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Morphology and chemical analysis of raw fuel and its combustion residue of *Spirulina* (*Arthrospira*) *platensis* and synthetic waste blend at a 70/30 mass ratio

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Abstract. This study delves into the morphological characteristics of the cyanobacterium *Spirulina* (*Arthrospira*) *platensis* (SP) and the synthetic waste (SW) ashes generated from co-combustion in a circulating fluidized-bed combustor (CFBC). Specifically, it addresses the ash attributes, including particle size, shape, and structural composition. The research focuses on the morphological and chemical transformations occurring in a 70:30 mass ratio blend of SP and SW during thermal processing in a CFBC. Scanning electron microscopy (SEM) was used to examine its surface structure and morphology, which indicated a transformation in particle morphology. The resulting ash exhibited a coarser surface texture, with an average particle size distribution of approximately 3 μm. Chemically, the ash composition showed reduced concentrations of carbon (C), sodium (Na), phosphorus (P), sulfur (S), and chlorine (Cl), elements that predominantly volatilize during combustion, leading to emissions such as CO_2, SO_2, and fly ash. The residual non-volatile ash components may offer practical applications, potentially being converted into fertilizers and catalytic materials.

1 Introduction

Population growth has increased demand for fossil fuels in Indonesia. Around 795 million barrels of oil equivalent (MBOE) were consumed in 2016, and this figure is expected to increase to 4.569 MBOE in 2050 [1]. The high energy demand is not proportional to the availability of Indonesia's energy reserves. Solid fossil fuels, such as coal, are often used as energy sources for power generation. However, it is estimated that coal resources will be depleted in 65 years [2]. Fossil-based energy sources significantly contribute to global warming by releasing greenhouse gases during combustion [3].

On the other hand, environmental problems, along with the significant increase in waste volume, have posed critical challenges in Indonesia. Based on data from the Ministry of

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Environment and Forestry, total waste in 2019 was 68 million tons, with plastic waste estimated at around 9.52 million tons [2]. This waste growth is linear with the extent of residential development and changes in lifestyle orientation of the current society. Converting waste to energy has become an attractive choice for addressing the depletion of fossil fuel resources and the increasing energy demand. Waste combustion has become a primary option because it significantly reduces waste volume and enables energy recovery [4]. Synthetic waste (SW) co-combustion with biomass is a promising method to further reduce the carbon footprint [3]. *Spirulina* (*Arthrospira*) *platensis* (SP) is a proposed feedstock due to its abundance, renewable, CO2-neutral fuels, and high growth rate compared to wood and other terrestrial plants [3].

Co-combustion is a common method for increasing decarbonization rates. Soares et al. [5] added acai seed to coal combustion in a circulating fluidized bed combustor (CFBC), decreasing SO_2 and CO emissions. A study on the kinetics of *Spirulina* and plastic waste co-combustion was conducted by Sukarni et al. [3], in which the activation energy decreased as the Spirulina proportion increased. Biomass addition improves combustion characteristics and reduces emissions. However, there is limited research on the ash characteristics of a *Spirulina*-plastic waste blend in CFBC. Examining the fundamental properties of the fuel material will provide the dataset needed to properly design a suitable combustion reactor and to appropriately handle the by-products. The chemical composition and morphology of the feedstock and its ashes are needed to understand the SP/SW mixture's potential as a fuel and to assess the reutilization of its combustion by-products. Scanning electron microscopy (SEM) paired with an energy-dispersive X-ray (EDX) spectrometer is commonly used to examine particle shape and chemical composition, which affect the combustion rate of solid fuel.

This study investigated changes in morphology and chemical composition during the combustion of an SP-SW mixture in a CFBC. Both materials are mixed in a 70SP/30SW mass ratio.

2 Method

2.1 Material

SP samples were obtained from the Center for Development of Brackish Water Aquaculture (Balai Besar Pengembangan Budidaya Air Payau, BBPBAP), Situbondo, Indonesia. Drying process conducted using an oven at 100 °C for 24 h. The dried biomass is then pulverized and sieved using a mesh-60 filter (<0.25mm), then subsequently stored in the insulated bottle.

Fig. 1. 70SP/30SW combustion feedstock preparation

SW was collected from the dumpsters in Malang City, Indonesia. SW is composed of engine oil bottles (EOB), plastic buckets (PB), and food containers (FC), which are cleaned using water and then sun-dried for two days. Dried SW was crushed to a mesh size 20 (<0.84mm). Both samples were mixed in a mass ratio of 70SP/30SW by using a mechanical mixer at 1200 rpm for 15 minutes, then weighed with a total mass of 1 g for characterization and 100 g for each combustion test (Figure 1).

