

PREPARATION AND PHYSICO-CHEMICAL PROPERTIES EVALUATION OF BIODIESEL FROM PITHRAJ (*APHANAMIXIS POLYSTACHYA*) SEEDS AVAILABLE IN BANGLADESH

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Abstract

In this study, Pithraj (*Aphanamixis polystachya*) seed (PS) oil was used to produce biodiesel via transesterification process. The PS oil was extracted from seed using a soxhlet solvent extraction technique and the effect of temperature and heating rate on product distribution was investigated. The PS oil was pretreated (esterified) to combat the saponification reaction and other associated problems e.g., phase separation. The transesterification reactions were carried out and the optimum biodiesel yield was found 93.87%, when the reaction condition was as follows: addition of 50 wt.% methanol, 0.8 wt.% NaOH (both are on the basis of wt.% of PS oil addition), 60 °C reaction temperature and 90 min reaction time. Biodiesel produced from PS oil was characterized by various physico-chemical means and compared with international standards. The use of the produced biodiesel in blend with commercial diesel will bring a remarkable change in fuel economy of the country, will ensure a clean and safe environment and will demonstrate a way for 'Waste to Energy'.

Keywords: Biodiesel, Transesterification process, Pitharaj Seed, Waste management, Physico-chemical properties, Clean energy

1. Introduction

The global scarcity of fossil fuel, its increasing cost and pollution associated with conventional fuel make biomass as an attractive source for renewable fuel production. Currently, about 86% of the world energy consumption is met by fossil fuels [1]. Bio-fuel, produced from biomass, can resolve the issues of defensible development, energy security and reduction of greenhouse gas emissions [2]. Among the biofuel (e.g., biodiesel, bio-oil, bio-ethanol, biogas etc.), biodiesel can decrease the net carbon-dioxide (CO₂) emissions by 78% on a lifecycle basis when compared to conventional diesel fuel [3]. Biofuels, predominantly produced from different biomass in solid, liquid or gaseous forms, have been increasingly attracting attention as alternative sources of fuels and chemicals [4]. Among liquid biofuels e.g., bio-alcohols, vegetable oils, biodiesels, bio-crude and synthetic oils, biodiesel offers promising alternative [5]. The use of biofuels decreases the external energy dependence, promotes regional engineering, increases research & development, decreases impact of electricity production and transformation; increases the level of services for the rural population, creates employment and so on.

Biodiesel, mainly fatty acid methyl esters, can be derived from a renewable lipid feedstock. Non-edible oil from various plant seeds is known as second-generation feedstock for the production of biodiesel. Vegetable oil from *Jatropha*, *Rubber*, *Mahua* and *Karanja* seeds are the most commonly used for biodiesel production [6]. Although, the second-generation biodiesel production focused mainly on the utilization of oil from seed without much consideration to residue from the seed after oil extraction, the proper utilization of these residue as well as other parts of source plant will reduce solid waste generation and will lower the total investment costs.

Vegetable oils (edible/ non-edible), extracted from seeds, have high viscosity (may be due to presence of higher molecular weight free fatty acid substances) which causes major problems in their direct use as fuels in Internal Combustion (IC) engines. Among various processes (e.g., trans-esterification, pyrolysis, micro-emulsification and dilution) to split the oil into simpler molecules to achieve required viscosity and other properties comparable to standard diesel oils, trans-esterification is the most commonly used commercial process to produce light vegetable oil fuel i.e., biodiesel [7].

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The process proceeds well in the presence of homogenous catalysts e.g., NaOH, KOH, H₂SO₄ etc.[8]. A simplified transesterification process is shown in Figure- 1. Biodiesel production from -

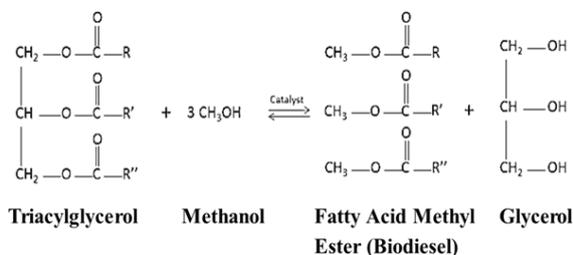


Fig. 1: An illustration of trans-esterification reaction for biodiesel production



Fig. 2: An overall process illustration from seed collection to raw oil extraction system

Jatropha oil [9], Pongamia oil [10], Cornus wisoniana oil [11], Cerbera oil [12], Rubber seed oil [13] etc. had been reported and the yield was found 85-96%. Although non-edible renewable pithraj (*Aphanamixis polystachya*) seed and oil from it is accessible in many parts of Bangladesh, so far, no study on the production of biodiesel from it has been reported. The oil content in the pithraj seed is about 43-46% which is comparable to other non-edible seeds like Jatropha seed, rubber seed and the weather and soil conditions of Bangladesh is suitable for the cultivation of this plant around the country. Hence, biodiesel from pithraj seed oil will be a cheap and marginal substitute to diesel fuel. Hence, this study aims to produce biodiesel from pithraj seed oil, to evaluate its physico-chemical properties and to compare it with international standards.

