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Efficient Bio-Oil Production from Coconut Shells Using Parabolic Solar Pyrolysis

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ABSTRACT

The study provides valuable insights for the potential of coconut shell as a renewable energy source for bio-oil production using parabolic solar pyrolysis The primary objectives of this study were to assess the efficacy of parabolic solar pyrolysis in bio-oil production, analyze coconut shells and biochar, conduct pyrolysis experiments, identify parameters influencing pyrolysis, carry out performance tests, and analyze the composition of bio-oil compounds. The research methods used include energy analysis, optimization of parabolic solar pyrolysis systems, performance calculations, analysis of GC/MS of bio-oil compounds, and the assessment of biochar. The proximate analysis of the coconut shells revealed that they consisted of 47.37% fixed carbon, 1.89% ash, 11.32% moisture content, and 77.8% volatile matter. The heating rate during the process was in the range of 5-150°C/min. The factors affecting the performance of parabolic solar pyrolysis include the light radiation intensity, parabolic area, receiver, and reactor material. The temperature generated by the solar pyrolysis concentrator was in the range of 300-650°C. The study found varied bio-oil, biochar, and gas yields influenced by the particle size and pyrolysis temperature. The main compounds in the bio-oil were phenol, furfural, cresol, creosol, syrigol, guaiacol, pentadecanoic acid, and carbonyl compounds.

1. INTRODUCTION

Coconut shell is one of the biomass wastes that has the potential to be developed into a renewable energy source. The potential for coconut shells in West Sumatra and Indonesia is very large because coconuts are necessary in everyday life. Coconut shells have good thermal diffusion properties compared to other materials, such as wood, so they have a great opportunity to be used as a substitute fuel [1]. In addition, coconut shells have a calorific value of 18,388 kJ/kg and has 18.29% carbon components and 67.67% volatiles, which are more easily converted into liquid [2]. The chemical composition of the coconut shell includes 29.4% of lignin, 27.7% of hemicellulose, 26.6% of cellulose, 8.0% of water, 0.6% of ash content, 4.2% of extractive components, 3.5% of uronic anhydrous, and 0.1% of nitrogen.

Coconut shells possess a higher carbon and volatile content, allowing for more liquid and charcoal production. It is an ideal material for physical processing due to its tough natural structure and low ash content, making it an ideal material with a minimal environmental impact and ease of processing [3]. Like other biomass materials, coconut shells contain lignin, cellulose, and hemicellulose. Therefore, understanding the pyrolysis characteristics of these compounds is imperative. The significance of coconut shells in pyrolysis arises from their role as a sustainable source of biomass that can be efficiently utilized in producing bio-oil and valuable by-products.

One of the energy conversion techniques for coconut shells is pyrolysis, which converts coconut shells into bio-oil, biochar, and gas using a closed combustion method at high temperatures. The pyrolysis technique is a thermochemical method in which biomass waste is converted into solid fuel (char), gas (syngas), and liquid (bio-oil) without the presence of oxygen in a reactor [4]. In other words, pyrolysis is a process of thermochemical decomposition of organic matter that takes place without air or oxygen. According to Basu [5], pyrolysis of biomass generally takes place in the temperature range of 300°C to 600°C. This process is more efficient and flexible compared to other thermochemical conversion processes. Based on Li et al. [6], the amount of bio-oil yield produced increases in line with the increase in optimal temperature, after which it decreases if the temperature is too high.

The pyrolysis process requires high temperatures for its thermochemical decomposition, so it uses wood or gas stoves as a source of heat energy. Research by Novita et al. [7] involved the design of a pyrolysis device to produce bio-oil through the use of a gas stove and a firewood-burning stove. Burning stoves used gas and firewood, but the operating costs were quite high. Moreover, firewood was difficult to collect. This high cost increased the production cost of bio-oil. Moreover, Novita et al. [8] conducted research using a wood stove to pyrolyze rice husks into bio-oil with a combustion temperature of 300-500°C. It was found that the utilization of this heat energy required big costs and temperatures that could not be controlled.

Concentrated solar energy is one source of heat energy capable of producing high temperatures. Solar energy can be increased in intensity if a solar collector with concentrated solar power (CSP) is used. CSP is considered a very promising renewable energy technology because of its ability to generate heat and electricity and easily store heat energy in thermal storage devices [9]. Concentrated solar radiation can produce high temperatures to heat biomass pyrolysis [10]. As also stated by Zeng et al. [11], solar energy has the potential to make bio-oil with a high heating value and lower CO_2 emissions compared to conventional pyrolysis.

Solar energy and biomass are the two main energy sources in renewable energy, which can be integrated to produce heat, power, transportation fuels, chemicals, and biomaterials using pyrolysis [12]. Parabolic dish solar collectors are a type of CSP system developed in many countries because, until now, this technology is considered the most mature and has proven its use to be effective [13]. Solar power generates heat energy by using mirrors or lenses to concentrate a large area of sunlight or solar thermal energy into a smaller area. CSP generally requires large amounts of direct solar radiation, and its energy generation drops significantly if clouds cover it. Pyrolysis using CSP parabolic is economically feasible, environmentally friendly, practically for dry countries, and has agricultural potential [14].

Based on this consideration, this study was carried out using concentrated solar energy to heat a pyrolysis reactor using coconut shells as a raw material. The solar concentrator used was a parabolic dish that used a stainless steel mirror as a reflector. The study provides valuable insights for the potential of coconut shell as a renewable source for bio-oil production using parabolic solar pyrolysis. The primary objectives of this study were to assess the efficacy of parabolic solar pyrolysis in bio-oil production, analyze coconut shells and biochar, conduct pyrolysis experiments, identify parameters influencing pyrolysis, carry out performance tests, and analyze the composition of bio-oil compounds.

