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Fast Pyrolysis of Lignin Extracted by Different Lignocellulosic Biomass after the Pretreatment Process

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ABSTRACT

The manufacturing of aromatic chemicals and fuels through the rapid pyrolysis of lignin looks promising. Product selectivity and liquid yield are determined by the lignin structure and pyrolysis conditions. Lignocellulosic biomass is a carbon-containing renewable and long-lasting energy source that can be found naturally. Pyrolysis has received a lot of attention for its efficient thermal decomposition of lignocellulose biomass—which includes components of cellulose, hemicellulose, and lignin—into solid, liquid, and gas products. The formation of char is one way to describe the conversion mechanism of pyrolysis. A pre-treatment process was used to extract lignin, and the maximum yield was achieved by varying the time and temperature in a material-to-material ratio of 1:20. Without the use of any inert gas for fluidization, the first set of experiments was carried out at temperatures ranging from 400 to 650 °C. In continuous fast pyrolysis, the heating rate has an excessive rank in converting biomass into liquid, gas, and char yield when the pyrolysis temperature is increased from 600 to 700 and then 800 °C. This research provides a deeper comprehension of the

interactions that take place between various components during the rapid pyrolysis of biomass. With an optimal yield of 11.96 percent being NTB, walnut shell (WNS), almond shell (AS), and babool tree bark (BTB) were produced at 600 °C with yields of 11.21, 11.73, 11.88, and 11.96%, respectively. With an optimal yield of 11.17 percent being BTB, walnut shell (WNS), almond shell (AS), and neem tree bark (NTB) were produced at 700 °C at yields of 10.89, 11.23, 11.17, and 10.88%, respectively. For walnut shell (WNS), almond shell (AS), babool tree bark (BTB), and neem tree bark (NTB), respectively, an optimal yield of 11.55 percent was obtained at 800 °C for NTB. Neem tree bark (NTB) produced the highest yield of 11.96 percent when compared to the biomass when heated to 600 °C.

Keywords: Fast pyrolysis, Lignocellulosic biomass, Lignin, Resins, Catalyst, Renewable energy

1. INTRODUCTION

Since the world's population has been growing, there have been growing concerns about the depletion of fossil fuels and the negative effects they have on the environment. As a consequence of this, procedures that make it simpler to make use of alternate sustainable feedstocks are receiving a growing amount of attention. Biomass is a promising raw material and alternative resource for the purpose of producing valuable goods, low-carbon fuels, chemicals, and energy (Jampa *et al.*, 2019). Through biochemical or thermochemical transformations, lignocellulosic biomass is an excellent renewable feedstock for the production of energy and useful products like fuels and chemicals. The significance of a particular kind of biomass in a particular area is frequently determined by (Steubing *et al.*, 2010).

The primary by-products of lignin pyrolysis are gaseous hydrocarbons that contain carbon monoxide and carbon dioxide, volatile liquids like methanol, acetone, and acetaldehyde, monolignols, and monophenols like phenol, guaiacol, syringal, and catechol. A portion of lignin is used to produce the thermally stable product known as char (Yao *et al.*, 2022). Char production increases at lower pyrolysis temperatures. In comparison to cellulose pyrolysis, the temperature range that lignin pyrolysis covers is rather extensive. H₂, CO, CO₂, CH₄, and C²⁺ made up the majority of the gaseous product at a pyrolysis temperature of 800 °C. It was observed that as the temperature rose, the overall conversion increased. Conversion is higher for lower heating rates at lower temperatures. However, the conversion rate eventually decreases at temperatures above 600 °C and 700 °C as the pyrolysis temperature rises (Mushtaq *et al.*, 2017). In terms of conversion, faster pyrolysis has more advantages over slower heating rates. This is because chars and coke are more likely to form at lower temperatures and over longer periods of time (Dharmaraja *et al.*, 2023).

