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Evaluating the Role of Extractives in Biomass Pyrolysis for Enhanced Hydrogen Syngas Production

Teguh Suprianto*, Muhammad Kasim, Darmansyah

Mechanical Engineering, Banjarmasin State of Polytechnic, 70123, Banjarmasin, Indonesia

teguh.suprianto@poliban.ac.id

Abstract. This study explores how extractive content in lignocellulosic biomass affects syngas quality during fixed-bed pyrolysis-gasification, specifically focusing on hydrogen (H_2) concentration. While woody biomass is a known energy source, the link between its non-structural organic compounds (extractives) and H_2 in syngas is often overlooked. We investigated teak, coconut, and jackfruit wood to understand this influence and optimize temperature for better biomass-to-hydrogen conversion. An MQ-8 sensor detected H_2 levels. Results show that biomass with high extractive content significantly boosts syngas H_2. Jackfruit wood yielded the highest H_2 concentration (2898 ppm at 471°C), outperforming coconut wood (1965 ppm at 444°C) by 41.7% and teak wood (1931 ppm at 395°C) by 50.1%. This is due to jackfruit's high cellulose and extractive content, which decompose efficiently at higher temperatures. Overall, high-extractive biomass improves syngas quality and expands sustainable options for hydrogen production.

Keywords: biomass pyrolysis, extractive content, hydrogen yield, syngas quality.

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1. Introduction

The importance of anticipating the scarcity of non-renewable fossil fuels has sparked interest in the use of alternative fuels [1]. Yet, 2022 electricity relied heavily on coal (37.6%), oil (33.4%), and gas (16.8%), with renewables at just 12.2% [2], highlighting the urgent need for sustainable energy transition [3]. Among the fuel conversion technologies, biomass gasification presents an attractive alternative for the production of synthesis gas (syngas).[4]. Biomass can be transformed into valuable energy sources via gasification. This thermochemical conversion process improves the hydrogen-to-carbon ratio of the raw material by cleaving carbon bonds and incorporating hydrogen into the resulting gas products. When biomass containing high carbon reacts at temperatures exceeding 600°C, it generates carbon monoxide (CO) and hydrogen (H_2). The resulting gas mixture from gasification is known as synthesis gas or syngas. This process comprises numerous reactions and produces a variety of gases and by-products. It is expected that this conversion process will become a key energy source in the future, replacing fossil fuels while offering an eco-friendly fuel alternative [5].

Indonesia has significant potential to replace fossil fuels with renewable energy resources, particularly biomass. While biomass encompasses a variety of feedstocks, wood is the dominant resource due to its abundant supply. In Kalimantan, wood is a crucial commodity used for construction and industrial materials. According to data from the Central Statistics Agency in 2011, South Kalimantan produced 112,116.26 m^3 of wood. The numerous wood processing industries generate a substantial amount of wood waste. In the province, there are 83 sawmill industries, with the majority of sawmills processing less than 6,000 m^3. These sawmills produce waste ranging from 20% to 30% of the total log volume. [6].

The large volume of wood waste can be utilized as an alternative fuel through gasification to produce syngas. An important advantage of biomass over fossil fuels is its low cost and potential to reduce environmental pollution [7], [8].Therefore, research is necessary to generate syngas from wood waste. Syngas, short for synthesis gas, is the primary product of gasification and refers to a mixture that primarily consists of CO and H_2 in varying proportions. It also contains other gases such as CO_2, CH_4, H_2O, and N_2, as well as organic (tar) and inorganic compounds (H_2S, HCl, NH_3, and alkali metals). [9].

Most research in the field of syngas utilization has focused on its use as a direct fuel and for chemical production. The application of syngas as fuel for internal combustion engines is still quite limited. However, in addition to reducing pollutant emissions, the use of solid fuels through gasification offers other advantages, such as ease of handling and the flexibility of feedstocks, ranging from agricultural residues to urban waste. [10]. Various installations employ biomass waste and solid waste as their feedstocks. General Electric (GE) has been at the forefront of developing syngas technology and turbine technology. [11].

