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Potential assessment of microalgal oils for biodiesel production: A review

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Abstract
In view of increasing energy demand, climate change, increasing price of petroleum and fast depleting fossil fuel resources, the urgent need of finding alternatives fuels is being felt all over the world. Presently, the microalgae, are viewed as potential 3rd generation source of biodiesel due to significant advantages over terrestrial seed oil plants. The paper attempts theoretically to assess the potential of oils from six microalgae species available in north part of India for the production of biodiesel on the basis on oxidation stability index and Oxidizability. Based on the fatty acid compositions, APE and BAPE are find theoretically. On the basis of APE and BAPE, oxidation stability index and oxidizability have been assessed. The grading of oils in terms of OSI and OX helps to select the potential feed stocks for biodiesel production and discard the other feed stocks that may require considerable efforts to improve the oxidation stability. It is concluded that the oils can be arranged in the decreasing order of oxidation stability index: Pithophora> Spirogyra> Hydrodictyon> Cladophora> Tolypothrix> Rhizoclonium and on the basis of oxidizability.: Pithophora> Spirogyra> Hydrodictyon> Cladophora> Tolypothrix> Rhizoclonium which means that Pithophora takes more time to oxidize and best suited for biodiesel production while the other oil needs antioxidant to increase their stability for biodiesel production.

Keywords: Cultivation, Harvesting, Extraction, Oxidation stability, Oxidation stability index (OSI), Oxidizability

1. Introduction
Energy is the basic requirement for economic development and every sector of global economy like agricultural, industrial, transportation etc. needs energy and consequently, the energy consumption is rapidly increasing globally. Rapid depletion of conventional energy resources, increasing costs and associated environmental degradation has led to the concern about energy security. This situation has resulted into the search for liquid renewable fuels like bioethanol/ biodiesel as substitute of gasoline/ diesel respectively. Biodiesel, an eco-friendly renewable fuel, is monoalkylesters of long chain fatty acids derived from vegetable oils or animal fats. The biodiesel from edible oil resources is impractical and infeasible as more than 50% of edible oil is imported to meet for food requirement in India [1]. The non edible oil resources like *Ratanjot(jatropha curcas.L), Karanja(pongamia piñata), sal(shorea robusta), mahua(madhuca indica), and neem(azadirachta indica)* etc are viewed in India as potential feed stocks for biodiesel. Recently, microalgae is being viewed as future source of biodiesel, as it requires very less land area, less time (24 hrs to 48 hrs) for maturity and gives about 30 times or more oil yields than terrestrial oil seed crops. The present review is focussed on the potential assessment of microalgal oil for biodiesel production [2-6] and covers the classification of algae, cultivation, harvesting, oil extraction and evaluation of Oxidation stability index. The potential of selected algal species for biodiesel production has been assessed with respect to stability, usability and storability of these oils similar to diesel.

1.1 Importance of algal oil as source of biodiesel
Microalgae production based on CO_2 fixation is much faster and more efficient than terrestrial oil seed crops and therefore, is considered to serve as a commercial feasible process for CO_2 mitigation. Majority of the microalgae have much higher cell growth and 10-50 times high CO_2 fixation rate and are accompanied by high algal biomass productivity which can be used to produce variety of biofuels, pigments, cosmetic and nutritious food. The maturity time of (24 hrs-48 hrs) and need of wastelands and waste water are other added advantages of microalgae compared to terrestrial plants [7]. The table 1 gives the oil productivities of some of oils and the land requirement.
The table 1 shows that microalgae has the ability to give highest yield of about 1,36,900 l/ha/yr with a land area of only 2 Mha compared to terrestrial plants while the corresponding non-edible oils like *Jatropha* has the oil productivity of 1892 l/ha/yr and needs 140 Mha of land. The productivity of other edible oils varies with land requirement but the edible oils cannot be used for biodiesel production. Microalgae have faster growth rates, capable of growing in highly saline waters that are unsuitable for agriculture, fixing large fraction of solar energy, have higher photosynthetic efficiency and require little simple nutrients supply for the growth compared to terrestrial oil seed plants [9]. The lipid

oil content of microalgae varies between 20 and 40% (dry wt basis) and lipid contents as high as 85% is also reported for certain microalgal strains [10–12]. Microalgae have the potential to produce 25–220 times more triglycerides that can be readily converted to biodiesel [4, 11, 13 and 14]. Due to these advantages, the third generation microalgal biodiesel is getting more & more attention of the researchers of the world including India.