Fossil resources play a significant role in the industries that make polymers and synthetic chemicals. Biomass can be used to produce petrochemical precursors in place of fossil fuels because it is abundant everywhere. It is established that the primary source of lignin formation is the component of lignocellulose biomass (Dharmaraja *et al.*, 2023). Almond shells, walnut shells, neem trees, babool trees, and rice straw have the potential to be transformed by pyrolysis into bio-oils and derivative products toward biomass due to their high content of cellulose, hemicellulose, and lignin (Wu *et al.*, 2022).

The lignocellulosic biomass's organic vapors are transformed into char and total gases with increased residence time. At temperatures below 800 °C and 750 °C, tar and gases rise as

residence time increases (Yang *et al.*, 2022). Fast pyrolysis is a method of burning biomass at high temperatures (between 600 °C and 800 °C) without the use of oxygen. It has the advantages of higher combustion efficiency and lower storage and transportation costs (Soomro *et al.*, 2021). During pyrolysis, biomass is thermally decomposed without oxygen, resulting in the production of bio-oil, gaseous and charred products. With a yield of up to 78% by weight, it is thought to be a promising approach for the short-term valorisation of biomass bio-oil, made from dried biomass (Siddique *et al.*, 2021). Depending on the preferences of the product, the pyrolysis process can be divided into slow pyrolysis and fast pyrolysis between 400 and 650°C. In contrast, slow pyrolysis favors the production of solid bio-char and can take several hours (Siddique *et al.*, 2022).

Fast pyrolysis, on the other hand, is the process of increasing the amount of bio-oil (condensable vapors) produced. It quickly reaches the process temperature and works at an extremely high rate of heating. In addition, for fast pyrolysis, the maximum feedstock particle size is 2 mm (Akhter *et al.*, 2021). The conversion of biomass through incomplete combustion at a temperature of 700 °C in a controlled atmosphere of steam and oxygen environment is the final and most important process known as gasification. By-products of the process include char, condensable vapors, syngas, and the primary product. A mixture of hydrogen, carbon dioxide, and carbon monoxide is called synthesis gas or syngas. Because syngas can be easily converted into electricity through the use of gas engines, gas turbines, or fuel cells, gasification is a more effective method of producing electricity than conventional incineration (combustion).

In addition, gasification is superior to biological methods because it can convert any kind of biomass, unlike fermentation (Siddique *et al.*, 2021). In conclusion, the primary advantages of gasification are the conversion of the entire biomass's carbon content, the production of valuable fuels like hydrogen and bio-oil, and the reduction of CO₂ emissions. Typically, it is linked to the moisture content, or amount of water in the lignin extracted from biomass (Jamaldheen *et al.*, 2021). The lignin loses its water content and becomes liquid-free during pyrolysis. In order to attain low-cost yield, numerous researchers have stated that biomass-derived lignin with economical steam content is desirable. The presence of too much water in the biomass may result in the formation of tar. As a result, both the quantity and quality of pyrolytic product yield are diminished (Zahid *et al.*, 2016). Economically, the high water content of biomass-derived lignin necessitates excessive heat energy for drying and raises the lignin's temperature. However, the primary disadvantage of pyrolysis is the moisture content of biomass-derived lignin (Siddique *et al.*, 2022).

Therefore, selecting lignin with less than 30% moisture content is preferable. Over the past ten years, pyrolysis has emerged as one of the thermochemical processes that hold the most promise for converting biomass into energy-enhancing biofuels to replace fossil fuels (Junior *et al.*, 2022). A process known as biomass pyrolysis involves the thermal degradation of a biomass feedstock in the absence of oxygen. Cotton straw (45.5%), corn straw (42.7%), and bamboo (39.8%) are all better options as raw materials for pyrolysis in order to achieve higher lignin yields (Safdari *et al.*, 2019). They all contain more lignin than a walnut shell.

However, Indonesia has a lot of biomass due to the country's annual production of 69 million tonnes (Azeta *et al.*, 2021). Stacking and burning biomass are wasteful uses that pollute the atmosphere and the environment. As a result, it is anticipated that using rice straw as a pyrolysis feedstock will be beneficial to the environment. The solid lignin yield from pyrolysis, which serves as a catalyst for lignin, was weighed (Douvartzides *et al.*, 2022).

