

Synthesis of Biodiesel by using marine Macro-algae of Karwar Region, Karnataka, India

K. Kishore Naik¹ and T. Prameshwara Naik²

¹Research Scholar, Dept. of Botany, Sahyadri Science College, Kuvempu University, Shivamogga, Karnataka, India

²Associate Professor, Dept. of Botany, Sahyadri Science College, Kuvempu University, Shivamogga, Karnataka, India

Abstract

In response to the world energy crisis, global warming and climate change, algal biodiesel production has received much interest in an effort to search for sustainable development. Using algae as a biofuel feedstock holds many advantages in relation to the environment, food security and land use. The lipid contents or oil in algae, once extracted and purified, represent an excellent sustainable feedstock for biodiesel production. In this study three different species of macroalgae (*Dictyota*, *Cladophora* and *Gracilaria*) were used for algal oil extraction. The algal oil was extracted by physical and chemical extraction method. The transesterification reaction of algal oil was carried out with methanol and NaOH as a catalyst for the production of biodiesel. The percentage of oil obtained per gram of biomass was measured. Burning test was carried out by using different blends of algal oil. It was shown that the burning rate of B100 was much lower compared to conventional diesel and B20. Physicochemical properties of algal biodiesel, such as, flash point, kinematic viscosity, water and sediment, density, cetane number, cloud point, acid value, free glycerin, total glycerin, sulphated ash, pour point, carbon residue, sulphur, copper strip corrosion, distillation temperature and phosphorus were examined using the American Standard Test Methods (ASTM D 6751-06)

Key Words : macroalgae, algal oil, biodiesel, transesterification.

Introduction

Recently, more and more concerns have been expressed regarding sustainable development. Sustainable development refers to a mode of human development where an activity can meet the needs of the present generation in an environmentally friendly manner while maintaining options for future generations (Brundtland 1987). The concept of sustainable development can be divided into four parts:

environmental sustainability, economic sustainability, social sustainability, and cultural sustainability. Today more than ever before, unpredictable environmental issues strongly bound with economic, social and cultural impacts are dominating the international agenda, and much importance has been attached in particular to the sustainability of industry. Identifying the core environmental, economic, social and cultural impacts is the first step in supporting the development of a sustainable industry.

Unsustainable aspects can be identified using the techniques of risk assessments (Gupta et al. 2002) and environmental impact assessments (Salvador et al. 2000). Potential risks can thus be forecast and then either mitigated or eliminated to some degree. It is a long-term goal to achieve sustainable economic development along with sustainability of energy. Many significant problems lie in energy production and consumption, such as shortage of resources, low energy efficiency, high emissions, damage to environment, and lack of effective management systems (Zhanget al. 2011). As an example of the scale of the challenge, from 1990 to 2006 China observed an increase of nearly 6% annually in CO₂ emissions, ending up with 5.65 billion tons CO₂ in 2006, accounting for 20.3% of the global amount (Jianget al. 2010). Therefore, it is a long journey for developing countries to optimize energy structures, improve energy efficiency, enhance environmental protection, and carry out efficient energy management in pursuit of sustainable development.

Biofuels have become a hot research topic due to their advantages over fossil fuels. The desire to reduce reliance on foreign oil imports, to improve energy security and to reduce the effects of global warming and climate change has sparked a lot of interest in terms of research and development (R&D) of alternative fuels (Coplin 2012). Policymakers, academics, business representatives, and members of relevant associations are pushing development of biofuels for various reasons. Some think of biofuels as a substitute for high-priced petroleum, while others emphasize their potential to extend available energy resources to confront the increasing world demand for fuels in the transportation sector. Others see biofuels as a substitute for carbon-neutral energy or as an economic opportunity for business. Nonetheless, there are still some skeptical voices arguing that not all biofuel types are sustainable. Many of the biofuels which are currently being supplied have been criticized on the basis of potential adverse effects on the natural environment, food security and land use. In response to the challenges outlined above, renewable energies have received a lot of attention and will hopefully become one of the main energy sources for the world. According to calculations, renewable energy in 2010 covered only 13% of the global primary energy demand (IEA 2012b).

Bioenergy is thought of as the renewable energy with the highest potential to satisfy the energy needs of modern society for both developed and developing countries (Ong et al. 2011). At present, bioenergy contributes around 10–15% of the world energy use (Demirbas et al. 2009). Biofuels, mainly in the form of biodiesel, bioethanol, biogas and biohydrogen, have therefore received increasing attention (Antoni et al. 2007; Johnson and Wen 2010).

