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Study of FRP Ship Waste Composite Materials and Its Combustion Residue

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***Abstract*— The escalating utilization of FRP materials ultimately gives rise to issues related to waste production. Waste disposal typically involves incineration, as practiced at UD Wahyu Asih Fiberglass. The combustion process yields thick black smoke and a pungent odor. Incineration does not annihilate fiberglass material but generates combustion byproducts, such as solid ash. This study aims to elucidate the material type, chemical element content, and associated properties inherent in FRP shipbuilding materials at UD Wahyu Asih Fiberglass Shipyard. The methodology commences with the identification of materials utilized in FRP ship manufacture through field observations at the shipyard. Another objective of this study is to quantify the ash content and ascertain the total particulate matter during the incineration process of FRP shipbuilding material waste via laboratory tests. The total particulate data obtained will be compared with applicable emission quality standards.**

Keywords— ash content, combustion residue, fiberglass, FRP, waste.

I. INTRODUCTION

Composites are materials with new mechanical characteristics made by mixing several components. In general, composites comprise binder material (matrix) and reinforcing material, also called filler material. Composites have favorable properties, such as lightweight construction, strength, and no corrosion [1]. Fiberglass composites have some mechanical properties that are better than metals. These composites can achieve higher values of specific stiffness (young modulus or density) and tensile strength than some metals [2]. Fiber Reinforced Plastics (FRP) is a structural composite material with synthetic resin as the matrix and fiber as the skeleton.

Fiberglass material (from now on referred to as FRP) in fisheries, such as new shipbuilding materials, is utilized in Indonesia. This happens because the availability of wood materials commonly used as shipbuilding materials is low, so there is a need for alternative materials in the construction of fishing boats. FRP ships have advantages in their application, including lighter weight, easier maintenance, weather resistance, and shorter production times. FRP ships are currently more economical than wood and metal for small shipbuilding materials [3].

The escalating utilization of FRP materials ultimately raises new issues related to the waste produced. The FRP waste in question comes from the remaining production and molding of ships made of FRP and FRP ships that are no longer suitable for use. Kusumawardani et. al. [4] stated that FRP waste could not be destroyed carelessly. FRP waste is inorganic waste that will not decompose quickly. Inorganic waste that is buried has the potential to pollute the soil, so it is suspected that polluted soil will be difficult to reuse or plant. This is supported by research by Setyaningrum [5] which states that contaminants entering the soil will decrease soil function and cause soil degradation. Plastic or resin is one of the components that can affect high levels of zinc (Zn) in the soil, affecting plant growth.

The primary materials for making FRP ships are Chopped Strand Mat (CSM) and Woven Roving, which have a direct impact in the form of itching if there is direct contact with the skin. Latief et al. [6] state that fiber and resin do not contain toxins but it is very difficult to break down microorganisms in the soil, so their presence in nature has the potential to damage the environment. In addition, other chemicals used in the manufacture of FRP ships are thought to have the potential to affect health.

Some shipyards try to burn pieces of ship bodies or unused FRP ship molds. This is done to reduce piles of shipbuilding materials and FRP ship molds. When burning, it causes thick white smoke with a reasonably sharp odor. The combustion process is straightforward, namely, a pile of FRP waste is ignited with fire until it burns. After the combustion, the burnt FRP shipbuilding materials and molds are not all burned out. There is solid ash as a residue of combustion. This raises the question: Can the combustion process destroy FRP material from the remaining production and FRP ship molds that are no longer used? Are the smoke and ash produced harmless?

Therefore, it is necessary to conduct a study to obtain information related to the content of smoke generated during the combustion process and combustion residue ash. The results of this study can answer the question of whether FRP ship material waste can be eliminated in the ordinary combustion process.

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II. METHOD

The research was conducted at the Integrated Chemistry Laboratory of IPB University with samples from UD Wahyu Asih Fiberglass Shipyard, Kebumen, Central Java. The tools used in the research are an electric furnace, porcelain cup, desiccator, and analytical balance. The material used is waste left over from the production of FRP shipbuilding. Determination of ash content was carried out using the AOAC (2012) 942.05 method.

The material that became the research sample was the remaining waste from the production of FRP shipbuilding on the side consisting of 4 layers with details of gel coat + CSM300 + WR600 + 2CSM300 weighing 2 grams obtained from UD Wahyu Asih Fiberglass Shipyard.