2. MATERIALS AND METHODS

2.1 Coconut shell feedstock

Coconut shells collected from the waste of coconut milk processing in the Harau District, Limapuluh Kota Regency, West Sumatra, Indonesia. The coconut shell was dried using a dryer at 70°C for ten days until the water content reached 8-12%. The dried raw materials were then ground using a grinder, resulting in 3, 5, and 10 mm sizes. Coconut shell particles of 3, 5, and 10 mm were selected to determine the optimal particle size for producing high levels of bio-oil while also considering that coconut shells are hardwood and relatively resistant to decomposition. Coconut fragments of sizes 0.1-1, 4-8, and 10-20 mm were placed in a digital thermostat-controlled oven at a temperature of 120°C for 12 hours before assessment [3]. Particle size had a predominant impact on transfer properties, with a critical size determining the shift in the regime for different components [15]. Bio-oil production is adversely affected by particle sizes that are either too small or too large [16].

The composition of the coconut shells was determined using proximate analysis. This analytical method was employed to determine the moisture content, volatile components, fixed carbon, ash content, and inorganic residue remaining after combustion. Theoretically, biomass with a high volatile fraction is deemed more suitable for bio-oil production, whereas biomass with a high fixed carbon content is considered more suitable for biochar production [17].

2.2 Solar pyrolysis experiments

The design of the pyrolysis reactor involved the development of both functional and structural aspects. The heat collector circuit was designed to achieve a combustion temperature of 300-600°C. It is important to note that the pyrolysis temperature significantly influences the characteristics of the bio-oil and the overall yield produced.

The functional design describes the function of each component of the pyrolysis reactor. Pyrolysis reactor components include:

1. A pyrolysis reactor served as a place to accommodate raw materials to be burned.
2. Smoke distribution pipe, which served to drain the air or smoke produced by the combustion in the reactor
3. Concentrated Solar Power (CSP), which serves to gather solar radiation and is focused at one point to heat the pyrolysis reactor in the form of a parabolic dish
4. The frame and stand of the concentrator, which functioned to support the position and seat of the concentrator
5. Thermocouple type K, which was used to measure the maximum temperature in the pyrolysis reactor
6. Arduino, which is a device that can display temperature automatically
7. The condenser, which functions to condense hot air streams (smoke) into liquid
8. The bio-oil discharge valve, which functions to remove bio-oil produced from the condensation process
9. The bio-oil reservoir, which serves to accommodate the bio-oil produced

The design of the parabolic dish solar pyrolysis can be seen in Figure 1.

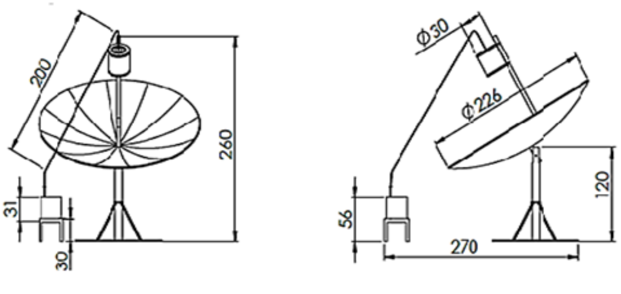


Figure 1. Parabolic dish solar pyrolysis reactor

2.3 The working principle of the parabolic dish concentrator

There are several working principles for parabolic dish concentrators, which include:

1) To concentrate the sunlight: in this study, the parabolic concentrator, which was covered by a stainless steel mirror plate, would absorb solar energy and reflect the light. The reflected light would be used to centralize the light and heat of the sun towards a focal point in the smaller area. The energy that was concentrated at one point would produce heat that could be used for the pyrolysis process.
2) To convert the light into heat energy.
3) To trap the heat.

2.4 Calculation of pyrolysis performance

1) Calculation of the optimal reactor temperature of 300-600°C
2) Heating rate, the rate of increase in temperature per minute is expected to be 5 - 200°C/min
3) Length of combustion time (retention time)
4) Calculation of yield of bio-oil, biochar, and gas can be seen in the equation below.

$$Y_{\text{Bio-oil}} = \frac{Wb \times 100\%}{WT} \tag{1}$$

$$Y_{\text{Biochar}} = \frac{Wc \times 100\%}{WT} \tag{2}$$

$$Y_{\text{Gas}} = \frac{Wg \times 100\%}{WT} \tag{3}$$

2.5 Analysis of bio-oil compounds using GC/MS

Gas chromatography and mass spectrometry (GC/MS) enable the identification of the constituent compounds present in bio-oil. The experimental protocol comprised the use of an Rtx 5MS 30-m column, with the injector temperature set at 280°C, column temperature at 50°C, and temperature increase at a rate of 10°C/min until it reached 270°C. The interphase temperature was maintained at 280°C. Before injection, the bio-oil underwent a series of preparatory steps, including storage at ambient temperature, homogenization, folding, and humidification. Finally, the prepared bio-oil was injected into the GC-MS system for analysis. Compounds derived from bio-oils can be identified using retention time and mass spectral analysis.

2.6 Analysis of biochar compound and energy

Analysis of compounds contained in biochar was carried out using proximate analysis and analysis of energy was done using a bomb calorimeter.

3. RESULTS AND DISCUSSION

3.1 Coconut Shells characterization

Proximate analysis was carried out to determine the coconut shell's characteristics, including moisture, volatile matter, fixed carbon, and ash content. Meanwhile, the ultimate analysis test determined the amount of carbon, hydrogen, nitrogen, sulfur, and oxygen (CHNSO) in coconut shells and biochar. Based on Rout et al. [18], proximate and ultimate analysis can determine the characteristics of the resulting pyrolysis products. Moreover, the characteristics of the coconut shell can determine the amount of bio-oil, biochar, and gas produced by the pyrolysis process. The main properties of coconut shells with proximate, ultimate, and energy analysis with a bomb calorimeter are shown in Table 1.

