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Caulerpa peltata Methyl Esters as A Renewable Source of Energy

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In this paper, ten species of macroalgae comprising of four green algae, three brown algae and three red algae collected from Gulf of Mannar were evaluated for their lipid content and this paper strives to suggest an alternate to diesel fuel from bio-diesel derived from the green macro algae, *Caulerpa peltata*. Biodiesel characterization was based on ASTMD6751 and the glycerine content and flash point was found to be little bit higher than the standards. Kinematic viscosity, iodine value, neutralization value were within the permissible limits.

Key Words: Macro algae, *Caulerpa peltata*, Transesterification, Biodiesel, Reaction conditions, Properties.

INTRODUCTION

Crude oil reserves are suspected to be depleted in less than 50 years at the present rate of consumption[1]. Petroleum based fuels are limited reserves concentrated in certain regions of the world. Therefore , countries lacking such resources are facing foreign exchange crises, mainly due to the import of crude oil. Hence alternatives for sustainable energy resources are researched upon. Bio-diesel offers a prospective alternative to commercial diesel because of its clean burning qualities. It is carbon-neutral, non-toxic and bio-degradable. Algae being the best source of bio-diesel is also the highest yielding feed-stock in comparison to its competitors. Macroalgae are multi-cellular organisms, which like plants use photosynthesis to convert the sun's energy into chemical energy. They could be a useful natural solar panel transforming sunlight into the chemical energy of oil. The yields of oil from algae are orders of magnitude higher than those for traditional oilseeds, it can produce 250 times the amount of oil per acre as soybeans[2]. Algae can grow in places away from farmlands and forests, thus minimizing the damages caused to the eco and food chain systems. Algae are the best sources for carbon sequestration. Algae can be grown in sewages and next to power plant smoke-stacks where they digest the pollutants and give bio-fuel[3]. Macroalgae growing in water have fewer and more predictable process parameters like sunlight and temperature than higher plant systems allowing easier extrapolation from one site, even climatic conditions to others. They can doubles itself in 3-8 h and they require much less land areas. Vehicles that run on alternative fuels such as biodiesel are the most efficient in terms of mileage and exhaust emissions. Bio-diesel runs in any conventional diesel engine without any major modifications.

EXPERIMENTAL

Ten species of macro algae comprising of 4 green algae, 3 brown algaeand 3 red algae were collected from mandapam regions, Gulf of Mannar marine biosphere reserve along south-east coast of India. Algae were washed in sea water to remove sand and other impurities. The cleaned algae were dried in a tray drier at 55 ºC to remove moisture. The species were evaluated for their lipid content by Bligh and Dyer method[4] and the results are shown in Table-1.

TABLE-1
LIPID CONTENTS

Sea weed species	Total lipid (%)
Geliediella acerosa	3.6
Chaetomorpha aerea	8.6
Gracilaria edulis	2.4
Gracilaria crassa	0.9
Caulerpa peltata	11.4
Caulerpa racemosa	10.6
Turbinaria conoides	3.6
Enteromorpha compressa	11.4
Sargassum myriocystum	0.5
Sargassum wightii	1.2

Since *Caulerpa peltata* had a good lipid content , it was decided to investigate it for bulk preparation and characterization.

Grinding: 1 kg of wet algae was shade dried and then finally dried in an oven at 60 ºC. About 880 g of dry algae was obtained, which was finely chopped into pieces and then ground into fine powder using mortar and pestle.

Algal oil extraction: The algal mass solvent was extracted to separate the lipid content. Chloroform and methanol were added in the ratio of 2:1 (v/v) and allowed to percolate through the algal mass for 24 h. Then the algal bio-mass was separated using a Whatmann filter paper. The extracted oil was evaporated in vacuum to release chloroform and methanol solutions using rotary evaporator. The extraction was done for three times to ensure complete extraction of algal oil.