A 2-gram sample of the FRP ship side was put into a porcelain crucible and ignited over a flame. After that, it was put into an ashing furnace at 600° C for 2 hours. Then, calm in a desiccator and weigh until a constant weight is obtained. The following formula determined the calculation of ash content.

$$\text{Ash content (\%)} = \frac{W_1 - W_2}{W} \times 100 \quad (1)$$

With:
W = weight before fumigation, in grams
W_1 = sample weight + porcelain vrucible after fumigation, in grams
W_2 = weight of empty porcelain vrucible, in grams

III. RESULTS AND DISCUSSION

Before discussing the smoke content produced during combustion and the ash content as a combustion residue, describe the materials that form the shipbuilding FRP composite material.

A. *FRP Composite Materials*

All script should Fiber Reinforce Plastic (FRP) composite is a type of composite material resulting from a combination of glass fiber, resin, gelcoat, and pigments with a specific composition. Glass fiber types are divided into 4, namely, S-glass and R-glass, A-glass (high alkali glass), C-glass (Sodium Borosilicate), and E-glass (Aluminum Borosilicate) [7]. Based on observations and literature studies, the materials, types, and chemical content of FRP materials used in making FRP ships are presented in Table 1.

TABLE 1.
MATERIALS, TYPES, AND CHEMICAL COMPOSITION OF FRP MATERIALS USED BY UD WAHYU ASIH FIBERGLASS SHIPYARD

No	Materials	Types	Chemical Composition
1	*Chopped strand mat* (CSM)	300	SiO_2, CaO, Na_2O
2	*Woven Roving*	600 and 800	SiO_2, CaO, Na_2O
3	Resin	Yukalac 235 series	$C_{10}H_8O_4$
4	Katalis	*Mepoxe*	$C_4H_{10}O_3$
5	Aerosil		SiO_2
6	Miracle gloss		
7	*Talc*		$Mg_3Si_4O_{10}(OH)_2$
8	*Cobalt napthanate*		$Co(C_{11}H_7O_2)_2$
9	Pigmen		
10	Gelcoat	Yukalac G-123 T-EX	

1) Chopped Strand Mat

Chopped strand mats (CSM), often called mats, are pieces of glass fiber with a length of about 50 mm arranged irregularly and formed into sheets with an adhesive containing seizing material [7]. In Fig 1, an example of a CSM300 matt sheet is presented. The mat composition contains silica, which can provide hardness, flexibility, and stiffness. The addition of mat laminates can increase the tensile strength [8]. Sari et al. [9] states that the most considerable oxide content in the mat is SiO_2 (56.88%), CaO (16.24%), and Na_2O (12.91%). Based on the Material Safety Data Sheet (MSDS), the mat is not classified as hazardous but can potentially irritate the skin and eyes. The mat used by shipyards in Kebumen is CSM300, meaning the mat has a 300 g/m² density. Jushi Group Co., Ltd manufactures the mat.

Figure. 1. CSM300

2) Woven Roving

Woven roving (WR) comprises long fibers that resemble a plait in a perpendicular direction (Fig 2). Woven roving is the main laminate to add higher tensile and bending strength than Mat laminates. In the process of laminating woven roving fibers, it is relatively tricky for resin solutions to fill the woven roving fiber webbing. The lack of resin content makes the woven roving resistance to water absorption less suitable. Types of woven roving include WR400 (400 g/m²), WR600 (600 g/m²), and WR800 (800 g/m²) [10]. The types of WR used by UD Wahyu Asih Fiberglass Shipyard are WR600 and WR800. This fiber has greater strength and stiffness than CSM. In the lamination process, the weight ratio between woven roving fibers and resin is around 45-50% woven roving and 50-55% polyester resin from the weight fraction [7]. Sari et al. [9] states that the most considerable oxide content in woven roving is SiO_2 (56.86%), CaO (18.71%), and Na_2O (11.80%). Based on the Material Safety Data Sheet (MSDS), woven roving is not classified as hazardous but can potentially irritate the skin. Jushi Group Co., Ltd. produces woven roving used by shipyards in Kebumen.

(a) WR600 (b) WR800

Figure. 2. Types of woven rovings used

3) Resin

Resin is a liquid material used as a fiber binder in lamination. The resin has a tensile strength and stiffness lower than the reinforcing fiber. Generally, shipyards use polyester resin with the advantages of being transparent, waterproof, colorable, flexible, resistant to extreme weather, and chemical resistant [11]. The polyester resin consists of long chains of $C_{10}H_8O_4$ monomer molecules bonded through a polymerization reaction. The resin reaches the curing phase faster if the resin is used by adding catalysts and accelerators. Adding these liquids into the resin causes a chemical reaction known as polymerization. The resin used by shipyards in Kebumen is Yukalac 235 series, a type 2 resin with fast drying characteristics and is very suitable for making FRP products with hand lay-up and spray-up molding processes. This type is commonly used as a structural material in manufacturing yachts, fishing boats, building materials, and other FRP products. Based on the Material Safety Data Sheet (MSDS), polyester resin is hazardous because it can cause skin irritation, severe eye irritation, flammable liquids, and damage to organs through prolonged or repeated exposure.