Table 1. The main properties of coconut shell

Analysis	Cococnut Shell
Proximate Analysis (% mass, dry)	
Fixed carbon (%)	47.37
Ash (%)	1.89
Volatile matter (%)	77.8
Moisture (%)	11.32
Dry matter content (%)	88.68
Ultimate Analysis (% mass, dry)	
C (%)	47.37
H (%)	-
N (%)	0.6
Organic matter (%)	98.11
Energy Analysis (cal/gr)	3543.46

Based on the analysis carried out in this research, the compounds contained in the coconut shells were 47.37% fixed carbon, 1.89% ash content, 11.32% moisture content, and 77.8% volatile matter. However, several previous studies that had been conducted provided different results. Research done by Rout et al. [19] found that coconut shells had characteristics of 10.1% moisture content, 75.5% volatile content, 11.2% fixed carbon content, and 3.2% ash content. Meanwhile, a study by Sarkar [20] stated that coconut shells contained 7.82% moisture, 79.91% volatile matter, 12.04% fixed carbon, 0.23% ash, 39.22% carbon, 4.46% hydrogen, 0.22% nitrogen, 56.10% oxygen, and a heating value of 9.62 MJ/kg. Monir et al. [21] found that the elemental composition of coconut shells, which are assumed to be C, H, and O, was 45.03%, 6.94%, and 47.47%, respectively.

Another finding was from Azeta et al. [22] that stated that the composition of coconut shell compounds included 29.7% of lignin, 23.8-27.71% of hemicellulose, 29.58-65% of cellulose, 1.7-3.8% of ash, and 4.2% of extractive content. Theoretically, biomass characterized by a substantial volatile component is considered more appropriate for generating bio-oil, whereas biomass featuring a high fixed carbon content is deemed more suitable for biochar production [17]. In this study, the coconut shell exhibited a sufficiently elevated volatile fraction, making it well-suited for bio-oil production.

3.2 Parabolic dish solar pyrolysis design

The described solar pyrolysis system employs a parabolic design to harness direct sunlight, concentrating heat at a single focal point through an open parabolic reflector. This parabola absorbs solar energy and directs it to a focal point within a pyrolysis reactor. The reflective surface of the parabolic dish is composed of a 1-inch stainless-steel mirror that effectively transforms sunlight into heat energy. The parabola has a base diameter of 2.26 m, an arch height of 0.32 m, and total area of 0.482 m^2. The stainless-steel mirror plate is an excellent reflector for absorbing and reflecting energy in pyrolysis reactors. This parabolic solar concentrator is specifically designed to produce heat or high-temperature energy.

The parabolic dish solar pyrolysis reactor is a tool for decomposing organic compounds, which is performed through a heating process without direct contact with outside air at a temperature of 300-600℃. The reactor determines the heat transfer quality, processing time between the gas and liquid phases, and main product output [23]. Solar pyrolysis is the same as conventional pyrolysis, which uses external heat energy but uses concentrated solar energy to heat the pyrolysis reactor system [24]. The primary components of the solar pyrolysis system include a fixed-bed fire-tube heating reactor, liquid condenser, and collectors [19].

The system of parabolic dishes is similar to a trough, utilizing the geometric properties of a three-dimensional parabola (Figure 2). The reflected direct beam radiation is concentrated on a point focus receiver, and the CST system can heat it to an operating temperature of over 1000℃, similar to a tower system. The concentrator mirrors produced are made of thin glass with a reflectance of 93.5%. Efforts to increase the reflectance value can reach 95% by the end of 2015 using polymer materials or aluminum coating techniques [25].

According to Abu Bakar et al. [26], the refractive index is another factor that can change the optical efficiency and reception angle of the concentrator. A parabolic concentrator absorbs light that enters the receiver through reflection, and concentrates it at a single focal point of the concentrator [27]. The main advantage of using a parabolic concentrator is that it can obtain a higher geometric concentration with a smaller field of view [28]. The dish system offers the highest potential solar conversion efficiency among all CSP technologies, as it displays the aperture directly towards the sun.

The main products of solar pyrolysis are bio-oil, biochar, and gases. Solar pyrolysis products have a higher calorific value for storing solar energy as chemical energy [29]. Using solar energy is profitable and reduces the production costs for the pyrolysis process because it uses concentrated solar power. As reported by Joardder et al. [30], solar pyrolysis (Figure 2) can reduce the production cost of a pyrolysis system by one-third.

Figure 2. Parabolic solar pyrolysis

The parameters that influence the performance of solar pyrolysis include drying and reducing the size of the coconut shell, moisture content, light intensity, reflector material, wind speed, temperature, reactor type, heating rate, residence time, and pyrolysis temperature. In the technique of pyrolysis, several parameters that affect the pyrolysis process are the pretreatment of biomass, moisture content, particle size of the material, composition of the biomass compounds, temperature, heating rate, gas flow rate, residence time, type of pyrolysis, type of pyrolysis reactor, and final pyrolysis product [31]. The parameters considered in this study were as follows:

1) Pretreatment: drying and reducing the material size

The initial treatment for the coconut shell involves drying and reducing the size of the material, which affects the quality of the bio-oil produced and the performance of solar pyrolysis. Hassan et al. [32] stated that the pretreatment of biomass carried out in the fast pyrolysis process has been proven to change the structure and chemical composition of biomass, which causes changes in the mechanism of the thermal decomposition of biomass.

In this study, the coconut shells were cleaned to remove all impurities and broken into pieces to reduce their size. Then, they were dried for two weeks at 80-100℃ to obtain a moisture content of 8-11%. As Wang et al. [33] stated, the biomass drying process to reduce moisture content uses hot airflow at 150℃. The lower the moisture content of the material, the faster the combustion process in the reactor, and the better the quality of the bio-oil and bio-charcoal produced. When the moisture content of the material in this study was higher than 10%, the water content of the bio-oil was also higher. Therefore, it would prolong the bio-oil purification process. Thus, it can be said that a low water content can accelerate the thermochemical decomposition of materials. The effect of low water content on the material can increase the amount of bio-oil produced and phenol compounds produced during the pyrolysis process [34]. In addition, a significant increase in temperature accelerates the reduction of the water content in the material [35].