Table 1 Oil productivity and land area required for growth of oil producing plants [8]

SI.No.	Crop	Oil yield ($l\ ha^{-1}yr^{-1}$)	Land area needed for oil yield (M ha)
1	Corn	172	1540
2	Soybean	446	594
3	Canola	1190	223
4	Oil palm	5950	45
5	Coconut	2689	99
6	Jatropha	1892	140
7	Microalgae	136,900	2

1.2 Oil yields of microalgae

Microalgae, the single-cell microscopic organisms naturally found in fresh water and marine environment, are at the bottom of food chains and are considered to be one of the oldest living organisms on the planet. More than 50,000 species of microalgae species exist today, but only 30,000 are identified as potential species for the biodiesel production point of view [15]. Table 2 gives oil yields of some of the potential algae species.

Table 2 Oil contents of microalgae [8]

S.No.	Microalgae	Oil content (% dry weight)
1	*Botryococcus braunii*	25-75
2	*Chlorella sp.*	28-32
3	*Crypthecodinium cohnii*	20
4	*Cylindrotheca sp.*	16-37
5	*Dunaliella primolecta*	23
6	*Isochrysis sp.*	25-33
7	*Monallanthus salina*	>20
8	*Nannochloris sp.*	20-25
9	*Nannochloropsis sp.*	31-68
10	*Neochloris oleoabundans*	45-47
11	*Nitzschia sp.*	45-47
12	*Phaeodactylum tricornutum*	20-30
13	*Schizochytrium sp.*	50-77
14	*Tetraselmis sueica*	15-23

The above table shows that the *Schizochytrium sp.* has high oil content (50-77 %) while *Tetraselmis sueica* has low (15-23 %) oil contents but all are potential species.

2 Cultivation of Microalgae

Considerable work is reported in India and abroad on the identification & development of potential microalgae species for bio fuel production. The criteria of selection of potential species for culture and cultivation are [16]

- High photosynthetic efficiency utilising solar energy
- Capable of producing high yields of proteins, carbohydrates, lipids and pigments etc.
- Capable of grow in waste water under scarce conditions like fresh, sea water, brackish water and treated effluents
- Capable of having high adaptability to large constraints/ large climatic conditions

The figure 1 classifies various processes for cultivation of microalgae. In order to obtain higher biomass, suitable cultivation technique is required. On the basis of available literature, the cultivation techniques are classified into three main categories: Open pond, photo bioreactor and fermenter with their subsets.

All the three main types of processes are compared in table 3 in terms of number of parameter that helps to address the most common method.

Table 3: Comparison of cultivation processes for microalgae [17]

S.No	Parameter	Raceway ponds	Photo bioreactor	Fermenters
1	Cell density in culture	Low	Medium	High
2	Limiting factor for growth	Light	Light	Oxygen
3	Culture volume necessary to harvest unit weight of cells	High	Medium	Low
4	Surface area to volume ratio	High	Very high	-
5	Control of parameters	Low	Medium	Very high
6	Construction cost per unit volume of algae produced	Medium	High	Low
7	Operating costs	Medium	High	Low
8	Technology	Readily available	Under development	Readily available
9	Risk of contamination	High	Medium	Low
10	Evaporative water losses	High	High	Low
11	Weather dependence	High	Medium	Low
12	Maintenance	Easy	Difficult	Require specialized maintenance
13	Susceptibility to overheating	Low	High	N A
14	Susceptibility to excessive O_2 level	Low	High	N A
15	Ease of cleaning	Very easy	Difficult	Difficult
16	Ease of scale up	High	Variable	High
17	Land requirement	High	Variable	Low
18	Suitability to different species	Low	High	Low

