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Original Article

Optimizing pine cone pyrolysis in a fixed-bed reactor: Effects of temperature and product characterization

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ABSTRACT

Pyrolysis is a promising process for converting lignocellulosic materials to high-value-added products (bio-oil, biochar, and syngas). This study aimed to produce and characterize bio-oil obtained from pine cones via pyrolysis using a fixed bed reactor system (FBRS). This study investigated the effect of temperature (500, 600, and 850 °C) on the pyrolysis product yield. The findings showed that with increasing the temperature, the bio-oil and gas yield increase, and the bio-char decreases. The highest calorific value of bio-oil (23.74 MJ/kg) and bio-char (32.89 MJ/kg) was obtained at 600 and 850 °C, respectively. The optimal pyrolysis temperature is 850 °C, which maximizes syngas production at 45.5%, making it the most favorable condition for syngas-focused applications. At this temperature, the yields of bio-oil and biochar are 36.2% and 18.3%, respectively. The qualitative analysis conducted through gas chromatography-mass spectrometry (GC/MS) revealed that the bio-oil produced from the pyrolysis of pine cones is a complex mixture of various organic compounds, including but not limited to aldehydes, alcohols, organic acids, furans, phenolic compounds, and several aromatic substances. The presence of these bioactive compounds underscores the potential utility of this bio-oil as a viable biofuel, offering promising opportunities for renewable energy solutions and reduced dependence on fossil fuels.

1. Introduction

Industrialization and the growing population in developing countries have led to a surge in energy demand that is usually met by nonrenewable resources which can result in environmental pollution and climate change (Nazarpour et al., 2022; Taghizadeh-Alisaraei et al., 2023). The conversion of lignocellulose materials into fuels and chemicals as a renewable and environmentally friendly energy source, while being replaced by fossil fuels with the help of repairing global warming, has attracted the attention of researchers (Guedes et al., 2018; Kabir and Hameed, 2017).

There are many available technologies for producing biofuels from biomass, including the production of biodiesel from vegetable oils (Sajjadi et al., 2016), bio-hydrogen from algae (Nazarpour et al., 2022), pyrolysis (Shahnouri et al., 2024), SO_2-alcohol-water (SAW) fractionation (Dehghani Firouzabadi and Tatari, 2024; Tatari et al., 2024), fermentation (bioethanol) (Shafaei et al., 2024) and anaerobic digestion technology (Wang et al., 2024) and biogas production (Yaqoob et al., 2021), which are classified as first-generation fuels (de Almeida and Colombo, 2023). The production of first-generation biofuels has many problems, such as high costs and restrictions on the use of raw materials (Safari et al., 2024), while in the second-generation fuels, the problems with the availability of raw materials related to the first-generation fuels were solved, and a variety of raw materials could be converted to fuel (Aro, 2016; Saladini et al., 2016). In third-generation biofuels, the use of algae to produce high-value-added biofuels has been considered (Bajpai, 2019).

The pyrolysis process is a favorable method for producing chemicals and biofuels from lignocellulose materials among the available thermochemical conversion technology (Liu et al., 2020; Situmorang et al., 2021). Generally, slow pyrolysis is carried out in an oxygen-free atmosphere at 400-600 °C (Basu, 2018). Among the most important advantages of fast pyrolysis are higher conversion efficiency and environmental friendliness in which solid biomass can be directly converted to bio-fuels (Ahmed and Gupta, 2009). Bio-oil is the main product of the fast pyrolysis process. Usually, slow pyrolysis produces some gas and biochar (Chen et al., 2017; Silva, 2016).

Agricultural and forestry by-products are available in high quantities and are potentially affordable (Clauser et al., 2021; Valenti et al., 2020). These sources are environment-friendly due to their outstanding properties (biodegradable, biocompatibility, high chemical stability, and low cost) and chemical compositions (Li et al., 2016). Pines are one of the most widespread tree species distributed in the Northern Hemisphere with more than 100 different species. The fruit of the pine or pine cone is a dry, conical, brown, and scaly wood with seeds placed between the scales, and because of the shape of the seeds, pine is part of the family of gymnosperms (Mabaso et al., 2018; Song et al., 2015; Xu et al., 2012). In recent years, many studies have been done on the practical use of pine cones. For example, pine cone is used in decorative and handicraft applications (Mabaso et al., 2018), heavy metal adsorbent (Ofomaja et al., 2010), composite reinforcement (Agayev and Ozdemir, 2019), medical applications, food industry (Xu et al., 2012), papermaking (Gulsoy and Ozturk, 2016), fuel, etc. The pine tree and its waste (pine cone) in countries with large pine resources can be considered a precious resource for biofuels, papermaking production, and sustainable and renewable energies.

