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BIODIESEL PRODUCTION FROM *SARGASSUM*SPA SRI LANKAN MARINE FLORA AND OPTIMIZATION OF CONDITIONS FOR YIELD ENHANCEMENT

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Abstract

Biodiesel production from natural resources has drawn global attention due to its cost effectiveness, eco friendliness and sustainability compared to the conventional fossil fuels. This work was aimed to select the best marine flora available in the Northern Sri Lankan sea to produce biodiesel and to optimize the conditions to produce higher yield. Five species of macro flora such as *Sargassum* sp, *Ulva fasiata*, *Turbinaria ornata, Gellidium* sp, *Thallasia* sp were collected from the coastal area of the Jaffna peninsula and washed thoroughly with water(mixed with NaOH) and dried under direct sun light. The organic solvents used to extract oil from marine plant species were n-Hexane and Di-ethyl Ether, while alkaline catalysts were used to convert the extracted oil into biodiesel via trans-esterification reaction. Higher oil quantity was obtained from *Sargassum* sp compared to other marine macro floral species, and it was selected for further studies. Optimum conditions for biodiesel production were identified as molar ratio of methanol to algae (4:1), catalyst amount in the reaction mixture (0.6%), reaction temperature (60^{o}C) and reaction time (25minutes). When the optimum conditions were provided, the percentage of biodiesel production was significantly increased by 11.7-fold than the non-optimized conditions from *Sargassum* sp. Therefore, optimization of conditions during trans-esterification, significantly increased the biodiesel production from *Sargassum* sp.

Keywords: Biodiesel, Optimization, Oil extract, *Sargassum* sp, Trans-esterification

Introduction

Continued usage of petroleum sourced fuels is now widely recognized as unsustainable, because of depleting supplies. Contribution of the fossil fuels to the accumulation of carbon dioxide in the environment is significantly higher thus they lead to greenhouse effect. The cost of crude oil will continue to rise due to diminishing supply, therefore the production of fuels from alternate sources will be needed in the future decades. In this scenario, biodiesel could be considered as best alternative fuel due to its nontoxic and nature. Biodiesel has attracted attention during the past few years as a renewable and environmentally friendly fuel because of diminishing petroleum reserves and the deleterious environmental consequences of exhaust gases from petroleum diesel.

Biodiesel is the mono alkyl esters of long fatty acids, which is derived from trans-esterification of biological substances. The recent researches have proven that oil production from algae is clearly superior to that of terrestrial plants such as palm, grape seed, soybeans and has potential to completely displace fossil fuel (Abdel-moneim et al., 2010).Marine and freshwater algal species can contribute between 20-80% of the oil production by weight of their dry mass (Georgogianni *et al*, 2007). Algae show much faster growth rates than terrestrial crops. The per unit area yield of oil from algae is estimated to be from 20,000 to 80,000L per acre per year. The use of algae as energy crops has potential benefits, due to their easy adaptability to growth conditions, the possibility of growing in adverse environments, either in fresh or marine waters avoiding the use of land. Furthermore, two thirds of earth's surface are covered with water, thus algae would truly be renewable option of great potential for global energy needs. Different algal species better suited for different types of biodiesel. Algal biofuels appear to be the only current renewable abundantly available, natural source that could meet the global demand for fuels (Abdel-moneim et al., 2010). There is a need to explore promising sources for biodiesel production and proper trans-esterification methods for the efficient biodiesel production. Therefore, this study was aimed to select the best marine flora available in the Northern Sri Lankan sea for the biodiesel production and to optimize the conditions to enhance the biodiesel yield.

Materials and Methods

Sources of algal species

Five species of macro algae such as *Sargassum* sp, *Ulva fasiata, Turbinaria ornata, Gellidium* sp, *Thallasia* sp.were collected from the sea and the coastal area of the Jaffna peninsula.

Pretreatment of algal species

The samples were washed thoroughly two to three times using tap water. Then they were spread directly under sun in a light area for one week to get dried biomass. The dried samples were ground separately, and the fine powder was passed through a 500-micron sieve to remove oversized particles.

Treatment with solvent

Treatment with hexane

Oils were obtained by extracting the algae (10grams) with hexane in a Soxhlet extractor for 9 hours. The extracted oil was separated by evaporating the solvent in a rotary evaporator at 45^{o}C for 15mintues.

Treatment with di-ethyl ether

100 grams of fine powder of each algal sample were weighed and added in to 500ml brown bottle containing 200ml di- ethyl ether. The solution was covered and shaken every 30 minutes for six hours and allowed to stand for twenty-four hours in room temperature. Then it was shaken well and filtered through Buchner funnel suction pump using Whatsman (No1) paper.

Trans-esterification reaction

After filtration, the solvent was removed by evaporation using a rotary evaporator under reduced pressure and at a temperature below 35^{o} C. About 3.3 grams crude extract was obtained and separated through the extraction process from 10grams of algal biomass sample. The extracted oil was converted into biodiesel through transesterification reaction in the presence of methanol. In this process triglycerides reacts with alcohols to form the fatty acid ester (biodiesel) and the glycerol. During this reaction the algal oil was allowed to react with the methanol in the presence of alkaline NaOH.

Optimized condtion for transesterification reaction

Effect of molar ratio of methanol to algae

Oil extraction experimental setup was done by *Sargassum* sps,optimized solvent ratio (hexane:diethylether;200:0),optimized algal biomass 100g, and allowed for optimized time period (24 hours). Following mol ratio methanol to algal biomass was added to opitimized transesterification reaction.(2:1,3:1,4:1,5:1,6:1,7:1).