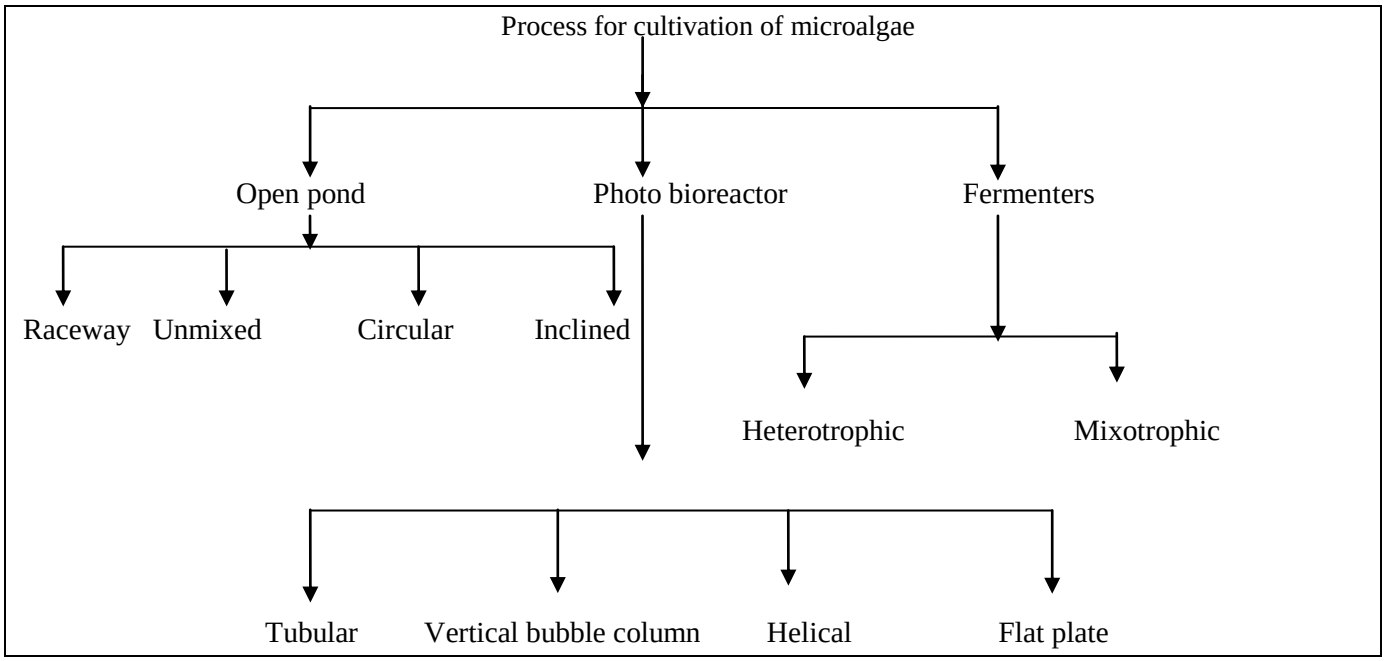

Fig. 1 Classification of cultivation process

The above comparison shows that the most suitable method for algae cultivation is photo bioreactor (PBR) as it has several advantages such as high surface to volume ratio, high efficiency of CO_2 conversion, ability for better CO_2 consumption, lower operating cost and less risk of contamination over the other systems. Because of these merits, considerable work is being done in India and other countries. Looking at these advantages, PBR is found as the most promising method of algae cultivation and is being developed all over the world [18, 19].

3. Harvesting Techniques

The algae, after cultivation, should be separated from the growing medium and drying so that the desired product can be obtained, this is known as harvesting. Harvesting processes mainly depends on the type of algae. The most common harvesting processes are flocculation, filtration, ultrasound, positively charged surface, gravity sedimentation, dissolved air flotation and centrifugation. A brief comparison between different harvesting processes is discussed in

table 4. It is concluded, from the available literature, that the harvesting of microalgal biomass is usually difficult due to its small size (2-20 µm) and it constitutes a major part of the cost of algae production (20-30 %) [20, 21]. It is, therefore, necessary to select most promising harvesting method to harvest the algae biomass effectively and efficiently.

Table 4 shows the various harvesting methods, each has certain advantage and disadvantages. Out of the above methods, the flocculation is reported as the most promising method for algae harvesting. The flocculants used in this method are polymers having higher molecular weights that can adsorb several particles at once [20].