In this study, walnut shell (WNS), almond shell (AS), neem tree bark (NTB), and babool tree bark (BTB) were used as lignocellulosic biomass sources for lignin extraction with a NaOH/H₂O solvent in the presence of sulfuric acid. The effect of the extraction conditions (time, temperature, sulfuric acid concentration, and NaOH/H₂O ratio).

The extracted lignin was then quickly pyrolyzed at a variety of temperatures, and the products that came out were found. In order to achieve the highest possible organic liquid yield through rapid pyrolysis, this study sought to determine the ideal conditions for extracting lignin from walnut shell (WNS), almond shell (AS), neem tree bark (NTB), and babool tree bark (BTB) using the NaOH/H₂O solvent.

2. MATERIALS AND METHODS

2. 1. Materials

As biomass feedstock, this study used walnut shell (WNS), almond shell (AS), neem tree bark (NTB), and babool tree bark (BTB). Chemicals such as Methanol, sulfuric acid (H₂SO₄), and sodium hydroxide (NaOH) were utilized. To get rid of moisture, the samples were first washed with tap water, then rinsed with distilled water, and sundried for ten (10) days. To reduce the amount of moisture in the samples, they were air-dried after being ground in a grinding mill to a particle size of 1–2 mm. Prior to the pyrolysis experiments, the feedstock was dried for 12 hours at 100 °C to lessen the moisture content to less than 10% by weight.

2. 2. Lignin extraction of different biomass

In this study, lignin was extracted from four distinct biomasses: walnut shell (WNS), almond shell (AS), neem tree bark (NTB), and bamboo tree bark (BTB). The lignin from a variety of biomasses was extracted using the following method. In this study, a NaOH solution with a W/V was used. For each experiment, 20 grams of NaOH were taken, mixed with 1000 mL of distilled water, 50 grams of biomass were added, and the mixture was dried for 5, 4, and 3 hours at 100 °C.

The extraction temperature was a major factor in increasing the amount of lignin that was recovered. After that, a mechanical stirrer was used to blend the liquor solution before storing it in a dry oven with babool tree bark, neem tree bark, walnut shell, and almond shell in a ratio of 1:20 before adding them into a beaker. The liquid was filtered through filter paper to get rid of water and extract lignin, and the pretreatment biomass was recovered through filtration. All four tests were carried out sequentially after being cleaned with distilled water to get rid of excess alkali.

The water was drained with filter paper, and the residue was dried. Using a pH meter and a pipette, concentrated sulfuric acid (H₂SO₄) was used to acidify the aqueous filtrate to a pH of 1. Sulfuric acid was used to lower the pH. After allowing the mixture to boil for an hour, it was cooled and the solid residue was washed with distilled water. Before drying, the precipitate was separated by filtering it through filter paper and washing it with distilled water to remove the lignin residue until a pH of 7 was reached. Unwanted materials were also washed away with distilled water to get rid of any impurities. The lignin samples were dried in an ISUZU (2-2050) drying oven at 105 °C for further processing. The sample was then measured, sealed, and filtered before being used again.



Figure 1. Drying oven



Figure 2. Raw material used like walnut shell (WNS), Almond shell (AS), Neem tree bark (NTB), Babool tree bark (BTB)