Transesterification: Algal oil viscosity is high is of the order of 8.2 CSt, which has to be reduced using a reaction known as the transesterification reaction. Conversion of a tri-glyceride molecule or a complex fatty acid to an alkyl ester and glycerol by reaction with alcohol over an acid or base catalyst is known as transesterification reaction. Base catalyzed transesterification is the most economical process requiring only low temperature and pressure giving a better yield and which is nearly 4000 times faster than acid catalysis. Before carrying out bulk tranesterification the oil: alcohol ratio has to be determined since the phase separation becomes a problem if correct oil:alcohol ratio is not followed. Different ratio of oil:alcohol was experimented (1:4, 1:5, 1:6, 1:7) and 1:7 oil:alcohol ratio with 5 % of base catalyst sodium hydroxide was found to give the optimum yield and a better phase separation (Fig. 1).

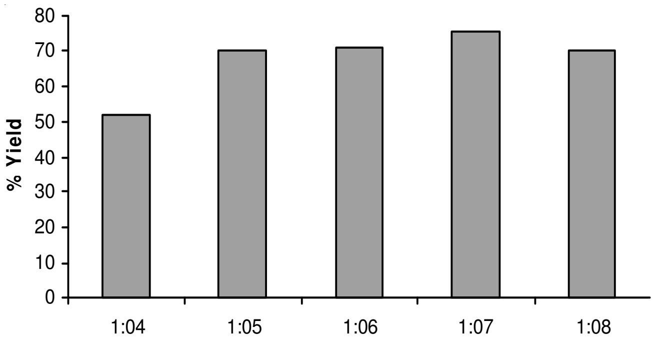

Fig. 1. Optimization of oil:alcohol ratio

The reaction time was optimized as 1.5 h. For 0.5 and 1 h a clear phase separation did not occur. Reaction for 1.5 h gave the best yield and a good phase separation (Fig. 2). After 2 h the yield started decreasing and the trials were stopped because higher reaction time is also not cost economical. Algal oil can also be transesterified to biodiesel by shaking in an electric shaker for three hours without heating[5]. The primary advantage of heating is to reduce the reaction time. However if the reaction temperature exceeds the boiling range of methanol, the alcohol starts vapourizing. So the reaction temperature has to be optimized for a cost comparative process.

The yield for temperature less than 60 ºC gave a less yield and the reaction temperature for *Caulerpa peltata* algal oil transesterification was optimized to be 60 ºC (Fig. 3). For temperatures higher than 60 ºC the yield was less because it exceeds the melting point of methanol which results in evaporation of solvent before reaction.