2. Materials and Methods

2.1. Collection and Processing of Seeds for Oil Extraction

The mature Pithraj Seeds (PSs) were collect from the local area of Badargonj Upazila of Rangpur District of Bangladesh. Raw PSs were de-hulled manually to separate the kernels from its shell. Then, the outer layer was removed from the kernels and the cleaned seeds were sundried, grinded, and sieved to a uniform size of < 0.4 mm. The grinded seeds were re-dried in oven at 105 °C for four hours and then kept in a desiccator until use. Chemicals including n-hexane, NaOH, H₂SO₄, methanol used in this study

were of analytical grades (Merck, Germany), purchased from Hatkhola, Dhaka, Bangladesh.

The oil extraction from the seeds can be carried out through mechanical press or chemical solvent extraction [8]. In this study, soxhlet solvent extraction process using n-hexane as solvent was carried out. The extraction period was 4 hours and the temperature was maintained at 60 °C. After the extraction process, a rotary evaporator (Boeco, Germany) was used to evaporate and collect the used solvent. The overall steps from seed collection to oil extraction is illustrated in Figure-2 and a details of the description is reported in the oil extraction section of our previous study by Hasan et al. [14] and also reported by *Setapar et al.* [15].

2.2. Acid Catalyzed Esterification

The raw oil extracted from seeds generally contain certain amount of free fatty acids (FFA), however, if the oil or fat feedstock has a FFA content of over 3 wt. %, a pre-treatment step is necessary before the transesterification process (alkali-catalyzed) for biodiesel production. Higher acid value i.e., higher percentage of FFA content in raw oil is one of the major drawbacks for biodiesel production directly from vegetable oil. The acid value of PS oil was found 52.82 mg KOH/g, which was unfavourable for direct base-catalyzed transesterification. Hence, a two-step process compromising acid esterification process (acid-catalyzed) followed by alkali-catalyzed transesterification was used. An acid catalyzed esterification process can reduces the FFA content (i.e., minimize the acid value) of the crude oil below 3%. To do this, a round bottom flask with a condenser attached to the neck of the flask was taken. Methanol and H₂SO₄ were used as esterifying agent and catalyst, respectively.

To carry out the acid-catalyzed esterification process, our previously studied optimum condition for esterification of Jatropha seed oil [16] were implemented which was as follows: oil to methanol ratio of 1: 0.9 (wt.% basis), oil to H₂SO₄ ratio of 1: 0.023 (wt.% basis), reaction temperature of 60°C, reaction time for 90 min and maintain continuous magnetic stirring of 400 rpm. After allowing the mixture to settle for 12 hr, two distinct layers formed where the bottom layer contained the esterified oil, which were collected (using a separating funnel), for transesterification process.

2.3. Base catalyzed transesterification

For base-catalyzed transesterification process, a three-necked round bottom flask (one neck was for charging raw materials e.g., esterified oil, catalyst and methanol and the other two of these necks were fitted with a condenser and a thermometer, respectively) was used and for uniform heating, the whole arrangement was kept in an oil bath. In the flask, required amount of esterified oil, methanol and catalyst were taken and the mixing (at 400 rpm using magnetic stirrer) were carried out at 60 °C for 90 min. Methanol and NaOH were added in the following ratio: 50 wt.% methanol, 0.8 wt.% NaOH (both are on the basis of wt.% of PS oil addition) [16] and the biodiesel yield was found 93.87%.

The produced methyl esters and glycerin via transesterification process were allowed to settle in a separating funnel for 8 hours. The upper layer in the separating funnel (biodiesel part) were separated out from bottom layer (glycerin, gums etc.) and was purified by distilling the residual methanol at 60°C.

The produced biodiesel was then washed with distilled water to remove remaining catalysts and to neutralize the pH of the biodiesel. Finally, the produced biodiesel was dried using a rotary evaporator and then stored and characterization and related experiments were carried out.