4) Catalyst

A catalyst is a chemical liquid mixed into the resin that accelerates the hardening process [12]. The catalyst must be proportioned so hardening occurs ideally at 16°C and 25°C. The catalyst used by shipyards in Kebumen is methyl ethyl ketone peroxide (mepoxy) with the chemical formula $C_4H_{10}O_3$ which is liquid and transparent in color. Mepoxe is a catalyst that must be minimized [13]. Based on the Material Safety Data Sheet (MSDS), catalysts are classified as hazardous substances because they can intensify fire and become oxidizers. Mepoxe catalyst has several advantages: low price, good corrosion rate value, long fluid resistance, and considerable tensile strength [14]. This catalyst can be stored at 30°C room temperature. PT Kawaguchi Kimia Indonesia produces mepoxe catalysts.

5) Aerosil

Aerosil, a fumed silica chemical, is one of the filler raw materials for making fiberglass composites. Aerosil is used as a fiberglass adhesive so that it has strength and does not crack easily [15]. The addition of aerosil makes the resin mixture soft, and the results are shiny. Based on the Material Safety Data Sheet (MSDS), aerosil is classified as a non-hazardous substance. Aerosil used by the shipyard is Pyrogenic Silica produced by Wacker Chemicals Fumed Silica (ZJG) Co., Ltd. with SiO_2 content reaching > 99%.

6) Miracle Gloss

Miracle gloss coating is carried out after the vessel mold is clean. The miracle gloss coating is done only once and is ensured to be evenly distributed throughout the body of the ship mold. This miracle gloss coating aims to make the mold easy to remove from the ship model [16]. This material contains a mixture of wax, oil, and other chemicals. Stoner Corporation produces the miracle gloss used. Based on the Material Safety Data Sheet (MSDS), miracle gloss is not classified as a hazardous substance.

7) Talc

Talc, as a filler material or material thickener, increases the composite's strength and stiffness. Talc consists of magnesium silicate hydrate with the chemical formula Mg3Si4O10(OH)2. Talc can be mixed with resins, color pigments, and catalysts [12]. Talc added to the resin mixture produces a putty with a slightly stiff and flexible texture when dry. Based on the Material Safety Data Sheet (MSDS), talc is not classified as a hazardous substance. However, exposure to large and repeated amounts of talc dust can cause pneumoconiosis, a lung disease that often affects people exposed to dust and chemical pollution.

8) Cobalt Naphthenate

Cobalt naphthenate is a bluish chemical liquid that functions as an active ingredient for mixing catalysts to dry quickly, especially if the quality of the catalyst is not good and too diluted. Cobalt naphthenate is an accelerator that functions as an ingredient to activate the catalyst so that the curing process (hardening) runs faster at room temperature [17]. This type of accelerator is usually combined with a Methyl Ethyl Ketone Peroxide catalyst. Cobalt naphthenate has the chemical formula Co $(C_{11}H7O_2)_2$ with a molecular weight of 418.33 gr/mol. Cobalt naphthenate cannot dissolve in water but in organic solvents such as acetone, ethanol, and methanol. Based on the Material Safety Data Sheet (MSDS), cobalt naphthenate is hazardous because it can cause skin irritation, severe eye irritation, flammable liquids, and is harmful if inhaled.

9) Pigments

Pigments are dyes whose use must be mixed with resin and other components to adhere to the outermost layer of fibreglass [18]. The pigment should differ from the boat mould, so it is easy to see the parts that have not been coated when coating the gel coat. The colour pigment used by the shipyard is the Matapel Unipol brand. These colour pigments have high brightness, are free of solvents, are not dispersed in polyester resins, are colourfast, resistant to UV light, and are environmentally friendly. Matapel Chemicals produces Matapel Unipol color pigments. Based on the Material Safety Data Sheet (MSDS), pigments are classified as hazardous substances because they can cause skin irritation, allergic skin reactions, severe eye disorders, and can cause respiratory irritation.