Biodiesel, which is usually produced from either animal fat or oil crops, such as soybean, corn, rapeseed, palm, and castor bean, is a non-toxic, renewable and biodegradable fuel, and thus one of the potential alternatives to fossil fuel. Nevertheless, this feedstock has low oil yield and entails high demand for land, water and fertilizer.

Macroalgae have received a great deal of attention towards biofuels production. Algae, which can absorb CO₂ photo-autotrophically, are ideal candidates for CO₂ sequestration and greenhouse gas during algae-based biofuels production. Nevertheless, biofuels, which are derived from food or non-food crops, are not thought of as renewable and sustainable energy types. The growth of these non-food crops targeted for biofuels production will lead to competition for arable farmland with food crops. Farms are limited and should be used to grow food crops. If the food crops grown in farmlands are used to produce biofuels, it will affect food security, and food prices will increase rapidly, subsequently impacting the access of poor populations to food (von Braun et al. 2008). Macroalgal biofuels can deal with most of the concerns connected to first- and second-generation biofuels, and are thus referred to as third-generation biofuels. Macroalgal biofuels are currently attracting a lot of research attention (Lam and Lee 2012).

Marine macroalgae is one such source of aquatic biomass and potentially represents a significant source of renewable energy. Macroalgal biomass can store large amounts of oil which can be exploited for the production of biodiesel (John and Anisha 2013). Marine macroalgae (kelp or seaweed) could be used for solar energy conversion and biofuel production (Ross et al 2008; Demirbas and Demirbas 2011). Macroalgal biomass is suitable feedstock for the production of biodiesel (Maceiras et al 2011; Singh and Olsen 2011; Zhou et al 2010). Many efforts have been dedicated toward producing biofuels from microalgae (Brennan and Owende 2010). However, less effort has been reported about macroalgae. Therefore we attempt to collect some of macroalgae for production biodiesel and characterised

MATERIALS AND METHOD

The feedstock used for biodiesel production in this study were macroalgae. Here we selected 3 macroalgal species from Karwar coast Karnataka, India, which were *Dictyota*, *Cladophora* and *Gracilaria* are shown in Fig. 1.

Figure-1

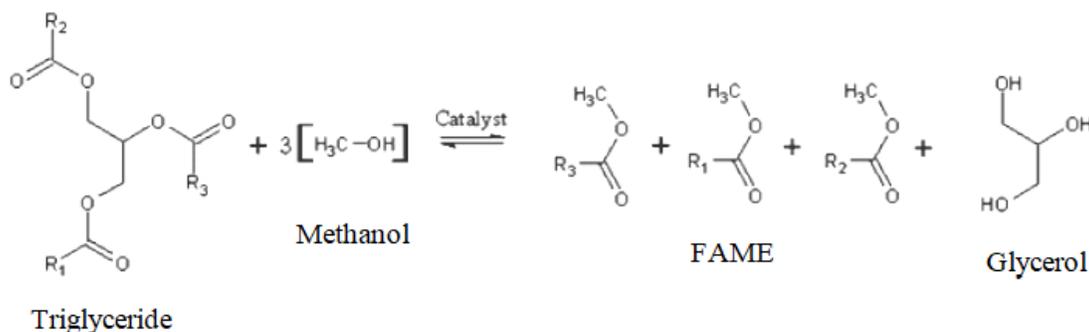


Dictyotaspp
Cladophoraspp
Gracillariaspp

The macroalgae were collected in polythene bags separately by hand picking and transported in wet condition to laboratory. The materials were cleaned thoroughly to remove debris and other foreign materials and preserved in 5% formaldehyde for further investigations.