2.2 Experimental setup

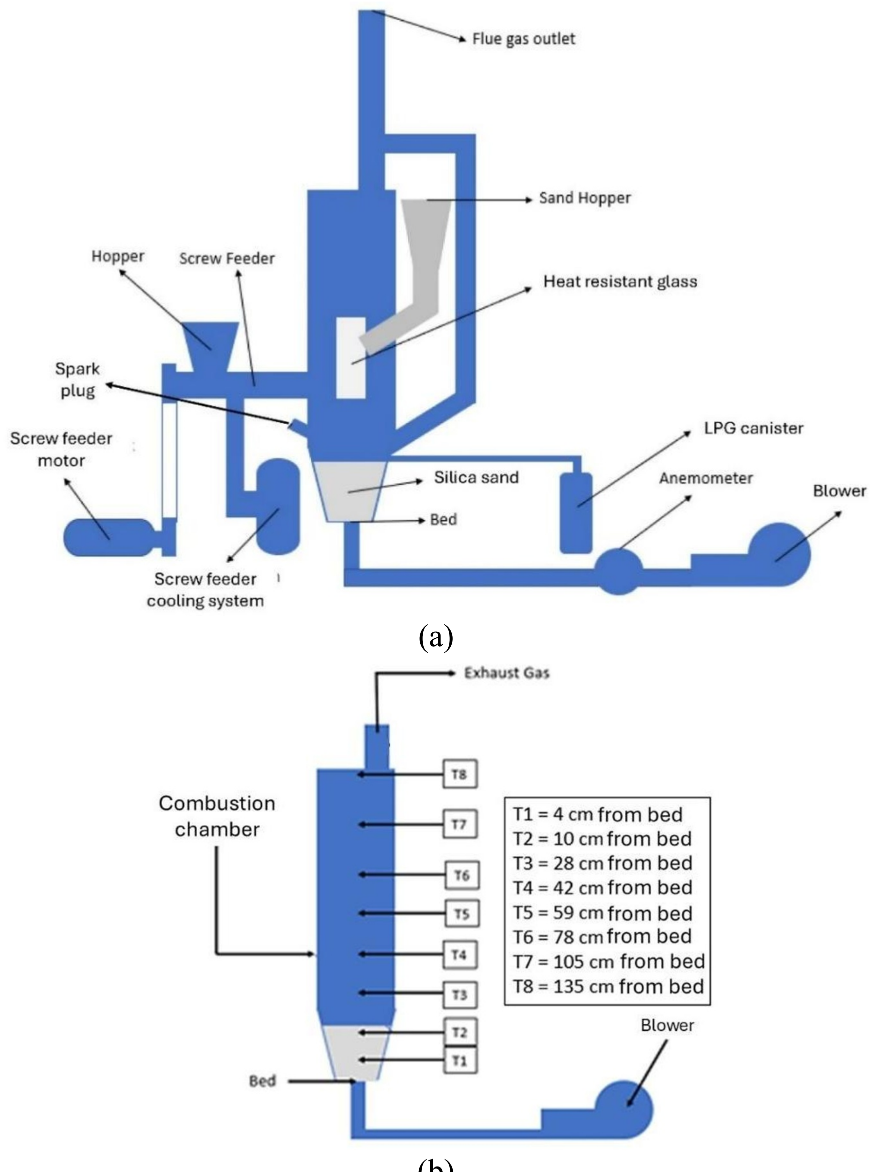


Fig. 2. (a) Experimental setup of the CFBC, (b) Configuration of the K-type thermocouple positioning

The combustion experiment is carried out by following the following procedure. First, connect it to a power source to turn on a blower that blows atmospheric air into the reactor, and install an exhaust gas line with an air speed of 7 m/s (Figure 2a). The speed of the resulting airflow is measured using an anemometer. The initial heating process begins by igniting the burner with LPG. The fluidized material, which is silica sand measuring less than 0.25mm with a specific gravity of 1520 kg/m^3, is fed into the reactor. The system is left until the 3rd K-type thermocouple (T3) reaches a stable temperature of 750°C (Figure 2b). Once the temperature stabilizes, the screw feeder is activated, and the test sample is introduced at a feed rate of 0.86 kg/min. Simultaneously, the cooling-water pump for the screw feeder is activated to maintain the sample's temperature stability. The fuel sample is then pushed into the combustion chamber by waiting for 25 seconds after the screw feeder is activated. Once the sample combusts stably, the LPG flow is turned off, and the combustion process ceases naturally. The final stage is cleaning and storing the appliance. The CFBC unit may cool until the 2nd thermocouple (T2) shows a temperature below 100°C. After that, the power source is disconnected, the exhaust duct is removed, and the ash is collected for further characterization.

