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Investigate the Potential Renewable Energy of Microalgae *Spirulina sp* Using Proximate Analyzer, SEM-EDX, and Thermogravimetry

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ABSTRACT

Microalgae *Spirulina sp* which has been cultivated by the Brackishwater Aquaculture Development Center, Situbondo Indonesia were tested for their potential energy performance using proximate analyzer, SEM-EDX, and thermogravimetry. The proximate analyzer showed volatile matter (VM), fixed carbon (FC), moisture, ash content (AC), total sulfur of microalgae *Spirulina sp* 68.15, 12.57, 11.22, 8.06, and 0.67 (wt%, ar), respectively, and the gross calorific value (GCV) is 4971 kcal/kg (dry basis). SEM-EDX test showed the morphology and chemical content of *Spirulina sp.* The content of microalgae *Spirulina sp* is dominated by carbon (C) and oxygen (O), then followed by chlorine (Cl), sodium (Na), potassium (K), sulfur (S), magnesium (Mg), and phosphorus (P). Thermogravimetry pyrolysis test of microalgae *Spirulina sp* resulted thermogravimetry (TG) analysis and derivative thermogravimetry (DTG) analysis curve, which is divided into three different steps. The moisture of microalga *Spirulina sp* was vaporized at the first step, started at 27 °C, and finished at 173 °C with a decomposed mass of about 13.81% of the total initial mass. The second step began at the end of vaporize moisture at about 173 °C and ended at around 618 °C. The gasification process occurred in volatile matter content and resulted mass loss of about 57.9% of *Spirulina sp* total mass. The last step showed the process of gasification of residual substances, started at the end of the volatile matter step, 618 °C, and stopped at 995 °C with a decomposed mass of 24.6% from total mass.

Keywords: *Microalgae, proximate, renewable energy, SEM-EDX, Spirulina sp., thermogravimetry*

I. Introduction

Russia's invasion of Ukraine not only caused damage to infrastructure but also caused an energy crisis in Europe Union (EU) and even the world. As is well known, Russia has become a global power in terms of providing energy sources [1]. Russia controls exports of energy sources to Asia 55.8% and 42% to the EU in 2020. Russia is now starting to limit exports of its energy sources to the western world as a form of retaliation for sanctions imposed on the country led by Vladimir Putin [2].

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The export restrictions resulted in a high price dispute. Oil prices on Tuesday, March 22, 2022, at 07:46 (Jakarta Time) showed Brent oil at US$ 117.49/barrel, up 1.62% from the previous day's closing position. Meanwhile, the light sweet type or West Texas Intermediate (WTI) costs US$ 114.16/barrel, an increase of 1.82%. In London, the fuel increase was over two euros or the equivalent of $2.2 per liter at each gas station. The price of Brent oil, the main international benchmark for oil, jumped past $130 on Tuesday, March 8, 2022, as Joe Biden banned Russian oil and gas from the United States. While Sweden faces the highest price increase in Europe, exceeding 25 kronor or 2.31 euros per liter. In addition, the average price of gasoline in Germany also rose to 1.83 euros per liter [3],[4],[5].

The energy crisis occurs shows that the world still relies on fossil energy sources and comes from certain countries. Indonesia, as the G20 presidency, must take decisive steps in an effort to overcome the global energy crisis. One of the efforts that can be done is optimizing new renewable alternative energy sources that can reduce dependence on fossil energy sources. Biomass is one of the promising new renewable energy sources to be converted as a substitute for fossil energy sources. Biomass has the character of being easily renewable, environmentally friendly, and has a high enough calorific value to be substituted into fossil fuels [6].

One type of biomass that can be used is the microalgae *Spirulina sp*. Microalgae have the characteristics not requiring a large area for the cultivation process and requiring a relatively short time for the harvesting process compared to other biomass [7]. Before being used as fuel, microalgae *Spirulina sp* needs to be characterized for its physical and chemical properties [8]. Characterization in this research using a proximate analyzer, a scanning electron microscope-energy dispersive x-ray (SEM-EDX), and thermogravimetric analysis (TG). A proximate analyzer is used to determine the physical properties and calorific value of the sample. SEM-EDX test was used to show the topography, morphology, and chemical composition of *Spirulina sp*., while the thermogravimetric test was used to determine changes in weight loss associated with changes in temperature. The data from this research is expected to be able to provide an overview of the character of microalgae *Spirulina sp*. Therefore, the resulting fuel product will be more optimal.