Thermochemical conversion is a method for transforming biomass into syngas. Of the different thermochemical processes, pyrolysis stands out due to its benefits, such as functioning at atmospheric pressure and low temperatures, which makes it more affordable and simpler to operate. Nevertheless, the products generated from biomass pyrolysis tend to have poor quality, marked by high levels of acidity, moisture, and viscosity, along with a low energy density [12]. A key parameter for evaluating the quality of syngas is its hydrogen content. As the hydrogen concentration in syngas increases, the quality of the syngas also improves[13]. On the other hand, an increased hydrogen content in syngas contributes to a higher specific calorific value [14], which is a crucial measure of its energy efficiency. This enhancement in calorific value means that the syngas can release more energy per unit mass when combusted, making it a more effective fuel source. Consequently, optimizing the hydrogen concentration in syngas not only improves its overall quality but also makes it more suitable for various energy applications and processes.

Many factors play a role in determining the yield and composition of the produced syngas. Some of these include the reaction temperature, reaction rate, and the type of reactor used. Additionally, the composition of the biomass material utilized, moisture content and the use of catalysts also have a significant impact on the gasification process [15],[16],[17]. Regarding pyrolysis products, gases were produced through the breakdown of specific functional groups. Hemicellulose contributed the most to CO2 production, while lignin had the highest CH4 output due to its aromatic rings and methoxy groups. In contrast, cellulose generated the highest CO levels at elevated temperatures (above 550°C) [18]. Hydrogen gas (H_2) produced during wood pyrolysis comes from the decomposition of organic compounds containing hydrogen, such as cellulose, hemicellulose, and lignin, which are the main components in woody biomass [14].

Cellulose and hemicellulose are carbohydrate polymers that contain significant amounts of hydrogen atoms, mainly in the form of hydrogen-carbon (C-H) and hydrogen-oxygen (O-H) bonds. During pyrolysis, these molecules undergo thermal decomposition, resulting in the release of hydrogen gas [14]. The main reactions that occur involve the breaking of bonds between hydrogen and carbon and oxygen. Cellulose $(C_6H_{10}O_5)n$ structure contains long chains of glucose bonded to hydrogen atoms. At pyrolysis temperatures, cellulose decomposes and releases light gases, including hydrogen, carbon monoxide

(CO), and carbon dioxide (CO_2). Hemicellulose, which has a more complex and diverse chemical structure than cellulose, also contains hydrogen bound to the polymer chain. The decomposition of hemicellulose produces a mixture of gases, including hydrogen, carbon monoxide, and methane (CH_4).

Lignin is a more complex component of wood, consisting of phenolic units that have hydrogen-carbon, hydrogen-oxygen bonds, and a hydrogen-rich aromatic structure. Lignin is more heat resistant than cellulose and hemicellulose, and decomposes at higher pyrolysis temperatures (around 280-500°C). Lignin decomposition produces a variety of pyrolysis products, including volatile gases such as hydrogen (H_2), carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), and several aromatic compounds. During pyrolysis, the primary volatile compounds from hemicellulose emerged first, followed by those from cellulose, and finally from lignin [18]. Lignin has a higher proportion of hydrogen atoms per molecule than cellulose, making it a significant source of hydrogen in the pyrolysis process.

In addition to direct biomass decomposition, hydrogen can also be produced through secondary cracking or further decomposition of tar and volatile compounds formed during pyrolysis. At higher temperatures, tar and pyrolysis oil rich in hydrocarbons can decompose into light gases such as hydrogen and methane [19]. Tar formed during pyrolysis can further decompose into lighter gases, including hydrogen. At high temperatures (over 500°C), tar tends to break down more easily into smaller volatile compounds, including H_2, CO, and CH_4.

In addition to the main content such as cellulose, hemicellulose and lignin, wood also contains extractive materials. Extractive content in wood refers to non-structural organic compounds found in wood, but not involved in the formation of the basic structure of cellulose, hemicellulose, or lignin. Extractives are compounds that can be extracted from wood using solvents such as water, ethanol, acetone, or other organic solvents. These compounds can be divided into three major subgroups according to their chemical composition: aromatic phenolic compounds, aliphatic compounds (fats and waxes), and terpenes and terpenoids. Although they do not play a role in the physical structure of wood, extractives have an important influence on the chemical properties and performance of wood, such as resistance to weathering, insect attack, and fungi [20]. The content of wood extractives varies depending on the wood species, and is usually influenced by factors such as the type of tree, the growing environment, and the part of the tree taken. The content of wood extractives can range from 5 to 20 percent [21].