To extract the oil from macroalgae, Hexane solvent extraction was used along with the expeller method. The algae were mixed with hexane and preceded to the grinding process. The ground algae were put into a container for settling for 24 hours. The oil was extracted by using the cloth filter which functioned as expeller. The extracts were kept into a beaker for 24 hours at room temperature to let the hexane evaporate. The residual crude algal oil was refined by washing with water. The amount of algal oil extracted was measured and recorded. The algal oil from macroalgae was converted into biodiesel by using the base-catalyzed transesterification reaction. In this reaction one molecule of each triglyceride in the algae oil reacted with three molecules of methanol to form three molecule of methyl esters (biodiesel) and one molecule of glycerol. The process was done separately for two samples of 50 ml algal oil so that comparison can be made. The catalyst used in this process was potassium hydroxide (NaOH) and the alcohol used was methanol. The amounts of methanol used were 2 to 7 times of 50 ml of algal oil. The amounts of potassium hydroxide (NaOH) used were 0.2 to 1.2 weight/volume (w/v) % of the feed algal oil. The mixture of alcohol and catalyst was then added to the algal oil. The reaction was carried out at the temperature below the boiling point of methanol (60°C) with continuous stirring for 40 minutes. After shaking the solution for two hours in orbital shaker, it was put into the separating funnel and was kept for 24 hours to settle the biodiesel and sediment layers clearly. Once the reaction was completed, two major products existed; glycerin and biodiesel. The biodiesel was collected

and the glycerin was removed. The biodiesel was purified by washing gently with warm water to remove residual catalyst or soaps. Finally the biodiesel was dried by heating.



The biodiesel was measured and stored in an aluminum foil sealed container for analysis. Physical properties of biodiesel from macroalgae were measured and compare with ASTM (D6751) standards in Table

3. RESULTS AND DISCUSSION

The algal oil was extracted from the selected macro algae species and continued to the conversion process to produce biodiesel. The comparison of the oil content for the selected three macro algae species are shown in **Table 1**. *Dictyotaspp*, had higher lipid content (8.67%) as compared to *Gracilaria*(8.87%) and *Cladophora*(3.48%): because of the lipid contents of macro algae are varied. The conversions of algal oil to biodiesel are also shown in **Table 1**

Table 1. Algal oil and biodiesel produced

macroalgae	Macroalgae weight (gm)	Algal oil (gm)	Algal oil %	Biodiesel (gm)	% of Biodiesel produced
<i>Dictyotaspp</i>	200	23.03	12.01	8.67	87.4
<i>Cladophora</i>	200	6.96	4.48	4.58	82.3
<i>Gracilaria</i>	200	15.74	9.87	6.39	82.4

Burning Test: Burning test was conducted to examine the difference between biodiesel blend (**Table 2**) of B100, B20 and B0. It was shown that the burning rate of B100 was much lower

compare to conventional diesel and B20. The conventional diesel burned vigorously because the energy density of conventional diesel is higher than the biodiesel.

Table- 2

No	Fuel	Biodiesel blend (% vol.)
1	B0	100% conventional diesel
2	B5	5% biodiesel + 95% conventional diesel
3	B10	10% biodiesel + 90% conventional diesel
4	B20	20% biodiesel + 80% conventional diesel
5	B30	30% biodiesel + 70% conventional diesel
6	B100	100% biodiesel

Physicochemical properties of biodiesel

Table -3

Fuel property	ASTM D 6751 standard.	Limits	Algal biodiesel
Specific gravity	D 1250-08	0.87-0.90	0.874 ± 0.0005
Free fatty acid	-	-	0.05 ± 0.004
Kinematic Viscosity (cSt) @ 40 ⁰ C	D 445	1.9-6	5.80 ± 0.004
Flash point ⁰ C	D 93	130 min	134.8 ± 0.44
Sulfur content, wt %	D 5453	0.05	0.01 ± 0.004
Cetane Number	D 613	47 min	48.73 ± 0.016
Acid number	D664	0.50 max	0.10 ± 0.008
Saponification value	-	-	184.0 ± 0.14
Water and sediments	D 2709	0.05	0.01 ± 0.0008
Copper corrosion	D 130	NO. 3 max	
Vacuum distillation@90 ⁰	D 1160	360 max	345.50 ± 0.22
Cloud point	D 2500	report	4.8 ± 0.44
Pour point	D 97	report	-8.8 ± 0.44
Total glycerol	D 6584	0.240max	0.21 ± 0.005

Free glycerol	D 6584	0.020	0.01 ± 0.0008
Carbon residue	D 4530	0.05	0.021 ± 0.005
Sulphated ash	D 874	0.02	0.01 ± 0.004
Calorific value	D 240-02	-	35.44 ± 0.08

4. CONCLUSIONS

In this work algal oil was extracted from different species of macroalgae, the biodiesel was produced from algal oil by using base-catalyzed transesterification reaction and the diesel engine performance test was also carried out for different blends of biodiesel from B0 to B30. Dictyota showed higher lipid content as compared to *Gracilaria* and *Cladophora*. Overall, the fuel consumption increased as the percentage of biodiesel blend increased. The reason is the lower energy content of the biodiesel as compared to ordinary diesel. In addition, the blend of 5% by volume of the biodiesel with the conventional diesel (B5) does not affect the performance of the engine. The reason of emission reduction is the increase in oxygen content of fuel blend when biodiesel blended with petro diesel and thus less oxygen is needed for combustion. This indicated that the addition of biodiesel to the conventional diesel was suitable for use in diesel engine.