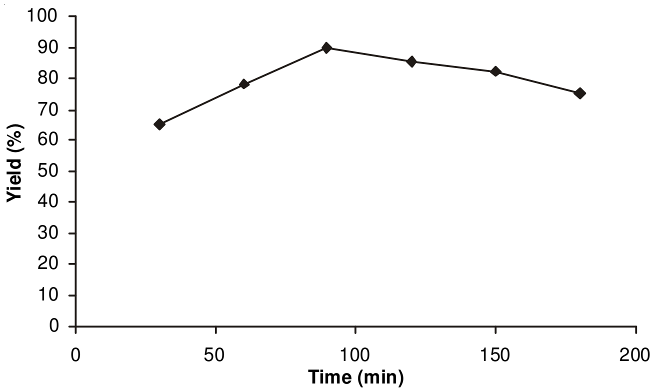

Fig. 2. Optimization of reaction time

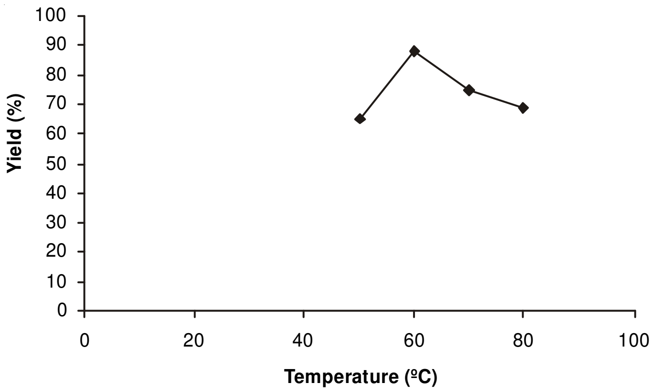

Fig. 3. Optimization of reaction temperature

Caulerpa peltata algal oil transesterification was optimized with volume ratio of 1:7 with oil:methanol with 5 % of base catalyst sodium hydroxide at 60 ºC for 1.5 h with constant stirring. After the reaction is complete, the mixture is kept in a settling flask for 16 h to separate the bio-diesel from the other layer which contains glycerine, pigment and impurities. The heavier co product glycerol after purification can be sold to pharmaceutical, cosmetic industries *etc.*,

Washing and drying: Biodiesel was washed by 5 % water twice until it is clean from catalyst, alcohol, impurities *etc.*, biodiesel was dried by using dryer and finally kept under the running fan for 12 h and stored for further analysis.

RESULTS AND DISCUSSION

Caulerpa peltata bio-diesel density is slightly higher than conventional diesel fuel. This allows use of splash blending by adding bio-diesel on top of diesel fuel for making biodiesel blends (Fig. 4).

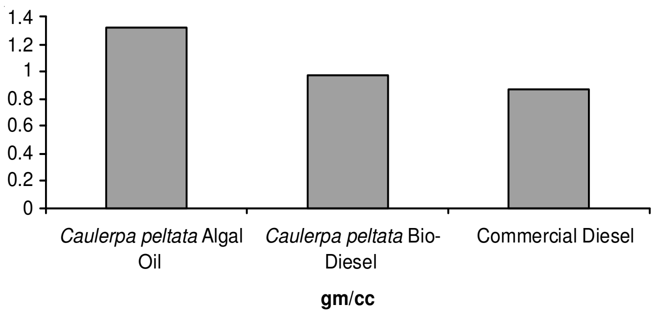

Fig. 4. Comparison of density

Acid value or neutralization number is the mass of potassium hydroxide in milligrams that is required to neutralize 1 g of a chemical substance. The acid number is a measure of the amount of carboxylic acid groups in a chemical compound such as a fatty acid. Acid number for bio-diesel should be lower than 0.50 mg KOH/g. This is because the free fatty acid (FFA) produced may corrode automotive parts and these limits protect vehicle engines and fuel tanks. Acid value of *Caulerpa peltata* bio-diesel was found to be in the permissible limits of ASTM (Fig. 5).