In the wood pyrolysis process, extractives are often the first components to decompose because their volatility is higher than the structural components of wood such as cellulose and lignin. This means that extractives can contribute to the amount of gas and tar formed during pyrolysis. Extractives decompose at low to moderate temperatures and exhibit distinct decomposition mechanisms compared to the primary biomass components such as cellulose and lignin [22]. Increased extractive content accelerates wood degradation by enhancing conversion rates at reduced temperatures, thereby lowering the overall thermal stability of the wood. [23]. During pyrolysis of Chinese cabbage scraps, which contain extractive components, five distinct stages were observed: a dehydration stage, three main weight loss stages, and a final char formation stage [24].

Many studies have been conducted to assess these effects; however, to the author's knowledge, there has been no research specifically exploring the influence of extractive content in wood on hydrogen production in syngas derived from biomass pyrolysis. Consequently, this research will examine how wood composition affects the quality of syngas generated from the gasification of sawdust, with a particular focus on the hydrogen gas yield during the pyrolysis-gasification process. The study specifically selected jackfruit (high), teak (medium), and coconut (low) woods to establish a controlled extractive-content gradient. This systematic variation enables isolation of extractives' effects on pyrolysis-gasification outcomes, as their organic compounds (tannins, flavonoids, terpenoids) are known to decompose into volatile gases that may enhance hydrogen production. These species represent economically significant tropical hardwoods with distinct lignocellulosic profiles. Jackfruit Wood

(*Artocarpus heterophyllus*) contains 8.3 % extractives [25], compared to 7.0% in teak wood (*Tectona grandis*) 7.0 % [26] and 6.1 % in coconut wood (*Cocos nucifera*) This gradient in extractive composition enables a controlled comparative analysis of their effects on syngas production.

The results of this study may provide valuable insights for identifying the most appropriate types of biomass for conversion into syngas, based on their wood composition levels. Our findings provide the first quantitative evidence linking specific extractive compositions to enhanced hydrogen production, offering a novel feedstock selection criterion for optimizing biomass-to-energy conversion.

2. Material and Method

2.1 Materials

Table 1. Wood Components

Component	**Teak Wood (%)** [27]	**Jackfruit Wood (%)** [28]	**Coconut Wood (%)** [29]
Lignin	29.22 – 32.80	28,76	26.58 – 36.35 (average 30,99)
Cellulose	46.72 – 50.90 (α-selulosa)	56,47	28.10 – 36.55 (average 31.95)
Hemicellulose	27.41 – 30.14	-	35.09
Holocellulose	75.76 – 79.74	-	69.51 – 80.07 (average 73.49)
Pentosan*	-	18,64	-
Extractive substance	4,03 - 9,26 (average 6.99) [26]	8.29 [25]	3.75-8.92 (average 6.06)

*. Pentosan is one of the components of the hemicellulose group.

The materials used in this study are wood with low, medium, and high extractive content. Jackfruit wood has high extractive content, coconut wood has low extractive content, and teak wood has medium extractive content. In this study, wood powder with a particle size of 20 mesh and a moisture content of approximately 10% was utilized as the raw material. Table 1 shows a comparison of each wood component.