II. Material and Methods

Material. The sample of microalgae *Spirulina sp* was cultivated, harvested, dried, and powdered by Balai Besar Pengembangan Budidaya Air Payau, Situbondo, Indonesia. Then the sample was crushed using a mortar and filtered through a size 60 mesh. Finally, the sample was put into a tightly closed bottle.

Procedure. The sample was tested using a proximate analyzer to find out the value of moisture, volatile matter (VM), ash content (AC), fixed carbon (FC), total sulfur, and gross calorific value (GCV). The proximate analysis method according to American standard testing and material (ASTM) with different procedures on each parameter is shown in Table 1. Another physical and chemical analysis was characterized using SEM-EDX FEI Inspect-S50 type. SEM was used to show the topography and morphology of the sample, while the chemical content was investigated using EDX test. A thermogravimetric Differential Scanning Calorimetry (DSC) analyzer, Mettler Toledo TG/DSC 1, was used to show the graph of TG analysis and derivative thermogravimetry DTG analysis of the sample with heating rate and nitrogen flow rate is 10°C/min and 100 ml/min, respectively.

III. Results and Discussions

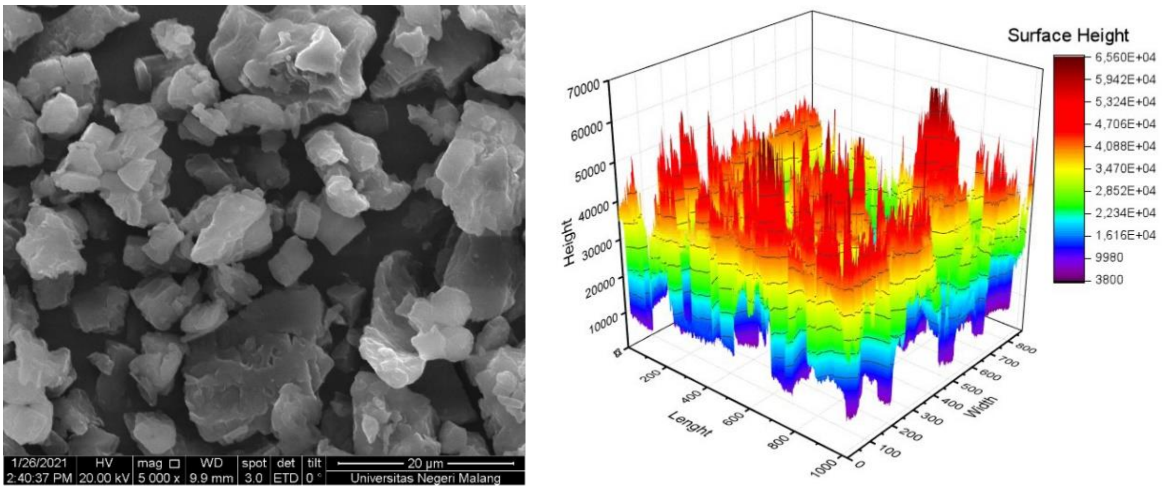
Proximate analysis results and test methods are shown in Table 1. The result shows that the most dominant content of microalgae *Spirulina sp* is VM, 68.15 wt% ar or 76.76 wt% db. It indicates that *Spirulina sp* is reactive during reaction process, and this condition is suitable for biomass combustion. VM value shows the convenience degree of biomass to be burned. The higher content of VM indicates that biomass is more sensitized to burn as a consequence of higher reactivity. On the other hand, a lower VM content makes the biomass hard to burn [9].

Table 1. The result proximate analysis of *Spirulina sp*

Parameters	Unit	ar*	db**	Test Method
Total moisture	%wt	11.22	--	ASTM D 2961 - 17
Ash content	%wt	8.06	9.08	ASTM D 3174 – 12(2018)el
Volatile matter	%wt	68.15	76.76	ASTM D 3175 – 20
Fixed carbon	%wt	12.57	14.16	ASTM D 3172 – 13
Total sulfur	%wt	0.67	0.75	ASTM D 4239 – 18el B
Gross calorific value	kcal/kg	4413	4971	ASTM D 5865 – 19

*ar: as received, **db: dry basis

FC becomes the second dominant content in *Spirulina sp*, about 12.57 wt% for ar and 14.16 wt% for db. FC is the remaining part of the evaporation process of volatile substances ends. Carbon in *Spirulina sp* is an organic substance that comes from the CO_2 fixation process during the photosynthesis process. Some organic carbon will turn into pyrolytic carbon during the photosynthesis evaporation process [10]. FC values can be used to determine the reactivity of solid fuels through a comparison of VM, VM/FC [11]. The comparison value of VM/FC on biomass is usually greater than 4.0, VM/FC > 4.0. The greater ratio value indicates that the solid fuel is more flammable and vice versa [12]. In this case, the ratio of VM/FC of *Spirulina sp* is 5.42.