Figure 3. Lignin taken from biomass



Figure 4. Lignin extraction residue of different biomass

2. 3. Fast pyrolysis

Experiments for fast pyrolysis were carried out in a CDS Analytical 5150 pyrolyzer. With 20 grams of biomass and other materials, lignin samples weighing 155.8 grams were pyrolyzed at a heating rate of 17 °C, with a residence time of 1 hour, and a pyrolysis temperature ranging from 600 to 800 °C. At the initial temperature of 23 °C, and the residence time of 1 h, the yield began to increase until it reached a final temperature of 600 °C, the required temperature, the yield began to drop. The sample was taken out of the furnace after it had cooled. It had a final weight of 11.21, 11.73, 11.88, and 11.96 for walnut shell, almond shell, babool tree bark, and neem tree bark, respectively with lignin catalyst loss of 43.95,41.35, 40.6, and 40.2% of its weight for walnut shell, almond shell, babool tree bark, and neem tree bark, respectively. The lignin catalyst loses more weight as the temperature rises from 700-800 °C. By using fast pyrolysis, biomass can be turned into fuel and a catalyst. In the absence of oxygen, this method offers the most appealing means of converting lignin yield into a catalyst by heating rate and temperature. To achieve pyrolysis conditions that call for an additional heat input source, the pyrolysis method necessitates the presence of an external heating source. Char mass was reduced while the temperature of pyrolysis was raised.



Figure 5. Pyrolysis of lignin (walnut shell, almond shell, neem tree bark, babool tree bark for catalyst preparation

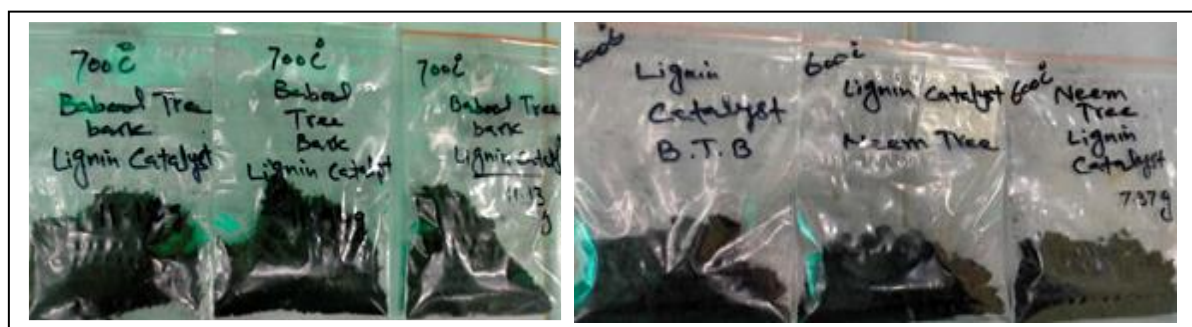


Figure 6. Lignin catalyst

3. RESULTS AND DISCUSSION

Table 1 provides a summary of the lignin yield. According to Table 1, the optimal yields for babool tree bark- 1 and neem tree bark- 1 are 6 and 5, respectively, at a temperature of 100

°C, a concentration of 2%, a ratio of 1:20, and constant speed. (Figure 7), shows the yield and lignin extraction. It is observed that yield initially increased, then decreased gradually and increased a little before finally decreased. Overall, the babool tree bark-1 produced more lignin. Table 2, which also provided a summary of the lignin yields of walnut and almond shells. (Figure. 8), shows the yield and extraction of the lignin. The findings demonstrated that, at a constant speed, a concentration of 2%, a ratio of 1:20, and a temperature of 100 °C, almond shell-1 and walnut shell-1 achieve optimal yields of 7 and 6 %, respectively. Tables 3, 4, and 5 provide a summary of the pyrolysis of lignin for catalyst preparation at various temperatures of 600, 700, and 800 °C, respectively. The graph of lignin pyrolysis for catalyst preparation at various temperatures are displayed in (Figure. 9, 10, and 11). The results in Table 3 demonstrated that neem tree bark has the highest yield. Overall, the neem tree bark at 600 °C yields 11.96% with a weight loss of 40.2%.

Table 1. Lignin yield from Babool tree bark and Neem tree bark at 100 °C for a different time interval

Biomass Sample	Temperature (°C)	Time (hr)	Liquid solvent concentration percent	Biomass to liquor ratio	Stirrer speed	Yield (wt.%)
Babool Tree bark-1	100	5	2%	1:20	Constant	6
Babool Tree bark-2		4				5
Babool Tree bark-3		3				4
Neem Tree bark-1		5				5
Neem Tree bark-2		4				3
Neem Tree bark-3		3				2