After drying, the coconut shells were reduced in size by using a grinder. The samples were placed in a pyrolysis reactor. The data obtained showed that 10 mm and 5 mm coconut shells were more flammable than finer raw materials. This shows that the size of the material significantly affects the combustion process in the pyrolysis reactor. This can be observed in the short time spent during the pyrolysis process for materials with larger sizes.

The particle size of the material usually used after cutting is 10-30 mm, and after milling, it is 0.3-1.5 mm [36]. Research conducted by Shen et al. [37] found that a smaller particle size of the material, 0.3-1.5 mm, could increase the amount of bio-oil produced. This is slightly different from the results described in previous articles, which stated that raw material sizes of 10 mm and 5 mm were more explosive than fine or very fine particle sizes. This study found that fine materials require a long combustion time. If the burning time on the finer material was the same as the more significant material size, then most of the finer material size was not entirely burned during the combustion process. The fine size of the material required a long time for the combustion process or a longer retention time.

2) Temperature

Temperature is a very influential factor in providing maximum results in the pyrolysis process. The function of temperature in the pyrolysis process is to provide the heat needed to decompose the chemical bonds of the biomass. The temperature generated by the parabolic solar pyrolysis concentrator was 300-650℃. The degree of temperature generated by this parabolic concentrator depend on the intensity of sunlight and wind speed. When the sun's intensity was high, the resulting temperature would increase, and vice versa. However, it was different from the wind speed. The stronger the wind, the lower the resulting temperature, even though the intensity of sunlight was very high.

Furthermore, the temperature can determine the conversion efficiency of the decomposition of biomass compounds. This is because the increase in temperature can accelerate the process of breaking the bonds of biomass compounds. Many studies have shown that a temperature of 450-550°C results in a high amount of bio-oil, but this result may change depending on the type of biomass used and other process variables [38].

3) Heating rate

The heating rate is important in determining the final product of the pyrolysis process because it affects the properties and composition of the final product. The low heating rate will reduce the pyrolysis reaction and prevent the thermal breakdown of the biomass, which produces more charcoal than bio-oil. The heating rate obtained during this process was 5-150°C/minute. This heating rate produced 25-37% of bio-oil yield.

A high heating rate will speed up the decomposition process of biomass compounds so that they produce more bio-oil and gas [39]. At a high heating rate, secondary pyrolysis helps the formation of gas components. The effect of a low heating rate can be seen by the more charcoal produced [40]. Uzun et al. [41] examined the pyrolysis of soybean meal using a fixed-bed reactor and obtained results that stated that a higher heating rate led to a higher increase in the amount of bio-oil. The increase in heating rate from 5-700°C/min increased bio-oil production by 23.36%.

4) Retention time

The factor that affects the decomposition of solid biomass materials into bio-oil and gas is the retention time of the materials in a reactor. Long residence times will produce a higher bio-oil yield. Jamaluddin et al. [42] and Tsai et al. [43] stated that retention time greatly affects the composition of the bio-oil and gas compounds produced from the pyrolysis process. Still, it does not significantly affect the charcoal produced. The incomplete repolymerization of the biomass components and the small production of charcoal is caused by the very short retention time of the vapour [44].

Low temperatures cause longer residence times, which results in higher charcoal products. In the fast pyrolysis of poplar wood, the amount of charcoal produced increases by residence time [45]. Thus, the effect of retention time is often greatly influenced by temperature, heating rate, and other parameters.

3.3 Performance test of parabolic solar pyrolysis

The performance test of parabolic solar pyrolysis was conducted using raw materials with different particle sizes and temperatures. The pyrolysis performance was calculated to determine the effect of the quantity and quality of the results obtained using solar pyrolysis tools on the bio-oil yield.

The products produced from testing raw materials with a size of 10 mm were 25.33-33% bio-oil, 56-72% of biochar, and 2.67-11.5% gas. As shown in Figure 3, the yield of bio-oil produced with this material at 600-650°C was 33%. The highest yield of biochar obtained at 300-350°C was 72%, and the highest yield of gas produced at 600-650°C was 11%.

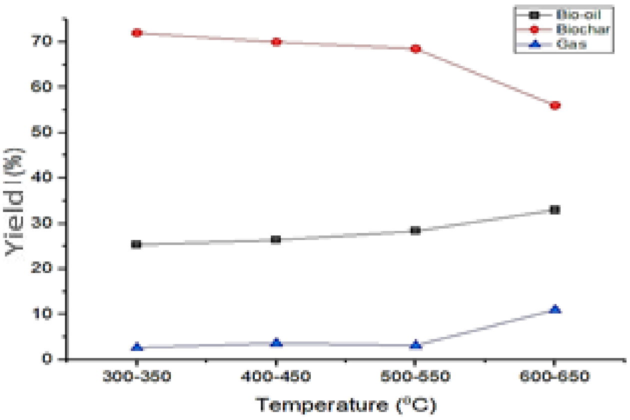


Figure 3. Effect of temperature and particle size of 10 mm on yield

Based on a performance test with a particle size of 5 mm and temperature of 300-650°C, 27.5-34.5% bio-oil, 47.5-69% biochar, and 3.5-18% gas were obtained. The highest bio-oil yield produced at 450-550°C was 34.5%, and the highest biochar yield at 400-500°C was 69%. Based on research conducted by Kato et al. [46], the pyrolysis temperature that has the most significant influence on determining the characteristics of bio-oil and increasing the yield of bio-oil is a pyrolysis temperature of 450-550°C. The highest oil yield of 75.74 wt% (including water) was achieved with a final temperature of 575°C, a heating rate of 20°C/min, and a particle size of 5 mm for the coconut shell. The results were higher because of the high water content of the material, which, as is known at this time, is higher than the results obtained for the other materials [3].

The concentration of bio-oil decreased significantly with increasing pyrolysis temperature; pyrolysis temperature and residence time played an important role in determining bio-oil characteristics. The performance test of solar pyrolysis with a particle size of 5 mm is shown in Figure 4.