Table 4 Comparison of harvesting techniques for microalgal biomass

S.No.	Algae harvest method	Basic principle	Merit/demerits	References
1	Flocculation	• A process of aggregating the microalgal cells to promote their separation, beginning with the addition of a material (a flocculant) into the medium, which disturbs the stability of the particles in suspension, including microscopic cells, causing them to aggregate . • Flocculants with higher molecular weights are generally more effective and can adsorb several particles at once forming a three-dimensional matrix, so the aggregated cells become easier to harvest. Due to this, the most effective flocculants are polymers either natural or synthetic.	Very high Relative cost	[20]
	a) Inorganic flocculation	• In this the inorganic flocculants neutralize the negatively charged surface to promote their separation. • Inorganic flocculants may be aluminium sulphate ($Al_2(SO)_3$), Ferric sulphate ($Fe_2(SO_4)_3$), Ferric chloride ($FeCl_3$) or lime $Ca(OH)_2$ etc.	Highly sensitive to pH	[21]
	b) Organic flocculation	• A process in which the organic flocculants neutralize the negatively charged surface to promote their separation. Organic flocculants may be okra mucilage, chitosan, modified cationic chitosan-polyacrylamide, greenfloc 120 or combination of starch and chitosan.	Used to flocculate the particles	[20]
	c) Microbial flocculation	• The microbe is fed with an organic substrate such as crude glycerol for harvesting.	Microbes can be reused	[22]
	d) Electro flocculation	• An electrically charged particle move in an electric field in which active coagulant species are produced by oxidation of a metal.	Consume less energy, no contamination by toxic flocculants	[23]
2	Centrifugation	• It makes use of the centrifugal force for the sedimentation of mixtures using centrifuge. More-dense components of the mixture migrate away from the axis, while the less-dense components migrate towards the axis of the centrifuge	Costly chemical/ equipment not required	[4]
3	Direct filtration	• It uses microbial membrane that only allows algal cells to pass through.	Time consuming	[20]
4	Ultrasound method	• In this method, the microalgal cells experience a force that drives them into the planes of pressure nodes, when exposed to an ultrasonic standing wave. When the field is switched off, the aggregated cells settle rapidly due to gravitational forces.	Coagulate the cell	[5]
5	Positively charged surface	• It is used to harvest positively charged surface acting as a magnet to attract and aggregate naturally the negatively charged microalgal cells.	Problem of finding suitable material	[20]
6	Gravity sedimentation	• This method is used for separation of microalgal biomass from larger volumes of water.	Slow process, deterioration of the biomass occur	[21]
7	Dissolved air flotation (DAF)	• The microalgal cells are subjected to flocculation using cationic polyelectrolytes to increase the floc size before applying DAF. Dissolved air flotation involves the generation of fine bubbles produced by a decompression of pressurized fluid. The fine bubble (<10 mm) adhere to the floc making them very buoyant and this buoyancy causes them to rise rapidly to the surface of a separation tank resulting in a concentrated cell foam (7-10% dry weight) which is removed as slurry.	Product extraction may be negatively affected	[21]

4. Extraction of Oil from Microalgal Biomass TNR 12

Various methods to extract the oil from algae are mechanical press, solvent extraction, supercritical fluid extraction and ultrasonic assisted. Each method is briefly discussed as below:

4.1. Mechanical press

It uses high pressure to cause the rupture of cell walls, easier to use and require no solvent. It can extract 70-75% of the oil from algal biomass [20, 24].

4.2. Solvent extraction

Organic solvents like benzene, cyclohexane, hexane, acetone, chloroform etc are mixed with microalgal biomass to extract the oil due to its high solubility in organic solvents that can be recycled. These are relatively inexpensive and the yields obtained are about 60-70 % [20, 24].

4.3. Supercritical fluid extraction

It is relatively more efficient than solvent extraction and is based on increasing the solvating power of supercritical fluid when raised above its critical temperature and pressure. It produces highly purified extracts free from potentially harmful solvent residues with quick extraction & separation and is safe for thermally sensitive products. In this method, CO_2 used as supercritical fluid, is liquefied under pressure and heated to attain the properties of both liquid and gases which acts as solvent for the extraction of oil [25-26].

4.4. Ultrasonic-assisted extraction

It is based on the phenomenon of cavitation which occurs, when vapour bubbles of a liquid are produced in an area in which the pressure of the liquid is lower than its vapour pressure. These bubbles grow when pressure is negative and compressed under positive pressure, causing a violent collapse of the bubbles. If the bubbles collapse, damage can be occurred and the cell contents are released. It has the advantages of requiring less solvent, greater penetration of solvent into cellular materials, improved release of cell contents into bulk medium and very less time. It gives 76-77% yield of oil [20]. From the above, it is clear that out of the above methods, solvent extraction and supercritical methods are the most promising extraction method when oil yields and other factors are taken into consideration.

5 . Fuel Properties of Algal Oils

The fuel properties of microalgal oil, *JCO* and diesel given in table 5 indicate that the density of the microalgal oil is more than the diesel but less than the *jatropha curcas oil* (*JCO)*. The viscosity of microalgal oil is more than both the diesel and *JCO.* This is due to their large molecular weight compared to both. The flash point is higher than diesel but lower than the *JCO*. The heating value and cetane number is almost similar to diesel.

Table 5 Comparison of Fuel properties of algal oil, *jatropha curcas oil* and diesel

SI.No.	Fuel properties	Unit	Microalgal oil [27-30]	Jatropha curcas oil [31-33]	Diesel [27-33]
1	Density at 15 °C	Kg m^{-3}	919	940	836
2	Flash point	°C	65-115	242	75
3	Cetane number	-	51	38	51
4	Saponification value	mg KOH g^{-1}	152	198	210
5	Peroxide value	Meg kg-1	1.00± 0.007	1.34 ± 0.01	-
6	Oxidation stability,110 °C	hours	8.83	2.36	17.3
7	Acid value	Mg KOH g^{-1}	0.13	28.0	<0.005
8	Iodine value	g I_2/100g	119.1	94.00	1.35
9	Heating value	MJ kg^{-1}	41	38	40-45
10	Kinematic viscosity at 40 °C	mm^2 s^{-1}	33.06	24.5	3.03
11	Solidifying point	°C	-12	-	-50 to -10
12	CFPP	°C	18	-	-6