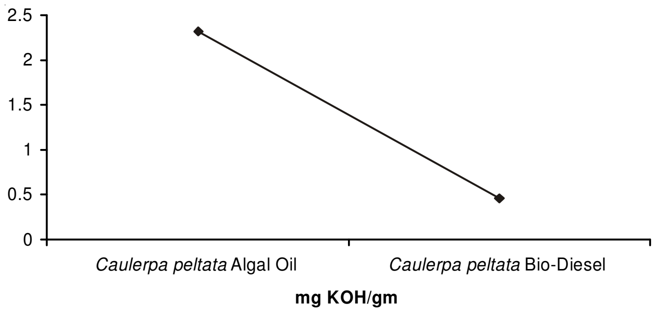

Fig. 5. Comparison of algal oil acid value and algal biodiesel acid value

Kinematic viscosity is an important property of all fuel oils. Higher viscosity results in negative impact on fuel injection system performance. Kinematic viscosity of *Caulerpa peltata* bio-diesel is 2.82 Cst, which is well within the permissible limits of ASTM standards (Table-2). Higher viscosity leads to poor atomization of the fuel, incomplete combustion, ring carbonization and coking of fuel injectors. Sulfur in diesel contributes to the formation of particulate matter in engine exhaust and affects the performance of vehicle emissions control equipment. Sulphur content in *Caulerpa peltata* bio-diesel is 0.0007 %, while the permissible limits according to ASTM Standards are .0015 mass % max, indicating it to be a clean burning fuel which does not contribute to global warming. The water content, glycerol content and iodine number of *Caulerpa peltata* bio-diesel is within the permissible limit. Higher water content will lead to corrosion and oxidation problems. The problem encountered in the long term storage of biodiesel are mainly due to hydrolytic and oxidative degradation. The first of them consisting of hydrolysis of methyl esters when water is present in the reaction mechanism can be influenced by the initial acid content of the product which has a catalytic effect on the above mentioned reaction, the quantity of water actually present and the temperature and form in which it is present *i.e.* dissolved, emulsified or separated on the bottom of the vessel. Higher glycerol content may lead to engine fouling, filter clogging *etc*. Iodine number is an indication of unsaturated fatty acids. A high content of unsaturation increases the danger of polymerization of engine oil leading to fuel thickening, clogging of filter pores *etc.* Flash point of *Caulerpa peltata* bio-diesel is higher than the commercial diesel. Flash point of a fuel is defined as the temperature at which it will ignite when exposed to a flame or spark. Since the flash point of *Caulerpa peltata* bio-diesel is higher, blending with commercial diesel is suggested. Thus in storage, biodiesel and its blends are safer than conventional diesel. Biodiesel can be mixed with regular petroleum diesel usually referred to as blends, B5, B10, B20 *etc.*, Modification to most diesel engines are not required when using B20 or less blends.

TABLE-2
PERFORMANCE STANDARDS

Parameter	*C. peltata Algal bio-diesel*	ASTM D6751	Units
Kinematic viscosity	2.82	2.5 - 6.0	CSt
Sulphur content	0.0007	.0015	% mass (max)
Water content	0.043	0.05	% vol. (max)
Total glycerol	0.26	0.24	% mass (max)
Iodine value	64	<115	g/100 g
Acid number	0.45	0.50	mg KOH/gm
Flash point	180	min 100	ºC
Visual appearance	Golden brown	Brownish yellow	-

Conclusion

Algal bio-diesel is a sustainable stock and a reliable option to meet the current automotive fuel usage. Vehicles that run on alternative fuels such as biodiesel are the most efficient in terms of mileage and exhaust emissions. Although microalgae has a better lipid content than macroalgae, the culturing conditions required for macroalgae offsets the less lipid content. It can double itself in a minimum of 8 h leading to a huge source of raw material for fuel. It also as an advantage of distilling the remaining cell constituents like carbohydrate, amino acids for food and pharmaceutical purposes. *Caulerpa peltata*, a green macroalgae was used to produce bio-diesel and the fuel was analyzed for various parameters like kinematic viscosity, sulfur content, water content, glycerol content, iodine number and acid number, which are well within the ASTMD6751. Flash point was slightly higher than commercial diesel indicating its safety in storage and a suggestion for blending with commercial diesel. Cost is the main obstacle for commercialization. If the economical and technical barriers are overcome ,then algal biodiesel could be the future fuel.

REFERENCES

1. K. Tsukahara and S. Sawayama, *J. Jpn. Petrol. Inst.*, 48, 251 (2005).
2. P. Spoalore, C.J. Cassan and E. Duran, *J. Bio. Sci. Bioenergy*, **101**, 87 (2006).
3. A.K. Bajhaiya, S.K. Mandotra, M.R. Susheela, K. Toppo and S. Ranade, *Asian J. Exp. Biol. Sci.*, **4**, 728 (2010).
4. E.G. Bligh and W.J. Dyer, *Can. J. Biochem. Physiol.*, **37**, 911 (1959).
5. I. Cohen and A. Neori, *Bot. Mar.*, **34**, 977 (1991).