10) Gelcoat

Gelcoat is a polyester resin explicitly used to coat the outside of FRP vessels because it has resistance to water, abrasion, and weather and is crack-free. One of the chemical compounds in gel coat is styrene with the chemical formula C_8H_8, an organic compound with a distinctive odour usually used as a solvent in making gelcoat [19]. The gel coat used by the shipyard is Yukalac G-123 T-EX, produced by PT Justus Sakti Raya. Based on the Material Safety Data Sheet (MSDS), gel coat is classified as a hazardous substance due to flammable liquids and vapors, is thought to damage fertility or fetuses in the womb, causes damage to organs through prolonged or repeated exposure, can cause respiratory irritation, skin irritation, and severe eye irritation. Workers are advised to use personal protective equipment to avoid potential hazards during the FRP shipbuilding process.

B. Chemical Element Content in FRP Composite Materials

The FRP shipbuilding process is related to the use of chemicals. The material contains several chemical elements, such as silicon, calcium, and magnesium. Chemical elements are pure substances that cannot be decomposed into simpler substances through ordinary chemical reactions [20]. Glass fiber used to manufacture FRP composites usually consists of silica (SiO_2), which contains silicon and oxygen. Data on chemical elements contained in FRP composite materials are presented in Table 2.

TABLE 2.
THE CONTENT OF CHEMICAL ELEMENTS IN FRP SHIPBUILDING MATERIALS AT UD WAHYU ASIH FIBERGLASS SHIPYARD

No	Chemical element	Group	Element	Boiling point (°C)	Melting point (°C)	Contained in
1	H (Hydrogen)	IA	Gas	-259,1	-252,9	Polyester resin, catalyst, talc, cobalt naphthenate, gelcoat
2	Na (Sodium)	IA	Solid	883	98	Chopped Strand Mat (CSM), woven roving
3	Mg (Magnesium)	IIA	Solid	1107	648,8	Talc
4	Ca (Calcium)	IIA	Solid	1484	842	Chopped Strand Mat (CSM), woven roving
5	Si (Silicon)	IVA	Solid	2355	1410	Chopped Strand Mat (CSM), woven roving, aerosil, talc
6	C (Carbon)	IVA	Solid	4827	3550	Polyester resin, catalyst, cobalt naphthenate, gelcoat
7	O (Oxygen)	VIA	Gas	-183	-218,8	Chopped Strand Mat (CSM), woven roving, polyester resin, catalyst, aerosil, talc, cobalt naphthenate
8	Co (Cobalt)	VIIIB	Solid	2870	1495	Cobalt naphthenate

Source: pubchem.ncbi.nlm.nih.gov

Based on Table 2, the elements contained in each material used to manufacture FRP composites vary greatly. Some elements, such as oxygen, hydrogen, silicon, and carbon, are found in substantial quantities in the materials used to manufacture composites. In contrast, other elements, such as sodium, magnesium, calcium, and cobalt, are found in relatively smaller quantities. Some elements have reactive properties, such as hydrogen, sodium, magnesium, calcium, cobalt, and oxygen. Reactive materials are dangerous because they can react directly with other substances or polymerize, which is exothermic [21].

Several elements are in the same class: hydrogen and sodium, magnesium and calcium, silicon and carbon. Elements in one group have similar properties because the element has the same electron configuration in its outer shell. Electrons located in the outermost shell are known as valence electrons. The similarity in the number of valence electrons makes the reactivity of elements in one group the same [20].

FRP materials contain two types of elements, namely solid and gas. Materials that are widely used have solid element types. Solid elements have a fixed volume and shape. Particles in solid elements have a strong force of attraction, and the space between particles is tiny, so they have a high density and density [21]. Two materials have a type of gas element, namely hydrogen and oxygen. The gas element has a volume and shape that is not fixed because the particles are not bound to each other and move freely. Gases have a much lower density compared to solids [20].

The temperature at which a substance undergoes a transition from the liquid phase to the gas phase is referred to as the boiling point. With increasing temperature, there is a proportional enhancement in the intensity of translational and rotational movements of molecules, as well as vibrations of atoms and groups of atoms within the molecules. The strength of intermolecular forces of attraction varies significantly, and the boiling point of a compound serves as an indicator of these forces' potency. Elevating the temperature of a sample to the characteristic boiling point of the compound is necessary to overcome the intermolecular forces of attraction that maintain the molecules in a condensed liquid state. According to the provided table, oxygen and hydrogen are the elements with boiling points below 0.

The melting point signifies the energy required to disrupt the bonds and transition a substance from its solid phase to a liquid state. Typically, the strength of bonds between atoms within an element dictates the energy needed for bond disruption. As temperature directly correlates with energy, higher bond dissociation energies align with elevated temperatures. Consequently, the greater the melting point, the stronger the bond among the element's atoms. Particles within such elements demand substantial energy to break these bonds during the transition from solid to liquid. Elements exhibiting robust molecular interactions typically feature high melting points, as significant energy is necessary to sever these interactions. Oxygen and hydrogen are examples of elements with melting points below 0.