2.2 Experiment Setup

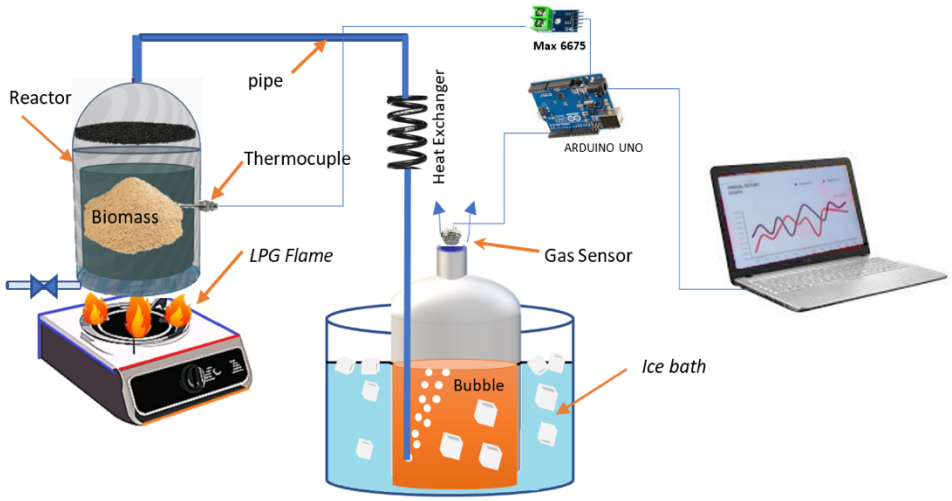

Figure 1. Pyrolyzer fixed bed reactor. Taken from [14]

In this study, the independent variable being measured is the concentration of hydrogen gas generated, whereas the manipulated variables include the type of wood used as feedstock. The quality of the syngas is evaluated based on the hydrogen gas concentration present in it. The experiment setup shown in Figure 1 The experimental procedure involves heating the biomass inside a gasification reactor until a temperature of 500°C is attained. Heating rate was 3 ^{0}C/min. After the temperature reached 500 °C, it was maintained for a residence time of 3 minutes. Heat is supplied to the gasification reactor by a continuously operating LPG stove. During this process, the biomass undergoes a phase transition (decomposition) from solid to gas, resulting in the formation of syngas and various unstable gases. A Type K thermometer is employed to measure the temperature within the reactor. The gases produced during gasification are channeled into a condenser to condense any vapor, yielding a more stable and cleaner gas. This gas is then directed to a collection chamber fitted with sensors for hydrogen (H_2). This experiment used MQ-8 as hydrogen gas sensors. MQ-8 is semiconductor (Metal Oxide, typically tin dioxide-based). Detection Range: 100–1000 ppm (H_2 gas). The MQ-8 sensor was chosen due to its proven sensitivity to hydrogen (H_2) gas and its reliable performance in real-time monitoring applications. It offers a practical balance between accuracy, response time, and cost, making it well-suited for experimental setups requiring continuous observation of H_2 concentration trends. While it has some cross-sensitivity to other gases, this limitation is minimized under the controlled conditions of the experiment. This sensor was calibrated by measuring output voltage and compared to reference values for accurate concentration readings. This sensor transmit the concentration data to a microcontroller, while a computer is used to display and record the resulting gas concentration values in ppm (parts per million). The rate of hydrogen concentration was measured every second. The experiment was repeated three times to ensure consistency and reproducibility of the results.

3. Results

Figure 2 shows the results of the experiment that has been carried out. The concentration of hydrogen gas is in ppm (parts per million).

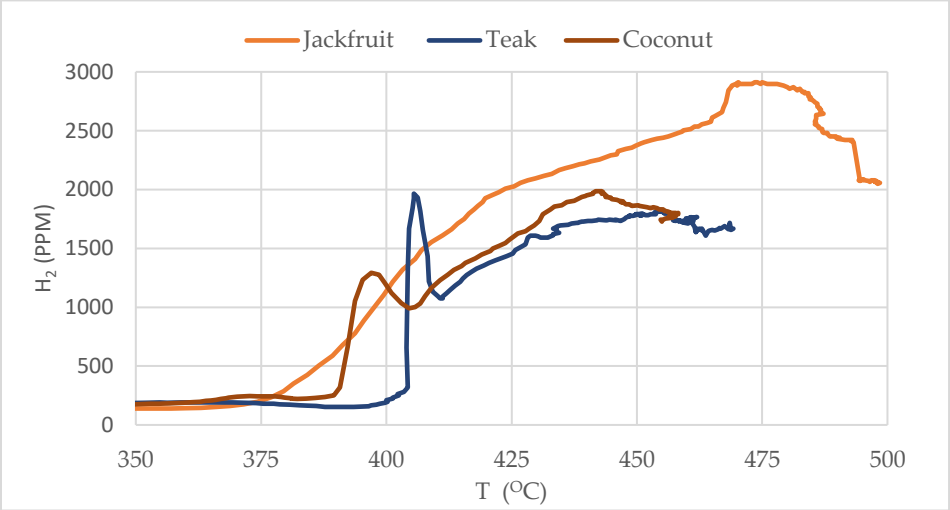

Figure 2. The concentration of hydrogen produced during the pyrolysis process.