(a) (b)

Fig.1. a) SEM surface image and b) topography of microalgae *Spirulina sp*

Moisture and ash content on the third and fourth position of *Spirulina sp* content with 11.22 and 8.06 wt% ar, respectively. Both of the values are lower compared to VM. The lower moisture value has an effect on the energy requirements used for the evaporation process on a smaller solid fuel [13]. While the low value of ash content will give the advantage of a low solid residual. Ash content in *Spirulina sp* is relatively small but contains alkali metals such as sodium and potassium, which can cause clumping and corrosion in a combustion system [14].

Visual analyses of microalga *Spirulina sp* surface via the micrograph is shown in Figure 1a. In this figure, the surface roughness of *Spirulina sp* is shown in two dimensions (2D) with width of 20 µm. Then imaged in 3D using the OriginPro 2017 software, as shown in Fig. 1b. The red graphs in Fig. 1b show the maximum peak, while the blue graphs show the lowest peak of the sample surface. Dominate red graph compare to the blue graphs indicates that the surface of *Spirulina sp* is rough. The level of surface roughness is proportional to the effective surface area, which causes an increase in the rate of intermolecular reactions [15]. It can shorten the reaction time. The higher surface area makes the evaporation process of VM on *Spirulina sp* faster [16].

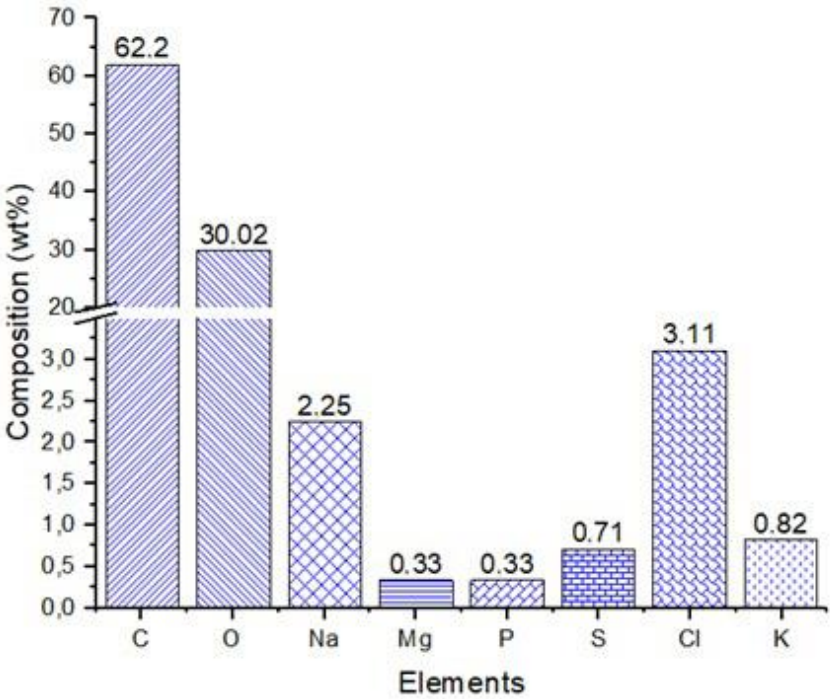


Fig. 2. Chemical content of microalgae *Spirulina sp*

Figure 2 shows the chemical content of microalgae *Spirulina sp* characterized by the EDX test. The content of microalgae *Spirulina sp* is dominated by carbon (C) and oxygen (O), then followed by chlorine (Cl), sodium (Na), potassium (K), sulfur (S), magnesium (Mg), and phosphorus (P). Element C leads the composition with 62,2 wt%. It is considered good condition because element C contributes positively to the formation of calorific value. The higher value of C makes the GCV value in microalgae *Spirulina sp* higher too [17].

The second dominant is element O with 30.02 wt%. It contributes negatively to the formation of the calorific value of microalgae *Spirulina sp*. This condition is caused by the character of the element O, which can cause the oxidation of carbon so that it obstructs the reaction [18]. The high oxygen content can be reduced using a metallic platinum (Pt) or palladium (Pd) catalyst [19]. Element Cl content in *Spirulina sp* is about 3.11 wt%. In combustion process, it will vaporize and react become hydrochloride (HCl), chlorine (Cl_2), and alkaline chloride compounds. The alkaline chloride will condense and bond to fly-ash particles when the temperature decreases [20].