The above table indicates that the kinematics viscosity of algal oil is 33.06 (mm^2 s^{-1}) and 24.5 (mm^2 s^{-1}) for *JCO* showing that algal oil is more viscous than the *JCO*. Therefore, it is difficult to use microalgal oil directly in engine due to piston ring sticking and gum formation. The iodine value of microalgal oil, which depends on unsaturation, is more than the diesel. The acid value of algal oil is less than *JCO* which means that the generation of free fatty acid are less linger life and less harmful for the skin. The oxidation stability of microalgal biodiesel is more than *JCO*, which means that it can be stored for a longer period of time without change in its quantity.

6. Fatty Acid Composition of Various Algal Oils

Table 6 presents fatty acid profile for all selected microalgae. It is clear from the table that the main components of oil were palmitic acid (16:0), oleic acid (18:1), linoleic acid (18:2), palmitoliec acid (16:1) and myristic acid (14:0). All the microalgal lipids were mainly composed of 40-50% saturated and 50-60% unsaturated fatty acids [34].

Table 6 Fatty acid profile of various microalgal oils [34]

SI.No.	Fatty acids	Molecular formula	X:Y	Tolypothrix	Pithophora	Spirogyra	Hydrodictyon	Rhizoclonium	Cladophora
1	Lauric acid	$C_{12}H_{24}O_2$	12:0	0.7	1.3	1.1	0.9	1.4	1.2
2	Tridecanoic acid	$C_{13}H_{26}O_2$	13:0	0.2	0.4	0.3	0.1	0.3	0.7
3	Myristic acid	$C_{14}H_{28}O_2$	14:0	5.8	5.5	6.4	7.0	6.2	9.7
4	Pentadecanoic acid	$C_{15}H_{30}O_2$	15:0	-	0.8	0.6	0.4	0.6	-
5	Palmatic acid	$C_{16}H_{32}O_2$	16:0	31.8	29.7	25.2	26.9	30.4	27.5
6	Heptadecanoic acid	$C_{17}H_{34}O_2$	17:0	2.8	0.4	0.3	0.4	1.7	0.8
7	Stearic acid	$C_{18}H_{36}O_2$	18:0	2.7	3.9	4.5	2.6	6.1	4.3
8	Arachidic acid	$C_{20}H_{40}O_2$	20:0	1.4	1.2	1.3	1.1	1.9	1.6
9	Heneicosanoic acid	$C_{21}H_{42}O_2$	21:0	0.6	0.1	-	0.2		0.8
10	Behenic acid	$C_{22}H_{44}O_2$	22:0	0.9	1.6	1.4	0.9	1.2	1.3
11	Myristoleic acid	$C_{14}H_{19}O_2$	14:1	1.9	0.9	1.1	0.3	2.1	1.2
12	Palmitoleic acid	$C_{16}H_{30}O_2$	16:1	4.7	6.2	5.4	3.8	4.8	5.4
13	Oleic acid	$C_{18}H_{34}O_2$	18:1	23.4	28.4	33.3	34.8	18.9	22.9
14	Gondoic acid	$C_{20}H_{38}O_2$	20:1	0.6	0.9	0.7	1.2	0.4	0.8
15	Erucic acid	$C_{22}H_{42}O_2$	22:1	0.1	-	0.2	0.1	-	-
16	Nervonic	$C_{24}H_{46}O_2$	24:1	0.3	0.2	0.6	0.5	-	0.1
17	Hexadecadienoic	$C_{16}H_{28}O_2$	16:2	2.4	3.6	3.8	2.8	1.6	2.3
18	Linoleic acid	$C_{18}H_{32}O_2$	18:2	8.6	11.2	10.8	9.3	9.7	8.6
19	Eicosadienoic acid	$C_{20}H_{36}O_2$	20:2	0.4	0.1	-	0.2	-	0.3
20	Linolenic acid	$C_{18}H_{30}O_2$	18:3	8.4	0.4	0.7	2.5	9.6	6.1
21	Eicosadienoic acid	$C_{20}H_{36}O_2$	20:3	0.6	1.2	0.6	2.1	0.6	0.6
22	Docosahexaenoic acid	$C_{22}H_{38}O_2$	22:3	0.2	0.3	0.2	0.4	0.6	0.4
23	Trans Docosa-hexaenoic acid	$C_{22}H_{38}O_2$	22:3	1.4	1.7	1.4	1.5	1.9	3.2
24	Eicosatetraenoic	$C_{20}H_{32}O_2$	20:4	0.1	-	0.1	-	-	-
25	Eicosapentaenoic	$C_{22}H_{32}O_2$	20:5	-	-	-	-	-	0.2
26	% Saturation			**46.9**	**44.9**	**41.1**	**40.5**	**49.8**	**47.9**
27	% Unsaturation	Mono Unsaturated		31.7	36.6	41.3	40.7	26.2	30.4
		Di Unsaturated		11.4	14.9	14.6	12.3	11.3	11.2
		Poly Unsaturated		10.0	3.6	3.0	6.5	12.7	10.5
28	Total Unsaturation	Total		**53.1**	**55.1**	**58.9**	**59.5**	**50.2**	**52.1**