2.4. Characterization of oil and biodiesel from Pithraj Seeds

The PS Oil as well as produced biodiesel were characterized to evaluate the quality of oil and feasibility to use as a fuel. Viscosity (both of raw oil and biodiesel) at 40°C and 100°C was measured using a capillary U-tube viscometer (COMECTA, Spain) keeping in a heating bath (Selecta VB-1423, Spain) following the procedure of ASTM D445-65 method.

For flash point determination, ASTM D64-50 method was followed with a flash point tester (Eralytics, Austria). Pour point and acid value were determined following ASTM D97-57 and D974-02 methods, respectively. Density of the oil and biodiesel was measured using a pycnometer (25 mL) at 15°C. A bomb calorimeter (Model-NW 21, Julius Peter, Berlin, Germany) was employed to measure the calorific value.

2.5. FTIR Spectra of PS oil

Different functional groups present in the PS oil and biodiesel were measured with a FTIR Spectrophotometer (Shimadzu, Japan). The IR light passed through the sample within the wavenumber range of 400 cm⁻¹ to 4000 cm⁻¹.

3. Results and Discussions

3.1. Effect of Extraction Time on PS Oil Yield from Seed

Oil from the PS was extracted with solvent extraction technique (using n-hexane) as solvent. Among various solvents for oil extraction, n-hexane gives relatively higher oil yield [17]. Here the oil extraction was carried out for three different periods of time: 2 hr, 4 hr and 6 hr. The oil yield was 33.5 %, 44.12% and 46.03% for 2 hr, 4 hr and 6 hr extraction period. An increase in 2.04% oil yield occurred for six hr extraction period in comparison to 4 hr extraction time, which was not significant. Hence, four hours extraction time was used for further oil extraction in this work.

3.2. Physicochemical Characterization of Extracted PS Oil

The physicochemical parameters of PS oil have been listed in Table-1. The color of the oil was pale yellow. The kinematic viscosity of the oil was found 28.57 cSt at 40 °C, which was high enough to restrict direct engine application. Therefore, it was required to transform vegetable oil into corresponding methyl esters to reduce the viscosity in desired level [14]. For biodiesel production from PS oil, acid catalyzed esterification was required prior to base-catalyzed transesterification as due to higher acid value as well as Free Fatty Acid (FFA) content. The FFA content was found 28.84%, which was needed to be minimized below 3% as high FFA could cause saponification during base catalyzed transesterification [18].

Table-1:

Physicochemical parameters of Pithraj seed (PS) oil

Parameters	Units	Values	
Color	-	Amber / pale yellow	
Density at 15 °C	gm/cc	0.85	
Kinematic Viscosity	40 °C	cSt	28.57
	100 °C	cSt	6.74
Pour point	°C	< -18	
Flash point	°C	31	
Acid Value	mg KOH/g	52.82	
Free Fatty Acid (FFA) (0.546 times of acid value)	%	28.84	
Calorific Value	MJ/kg	39.50	

3.3. FT-IR Spectra Analysis of PS Oil and Produced Biodiesel

To determine the functional groups presence in the extracted pithraj seed oil as well as biodiesel produced from the oil by transesterification process, the FTIR Spectroscopic analysis method was employed. Appropriate quantities of KBr and pithraj

seed oil (in the ratio of 100:0.1) were mixed by grinding in an agate mortar and pellets were made with about 100 mg mixture. FTIR relies on the fact that the most molecules absorb light in the IR-region of the electromagnetic spectrum. This absorption corresponds specifically to the bonds present in the molecule.

Figure-3 represents the FT-IR spectrum of the PS oil where the most dominant peak was observed at 2916.37 cm^{-1} indicates the C-H stretching vibration of fatty acids carbon chains. As this type of bonding is prominent in oil, the area covered by this peak is also larger than other peaks. The second dominant peak is at 1782.23 cm^{-1} , which basically denotes the C=O stretching vibration of fatty acids present in the oil [14]. Peak at 1620.21 cm^{-1} confirms the existence of unsaturated fatty acid in the oil as peak at that point is present due to C=C stretching vibration of alkene. All peaks below 600 cm^{-1} are basically from the trace amount of inorganic compounds present in the oil mixture [19].

