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CHARACTERIZATION OF RUBBER SEED (*HEVEA BRASILIENSIS*) AS RAW MATERIAL FOR THE PRODUCTION OF BIOFUEL

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Abstract. *Rubber seeds from the Musi Rawas region in South Sumatera have great potential for rubber seed plantations. However, their utilization has not been maximized and they are often treated as plantation waste. This research aims to obtain the characteristics of rubber seeds as raw materials for biofuel production, so that the rubber seeds from the South Sumatera region can be utilized by the community and not just considered as plantation waste. In the first treatment, the rubber seeds are crushed to obtain the seed coat and the kernel. The crushed rubber seed shells are finely ground and sieved, while the kernel is pressed to extract vegetable oil using a pressing tool. The test methods used to determine the characteristics of the rubber seed shells include proximate analysis and calorific value, while GC-MS analysis is employed for the rubber seed oil. The proximate analysis of the rubber seed shell (RSS) yielded the following results: moisture content of 15.97 wt%, volatile matter of 47.43 wt%, fixed carbon of 32.45 wt%, and ash content of 4.15 wt%. The calorific value of the rubber seed shell was found to be 3312.8694 calories per gram. For the GC-MS yield of the rubber seed oil, the composition is as follows: palmitic acid 7.32%, linoleic acid 34.69%, oleic acid 45.35%, and pentadecanoic acid 8.86%. Based on the obtained results, rubber seeds show promising potential as raw materials for biofuel production through the pyrolysis process.*
Keywords: *rubber seed; proximate analysis; calorific value; GCMS analysis; pyrolysis*

1. Introduction

Energy is a crucial necessity for human survival that is in constant demand. The majority of this energy is derived from non-renewable resources, commonly referred to as fossil fuels. Fossil fuels account for 94% of Indonesia's total energy requirements. (Budiastuti *et al*., 2022). The increase in the price of fossil fuels in Indonesia is driving savings and research efforts to find alternative fuel sources. The government is starting to support activities to find new fuel sources such as biodiesel, bioethanol, bio-oil, bio-gas, and fuel from natural gas. (Widayat & Suherman, 2012). Alternative raw material to produce biofuel is biomass. Biomass is defined as all types of carbon materials, excluding fossil fuels. Biomass plays a significant role in the field of environmentally-friendly energy technology due to its abundant availability, renewable nature, and sustainable energy source. (Özyuğuran *et al*., 2018). Biomass pertains to organic material obtained from plants, animals, and microorganisms that has not undergone fossilization. Biomass can come from mining, agriculture, aquaculture, animal husbandry, or in the form of industrial waste and household waste. (Hermiati, 2019). One example of biomass derived from plantation waste is rubber seed waste.

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The rubber plant (*Hevea Brasiliensis*) is one of the tropical plants plantation that is widely cultivated, a part from rubber being used from rubber plants also has another potential, namely in its seeds. Rubber seed kernels contain quite a lot of vegetable oil, with an oil yield of 37.5%. (Widayat & Suherman, 2012). The rubber plant produces shiny, speckled brown seeds 2.5–3 cm long and 2–4 g in weight. The seeds are contained within three ellipsoidal pods, with each pod enclosing three seeds. (Pizzi *et al*., 2020) The rubber seed is an underutilized byproduct, as only a small portion of it is typically used for seeding purposes, The availability is abundant but has not been applied optimally. Rubber seed production in Indonesia presently reaches 5 million tons per year, with an oil rate of 40-50% that can be produced by rubber seeds. (Pulungan *et al*., 2021). Rubber seeds are characterized by their significant size and tough outer skin, weighing approximately 3-5 grams depending on factors such as the type, age, seeds, and moisture content (Nazaruidin & Paimin, 2006). These rubber seeds are composed of approximately 45-50% shell and 50-55% seed kernel (Setyawardhani *et al*., 2010).