The above table shows that all the algal oil has 40-48% saturated while 52-60% unsaturated fatty acids. Almost all the oils contain palmatic, oleic and linolenic acids in significant quantities while the other acids are present in smaller amount. The mechanism of OS is discussed below:

6.1 Oxidation stability (OS) of microalgal oils

Oxidation of oil occurs when it is exposed to air/ O_2 and is accelerated by light, high temperature, presence of water, acids, catalysts (eg Cu), natural antioxidant etc. The shelf life of oil is reduced with temperature as indicated by an increase in the viscosity and deposits in the oils. OS, an important oil/ biodiesel quality parameter, is expressed by the induction period (IP). The auto oxidation process may occur during the storage of oil/fatty acid methyl esters (biodiesels). The peroxide and hydroperoxides formed during primary oxidation are converted to ketones and aldehydes which are finally polymerized into polymers detected as deposits/ sludges in oils/biodiesel, thereby making the later unsuitable as engine fuels due to clogging of fuel filters [35]. Oxidation stability is of industrial concern, because the byproducts formed during decomposition contribute to deposit formations in tanks, fuel systems and filters [36]. The oxidation products include hydroperoxides which eventually polymerize and form the insoluble sediments that are capable of plugging filters, fouling injectors, and interfering with engine performance [37, 38].The polymerization reaction can also lead to an increase in viscosity [39]. Furthermore, very high levels of oxidation in biodiesel can cause separation of two phases causing fuel pump and injector operation problems [40]. Thus, companies, that transport and store biodiesel, are very concerned about oxidative stability. Factors promoting oxidation are the presence of air, light, elevated temperatures, and the presence of extraneous materials [41]. The oxidative stability of biodiesel can also be influenced by the production. It has been noted that major natural antioxidants are removed during distillation purification and the biodiesel produced by distillation typically contains little or no natural antioxidants [36, 40]. Oxidative stability is determined in biodiesel using the EN 14112 method [47]. This measures an induction period for oxidation when the fuel is subjected to oxidation at elevated temperature [41, 42]. The induction period is defined as the period (measured in hours) during which no oxidative, volatile components are generated under certain defined conditions. It is also known as oxidation stability index (OSI). The mechanism of OSI is discussed below:

6.2 Oxidation Stability Index (OSI)

OSI method determines the time also known as "induction time", which is the time when the maximum rate of oxidation occurs indicated by an increase in conductivity of deionised water caused by passing dry air through a heated oil biodiesel sample. The effluent air carries volatile acids into a separate container with the deionised water. The details are available in paper [43].

6.2.1 Evaluation of Oxidation Stability Index

The rate of oxidation of fatty compounds depends on the number of double bonds per mole and their relative positions. Two relative positions can be determined by APE & BAPE as given below:

6.2.1.1 Allylic Position equivalent (APE)

An allyl group is a substituent with the structural formula $-H_2C=CH-CH_2-$ and consists of a methylene group ($-CH_2-$) attached to a vinyl group ($-CH=CH_2$). An allylic position is the position of a carbon bonded to a carbon atom, which in turn is bonded with another carbon atom. A position on the saturated carbon is called the "allylic position" or "allylic site." A group attached at this site is called as "allylic." For example, $CH_2=CHCH_2OH$ "has an allylic hydroxyl group."

6.2.1.2 Bis-Allylic position equivalent (BAPE)

Bis-Allylic are hydrogen atoms bonded to the carbon that are in allylic positions with respect to two different C=C double-bond. For example, the highlighted hydrogen atoms represent bis-Allylic position, because these are in an allylic position with respect to the C=C bonds on both LHS and RHS.

R-CH=CH-C**H$_2$**-CH=CH-R

BAPE

The APE and BAPE are calculated using fatty acid compositions. The member of APE & BAPE calculated for all Fatty acids present in different oils is given in table 7.