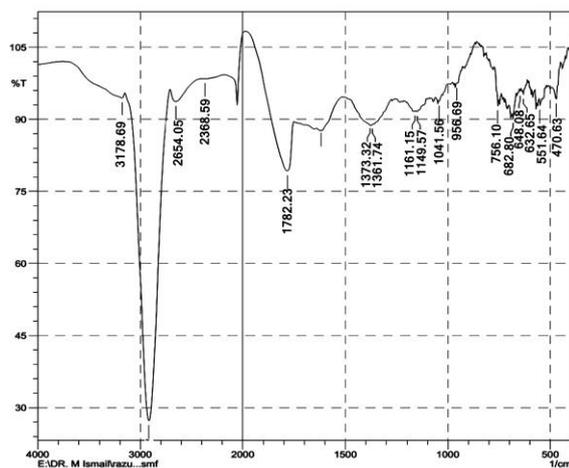


Fig.3: FTIR spectra of Pithraj seed oil

Table-2:

Analysis of FT-IR peaks of PS oil

Peak (cm^{-1})	Functional group
632.7, 682.8	Inorganic Compounds
956.69, 1041.56, 1149.57, 1161.15	C-C(O)-C stretching vibration of alcohol, ester
1361.74, 1373.32	C-H bending vibration of alkanes
1620.21	C=C stretching vibration of alkene
1782.23	C=O stretching vibration of ester, aldehyde, carboxylic acid, α , β -unsaturated ketone
2916.37	C-H stretching vibration of fatty acids carbon chains
3178.69	O-H stretching vibration of strong broad carboxylic acid

Figure-4 illustrates the FT-IR spectrum of the PS oil where the major dominant peaks were observed at 1762.94 cm^{-1} and 2920.12 cm^{-1} indicate the ester (C=O) of PS oil biodiesel and C-H stretching vibration of medium alkane (SP^3 absorption), respectively.

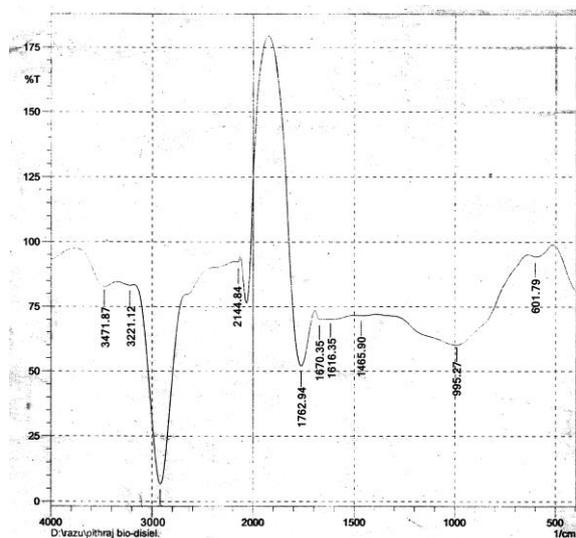


Fig. 4: FTIR spectrum of produced biodiesel from PS oil

Table 3:

Analysis of peak obtained in FTIR of Pithraj seed oil Biodiesel:

Peak (cm^{-1})	Functional group
601.79	C-Br stretching vibration of strong halo compound
995.27	C=C bending vibration of strong alkene
1465.9	C-H bending vibration of medium alkane ($-\text{CH}_2-$)
1670.35	C=C stretching vibration of weak alkene
1762.94	C=O stretching vibration of carbonyl group of triglyceride
2920.12	C-H stretching vibration of medium alkane (SP^3 absorption)
3221.12	C-H stretching vibration of medium alkane
3471.87	O-H (Hydrogen bonded)

The FT-IR spectra of the PS oil and biodiesel produced from it are comparable to each other because of the presence of triglycerides and esters. However, some differences were observed where the peaks appeared at 956.69 , 1620.21 , 1782.23 and 2916.37 cm^{-1} in the PS oil were shifted to 995.27 , 1670.75 , 1762.94 and 2920.12 cm^{-1} in the biodiesel respectively. Furthermore, the disappearance of the peaks from the spectrum of the PS oil at 1041.56 , 1149.57 , 1161.15 , 1361.74 and 1373.32 cm^{-1} and the formation of new peaks at 1465.9 , 1670.35 and 3221.12 cm^{-1} in the produced biodiesel evidently confirm the conversion of PS oil into biodiesel.