Despite the awareness of the beneficial properties found in rubber seeds, their application has not been fully realized. Rubber seeds possess favorable nutritional content, with 68.53 g/100 g of fat, 17.41 g/100 g of proteins, and 6.99 g/100 g of carbohydrates. However, it is important to note that rubber seeds also contain toxic and hazardous substances, specifically cyanide acid (HCN), which can be harmful if consumed (Putri *et al*., 2019).

The Directorate General of Plantations of the Republic of Indonesia reports that in 2020 the area of rubber plantations in Indonesia is measurable to achieve around 3.6 million hectares, include of smallholder plantations (88.12%), nation plantations (5.17%), and private plantations (6.71%) (Junaidi, 2022). According to the 2019 Plantation Statistics Agency, the area of rubber plantations in South Sumatera is 722,054 ha. As many as 400 rubber trees can be planted on 1 hectare of land. So, it is estimated that it can produce 5,050 kg of rubber seeds per year. Therefore, rubber seed has a very large potential as a source of biomass, but its utilization is not maximized and only becomes plantation waste (Direktorat Jenderal Perkebunan, 2018).

There are several methods of converting biomass into an energy source, especially direct combustion which produces heat, gasification produces gases (such as methane, carbon monoxide, and hydrogen), and liquefaction/pyrolysis which produces liquid fuels. (Ram & Mondal, 2022). One of the conversions of biomass into energy is the pyrolysis process.

2. Methods

2.1. Material Preparation

The material used is rubber seeds, a side product by rubber plantations in Musi Rawas Regency, South Sumatera. The rubber seeds are crushed to obtain the seed shells and seed kernels, the shells are finely ground and then sieved, and the kernels are squeezed using a screw press to obtain the vegetable oil contained in the kernels. Then proximate analysis and calorific value was performed on the rubber seed shell and GCMS (Gas chromatography–mass spectrometry) analysis to determine the fatty acid content of the rubber seed.

2.2. Proximate analysis

The Rubber seed shell was weighed and subsequently transferred to stainless steel trays. These trays were then placed inside a drying oven maintained at a constant temperature of 105°C for one hour. Afterward, the biomass was cooled to room temperature using a desiccator and weighed once more. The moisture content is subsequently determined by applying the Equation (1).

$$A = \frac{(\mathrm{WI-Wf})}{WI} \times 100\% \quad (1)$$

Where A represent moisture, WI represent the initial weight of the sample (before drying), and Wf represent the weight of the sample after drying.

The laboratory muffle furnace (Carbolite Type 301) was used to determine the ash content following the standard ([ASTM] D-3174, 2012). A biomass sample weighing 1.0 g was placed in a crucible and placed inside the furnace, which was maintained at a temperature of 600 ± 10 °C for 4 hours. Subsequently, the crucible was removed from the furnace and placed into a desiccator for cooling. This cycle of heating and cooling was repeated until a consistent weight was attained, indicating the presence of ash content.

The determination of volatile matter in the biomass followed the procedure described in ([ASTM] D-3175, 2011). A biomass sample weighing 1g was placed inside a muffle furnace, which was kept at a constant temperature of 950 ± 10°C for a duration of 7 minutes. Subsequently, the crucible was removed from the furnace and transferred to a desiccator. The volatile matter content was determined by measuring the weight loss incurred during the process.

The results for ash content and volatile matter are reported based on a wet basis.

2.3. Calorific Value

The bomb calorimeter is a device utilized to quantify the heat released during the complete combustion (in the presence of excess oxygen) of various substances such as compounds, food, and fuels. Multiple samples are placed inside an oxygen-filled tube, which is submerged in a heat-absorbing medium known as a calorimeter. An electrically heated wire within the tube ignites and burns the samples.

2.4. GCMS (Gas chromatography–mass spectrometry)

GC-MS (Gas Chromatography-Mass Spectrometry) is used to determine the fatty acid content in rubber seed oil.

3. Results and Discussion

3.1. Proximate analysis

Proximate analysis was used on rubber seed shell samples to determine moisture content, volatile matter, ash content, and fixed carbon. The results of the Proximate Analysis can be seen in Figure 1.