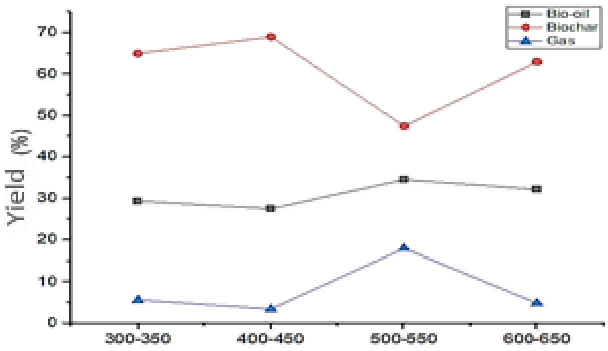


Figure 4. Effect of temperature and particle size of 5 mm on yield

The products produced from testing with a particle size of 3 mm were 26.83-37.67% bio-oil, 46.5-61% biochar, and 12.17-21.07% gas. The amount of bio-oil produced with a particle size of 3 mm at 600-650°C was 37.67%. The highest amount of biochar obtained at 300-350°C was 61%, and the highest amount of gas produced at 400-450°C was 21.07%. The performance test of solar pyrolysis with a particle size of 3 mm is shown in Figure 5.

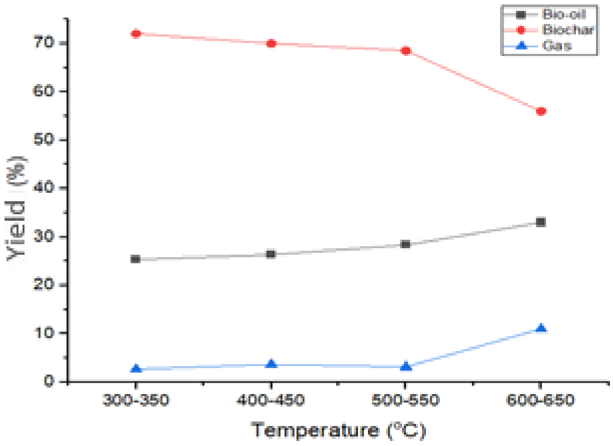


Figure 5. Effect of temperature and particle size of 3 mm on yield

From the performance tests conducted, it can be concluded that smaller particle sizes and high-temperature factors of ≥ 650℃ can increase the yield produced in this solar pyrolysis process. The study found varied yields of bio-oil, biochar, and gas, influenced by the particle size of the coconut shells and pyrolysis temperature.

The bio-oil yield varied from 21.9% to 75% depending on the biomass used, reactor type, and reactor temperature [47]. Differences in yield from the above tests are caused by several factors, including weather conditions at the time of testing, changing wind speeds, human error, and the conditions of the measuring instruments. Coconut shell fragments with sizes less than 1 mm, 4-8 mm, and 10-20 mm were examined at a heating rate of 10℃/min, reaching a final pyrolysis temperature of 575℃. The optimal yield was observed for particles of intermediate sizes. The variation in yield based on size has been attributed to the distinct heat transfer rates in materials of different sizes [3].

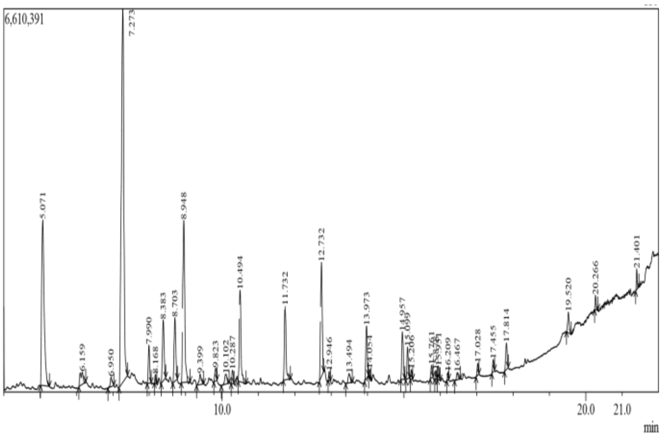
The resulting char, bio-oil, and gas yields ranged from 22 to 31%, 38 to 44%, and 30 to 33% under various pyrolysis conditions. These findings suggest that the impact of pyrolysis temperature and particle size on the yield is more pronounced than that of heating rate and residence time [19]. Pyrolysis experiments were conducted at various temperatures and particle sizes to maximize the liquid yield from the coconut shell pyrolysis. The highest yield was achieved at 550℃, with varying yields of char, liquid, and gas [48].

3.4 Bio-oil characterization

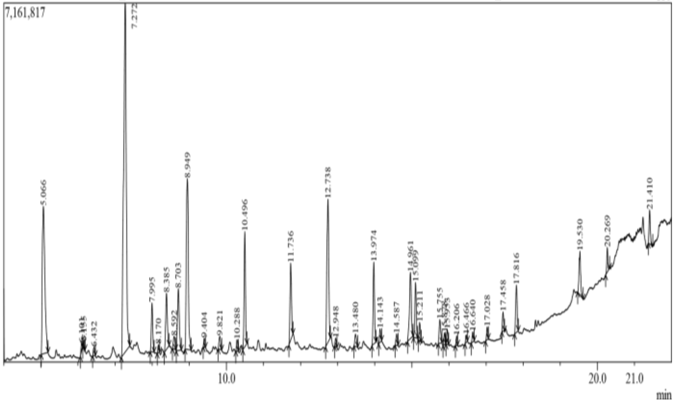
The pyrolysis of coconut shells produces bio-oil, which can be used to create value-added products and chemical raw materials. Bio-oil, which is categorized as a type of tar, typically contains elevated oxygen levels, rendering it non-hydrocarbon in nature. Consequently, it differs significantly from analogous petroleum products. Their naturally strong structure and low ash content make coconut shells ideal for simple physical processing, resulting in a low environmental impact. Bio-oil is a liquid fraction produced from pyrolysis with a combustion temperature with solar pyrolysis of 300-650℃. The bio-oil (Figure 6) produced from this solar pyrolysis process had different characteristics from the bio-oil produced from the pyrolysis process, which used wood or gas stove fuel.