2.3 Characterization

SP and SW were analyzed on their raw material and combustion byproducts. The calorific value of 70SP:30SW was analyzed using a Parr Instrument 1341 plain-jacket bomb calorimeter. The surface morphological structures of the raw material and pyrolysis by-product were examined using SEM (Scanning Electron Microscopy) with an FEI Inspect S50, coupled with EDS (Energy-dispersive X-ray Spectroscopy), using an X-ray Ametek EDAX TSL for surface element analysis. SEM-EDS specimen selected using random sampling where five different primary particles are analyzed during testing, while ensuring homogeneity of particle’s morphology and chemical composition. The EDS result is averaged to obtain the final reading.

3 Results and discussion

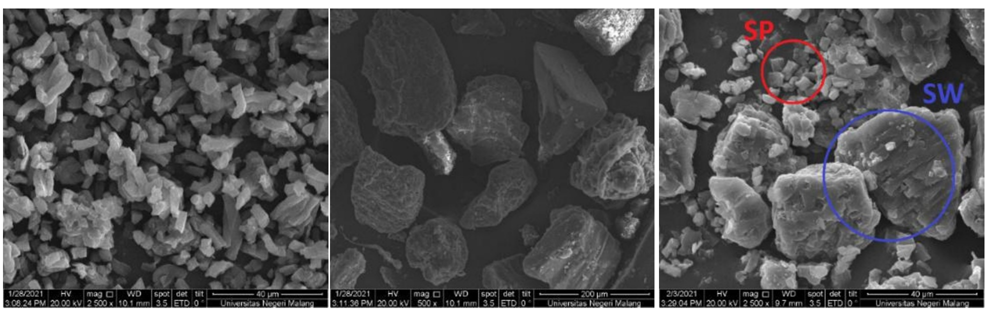
The calorific value (CV) of the 70SP/30SW mixture is 28.78 MJ/kg (Table 1). Co-combustion feedstock has a higher CV compared to biomass, while comparable to bituminous coal, which is often used as the main fuel in coal-fired power plants [6]. The higher calorific value (CV) of the 70SP/30SW blend is attributed to its polymer content, which typically has a higher carbon-to-hydrogen (C/H) ratio than other biomass fuels. Polymer also has a lower oxygen and carbon ratio (O/C) compared to biomass. This is advantageous because less fuel is required to produce the same amount of thermal energy when compared to low-calorie fuels. Fuel with high CV often has better combustion efficiency due to higher flame temperature, which surpasses unburned fuel activation energy, resulting in sustainable combustion and yields better flame stability compared to low CV fuels [3].

Morphological analysis of SP revealed cylindrical particles with diameters less than 40 μm (Figure 3a). SW had circular particles with diameters larger than those of SP microalgae (Figure 3b, c). Particle shape and size play an important role in combustion rate and mass transfer because the larger the particle surface area, the higher the reaction rate, thereby reducing thermal gradients between particle surfaces and the nucleus and avoiding incomplete combustion. Particle shape also affects the volatile release mechanism, in which volatile gases form at elevated temperatures, thereby generating internal pressure at the particle wall. A higher surface area promotes greater volatile release, thereby accelerating combustion.

Figure 4 shows the morphology of 70SP/30SW ash, which undergoes drastic changes during thermal degradation. The ash particles have noticeable pores due to the loss of key components such as lipids, proteins, and carbohydrates in the SP microalgae, as well as the depolymerization process in SW due to high temperatures that cause a phase change from solid to gas, leaving holes in the 70SP/30SW particles. Agglomerates are also formed due to ash sintering, in which melted inorganic elements, usually alkali-based compounds [7], bind to other particles, reducing the surface area of the ash particles. Ash sintering also indicates the violent release of volatiles during combustion.

Table 1. Calorific values comparison of common combustion feedstock

Feedstock		Calorific value (MJ/kg)	Reference
Type	**Material**		
Mixture	70SP/30SW	28.78	This study
Biomass	*Spirulina platensis*	20.97	[3]
	Nannochloropsis oculata	16.80	[7]
Polymer	LDPE	46.4	[8]
	PET	30.2	[8]
Coal	Lignite	17.7	[9]
	Bituminous	26.5	[10]



(a) (b) (c)