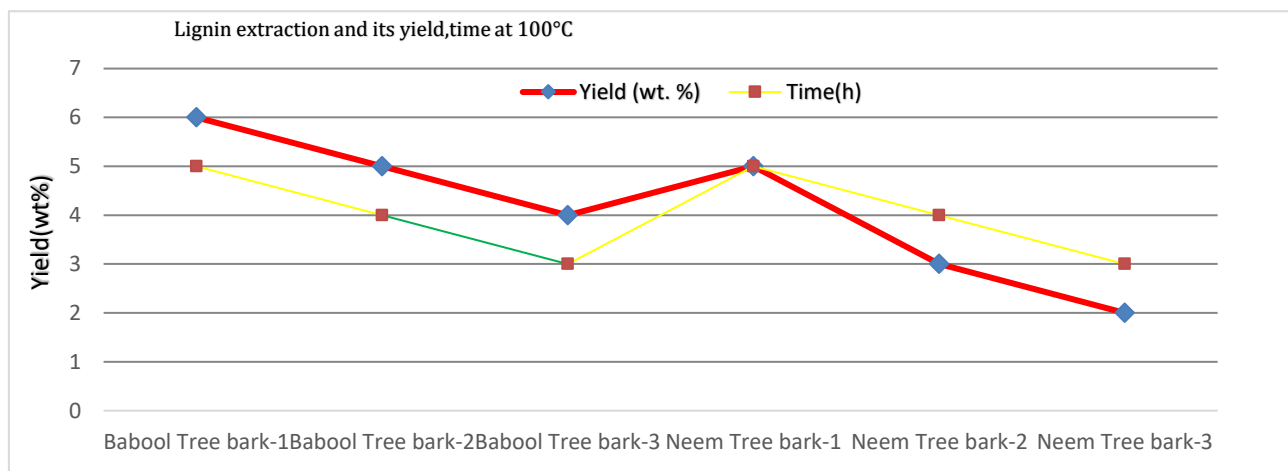


Figure 7. Lignin extraction and its yield

Table 2. Lignin yield from walnut shell and almond shell at 100 °C for a different time interval

Sample	Temp (°C)	Time (hr)	Liquid Solvent concentration percent	Biomass to Liquor ratio	Stirrer speed	Yield (wt. %)
Walnut shell-1	100	5	2%	1:20	Constant	6
Walnut shell-2		4				3
Walnut shell-3		3				1
Almond shell-1		5				7
Almond shell -2		4				3
Almond shell -3		3				4