The characteristics of bio-oil are shaped by its physical and chemical attributes and the pyrolysis method employed in converting lignocellulosic biomass [49]. The composition of bio-oil is complex and comprises numerous chemicals. Identification was carried out using GC/MS, classifying them into various families based on their functional groups, such as acids, ketones, aldehydes, phenols, furans, anhydrosugars, and hydrocarbons, based on their functional groups [50]. There are hundreds of organic compounds in the bio-oil, including alkanes, aromatic hydrocarbons, and phenol derivatives, as well as small amounts of ketones, esters, ethers, sugars, amines, and alcohols with H/C molar ratios greater than 1.5 [51]. Over 300 molecules are present in bio-oil, mainly resulting from decomposing three primary biomass constituents: cellulose, hemicellulose, and lignin. These compounds are susceptible to thermal and chemical degradation [52]. During the pyrolysis of lignocellulosic materials, phenolic compounds were identified in the resulting bio-oil. This section overviews the research efforts to produce phenolic compounds and bio-oil fractionation.

Figure 6. Bio-oil



(a) Compounds Contained in Bio-oil at temperature 600℃



(b) Compounds Contained in Bio-oil at temperature 500℃

Figure 7. GC-MS spectra of the bio-oil at different temperatures

Bio-oil quality factors include combustion temperature, moisture content, and raw material size. The characteristics of this bio-oil were that it had a more transparent color, a slight smell of smoke, and contained little tar. The features of the compounds in bio-oil were determined using GC-MS. The bio-oil components under examination are derived from solar pyrolysis products. The analysis focused on temperature variations (600 and 500°C) used in bio-oil production. The graph in Figure 7 illustrates the compounds identified by the GC-MS.

Figure 7 presents a graphical representation of the results of GC/MS testing conducted over a specific period, which helps identify and quantify the various compounds present in bio-oils. The chart displays a high curve, indicating the prevalence of compounds in the bio-oil, and a low curve representing compounds found in lower amounts. It is essential to note that the bio-oil subjected to GC/MS testing was obtained from the parabolic dish solar pyrolysis process, which employed combustion temperatures of 400, 500, and 600°C. The graph revealed that many compounds were present in substantial quantities. The wealth of information derived from the chart highlights the effectiveness of GC/MS in characterizing the composition of the bio-oil samples.

The composition of bio-oil was determined by the curve in the GC/MS graph, and a comparison of the quantity of compounds is provided in Table 2.

Table 2. Compounds identified by GC-MS at different temperatures

Compounds Detected at 600℃			**Compounds Detected at 500℃**		
R Time	**Name of the Compound**	**Area (%)**	**R Time**	**Name of the Compound**	**Area (%)**
5.071	2-Furancarboxaldehyde ($C_5H_4O_2$)	13.56	5.066	2-Furancarboxaldehyde	11.29
6.159	2-Furancarboxaldehyde ($C_5H_4O_2$)	1.23	7.272	Phenol	19.75
7.273	Phenol (C_6H_6O)	31.55	7.995	2-Cyclopenten-1-one, 2-hydroxy-3	2.15
7.990	2-Cyclopenten-1-one ($C_6H_8O_2$)	1.84	8.385	O-Cresol	2.93
8.383	O-Cresol (C_7H_8O)	3.49	8.949	Phenol, 4-methoxy-	13.90
8.703	M-Cresol (C_7H_8O)	3.62	10.496	Creosol	4.91
8.948	Phenol, 4-methoxy (C_7H_8O)	10.82	11.736	Guaiacol, 4-ethyl-	3.37
10.494	Creosol ($C_8H_{10}O_2$)	5.33	12.738	Phenol, 2,6-dimethoxy-	7.93
11.732	Guaiacol, 4-ethyl ($C_9H_{12}O_2$)	4.04	13.974	1,2,4-Trimethoxybenzene	3.54
12.732	Phenol, 2,6-Dimethoxy ($C_8H_{10}O_3$)	6.37	14.961	Trimethoxyamphetamine, 2,3,5- ($C_{12}H_{19}NO_3$)	3.70
13.973	1,2,4-Trimethoxybenzene ($C_9H_{12}O_3$)	2.70	15.099	2-Propanone ($C_{10}H_{12}O_3$)	2.40
14.957	4 - Ethyl - syringol ($C_{10}H_{14}O_3$)	2.46	15.755	1,2-Benzenedicarboxylic acid, diethyl ($C_{12}H_{14}O_4$)	1.14
15.099	2-Propanone ($C_{10}H_{12}O_3$)	1.46	17.816	Syringyl acetone	2.09
17.814	Syringyl acetone ($C_{11}H_{14}O_4$)	1.32	19.530	Pentadecanoic acid	2.15
19.520	Pentadecanoic acid	1.01	20.269	Hexadecanoic acid ($C_{16}H_{32}O_2$)	0.82
			21.410	Octadecanoic acid ($C_{18}H_{36}O_2$)	1.26

As shown in Table 2, the two bio-oil samples analyzed displayed similar compound profiles, albeit with varying concentrations. The primary compounds identified included Phenol, 2-Furancarboxaldehyde, 2-Cyclopenten-1-one, Cresol, Phenol, 4-methoxy, Creosol, Guaiacol 4-ethyl, phenol 2,6-dimethoxy, 1,2,4-Trimethoxybenzene, 4-Ethyl-syringol, 2-Propanone, Syringyl acetone, and pentadecanoic acid. Some differences were observed in the compounds produced at500°C, such as 1,2-benzene dicarboxylic acid, diethyl, hexadecanoic acid, and octadecanoic acid.

Coconut shell oil primarily consists of water (about 50 wt%), aromatics, phenols, acids, ketones, and ethers [45]. The main bio-oil compounds from rice husk include methyl esters, ethanol, silane, acetic acid, oleic acid, phenol, and trans-2-undecane [6].