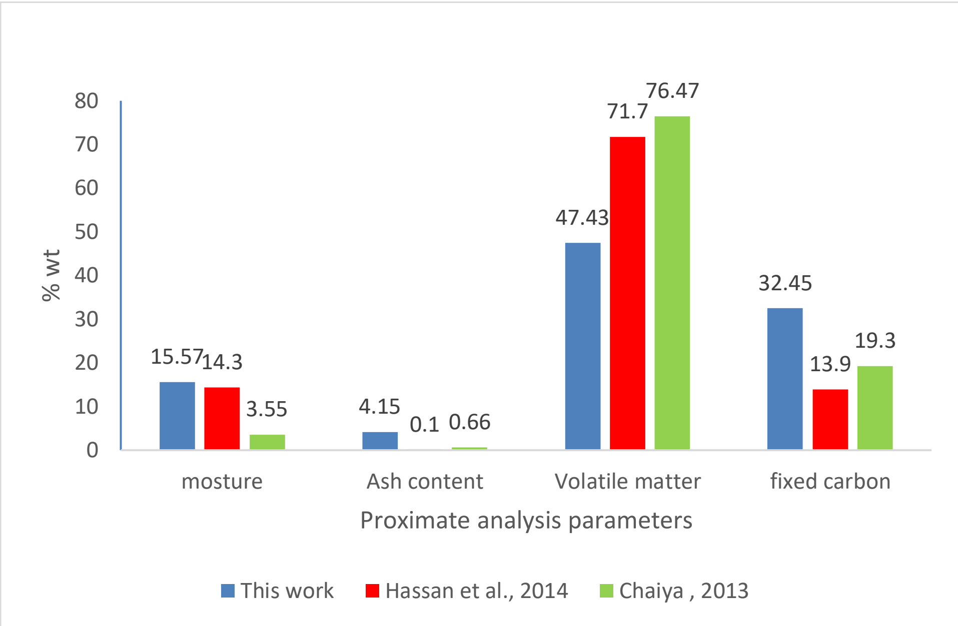

Figure 1. Graph Comparasion Proximate analysis of rubber seed shells with (Hassan *et al.*, 2014) (Chaiya & Reubroycharoen, 2013)

Figure 1 above illustrates that the immediate outcomes of the rubber seed shells indicate a water content ranging from 15.97% by weight. This value is higher compared to the water content of 14.3% wt (Hassan *et al.*, 2014) and 3.35% wt (Chaiya & Reubroycharoen, 2013). The study revealed that the relatively high water content was attributed to imperfect drying of the material. The moisture content of biomass is a significant operational parameter that frequently fluctuates, as noted in the report by (Hermansson *et al.*, 2011). The presence of water content complicates the processing in the reactor and leads to increased energy consumption during reactor pyrolysis

The ash content of the rubber seeds in the study was found to be 4.15% by weight. This result is higher compared to the ash content of 0.1% wt (Hassan *et al.*, 2014) and 0.6% wt (Chaiya & Reubroycharoen, 2013). The elevated ash content can be attributed to the presence of non-combustible materials, such as minerals or inorganic compounds, which are relatively abundant. According to (Sasmal *et al.*, 2012), a high ash content hinders enzymatic hydrolysis, specifically biomass saccharification. Given the relatively high ash content in the rubber seed sample, it is anticipated that the sample will undergo a slight decrease in enzymatic hydrolysis.

The Volatile Matter content of the rubber seed coat was determined to be 47.43% wt. This result is lower compared to the research conducted by (Hassan *et al*., 2014), which showed a result of 71% wt, and (Chaiya & Reubroycharoen, 2013), which showed a result of 76.7% wt. A substantial amount of volatile matter signifies the material's high susceptibility to melting. Therefore, it is expected that the pyrolysis results will be more optimal. Biomass with a higher fraction of volatile matter exhibits higher conversion rates compared to biomass with a higher fixed carbon content. In theory, biomass with a high volatile matter content is more suitable for bio-oil production, Biomass possessing a considerable concentration of fixed carbon is better suited for the production of biochar. (Vassilev *et al*., 2010)

3.2. Calorific Value of Rubber Seed Shells

The calorific value of rubber seed shell samples was determined using the bomb calorimeter method. The high calorific value of rubber seed shells indicates that it has the potential as a biomass for biofuel production. The high calorific value of rubber seed shells indicates that comparatively, it is a potential biomass for biofuel production (Hassan *et al*., 2014). The results of the calorific value of Rubber Seed Shells can be seen in Table 1.