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Many reports have been made of the use of pine cones to produce biofuels using the pyrolysis process, which is described below. Boutaieb et al (2020) reported the pyrolysis of pine cones at various temperatures (500-800 °C) in an FBRS. They found that the temperature had a lesser or more specific effect on the distribution of the product phase as a result of increased decomposition and also more cracking reactions, particularly at higher temperatures, causing more gas to be produced. It was found that the increase in temperature leads to a decrease in the bio-char yield (from 29.4 to 20.9%) and an increase in the gas yield (34.4-44.4%), while the bio-oil yield reaches a maximum of 37.6% in 600 °C. Jeong et al (2019) reported that the fast pyrolysis for pine cones improved with in-situ catalytic over H-Y zeolite catalysts. In this study, they used silicon dioxide (SiO_2) and aluminum oxide (Al_2O_3) catalysts. Their results showed that with increasing temperature, aromatic hydrocarbons increased at 500-600 °C and increased catalyst value due to increased cracking ability and overall acidity. Dawood et al (2017) investigated bio-char production using a slow pyrolysis process of pine cones at 500 °C to be used in the absorption of heavy metals and dyes. Their results showed that the pine cone is a cheap, environmentally friendly, and cost-effective absorber. The maximum absorption capacity of Langmuir for methylene blue and nickel ions was 10.46 and 11.77 mg/g, respectively. Brebu et al (2010) reported the co-pyrolysis of pine cones with fabricated polymers at 500 °C. Polymer type has a significant role in the pyrolysis product yield. The calorific value of biochar resulting from co-pyrolysis was higher than bio-char without mixed polymers.

Despite the extensive research conducted on biomass pyrolysis for sustainable bioenergy and value-added product generation, the pyrolysis of pine cones a highly abundant yet underutilized lignocellulosic biomass has received minimal attention in the scientific literature. Existing studies have predominantly focused on conventional feedstocks such as wood, agricultural residues, and algae, leaving a critical research gap in understanding the thermal conversion behavior and product potential of pine cones. Additionally, while the effect of pyrolysis temperature on product yields has been explored for other biomass types, there is a paucity of studies that provide a comprehensive analysis of the temperature-dependent physicochemical properties of biochar, bio-oil, and syngas specifically derived from pine cones. This research endeavors to bridge these gaps by optimizing the pyrolysis temperature in a fixed-bed reactor, conducting an in-depth characterization of the resultant products, and elucidating the underlying mechanisms that govern the influence of temperature on product properties. The study's innovative approach and emphasis on pine cones as a feedstock contribute to its superiority over prior research by offering novel insights into the valorization potential of an otherwise overlooked biomass resource, thereby advancing the scientific and practical understanding of biomass pyrolysis.

2. Material and Methods

2.1. Raw materials

In this study, the pine cone of *Pinus eldarica* was used as feedstock material. The mature pine cone (5-7 cm long) was harvested from Naharkhoran forest park in the Gorgan area (Golestan province, Iran). The pine cone collected was crushed and sieved to a particle size of less than 2 mm and dried in air for several days (Figure 1). The physicochemical characteristics of the pine cone were determined by proximate and ultimate analysis.

2.2. Physicochemical characteristics of pine cone and pyrolysis products

The proximate analysis was determined according to the following analytical standards: Moisture content (ASTM D3173), ash (ASTM D3174), and volatile materials (ASTM D3175). The fixed carbon was determined by the difference. The ultimate analysis such as C, H, N, S, and O (carbon, hydrogen, nitrogen, sulfur, and oxygen) content of pine cone, bio-oil, and bio-char was determined by an elemental combustion system (Costech, ECS 4010 CHNSO). The pine cone chemical compositions were determined according to the following analytical standards: cellulose according to the Kurschner–Hoffer method (Rowell, 1984), and lignin (TAPPI T222 om-02). Using the Dulong formula (Eq. 1), the calorific value of various pyrolysis products was calculated (Chen et al., 2012)

$$\text{Calorific value } (\text{MJ.kg}^{-1}) = 0.3383C + 1.442(H\text{-}O/8 \qquad (1)$$

where C, H, and O are the weight amounts of carbon, hydrogen, and oxygen, respectively.