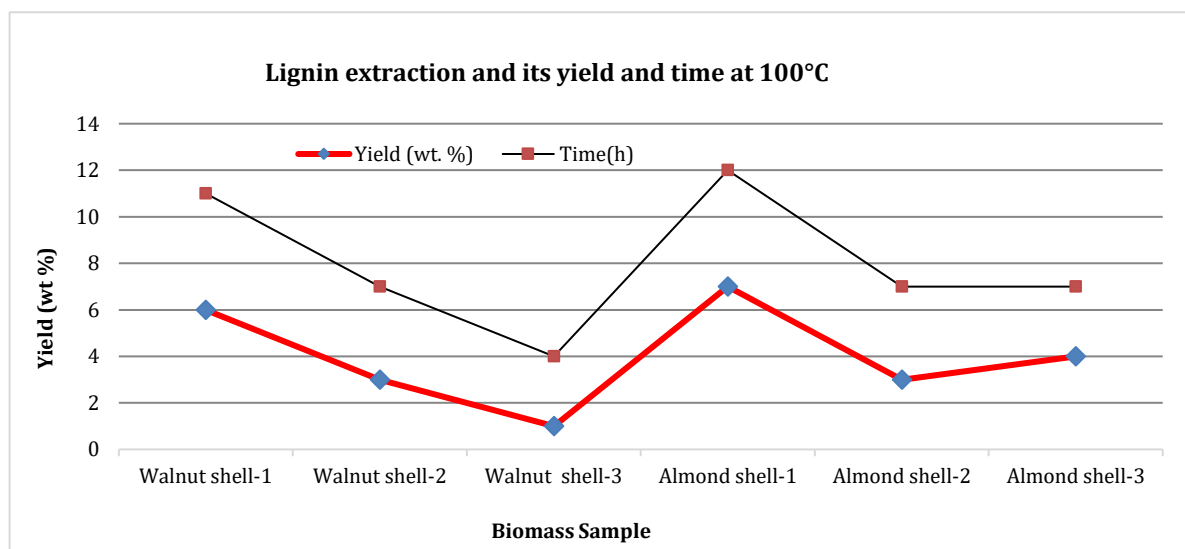


Figure 8. Lignin extraction and its yield

Table 3. Pyrolysis of lignin for catalyst preparation

Type of pyrolysis	Biomass type	The initial weight of lignin	Heating time	Heating Temp		Final weight % of lignin product yield	Change in weight (weight Loss %)
				Initial Temperature	Final Temperature		
Fast pyrolysis	Walnut shell - (WNS)Lignin	20 g	1hr	23 °C	600 °C	11.21	43.95

	Almond shell - (AS)Lignin					11.73	41.35
	Babool tree bark - (BTB)Lignin					11.88	40.6
	Neem tree bark - (NTB)Lignin					11.96	40.2

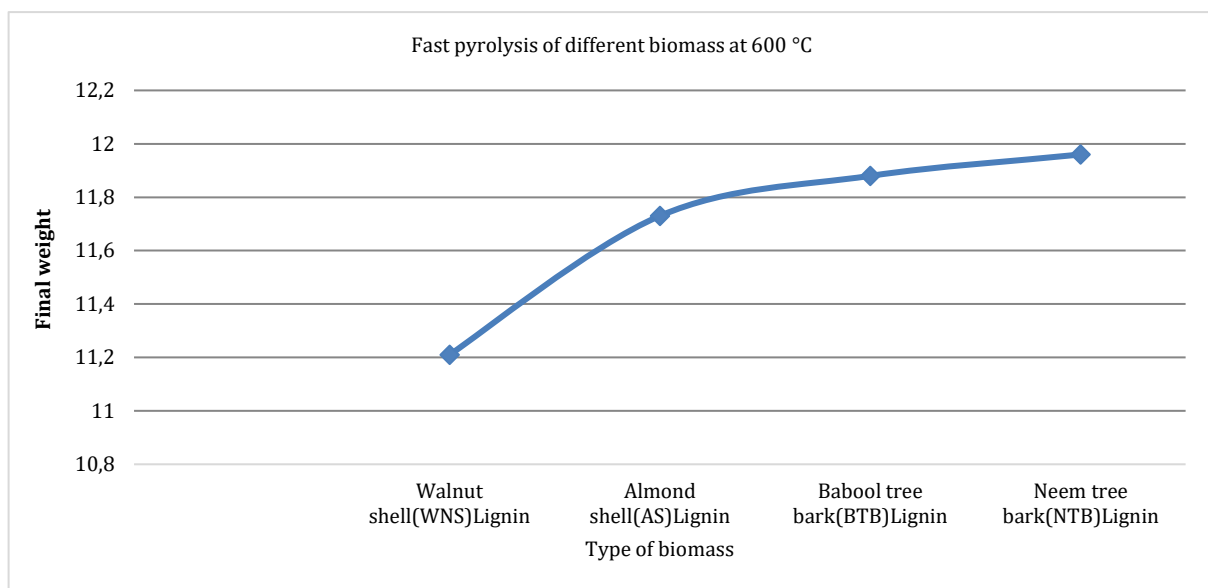


Figure 9. Pyrolysis of lignin for catalyst preparation

Table 4. Pyrolysis of lignin for catalyst preparation

Type of pyrolysis	Biomass type	Initial weight of lignin	Heating time	Heating Temp		Final weight % of lignin product yield	Change in weight (weight loss %)
				Initial Temperature	Final Temperature		
Fast pyrolysis	Walnut shell-(WNS)lignin	20 g	1hr	23 °C	700 °C	10.89	45.55
	Almond shell-(AS)Lignin					11.23	43.85
	Babool tree bark-(BTB)Lignin					11.17	44.15
	Neem tree bark-(NTB)Lignin					10.88	45.6