Table 7: APE & BAPE in various Fatty acid molecule

Common name	**Molecular Formula**	**APE**	**BAPE**
Myristoleic acid	$CH_3(CH_2)_3$**CH=CH**$(CH_2)_7COOH$	1	0
Palmitoleic acid	$CH_3(CH_2)_5$**CH=CH**$(CH_2)_7COOH$	1	0
Oleic acid	$CH_3(CH_2)_7$**CH=CH**$(CH_2)_7COOH$	1	0
Gondoic acid	$CH_3(CH_2)_9$**CH=CH**$(CH_2)_7COOH$	1	0
Erucic acid	$CH_3(CH_2)_{11}$**CH=CH**$(CH_2)_7COOH$	1	0
Nervonic acid	$CH_3(CH_2)_{13}$**CH=CH**$(CH_2)_7COOH$	1	0
Hexadecadienoic	$CH_3(CH_2)_2$**CH=CH**CH_2**CH=CH**$(CH_2)_7COOH$	2	1
Linoleic acid	$CH_3(CH_2)_4$**CH=CH**CH_2**CH=CH**$(CH_2)_7COOH$	2	1
Eicosadiensic acid	$CH_3(CH_2)_6$**CH=CH**CH_2**CH=CH**$(CH_2)_7COOH$	2	1
Linolenic acid	CH_3CH_2**CH=CH**CH_2**CH=CH**CH_2**CH=CH**$(CH_2)_7COOH$	3	2
Eicosadienoic acid	$CH_3(CH_2)_2$**CH=CH**CH_2**CH=CH**CH_2**CH=CH**$(CH_2)_7COOH$	3	2
Docosahexaenoic	$CH_3(CH_2)_4$**CH=CH**CH_2**CH=CH**CH_2**CH=CH**$(CH_2)_7COOH$	3	2
Trans Docosahexaenoic	$CH_3(CH_2)_4$**CH=CH**CH_2**CH=CH**CH_2**CH=CH**$(CH_2)_7COOH$	3	2
Eicosatetraenoic	$CH_3CH=CHCH_2$**CH=CH**CH_2**CH=CH**CH_2**CH=CH**$(CH_2)_7COOH$	4	3
Eicosapentaenoic	$CH_2=CHCH_2CH=CHCH_2$**CH=CH**CH_2**CH=CH**CH_2**CH=CH**$(CH_2)_7COOH$	5	4

Based on the presence of different fatty acids in different oils/algal oil, the APE & BAPE can be easily computed. However, unsaturated fatty acids are oxidatively unstable compared to saturated. Due to reactivity of double bond with O_2 of the air, the fatty acids with methylene-interrupted double bonds (linoleic and linolenic acids) are susceptible to oxidation than other fatty acids [44]. The data of table 6 has been used to compute APE and BAPE using the following correlations [36]:

$APE = 2\times (A_{C18:1} + A_{C18:2} + A_{C18:3})$ (1)

$BAPE = A_{C18:2} + 2 \times A_{C18:3})$ (2)

Where 'A' is the % fatty acids containing one, two or three double bonds.

$OSI = 3.91 - 0.045 \times BAPE$ ($R^2 = 0.983$) (3)

6.3 Oxidizability (OX)

The Oxidizability (OX) measures the relative rate of oxidation of oils/ biodiesel [45] and can be computed as:

Oxidizability (OX) = [0.02 (% O) + (% L) + 2 (% Ln)]/100 (4)

where 'O' refers to oleic acid (18:1), 'L' refers to linoleic acid (18:2) and 'Ln' refers to linolenic acid (18:3).

Finally, the BAPE is used to calculate OSI using equation (3) while OX is computed using equation (4) and the results are given in table 8.

Table 8 APE, BAPE, OX and OSI of different main algal oils

SI.No.	Oil	APE	BAPE	OSI	OX
1	Pithophora	80	12	3.37	12.57
2	Spirogyra	89.6	12.2	3.36	12.87
3	Hydrodictyon	93.2	14.3	3.26	14.99
4	Cladophora	75.2	20.8	2.97	21.26
5	Tolypothrix	80.8	25.4	2.76	26.27
6	Rhizoclonium	76.4	28.9	2.60	29.28

The above table shows that with increase in BAPE, the OSI decreases while the oxidizability increases. The poor oxidation property leads to formation of gums and choking of fuel line leads to operational problem in engine. [47-49] The increase in unsaturation leads to decrease in OSI indicating that there exists significant relation between BAPE & OSI as indicated by the increase in BAPE, decrease in OSI increase in OX.