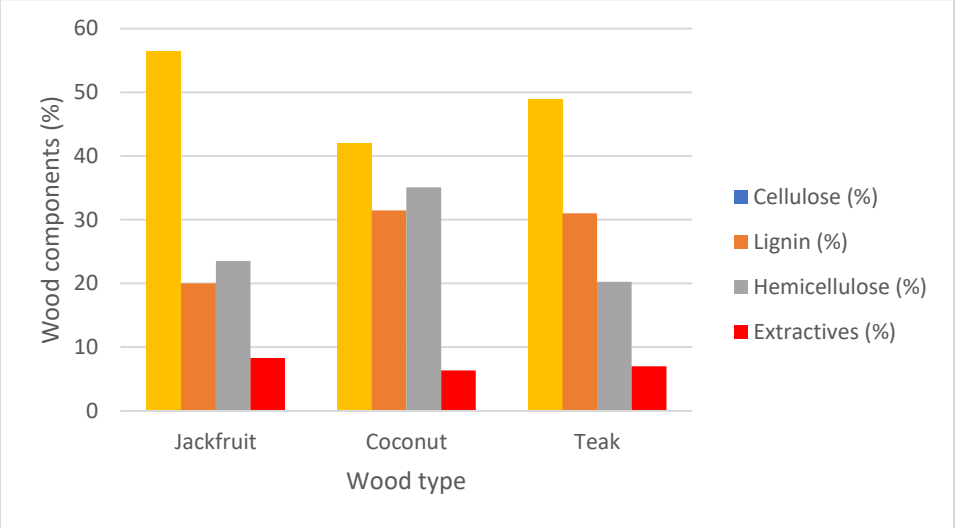

Figure 3. Wood composition by type.

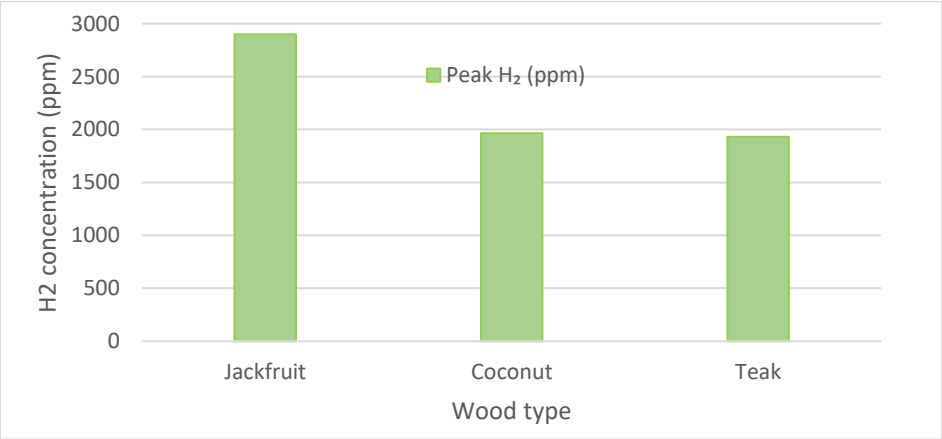

Figure 4. Wood composition by type.

The comparative data visualization illustrates two key aspects: wood composition and peak hydrogen gas production. Figure 3 reveals that jackfruit wood contains the highest cellulose content, coconut wood has the highest hemicellulose content, while teak wood exhibits the highest lignin concentration but lower extractive levels. These differences in chemical composition influence the hydrogen yield profiles. Figure 4 demonstrates that jackfruit wood produced the highest hydrogen concentration (2898 ppm at 471 °C), followed by coconut (1965 ppm at 444 °C) and teak (1931 ppm at 395 °C), highlighting a strong relationship between wood constituents and their thermal decomposition behavior.

The correlation between wood composition and hydrogen output can be explained through the decomposition characteristics of each component. Cellulose decomposes at higher temperatures (~300–400 °C) and generates significant hydrogen [18], which explains the extended and elevated hydrogen release from jackfruit wood, given its high cellulose content (56.47%) and notable extractives (8.29%). Hemicellulose, which breaks down earlier (200–350 °C)[18], supports initial hydrogen generation, as observed in coconut wood, although its lower cellulose limits hydrogen production at higher temperatures. Lignin decomposes across a broad range (200–500 °C), but contributes more to tar and aromatic compounds than hydrogen [30]. In teak wood, its high lignin content (29.22–32.80%) results in a rapid but limited hydrogen release due to lower extractive levels and the fast depletion of reactive components.