Other chemical contents of microalgae *Spirulina sp* contribute to the formation of the ash content. Elements of calcium and magnesium can increase the melting temperature of the ash, while elements of potassium and sodium can decrease the melting temperature at the ashes [16].

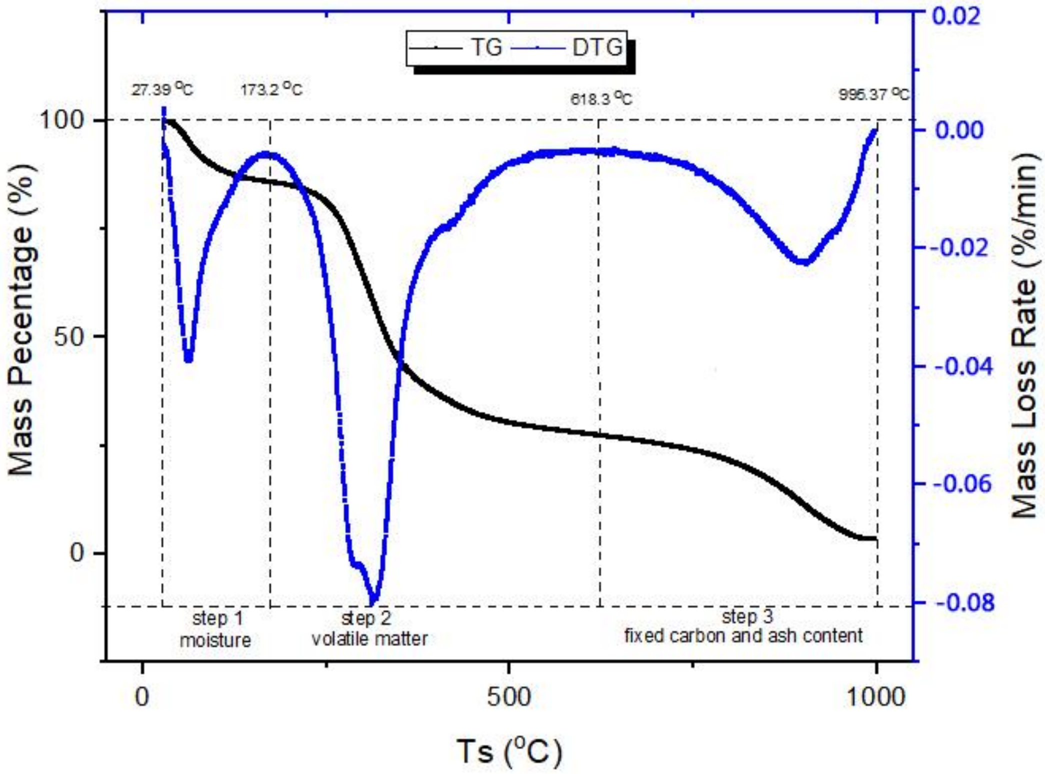


Fig. 3. The TG and DTG curve of pyrolysis *Spirulina sp* at heating rate of 10 °C/min

Figure 3 shows the curve of TG and DTG pyrolysis *Spirulina sp* at heating rate of 10 °C/min. The pyrolysis process occurs between an initial temperature of 27 °C until 995 °C for the final temperature. The decomposed process of *Spirulina sp* is divided into three different steps. The first step started at 27 °C and finished at 173 °C. The moisture of *Spirulina sp* was vaporized at this stage. In the first step, the mass of *Spirulina sp* was decomposed at about 1.44 mg or 13.81% of the total initial mass, and the DTG peak at 62.04 °C.

The second step began at the end of vaporized moisture at about 173 °C and ended at around 618 °C. In this step, a gasification process occurred in the volatile matter content of *Spirulina sp*. The dominant elements gasified in this stage are carbon and oxygen. The gasification process resulted in mass loss of about 6.06 mg or 57.9 % of *Spirulina sp* total mass. There are two peaks of DTG curves at this step. The first peak, at 286.47 °C, is degradation and combustion between carbohydrates and protein of *Spirulina sp*. While the second peak, at 311.6 °C, shows the further decomposition and combustion between protein and lipid [21]. This observation is considered by the fact that the temperature degradation of lipids is higher than others [22].