There are a number of compounds that are found in bio-oil, including:

1) Phenol

Phenol is a compound with a hydroxyl group directly attached to the aromatic ring. These compounds are classified as alcohols because of an OH group, making them the simplest aromatic compounds in this category. The acidity of phenol is attributed to its hydroxyl group, while the benzene ring influences its basicity.

The main constituent of this pyrolyzed diesel compound is phenol, which presents several advantages. Phenolic resins are widely used as cross-linked polymeric resins. However, due to the cost and availability of phenol compared to petroleum, products using phenolic resins tend to be relatively expensive. Therefore, further investigation is needed to replace petroleum-based phenols in phenolic resins with cost-effective alternatives derived from coconut shell pyrolysis [19]. Several methods have been developed to separate the phenol fraction and produce phenolic resins from bio-oil generated through pyrolysis [53].

2) 2-Furancarboxaldehyde (Furfural)

2-Furancarboxaldehyde, commonly known as furfural, is a cyclic organic compound with a five-carbon atom framework. This saccharide is known to activate taste buds, resulting in a sweet sensation on the tongue. Due to its extensive applications in the food, cosmetics, and pharmaceutical industries, furfural, primarily derived from agricultural residues of cereal crops, has emerged as a significant commodity in trade. Corn cobs are a primary source of this compound and are also found in vanilla. From a chemical perspective, furfural is classified as a heterocyclic aldehyde. It is a clear, slightly viscous liquid with an almond-like fragrance at room temperature. However, upon exposure to air, it changes to a yellowish hue.

3) Phenol, 4-methoxy (Mequinol)

Mequinol, or 4-methoxyphenol, is an organic compound with the chemical formula $C_7H_8O_2$. This phenol features a methoxy group in the para position and is typically presented as a colorless solid. Mequinol has applications in both dermatology and organic chemistry. It is frequently combined with the topical retinoid tretinoin in dermatological formulations to address skin depigmentation issues. The mixture typically comprises a 2% mass fraction of mequinol and 0.01% tretinoin in an ethanolic solution. Dermatologists often prescribe this medication to treat liver spots. Additionally, when used alongside a Q-switched laser, lower concentrations of mequinol have been demonstrated to be efficacious in depigmenting the skin for patients with disseminated idiopathic vitiligo. In organic chemistry, 4-methoxyphenol acts as a polymerization inhibitor, particularly for acrylates or styrene monomers.

4) Cresol

Cresol, also known as hydroxytoluene or methylphenol, is a class of organic compounds that are natural aromatic organic compounds classified as phenols or phenolics. These compounds are widely manufactured and can exist in solid or liquid states depending on temperature, as their melting point is near room temperature. Similar to other phenols, they undergo gradual oxidation upon prolonged exposure to air, and when contaminated, they tend to acquire a yellowish or slightly brownish color. Cresol possesses an odor typical of other simple phenols.

5) Creosol

Creosol is a chemical compound with the molecular formula $C_8H_{10}O_2$, a constituent of creosote. It is a disinfectant with lower toxicity than phenol and has a distinctive profile with a spicy vanilla aroma accompanied by leathery nuances and medicinal, balsamic undertones. Creosol is a modifier in white floral accords and exhibits intriguing properties in compositions featuring floral, leather, and animal notes.

6) Phenol, 2,6-dimethoxy (Syringol)

Phenol, 2,6-dimethoxy (Syringol), features methoxy groups in the adjacent (2 and 6) positions. It is the symmetrically dimethylated derivative of pyrogallol and is typically a colorless solid, although impurities can cause samples to appear brown. Syringol and its products are generated through the pyrolysis of lignin alongside guaiacol. Specifically, syringeal originates from the thermal breakdown of sinapyl alcohol.

Lignin, a prominent biomass constituent, can be categorized based on its syringyl content, indicating its source. Syringol is obtained through the pyrolysis of lignin derived from sinapyl alcohol, replacing the propenyl alcohol group with hydrogen. Consequently, syringol holds significance as a component in wood smoke. Lignin, a substantial portion of biomass, is sometimes categorized based on its syringyl component. Syringol is obtained from the pyrolysis of lignin derived from sinapyl alcohol, substituting the propenyl alcohol group with hydrogen. A high syringyl content indicates lignin sourced from angiosperms, while the pyrolysis of lignin from gymnosperms yields more guaiacol, resulting from the conversion of coniferyl alcohol.

7) Guaiacol, 4-ethyl

Guaiacol, 4-ethyl, is a phenolic compound with the molecular formula $C_9H_{12}O_2$. It is commonly found in bio-oil resulting from the pyrolysis of lignocellulosic biomass and is generated by Brettanomyces in wine and beer. The production of 4-Ethylguaiacol occurs during the pyrolysis of lignocellulosic biomass, originating from lignin and other phenolic compounds in bio-oil. Specifically, 4-ethyl guaiacol is derived from guaiacol in the lignin. When its concentration exceeds 600 µg/L due to yeast activity, it imparts bacon, spice, clove, or smoky aromas to the wine.

The bio-oil resulting from pyrolysis can be used as an alternative to diesel fuel when blended at 20%, demonstrating comparable performance characteristics and a more effective reduction of harmful emissions than conventional diesel oil [49]. However, bio-oil cannot be used directly as a fuel substitute and must be purified to meet diesel oil standards. Its limited applicability is due to its high water content, low heating value, high viscosity, and corrosiveness. An alternative approach is to utilize catalytic steam reforming of bio-oil to produce syngas and hydrogen [50].

Coconut shell oil primarily comprises water (50 wt%), aromatic compounds, phenolics, acids, ketone-containing compounds, hydrogen-containing compounds, and ether-containing compounds [20]. Bio-oil characteristic tests were conducted at the Center for Fuel Technology and Design Engineering, Indonesia. The characteristics of bio-oil obtained from coconut shells are presented in Table 3.