It is recommended that potential algal oils for biodiesel production due to considerable oxidation stability, while the other microalgal oils like *Cladophora, Tolypothrix and Rhizoclonium* are not suitable due to stability issue because when converted to biodiesel, the resulting biodiesel would require considerable efforts to improve their stability by adding antioxidants. However, these can be arranged in the order of increasing OSI as ***Rhizoclonium>Tolypothrix> Cladophora> Hydrodictyon> Spirogyra> Pithophora.*** In terms of OX the *Pithophora* (12.57) is found to have lower oxidation rates than *Rhizoclonium* (29.28) meaning that the former is degraded slowly than the later. Accordingly, the algal oil can also be arranged in increasing OX as follow: ***Pithophora> Spirogyra> Hydrodictyon> Cladophora> Tolypothrix> Rhizoclonium.***

It clearly demonstrates that increases in % unsaturation leads to decreases in OSI as shown in **Fig. 2** which shows that significant correlation between OSI & BAPE exists. (R^2 = 0.94).

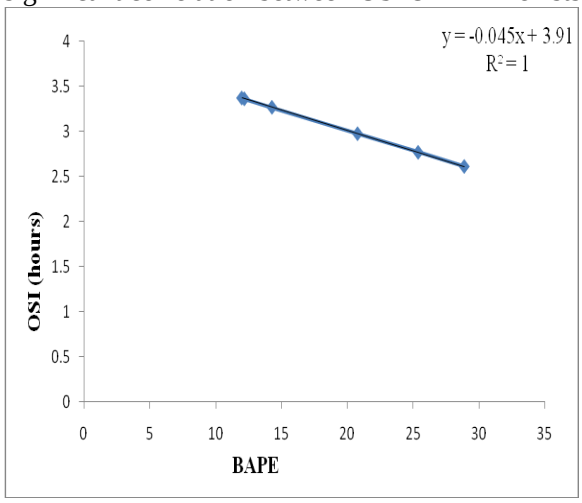

Fig. 2 Oxidation stability index as a function of BAPE

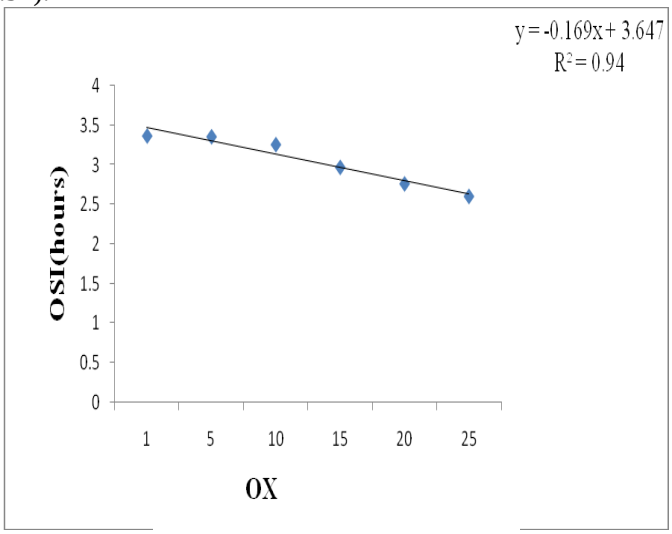

Fig. 3 Variation of OSI with OX

A plot of OSI vs BAPE calculated using eq. (3) for different algal oils to check the credibility of the equation as shown in fig. 2. The value of R^2 is 1 indicates that the relation is applicable to all the algal oil given in table 8. The relation between OSI & OX shown by fig. 3 further indicates that OSI is reciprocal to OX. Based on OSI, the three microalgal oils *Pithophora, Spirogyra and Hydrodictyon* have OSI more than 3hrs as per European standard [47].

Fig. 3 shows the relation between OSI and OX which indicates that OSI decreases with increase in OX and since the value of R^2 is equal to 0.94.

Conclusions

The paper reviews the work on cultivation, harvesting of algae and oil extraction. Looking at the high oil productivities from microalgal biomass, the paper attempts to assess the potentials of selected algal oils on the basis of chemical composition, % saturation & unsaturation, OX and OSI. It is concluded that the oils can be arranged in decreasing order of OSI: P*ithophora> Spirogyra> Hydrodictyon> Cladophora> Tolypothrix> Rhizoclonium* indicates that *Pithophora, Spirogyra and Hydrodictyon* oils may be recommended for biodiesel production as it would be more stable than others microalgal oils and require less effort for its stabilization. The oils can also be arranged in increasing order of OX: *Pithophora> Spirogyra> Hydrodictyon> Cladophora> Tolypothrix> Rhizoclonium* indicates that the *Pithophora* (12.57) has lower oxidation rates than *Rhizoclonium* (29.28) means that the former is degraded slowly than the later means that *Pithophora* takes more time to

oxidize and its life is more than the other oils. The work helps to select potential microalgal oils suitable for biodiesel production based on oxidation stability index and oxidizability.

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