Fig. 3. SEM image of (a) SP, (b) SW, and (c) 70SP/30SW

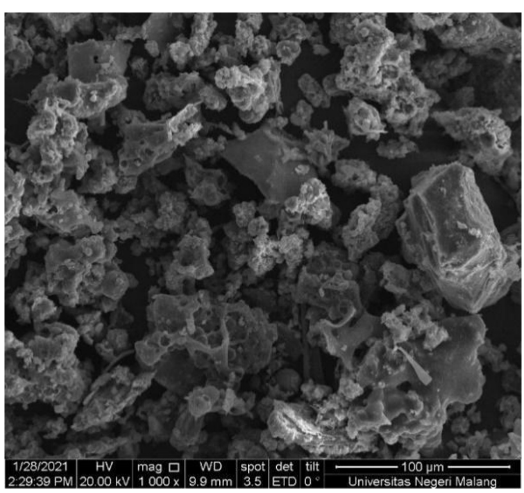


Fig. 4. Morphology of 70SP/30SW ash

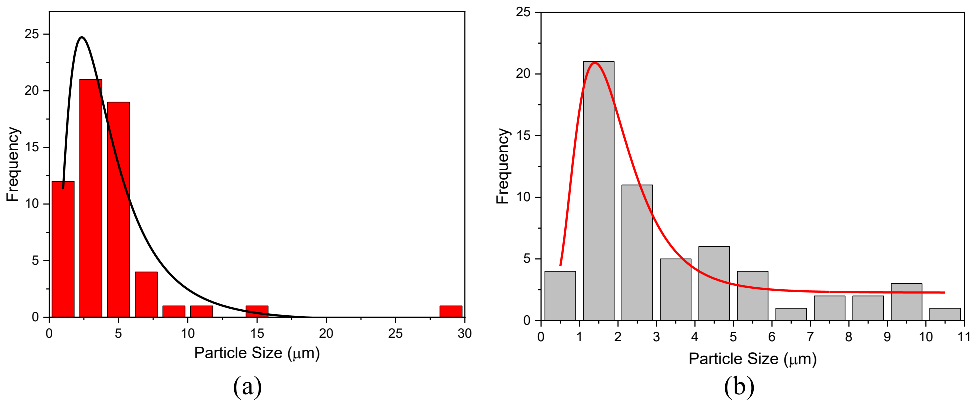


Fig. 5. Particle size distribution of 70sp/30sw (a) raw material and (b) ash

Particle distribution analysis was carried out on raw material and ash from 70SP/30SW as indicated in Figure 5. The residual ash from combustion has a smaller particle size than the raw material, with an average particle size of 1.5 μm, whereas the raw material has an average particle size of 2.5 μm. The decrease in particle size is caused by thermal degradation during combustion, which breaks molecules and complex structures into simpler forms by dissociating bonds with thermal energy exceeding the activation energy of each fuel component, so that the initially large particles split into several smaller particles. High thermal energy during combustion weakens covalent bonds in the polymer, leading to chain scission and the formation of reactive free radicals. Volatile fragments then react with oxygen, leading to a large thermal release from hydrocarbon oxidation. On the other hand, Spirulina decomposition begins with dehydration and is followed by devolatilization. Protein denaturation and lipid vaporization release volatile matter, which also oxidizes above 400°C until combustion is complete, leaving ash as a by-product.

Table 2. Elemental composition comparison of 70SP/30SW raw material and its ash

Sample	Chemical content (wt.%)							
	C	O	Na	Mg	P	S	Cl	K
Raw	63.25	28.36	2.18	0.64	1.36	1.18	3.9	1.29
Ash	62.6	27.99	1.97	0.58	0.82	0.97	3.42	1.27

Table 2 shows several chemical elements that are dominated by carbon and oxygen, both of which exhibit a marked decrease in post-combustion residues due to volatilization. Carbon elements are oxidized, resulting in exothermic reactions and emitting CO_2 and H_2O. Inorganic chemical elements would form ash as combustion residue, which is composed of Cl, S, Mg, P, K, and Na. 70SP/30SW combustion resulting in a decrease in inorganic content due to evaporation. Corrosion and fouling are often linked to inorganic compounds, especially Cl, S, and Na, which condense on the heat exchanger surface, reducing heat transfer rates and increasing maintenance downtime. The non-condensable fraction produces harmful emissions, such as HCl and SOx. However, phosphorus and potassium can be reutilized as fertilizers.

4 Conclusion

Based on a comprehensive analysis, the 70SP/30SW blend shows strong potential as a renewable fuel. Its high calorific value of 28.78 MJ/kg is comparable to that of bituminous coal, which is expected to reduce CO_2 emissions. Fuel morphology changes during combustion, with raw material particles having a cylindrical shape and sizes above 2.5 μm. Pores will form during thermal degradation, reducing the ash particle size to 1.5 μm. Pores are formed due to the loss of various core components of SP and SW, which are characterized by a decrease in carbon and oxygen content. Ash is composed of inorganic elements such as chlorine and sulfur, which need to be mitigated to reduce harmful emissions. However, the phosphorus and potassium content offer potential for reuse as fertilizer. The 70SP/30SW blend presents a promising alternative for cleaner, renewable energy production.

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