The elements' high melting and boiling points in FRP composite manufacturing materials can affect combustion. When the composite material burns, its elements will react with oxygen in the air to produce energy in the form of heat and gases such as carbon dioxide and water. Elements with higher melting and boiling points will require higher temperatures to burn completely. The combustion process will only be complete if the combustion temperature reaches these elements' melting or boiling point. It is essential to ensure that the combustion temperature reaches the melting and boiling point of each element contained in the composite material to ensure the combustion process occurs entirely and is safe for the environment and humans. This can be achieved by controlling the combustion temperature and ensuring that the combustion conditions allow all the elements in the composite material to burn completely. However, in reality, the combustion process is always flawed. If combustion at high temperatures uses air (containing 78% nitrogen), then a tiny part of the nitrogen will react with various types of harmful nitrogen oxides (NO_x) [22].

C. Ash Content of Combustion Residue of FRP Material

Ash is the remaining part of the combustion product. The determination of the ash content of the sample aims to determine the residue left after high-temperature combustion [23]. In laboratory tests that have been carried out, the ash content resulting from burning 2 grams of FRP ship samples on the side is 31.95% or around 15.97% per gram of material. The UD Wahyu Asih Fiberglass Shipyard destroys ship material waste by burning. The combustion produces dense white smoke and creates solid ash that cannot be removed. If the total weight of the ship produced by the shipyard is 99.14 kg, then if burning is carried out to destroy one FRP ship, solid ash will remain as much as ± 15 kg. Inorganic waste that is buried has the potential to pollute the soil, so it is suspected that polluted soil will be difficult to reuse or plant. This statement is supported by Setyaningrum [5], which states that contaminants entering the ground will decrease soil function and cause soil degradation. The display of ash from burning FRP material is presented in Fig 3.

Figure. 3. Ash from burning FRP material

D. Smoke Content of Combustion of FRP Material

U.S. EPA research shows several air pollutant parameters arise from open burning activities, such as CO, CH4, NOx, SOx, VOC, TSP, PM10, and PM2.5. This is one factor contributing to the greenhouse gas emission burden and hurts health. Calculating this emission load is also needed to determine how to manage waste to overcome air pollution problems.

The test results of the content of pollutants produced in the combustion process of the remaining FRP shipbuilding waste show the results of total particulates that exceed the Emission Quality Standard (BME). However, some are still below the BME, as seen in Table 3. BME has been determined in the Minister of Environment and Forestry Regulation Number 70 of 2016, which characterizes an emission to indicate certain air quality as a parameter. In this regulation, it can be seen that burning waste violates laws and regulations.

Particulate matter is a type of pollutant with non-carcinogenic and carcinogenic health risks that harm human health. Not only does particulate pollution affect human health, but it can also affect vision or visibility, damage plant life, and affect regional and global climate. The impacts of particulate pollution on human health include eye irritation, respiratory problems, allergies, and other health problems. The long-term impact of particulate pollution is to increase the risk of heart disease and more fatal respiratory diseases, including lung cancer, and can increase the risk of death [24].

TABLE 3.
THE CONTENT OF SMOKE FROM BURNING FRP SHIPBUILDING MATERIALS AT UD WAHYU ASIH FIBERGLASS SHIPYARD

Parameters	Concentrations (mg/Nm³)	BME (mg/Nm³)
Total particulate	135,8	120
Sulfur dioxide (SO_2)	38,8	210
Nitrogen dioxide (NO_2)	371	470
Hydrogen chloride (HCl)	0,88	10
Carbon monoxide (CO)	431,1	625
Carbon dioxide (CO_2)	10,1	-
Oxygen (O_2)	7,4	11

IV. CONCLUSION

Based on the results of the analysis and testing conducted by the author, the following conclusions can be drawn:

- UD Wahyu Asih Fiberglass Shipyard employs various materials in the construction of FRP ships, including CSM300, WR600, WR800, yukalac 235 resin, mepoxe catalyst, aerosil, miracle gloss, talc, cobalt naphthenate, pigments, and gel coat. Chemical elements detected in FRP materials consist of hydrogen, sodium, magnesium, calcium, silicon, carbon, oxygen, and cobalt.
- The ash content obtained from burning FRP ship waste on-site is 15.97% per gram of material.
- Total particulates emitted during the combustion process of remaining FRP shipbuilding waste surpass the Emission Quality Standard (BME), registering at 135.8 mg/nm³.

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