Spirulina sp at the last step shows the process of gasification of residual substances. In this process, the remaining carbon in Spirulina *sp* will continue to react together with the formation of charcoal from the remaining chemical elements that did not react in the two previous steps. This process occurred at the end of the volatile matter step, 618 °C, and stopped at 995 °C with a decomposed mass of 2.57 mg or 24.6%.

Table 2. Compare the physical properties of biodiesel *Spirulina sp* and diesel fuel [21]

Properties	Spirulina sp	Diesel
Density (kg/m^3)	860	830
Viscosity (mm^2/s) at 40 °C	5.6	2.6
Calorific value (MJ/kg)	41.36	43.8
Flashpoint (°C)	130	50

Regarding the potential of spirulina as a biofuel, Table 2 display the comparison physical properties between biodiesel Spirulina sp and diesel fuel by Rajak. The comparative value of the two fuels is not far apart. It's just that the flash point value of spirulina sp is higher. A higher flash point value indicates that the fuel is more difficult to ignite. The difficulty level is due to the carbon bonds in the fuel, which are difficult to decompose [22]. Spirulina sp has more complex carbon bonds than diesel fuel, $C_6H_{10}O_5$, so it will be more difficult to decompose than diesel fuel, $C_{16}H_{34}$ [23],[24]. Furthermore, the lower calorific value and kinematic viscosity value of fatty acids increased proportionally with chain length and decreased as the level of fatty acid alkyl chain saturation decreased. Figure 3 in step 2 also confirms that there is a low-temperature reactivity due to the increased carbon-to-hydrogen ratio present in the fatty acid alkyl chains [22].

IV. Conclusions

Based on the test results, the microalgae *Spirulina sp* has great potential to be converted as fuel. The chemical content and physical properties of microalgae *Spirulina sp* have the characteristics needed to be used as fuel to substitute fossil fuels. The main component that must be optimized in Spirulina sp microalgae is lipid because it plays a large role in the biofuel formation process, as shown in the thermal decomposition of volatile matter. Potential fuel products from microalgae *Spirulina sp* could be optimized more by researching better cultivation methods.

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Reference

[1] T. Lancet and R. Health, “Editorial The regional and global impact of the Russian

invasion of Ukraine," *Lancet Reg. Heal. - Eur.*, vol. 15, p. 100379, 2022, doi: 10.1016/j.lanepe.2022.100379.

[2] F. Sassi, and R. E. Geopolitics, "Structural power in Russia ' s gas sector : The commoditisation of the gas market and the case of Novatek," *Energy Strateg. Rev.*, vol. 41, no. November 2021, p. 100842, 2022, doi: 10.1016/j.esr.2022.100842.

[3] Z. Huang, X. Ming, and H. Duan, "Heterogeneous effects of energy poverty convergence in Europe," *Energy Strateg. Rev.*, vol. 41, p. 100822, 2022, doi: 10.1016/j.esr.2022.100822.

[4] V. Vasudev, X. Ku, and J. Lin, "Pyrolysis of algal biomass: Determination of the kinetic triplet and thermodynamic analysis," *Bioresour. Technol.*, vol. 317, no. June, p. 124007, 2020, doi: 10.1016/j.biortech.2020.124007.

[5] A. Parsy, C. Sambusiti, P. Baldoni-andrey, T. Elan, and F. Périé, "Cultivation of Nannochloropsis oculata in saline oil & gas wastewater supplemented with anaerobic digestion effluent as nutrient source," *Algal Res.*, vol. 50, no. March, p. 101966, 2020, doi: 10.1016/j.algal.2020.101966.

[6] E. Cano-Pleite, M. Rubio-Rubio, N. García-Hernando, and A. Soria-Verdugo, "Microalgae pyrolysis under isothermal and non-isothermal conditions," *Algal Res.*, vol. 51, no. May, p. 102031, 2020, doi: 10.1016/j.algal.2020.102031.

[7] A. A. D. Maia and L. C. de Morais, "Kinetic parameters of red pepper waste as biomass to solid biofuel," *Bioresour. Technol.*, vol. 204, pp. 157–163, 2016, doi: 10.1016/j.biortech.2015.12.055.

[8] P. Basu, *Biomass Gasification, Pyrolysis and Torrefaction*. London: Elsevier Inc, 2018.

[9] A. Prasetiyo, S. Sukarni, A. Irawan, A. A. Permanasari, and P. Puspitasari, "Physicochemical properties and porosity of coconut chell waste (CSW) biomass," *IOP Conf. Ser. Earth Environ. Sci.*, vol. 847, no. 1, 2021, doi: 10.1088/1755-1315/847/1/012017.