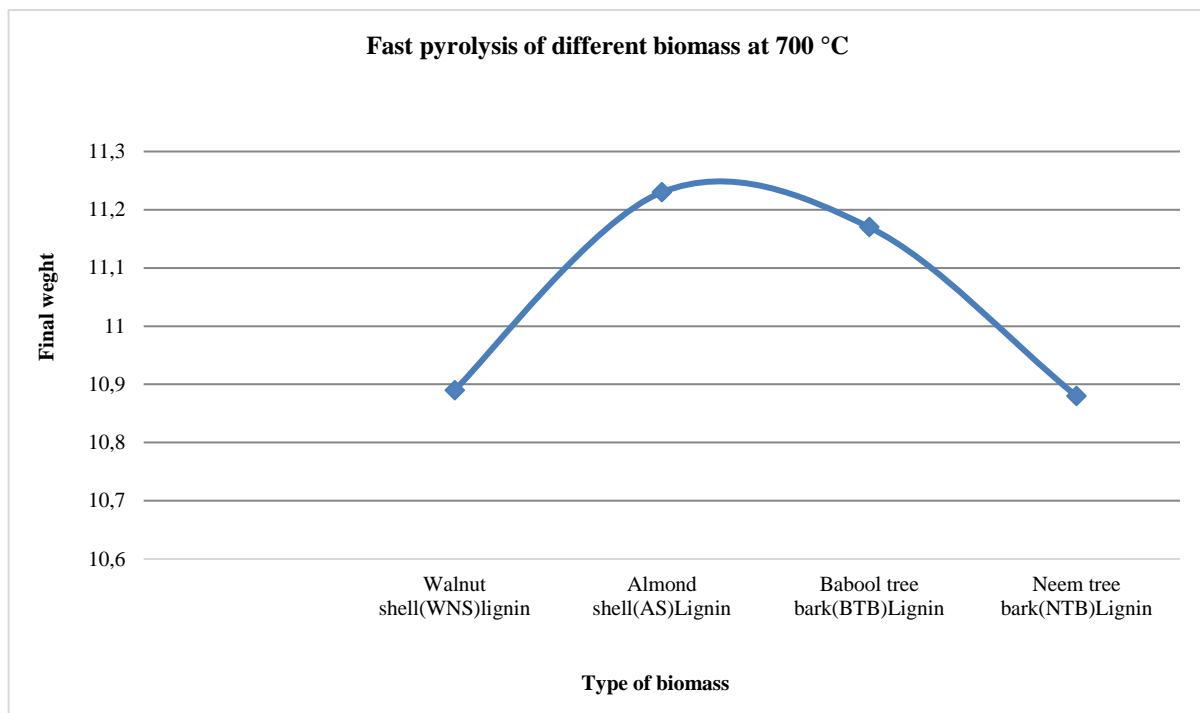


Figure 10. Pyrolysis of lignin for catalyst preparation

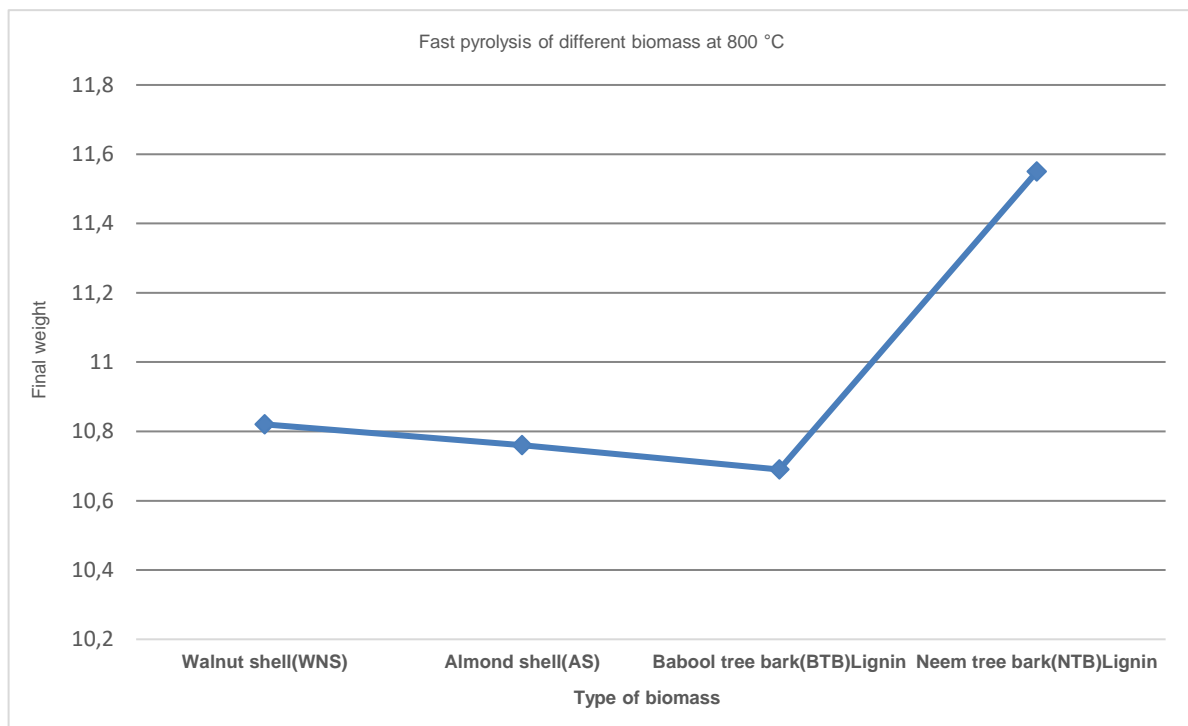


Figure 11. Pyrolysis of lignin for catalyst preparation

Table 5. Pyrolysis of lignin for catalyst preparation

Type of pyrolysis	Biomass type	The initial weight of lignin	Heating time	Heating Temp		Final weight % of lignin product yield	Change in weight (weight loss %)
				Initial Temperature	Final Temperature		
Fast pyrolysis	Walnut shell-(WNS)	20 g	1hr	23 °C	800 °C	10.82	45.9
	Almond shell-(AS)					10.76	46.2
	Babool tree bark-(BTB)Lignin					10.69	46.55
	Neem tree bark-(NTB)Lignin					11.55	47.25

4. CONCLUSIONS

In biomass pyrolysis, the materials are broken down through thermal decomposition at high temperatures without being completely burned. Pyrolysis oil and no condensable gas are the output products. As a potential feedstock for the production of phenolic bio-oil, which can be used as a renewable energy resource and a bio-replacement for phenol in the synthesis of adhesives, resins, and polymers, the rapid pyrolysis of lignin is a promising technology.

Due to the complexity of lignin's structure, no one knew how exactly pyrolysis occurred. However, the type of technical lignin and the pyrolysis, such as bubbling fluidized beds, that raises the temperature of the pyrolysis determine the composition and combination of the pyrolytic products.

The extraction of lignin from various types of biomass, such as; Almond shell, neem tree bark, babool tree bark, and walnut shell Lignin extracted from various biomasses at different temperatures 600 °C, 700 °C, and 800 °C showed that, in comparison to other lignin biomasses, lignin biomass obtained from neem tree bark (NTB) at 600 °C yielded the highest (maximum) yield of 11.96 %.

Almond shell biomass produced the highest yield (11.23 %) at 700 °C, while neem tree bark produced the highest yield (11.55 %) at 800 °C. In addition, increasing the temperature results in char formation and a decrease in yield. A product of higher quality is thought to benefit from a lower heating temperature. It has been observed that the optimal temperature and minimal residence time are necessary to achieve maximum yield. In conclusion, the extraction methods are mostly influenced by temperature and time, and lignin extracted from neem tree bark (NTB) produces superior results to other biomass.

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