Table 3. Characteristics of bio-oil from coconut shells

No	Parameters	Unit	Coconut Shell	Methods
1	Total Acid Number	mg KOH/g	20.3429	ASTM D664
2	Water Content (Karl Fischer)	%	88.73±0.32	ASTM D4017-15
3	Calorific Values	cal/gram	268	ASTM 5865
4	Volumetric Mass Density	kg/m^3	1.2	ASTM D1298

Table 3 indicates that bio-oil's total acid value and water content are relatively high. In contrast, its calorific value is lower than the fuel's, and its density is greater than that of oil. Due to the requirement for extensive purification, the presence of a long carbon chain in bio-oil renders it unsuitable as a substitute for biofuels, particularly biodiesel. However, it can be utilized as a fuel with a higher heating value than fossil fuels.

The bio-oil was generated through the condensation of smoke emitted by high-temperature combustion in a parabolic-dish solar pyrolysis reactor. This bio-oil has the potential to be transformed into various derivative products, including raw materials for biofuel production, substitutes for formalin in food preservation, wood preservatives, natural pesticides, antibiotics, and smoked products. The optimal temperature range for the combustion process that produces bio-oil is 400°C-600°C. Furthermore, bio-oil can be an alternative fuel for transportation engines [47].

3.5 Bio-char characterization

Biochar is a byproduct obtained from either slow or fast pyrolysis of biomass, with slow pyrolysis producing larger quantities of biochar. This carbonaceous pyrogenic substance is distinct from charcoal due to its application as a soil amendment for agronomic and environmental purposes [14]. Proximate and ultimate analyses were conducted to identify the compounds in biochar, while a bomb calorimeter was employed to determine the energy content in the charcoal.

The biochar exhibited a fixed carbon content of 51.46%, an ash content of 2.06%, and higher volatile matter compared to the proximate analysis of coconut shells. Additionally, the water content of biochar was 7.19%, significantly lower than coconut shells. Biochar possessed higher energy content than coconut shells, measuring 5816.95 calories/gram. Biochar from coconut shell pyrolysis demonstrated a higher calorific value than other biomass types [22]. The composition of biochar compounds and energy can be found in Table 4.

Table 4. Proximate and ultimate analysis of Biochar

Analysis	Biochar
Proximate Analysis	
Fixed Carbon (%)	51.46
Ash (%)	2.06
Volatile Matter (%)	70.6
Moisture Content (%)	7.19
Dry matter content (%)	92.81
Ultimate Analysis	
C (%)	51.46
H (%)	-
N (%)	0.3
Organic Ingredient Content (%)	97.94
Energy Analysis (cal/gr)	5816.95

Biochar is a porous solid material created by heating carbon-containing substances, comprising carbon, ash, water, nitrogen, and sulfur. Charcoal, a commercially valuable product produced through direct or indirect heating in piles or kilns, plays a crucial role. Understanding the interplay between microstructure, chemical composition, and physical properties is essential. In the solar pyrolysis process, temperatures exceeding 800°C can significantly impact the porosity of biochar, potentially affecting their adsorptive capacities [54]. Solid charcoal has diverse applications, both directly and in producing activated carbon and in manufacturing battery components and electrodes [3]. Coconut shell pyrolysis is primarily used to make char, commonly used to create activated carbon [19].

The study found that the biochar output decreased from 33.6% to 28.6% as the pyrolysis temperature increased from 400 to 600°C. However, the highest bio-oil yield was attained at 600°C, and gas production increased from 15.4% to 18.3%. Temperature significantly influenced the product yield and waste coconut shell's slow pyrolysis characteristics [20].

4. CONCLUSION

The pyrolysis reactor decomposes organic compounds through a heating process without direct contact with external air at a temperature ranging from 300 to 600°C. The system comprises parabolic dishes, similar to troughs, and utilizes the geometric properties of a three-dimensional parabola. The concentrated direct beam radiation is reflected onto a point-focus receiver, and CSP system can heat it to a temperature above 600°C.

Various parameters, including the drying and reduction of the size of the coconut shell, moisture content, light intensity, reflector material, wind speed, temperature, type of reactor, heating rate, residence time, and pyrolysis temperature, influence the performance of solar pyrolysis. The analysis revealed that the coconut shells comprised 47.37% fixed carbon, 1.89% ash content, 11.32% moisture content, and 77.8% volatile matter. On the other hand, biochar had 51.46% fixed carbon, 2.06% ash content, 7.19% water content, and 5816.95 cal/gram of energy.

The parabolic solar pyrolysis concentrator produced products with varying particle sizes, including 25-33% bio-oil, 56-72% biochar, and 3-11.5% gas, at temperatures ranging from 300-650°C. The study found that smaller particle sizes and high-temperature factors of ≥ 650°C can increase the yield in this solar pyrolysis process.

The bio-oil samples analyzed showed similar compound profiles, with primary compounds including phenol, but differences in compounds produced at 500°C, such as 1,2-benzene dicarboxylic acid, diethyl, hexadecanoic acid, and octadecanoic acid. The characteristics of bio-oil were a total acid number of 20.3429 mg KOH/g, water content (Karl Fischer) of 88.73±0.32%, calorific value of 268 cal/gr, and volumetric mass density of 1.2 kg/m^3.

Biochar, a byproduct of slow or fast biomass pyrolysis, has higher fixed carbon content, ash content, and volatile matter than coconut shells. It has a higher energy content and higher calorific value. However, biochar output decreases with temperature increase from 400 to 600°C.

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NOMENCLATURE

CSP	Concentrated Solar Power
CST	Concentrated Solar Thermal
GC/MS	Gas chromatography and mass spectrometry
kJ	Kilo Joule
CHNSO	Carbon Hydrogen Nitrogen Sulfur and Oxygen
C	Carbon mass fraction (%)
H	Hydrogen mass fraction (%)
N	Nitrogen mass fraction (%)
O	Oxygen mass fraction (%)
H/C ratio	Ratio Hydrogen/Carbon
KOH	Potassium hydroxide
cal	Calorie
ASTM	American Society for Testing and Materials