3.4. Physico-chemical Characterization of Produced Biodiesel

Table 4:

Competitive physico-chemical properties of bio-diesel produced from PS oil

Properties	Unit	Bio-Diesel from PS oil	Bio- diesel Standard [20]	Commercial diesel [20]
Kinematic Viscosity	40 °C	cSt	2.48	1.9-6
	100 °C	cSt	1.94	
Pour point °C	°C	-9.0	-15~16	-10
Flash point °C	°C	145	100-170	70
Density at 15 °C	g/cc	0.895	0.86~0.90	0.8445
Acid value	mg KOH/g	0.63	0.80 (max.)	0.34
Calorific value	MJ/Kg	38.90	40.20	44.50

The physico-chemical properties of the produced biodiesel differ from raw PS oil from various aspects. For instance, the kinematic viscosity of PS oil was 28.57 cSt and 6.74 cSt at 40°C and 100°C,

Pour point, the fluidity behaviour of a fuel at low temperature, of the produced biodiesel was found -9°C, which is in the range of the standard set for biodiesel as well as almost close to the pour point value of commercial diesel (-10°C). Flash point, the temperature at which the fuel starts to ignite, of the produced biodiesel was found 145 °C. Higher flash point of a fuel is considered as safe fuel and indicates that the fuel contains lower volatile components.

The presence of free acid in the fuel can affect the lubrication system and promotes corrosion in the engine [21]. Some unreacted fatty acids from the oil may stay in biodiesel mixture. The maximum acid value allowed is 0.80 mg KOH/g to inject in an engine. Here, the produced biodiesel showed 0.63 mg KOH/g as the acid value, which was satisfactorily lower than the maximum value.

The calorific value, a measure of energy produced by burning a unit mass of a fuel, of the produced biodiesel was found 38.90 MJ/Kg, which is very close to the biodiesel standard and lower than the commercial diesel. One of the reasons for lower calorific value of biodiesel compared to standard bio-diesel and commercial diesel may be the presence of the higher oxygen in the composition. However, higher oxygen content leads to complete combustion in the engine [22].

4. Conclusion

In this study, biodiesel was produced from locally available Pitharj seed. The findings are-

1. Well-known trans-esterification process was employed for biodiesel from pitharj seed oil - and the maximum yield was found 93.87% at 60°C reaction temperature.

2. The physico-chemical properties of PS oil and produced biodiesel from this oil were determined and compared with those of typical diesel fuel. The properties of produced biodiesel were on the brink of commercial diesel fuel and in some cases (e.g., flash point), produced biodiesel has better characteristics than those of diesel.

However, commercialization of the produced biodiesel requires more intensive study including pilot scale production and techno-economic feasibility study. Moreover, engine performance and emission characteristics of the produced biodiesel are yet to explore. Facing these challenges, PS oil biodiesel can be a competitive source of fuel in Bangladesh.

Acknowledgments

We would like to acknowledge the i) Bangladesh Bureau of Educational Information and Statistics (BANBEIS), Ministry of Education, Bangladesh (Project No: - PS2017594; 2018-2021) and ii) Ministry of Science & Technology, Bangladesh (Project No.: - 39.00.0000.009.06.024.19/(EAS-432)-448; 2019-20) for support in this study.

References:

- [1] Ibrahim, H., Agwara, J.N., Tukur, Y., Nwanya, K.O., Nwakuba, D.C., Ayilara, S., Adegbola, O.B., Zanna, A.S. and Aliyu, U.A., 2016. Production of Biodiesel from Calabash Seed Oil. *Chemical Science International Journal*, 14(4), pp.1-8.
- [2] Izah, S.C. and Ohimain, E.I., 2013. The challenge of biodiesel production from oil palm feedstock in Nigeria. *Greener journal of Biological sciences*, 3(1), pp.1-12
- [3] Carvalho, J., Ribeiro, A., Castro, J.D.F.D., Vilarinho, C. and Castro, F., 2011. Biodiesel production by microalgae and macroalgae from