Effect of catalyst amount

Oil extraction experimental setup was madewith*Sargassum* sps,with the optimized solvent ratio (hexane:diethylether;200:0), optimized algal biomass 100g and allowed for optimized time period (24 hours). Opitimied methanol to oil ratio 4:1 was added with the following catalyst amount(NaOH) respectively 0.3%,0.4%,0.5%,0.6%,0.7%,0.8% for transesterification reaction.

Effect of reaction temperature

Oil extraction experimental setup was madewith*Sargassum* sps,with the optimized solvent ratio (hexane:diethylether;200:0),optimized algal biomass 100g and allowed for optimized time period (24 hours) under optimized trasesterification reaction condition (molar ratio methanol to oil 4:1) with the optimized catalyst amount 0.7%(NaOH) were throught mixed using magnatic stirrer by various reaction time 5minutes to 30mintes(Khola and Ghazala, 2012) and that mixture was poured in to oil. This product was kept 35^{o}Cto 60^{o}C differnent temperature in a water bath.

Effect of reaction time

Oil extraction experimental setup was done with*Sargassum*sps,optimized solvent ratio (hexane:diethylether;200:0),optimized algal biomass 100g, allowed for optimized time period 24 hours,optimized trasesterification reaction condition molar ratio methanol to oil 4:1,optimized catalyst amont 0.7%(NaOH) were throught mixed using magnatic stirrer ,and the mixture was poured in to oil.this product was 60^{0}C with optimized temperature and allowing for 5minutes to 30minutes to reaction occurred in waterbath.

Biodiesel production after the optimization

The extracted oil was converted to biodiesel through trans-esterification reaction in the presence of methanol. The quality of biodiesel was assessed by measuring its properties such as flash point, viscosity, density, fire point and cloud point.

$$\text{Percentage of biodiesel yield} = \frac{\text{Biodiesel yield}}{\text{Oil used}} * 100$$

Biodiesel analysis

The quality of biodiesel was assessed by measuring its properties such as flash point, viscosity, density, fire point and cloud point.

Stastical analysis

All the experiments were done in triplicates. Statistical analyses were performed using Minitab 17.0 version. The data were analyzed using one way ANOVA. Tukey's multiple comparision test was used to determine significant difference at p _<0.05.

Results and Discussion

Effect of molar ratio of methanol to oil

The stoichiometric ratio for transesterification requires 3moles of alcohol and 1mole of triglyceride to yield three moles of fatty acid alkyl esters and one mole of glycerol. Significantly higher amount of biodiesel was obtained at 4:1 methanol to oil ratio than the non-optimized ratio (2:1). At higher molar ratio, the excess amount of oil promotes the forward reaction. When the range of methanol to oil ratio was 2:1 to 7:1, maximum yield was obtained (0.945%).

Effect of catalyst amount

When different amounts of catalyst (0.2,0.4,0.6,0.8,1.0%) were used, significantly higher amount of biodiesel production (0.93%) was obtained when 0.6%was used. The role of catalyst in transesterification reaction is very important. This reaction can be carried out with both, acid or alkali catalyst. However, using acidic catalyst has the disadvantages due to elevated rate of transesterification reaction and the reaction conditions are mild, consumption of methanol is significantly less, catalyst is less corrosive, and the acid catalyst process requires a high methanol to oil molar ratio and high acid catalyst concentration.

Effect of reaction temperature

The biodiesel production (after addition of methanol and alkali catalyst mixture to oil) at different temperatures ranging from 35^{o}C to 70^{o}C was given diesel yield. Maximum amount of biodiesel was produced in between 45^{o}C to 60^{o}C temperature range. Therefore, the temperature more likely gave a big effect for the yield produced. In this study, significantly higher biodiesel production was obtained at 60^{o}Cwhich is in the agreement with the available literature. When the temperature was optimized as 60^{o}C, biodiesel production was increased by 9.4 times(from0.1%-0.942%) than the non-optimized condition. The 70^{o}C for the system temperature excess the boiling point of the methanol (64.7^{o}CAt 60oC biodiesel gives 0.942%

yield, gives the maximum amount for producing diesel because there is a limitation of methanol boiling point. Biodiesel reduce the amount methanol, because of forward reaction in transesterification reaction. so that the methanol become insufficient. At 70oC, yield will be decreased 1.809% because, higher temperature could accelerate the saponification of triglycerides and had a negative effect on the product yield.

Effect of reaction time

When the reaction time was kept at 25minutes, biodiesel yield was significantly increased by1.2 times than the non-optimized reaction time. All the optimized conditions indicated that the reaction time required for the optimization of the alkaline catalyst transesterification reaction depend not only in the reaction temperature, but also on the degree of mixing in the process.

Biodiesel analysis

The quality of biodiesel was assessed by measuring its properties such as flash point, viscosity, density, fire point and cloud point, as shown in Table 1. The higher flash point of biodiesel as compared to Petro diesel makes it safer. The other properties of biodiesel are also very close to petro diesel.

Table 1. Biodiesel analysis: Comparison of the biodiesel properties with the petro diesel

Properties	Petro diesel	Biodiesel
Flash point (^oC)	134	142
Fire point (^oC)	154	159
Cloud point (^oC)	4	3
Density (KgM^{-3})	865.2	867.3

Conclusion

When the extracted oil was converted into biodiesel via trans-esterification reaction, after the optimization of conditions, such as molar ratio of methanol to algae (4:1), catalyst amount (0.6%), reaction temperature (60^{o}C) and reaction time (25minutes), the percentage of biodiesel produced was significantly increased by 11.7 times than the non-optimized conditions from *Sargassum* sp. Therefore, *Sargassum* sp brown macroalgae could be used as an efficient raw material for the biodiesel production, after the optimization of the conditions tested above.

Reference

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