constant temp. 65^{0}C, catalyst $NaOCH_3$

It was found that methyl ester yield was optimum at 90 minutes reaction time for both algal oils. Cladophora methyl ester yield was greater than spirogyra methyl ester. The time required to complete the transesterification process was 90 minutes beyond which, it gave minimal increment which was not feasible.

The transesterification reaction at temperature 65^{0}C and reaction time of 90 minutes using catalyst KOH gave maximum yield percentage of biodiesel for both cladophora oil (94%) and spirogyra oil (91%).

4. Analysis

The properties of produced algal biodiesel were analyzed as shown in table 4.

Table 4: Properties of produced biodiesel

Properties	Spirogyra biodiesel	Cladophora biodiesel
Cloud point	3^{0}C	3^{0}C
Pour point	-7^{0}C	-9^{0}C
Flash point	155^{0}C	148^{0}C
Fire point	159^{0}C	153^{0}C
Kinematic viscosity at 40^{0}C	3.5 mm^2/s	3.0 mm^2/s
Acid Value	0.472 mgKOH/g	0.434 mgKOH/g
Relative density	868.2 kg/m^3	864.3 kg/m^3
pH	7	7

The composition of the fatty acid methyl ester of produced biodiesel was analyzed using gas chromatography method shown in table 5.

Table 5: Fatty acid methyl ester (FAME) profile of spirogyra oblonga sp. and cladophora vagabunda sp. (g/100g of fatty acids)

Sample		Spirogra oblonga	cladophora vagabunda
Saturated Fatty Acids	C8:0	0.0	0.0
	C10:0	0.0	0.0
	C12:0	0.2	0.0
	C13:0	0.0	0.0
	C14:0	10.4	0.6
	C15:0	0.0	0.3
	C16:0	30.6	16.2
	C17:0	ND	0.4
	C18:0	3.2	0.9
	C20:0	1.8	ND
	C21:0	ND	ND
	C22.0	1.6	ND
	C23:0	ND	ND
	C24:0	ND	0.5
Mono Unsaturated Fatty Acids	C14:1	ND	0.23
	C15:1	ND	2.4
	C16:1	5.8	4.2
	C18:1	29.1	8.4
	C20:1	0.6	ND
	C22:1	ND	ND
	C24:1	ND	1.0
Poly Unsaturated Fatty Acids	C16:2	4.3	2.7
	C16:3	ND	1.4
	C16:4	ND	12.8
	C18:2	29.2	11.6
	C18:3	1.6	22.0
	C18:4	ND	3.1
	C20:3	0.9	0.8
	C20:4	ND	ND
	C20:5	ND	ND
	C22:6	ND	0.14

5. Conclusion

In the attempt of biodiesel production, two algae species were selected i.e. cladophora vagabunda and spirogyra oblonga. Among two methods of extraction of algal oil, solvent extraction chloroform: methanol (2:1 v/v) method was found better than hexane: ether (1:1 v/v) method. The optimum conditions for biodiesel production were observed at temperature 65^0C, reaction time 90 minutes and catalyst KOH (0.7 wt %) through transesterification reaction for both algal species. Cladophora algal species with higher biodiesel yield was the better choice as compared to spirogyra species. From the experimental work and analysis, algal biodiesel can be a superlative option over other biodiesel and a good alternative to the conventional fuels both economically and environmentally.

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