Detailed profiles from the experiment confirm these mechanisms. Jackfruit wood shows a steadily rising hydrogen production curve in Figure 2, reflecting prolonged decomposition and synergistic effects from both cellulose and extractives. In contrast, teak wood exhibits an early peak at 395 °C followed by a sharp decline, consistent with its lignin-dominated composition and lower extractive content. Coconut wood, with the highest hemicellulose content (35.09%), presents a moderate and earlier peak in hydrogen output, attributed to the early degradation of hemicellulose, with a maximum of 1965 ppm at 444 °C. Thus, wood types with high cellulose and moderate extractives, such as jackfruit, favor more stable and higher hydrogen production compared to those dominated by hemicellulose or lignin.

The pyrolysis pathways of lignocellulosic biomass are largely determined by the chemical structure of its main components. Cellulose, a crystalline polysaccharide, decomposes predominantly between 300–400 °C, yielding anhydrosugars and significant amounts of light gases such as H_2, CO, and CH_4. Its relatively uniform structure supports a predictable thermal breakdown, contributing substantially to hydrogen production. Hemicellulose, which is more amorphous and thermally labile, decomposes earlier (200–350 °C), generating volatile gases but with lower hydrogen yields due to its complex sugar composition.

In contrast, lignin, an aromatic and cross-linked polymer, degrades slowly over a wide temperature range (200–500 °C), producing mainly phenolic compounds and tar rather than hydrogen-rich gases. Extractives, which include small organic molecules like resins and terpenoids, volatilize below 300 °C and can promote early gas release. While their direct contribution to H_2 is limited, they may enhance gas-phase reactions and support hydrogen formation when present in moderate to high levels. Thus, wood with high cellulose and moderate extractives favors higher and more sustained hydrogen yields

4. Discussion

Extractives evaporate and decompose more readily at low to moderate temperatures (200°C to 400°C) during the pyrolysis process, resulting in the generation of various volatile gases, including hydrogen, carbon monoxide, and methane. In the initial stages of pyrolysis, extractives decompose before more complex components such as lignin, cellulose, or hemicellulose. Consequently, wood with higher extractive content tends to produce a greater volume of volatile gases, including hydrogen, at the early stages of pyrolysis.

One common type of extractive found in wood is phenolic compounds. Phenols and their derivatives tend to decompose at intermediate temperatures (approximately 300-400°C), during which hydrogen can be released as a byproduct of decomposition. Therefore, wood species with a higher concentration

of phenolic compounds in their extractives (e.g., jackfruit wood) are likely to release more hydrogen compared to those with lower phenolic content (e.g., teak wood).

Extractives, particularly those composed of hydrocarbon compounds, have shorter decomposition times. This indicates that in wood with high extractive content, the peak release of gases such as hydrogen can occur more rapidly; however, if the extractives decompose slowly alongside other wood components, such as lignin and cellulose, the gas release will be more gradual.

5. Conclusion

This study demonstrates that hydrogen production from wood pyrolysis varies notably with biomass composition. Among jackfruit, teak, and coconut wood, jackfruit wood yields the highest hydrogen concentration, reaching 2898 ppm at 471 °C. This value is 41.7% higher than coconut wood (1965 ppm at 444 °C) and 50.1% higher than teak wood (1931 ppm at 395 °C). The superior performance of jackfruit wood is attributed to its high cellulose and extractive content, which decompose efficiently at elevated temperatures and sustain hydrogen release. Teak wood produces a significant amount of hydrogen (1931 ppm) at lower temperatures, but its yield declines beyond 395 °C due to lower cellulose content. Coconut wood yields moderate hydrogen (1965 ppm), but its lower cellulose and extractive content limit production at higher temperatures. These findings highlight the critical influence of wood components on pyrolysis gas quality and indicate that high-extractive biomass, such as jackfruit wood, is a promising sustainable feedstock for efficient hydrogen production.

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