Table 1**.** Calorific value

Sample	Calorific value	SNI (Indonesian Standard)
Rubber Seed Shell	3312.8694 cal/gr	4000 cal/gr

The calorific value of the rubber seed shell sample ranges from 3312.8694 Cal/gr. However, this value does not meet the National standard SNI 8021:2014, which requires a minimum value of around 4000 cal/gr. A higher calorific value of biomass can generate energy-rich pyrolysis products, such as biochar, which can be utilized as a fuel source (Raveendran & Ganesh, 1996). As a result, if the sample is used as a raw material for pyrolysis, it will yield a small quantity. The lower calorific value is attributed to the relatively high humidity determined in the previous proximate analysis, which was approximately 15.97%. The presence of high moisture content can impede the pyrolysis process by affecting the raw material and subsequently reducing the fuel's calorific value (Wulandari, 2022). Increasing the calorific value can be done by maximizing drying in the pre-treatment process by using a long time and using a dryer or oven as a supporting tool.

3.3. GCMS analysis

Based on the GCMS data in Table 2, it can be seen that the primary fatty acid component found in rubber seed oil.

Table 2. The primary fatty acid component found in rubber seed oil

Composition	Molecular formula	% wt
palmitic acid	CH3(CH2)14COOH	7,32
Linoloic acid	CH3(CH2)4CH=CHCH2CH =CH(CH2)7COOH	34,69
Oleic acid	CH3(CH2)7CH = CH(CH2)7COOH	45,35
pentadecanoic acid	CH3(CH 2)13CO2H	8,86

The composition of triglycerides or fatty acids at rubber seed influences the structure of the hydrocarbon chain during the process of pyrolysis in liquid products. subjected stearic acid to pyrolysis, This leads to the formation of bio hydrocarbons, predominantly comprising a range of hydrocarbons from carbon numbers C1 to C4, with only a minimal presence of C8 alkane-alkene (5%) (Maher & Bressler, 2007). Conversely,when oleic acid and linoleic acid undergo pyrolysis, the resulting bio hydrocarbons consist of a considerably greater proportion of hydrocarbons spanning from carbon numbers C6 to C10. These findings indicate that the pyrolysis of unsaturated fatty acids generates a considerably larger fraction of gasoline-like hydrocarbons compared to the pyrolysis of saturated fatty acids (Asomaning *et al*., 2014).

4. Conclusions

Rubber seeds are a good raw material for biofuel production due to their relatively high content of volatile matter. However, the moisture content of 15% in the samples needs to be reduced as it can hinder the performance during the pyrolysis process. The moisture level can be reduced by choosing a more optimal drying method. The calorific value analysis of rubber seed shells shows a value of 3312.8694 calories per gram. This calorific value is considered low and does not meet the SNI (Indonesian National Standard) due to the relatively high moisture content. Biomass with a higher calorific value can generate pyrolysis products that are more energy-rich, such as biochar. The composition of triglycerides or fatty acids in rubber seeds affects the structure of the hydrocarbon chain in the liquid pyrolysis products. The fatty acid composition of rubber seed oil includes 7.32%wt of palmitic acid, 34.69%wt of linoleic acid, 45.35%wt of oleic acid, and 8.86%wt of pentadecanoic acid. Oleic acid and linoleic acid undergo pyrolysis, the resulting bio hydrocarbons consist of a considerably greater proportion of hydrocarbons spanning from carbon numbers C6 to C10. Based on the obtained results, rubber seeds show promising potential as raw materials for biofuel production through the pyrolysis process.

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