[10] M. V. Gil, D. Casal, C. Pevida, J. J. Pis, and F. Rubiera, "Thermal behaviour and kinetics of coal/biomass blends during co-combustion," *Bioresour. Technol.*, vol. 101, no. 14, pp. 5601–5608, 2010, doi: 10.1016/j.biortech.2010.02.008.

[11] K. Annamalai and I. K. Puri, *Combustion Science and Engineering*. New York: Taylor & Francis Group, LLC., 2007.

[12] V. Mettanant, P. Basu, and J. Butler, "Agglomeration of biomass fired fluidized bed gasifier and combustor," *Can. J. Chem. Eng.*, vol. 87, no. 5, pp. 656–684, 2009, doi: 10.1002/cjce.20211.

[13] H. Fatehi and X. S. Bai, "Effect of Pore Size on the Gasification of Biomass Char," *Energy Procedia*, vol. 75, no. 1, pp. 779–785, 2015, doi: 10.1016/j.egypro.2015.07.514.

[14] L. Leng, Q. Xiong, L. Yang, H. Li et al., "An overview on engineering the surface area and porosity of biochar," *Sci. Total Environ.*, vol. 763, p. 144204, 2021, doi: 10.1016/j.scitotenv.2020.144204.

[15] I. Obernberger, T. Brunner, and G. Bärnthaler, "Chemical properties of solid biofuels-significance and impact," *Biomass and Bioenergy*, vol. 30, no. 11, pp. 973–982, 2006,

doi: 10.1016/j.biombioe.2006.06.011.

[16] S. van Loo and J. Koppejan, *The Handbook of Biomass Combustion and Co-firing*. London: Earthscan, 2008.

[17] J. Yan, Q. Yang. L. Zhang. Z. Lei et al., "Investigation of kinetic and thermodynamic parameters of coal pyrolysis with model-free fitting methods," *Carbon Resour. Convers.*, vol. 3, no. December, pp. 173–181, 2020, doi: 10.1016/j.crcon.2020.11.002.

[18] Sukarni, Sudjito, N. Hamidi, U. Yanuhar, and I. N. G. Wardana, "Potential and properties of marine microalgae Nannochloropsis oculata as biomass fuel feedstock," *Int. J. Energy Environ. Eng.*, vol. 5, no. 4, pp. 279–290, 2014, doi: 10.1007/s40095-014-0138-9.

[19] S. Sukarni, "Heliyon Thermogravimetric analysis of the combustion of marine microalgae Spirulina platensis and its blend with synthetic waste," *Heliyon*, vol. 6, no. November 2018, p. e04902, 2020, doi: 10.1016/j.heliyon.2020.e04902.

[20] R. López, C. Fernández, J. Fierro, J. Cara, O. Martínez, and M. E. Sánchez, "Oxy-combustion of corn, sunflower, rape and microalgae bioresidues and their blends from the perspective of thermogravimetric analysis," *Energy*, vol. 74, no. C, pp. 845–854, 2014, doi: 10.1016/j.energy.2014.07.058.

[21] U. Rajak and T. N. Verma, "Spirulina microalgae biodiesel – A novel renewable alternative energy source for compression ignition engine," *J. Clean. Prod.*, vol. 201, no. X, pp. 343–357, 2018, doi: 10.1016/j.jclepro.2018.08.057.

[22] H. Y. Nanlohy, I. N. G. Wardana, N. Hamidi, L. Yuliati, and T. Ueda, "The effect of Rh3+ catalyst on the combustion characteristics of crude vegetable oil droplets," *Fuel*, vol. 220, no. December 2017, pp. 220–232, 2018, doi: 10.1016/j.fuel.2018.02.001.

[23] U. Rajak, P. Nashine, and T. N. Verma, "Characteristics of microalgae spirulina biodiesel with the impact of n-butanol addition on a CI engine," *Energy*, vol. 189, no. X, p. 116311, 2019, doi: 10.1016/j.energy.2019.116311.

[24] Y. Hu, M. Gong, S. Feng, C. (Charles) Xu, and A. Bassi, "A review of recent developments of pre-treatment technologies and hydrothermal liquefaction of microalgae for bio-crude oil production," *Renew. Sustain. Energy Rev.*, vol. 101, no. November 2018, pp. 476–492, 2019, doi: 10.1016/j.rser.2018.11.037.