- north littoral portuguese coast. WASTES: Solutions, Treatments and Opportunities 1st International Conference.
- [4] Demirbas, A., 2009. Biofuels securing the planet's future energy needs. *Energy Conversion and Management*, 50(9), pp.2239-2249.
- [5] Demirbas, A., 2007 "Comparison of transesterification methods for production of biodiesel from vegetable oils and fats," *Energy Convers. Manag.*, 49(1), pp. 125–130.
- [6] Takase, M., Zhao, T., Zhang, M., Chen, Y., Liu, H., Yang, L. and Wu, X., 2015. An expatiated review of neem, jatropha, rubber and karanja as multipurpose non-edible biodiesel resources and comparison of their fuel, engine and emission properties. *Renewable and Sustainable Energy Reviews*, 43, pp.495-520.
- [7] Rajamanickam, A. K., Lokesh, M., Ramaswamy, K., Sudharson, G. K., 2018. "A Review - Production Of Methyl Ester," *International Journal of Mechanical Engineering and Technology (IJMET)*, 9(9), pp. 749–754.
- [8] Demirbas, A., 2002. Biodiesel from vegetable oils via transesterification in supercritical methanol. *Energy conversion and management*, 43(17), pp.2349-2356.
- [9] Vyas, A.P., Subrahmanyam, N. and Patel, P.A., 2009. Production of biodiesel through transesterification of Jatropha oil using KNO₃/Al₂O₃ solid catalyst. *Fuel*, 88(4), pp.625-628.
- [10] Meher, L.C., Dharmagadda, V.S. and Naik, S.N., 2006. Optimization of alkali-catalyzed transesterification of *Pongamia pinnata* oil for production of biodiesel. *Bioresource technology*, 97(12), pp.1392-1397.
- [11] Qin, S., Sun, Y., Meng, X. and Zhang, S., 2010. Production and analysis of biodiesel from non-edible seed oil of *Pistacia Chinensis*. *Energy Exploration & Exploitation*, 28(1), pp.37-46.
- [12] Kansedo, J., Lee, K.T. and Bhatia, S., 2009. Cerbera odollam (sea mango) oil as a promising non-edible feedstock for biodiesel production. *Fuel*, 88(6), pp.1148-1150.
- [13] Zamberi, M.M. and Ani, F.N., 2016. Biodiesel production from high FFA rubber seed oil using waste cockles. *ARPJ Journal of Engineering and Applied Sciences*, 11(12), pp.7782-87.
- [14] Hasan, M.I., Mukta, N.A., Islam, M.M., Chowdhury, A.M.S. and Ismail, M., 2020. Evaluation of Fuel Properties of Sal (*Shorea - robusta*) Seed and Its Oil from Their Physico-chemical Characteristics and Thermal Analysis. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, pp.1-12.
- [15] Mohd-Setapar, S.H., Nian-Yian, L. and Mohd-Sharif, N.S., 2014. Extraction of rubber (*Hevea brasiliensis*) seed oil using soxhlet method. *Malaysian Journal of Fundamental and Applied Sciences*, 10(1).
- [16] Prodhan, A., Hasan, M. I., Sujana, S. M. A., Hossain, M., Quaiyyum, M. A., and Ismail, M., 2020. "Production and Characterization of Biodiesel from Jatropha (*Jatropha curcas*) Seed Oil Available in Bangladesh," *Energy Sources, Part A Recover. Util. Environ. Eff. Eval.*.
- [17] Jahirul, M.I., Brown, J.R., Senadeera, W., Ashwath, N., Laing, C., Leski-Taylor, J. and Rasul, M.G., 2013. Optimisation of bio-oil extraction process from beauty leaf (*Calophyllum inophyllum*) oil seed as a second generation biodiesel source. *Procedia Engineering*, 56, pp.619-624.
- [18] Chuah, L.F., Bokhari, A., Yusup, S., Klemeš, J.J., Abdullah, B. and Akbar, M.M., 2016. Optimisation and kinetic studies of acid esterification of high free fatty acid rubber seed oil. *Arabian Journal for Science and Engineering*, 41(7), pp.2515-2526.
- [19] Yuvarani, M., Kubendran, D., Salma Aathika, A.R., Karthik, P., Premkumar, M.P., Karthikeyan, V. and Sivanesan, S., 2017. Extraction and characterization of oil from macroalgae *Cladophora glomerata*. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 39(23), pp.2133-2139.
- [20] Banik, S.K., Rouf, M.A., Rabeya, T., Khanam, M., Sajal, S.I., Sabur, S.B. and Islam, M.R., 2018. Production of biodiesel from neem seed oil. *Bangladesh Journal of Scientific and Industrial Research*, 53(3), pp.211-218.
- [21] Atabani, A.E., Silitonga, A.S., Badruddin, I.A., Mahlia, T.M.I., Masjuki, H.H. and Mekhilef, S., 2012. A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renewable and sustainable energy reviews*, 16(4), pp.2070-2093.
- [22] Graboski, M.S. and McCormick, R.L., 1998. Combustion of fat and vegetable oil derived fuels in diesel engines. *Progress in energy and combustion science*, 24(2), pp.125-164.