Referencess

Antoni, D., Zverlov, V.V. & Schwarz, W.H. (2007). Biofuels from microbes. *Applied Microbiology and Biotechnology* 77, 23–35.

Benemann, J. & Oswald, W. (1996). *Final Report to the US Department of Energy*. Grant No. DEFG22-93PC93204, Pittsburgh Energy Technology Center, USA.

Bruntland, G.H. (1987). *Our Common Future: the World Commission on Environment and Development*. Oxford: Oxford University Press.

Bastianoni, S., Coppola, F., Tiezzi, E., Colacevich, A., Borghini, F. and Focardi, S. "Biofuel potential production from the orbetello lagoon Bioenerg., Vol.32, pp.619-628, 2008.

Chisti, Y. (2007). Biodiesel from microalgae. *Biotechnology Advances* 25, 294–306

Gupta, A.K., Suresh, I.V., Misra, J. & Yunus, M. (2002). risk mapping approach: risk minimization tool for development of industrial growth centres in developing countries. *Journal of Cleaner Production* 10, 271–281.

Copin, L.G. (2012). *Sustainable Development of Algal Biofuels: Biofuels in the United States*. Washington D.C., United States: The National Academies Press.

Demirbas, A. (2006). Oily products from mosses and algae via pyrolysis. *Energy Sources A* 28, 933–940.

Demirbas, A. and Demirbas, M. F. “Importance of algae oil as a source of biodiesel”, *Energy Convers. Manag.*, Vol.52, pp.163-170, 2011.

Demain, A.L. (2009). Biosolutions to the energy problem. *Journal of Industrial Microbiology & Biotechnology* 36, 319–332.

Demirbas, M.F., Balat, M. & Balat, H. (2009). Potential contribution of biomass to the sustainable energy development. *Energy Conversion and Management* 50, 1746–1760.

EEA (European Environment Agency). (2011). *Transport Emissions of Greenhouse Gases (TERM 002) – Assessment*. Report for European Environment Agency. Published in Jan 2011, Available at <http://www.eea.europa.eu/data-and-maps/indicators/transport-emissions-of-greenhouse-gases/transport-emissions-of-greenhouse-gases-7>.

Jiang, B., Sun, Z.Q. & Liu, M.Q. (2010). China’s energy development strategy under the low carbon economy. *Energy* 35, 4257–4264.

Johnson, M.B. & Wen, Z. (2010). Development of an attached microalgal growth system for biofuel production. *Applied Microbiology & Biotechnology* 85, 525–534.

John, R.P. and Anisha, G.S. “Macroalgae and their potential for biofuel”, *CAB Reviews: Perspectives in agriculture, veterinary science, nutrition and natural resources*, Vol.6, pp.1-15, 2011.

Long, S.P., Humphries, S. & Falkowski, P.G. (1994). Photoinhibition of photosynthesis in nature. *Annual Review of Plant Physiology and Plant Molecular Biology* 45, 633–662.

von Braun, J., Ahmed, A., Asenso-Okyere, K., Fan, S., Gulati, A., et al. (2008). *High Food Prices: The What, Who, and How of Proposed Policy Actions*. Policy Brief 1A. IFPRI, DC.

Maceiras, R., Rodriguez, M., Cancela, A., Urrejola, S. and Sanchez, A. "Macroalgae: Raw material for biodiesel production", *Appl. Energy*, Vol.88, pp.3318-3323, 2011.

Zhang, N., Lior, N. & Jin, H. (2011). The energy situation and its sustainable development strategy in China. *Energy* 36, 3639–3649.

Zhang, Y., Su, H., Zhong, Y., Zhang, C., Shen, Z., Sang, W., Yan, G. & Zhou, X. (2012). The effect of bacterial contamination on the heterotrophic cultivation of *Chlorella* in from the production of soybean products. *Water Research* 46, 5509–5516.