Figure 1. Pine cone used in this study.

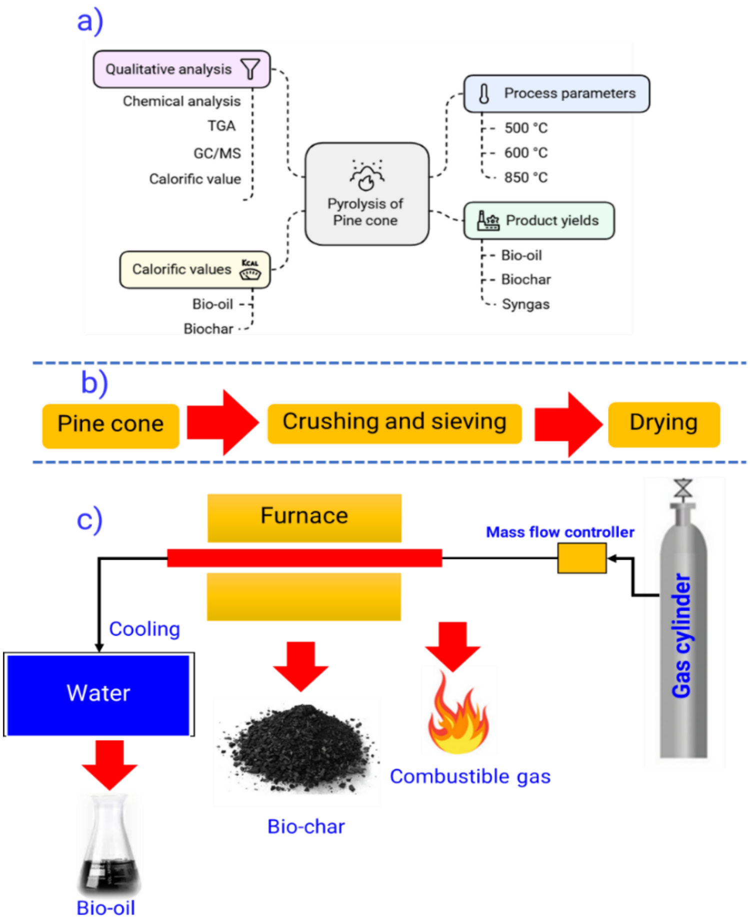

Figure 2. The schematic diagram of the experimental in this study, (a) design experiment, (b) raw material preparation, and (c) FBRS.

2.3. Thermal gravimetric analysis (TGA)

A thermogravimetric analyzer (Model: STA 503) was used to investigate the pine cone thermal degradation behavior and determination of pyrolysis temperature. Approximately 15 mg of pine cone under 0 to 600 °C temperature was heated according to the following: heating rate of 10 °C/min, carrier gas (CO_2) of 50 ml/min.

2.4. Pyrolysis process

The pyrolysis was carried out using an FBRS consisting of a stainless-steel tube (length 200 mm, outer diameter 100 mm), temperature and carrier gas controller, condenser, and gas components (Figure 2). The reactor was flushed with CO_2 (99.9%, 200 ml/min) before each trial. During the experiment, 50 g of pine cone sieved was placed into FBRS and then heated to the final temperature. Bio-oil collection equipment was cooled using an ice bath. Each component within the FBRS, including the char tank reactor and electrostatic precipitator, underwent individual weighing before and after each experimental run to ascertain the quantities of bio-char and bio-oil. The ratios between the final substances collected and the biomass employed in the FBRS were used to establish the quantities of bio-oil, bio-char, and syngas.

2.5. GC/MS analysis

The chemical composition of the bio-oil obtained at optimum conditions was investigated via GC/MS (Agilent HP 6890N GC coupled with 5973N). The oven temperature for GC/MS was programmed at 250 °C to injection of 2 µL of methanol (5%). GC/MS spectra peaks were identified by NIST 98.

2.6. Statistical analysis

The experimental data were analyzed using analysis of variance (ANOVA) to determine the statistical significance of the observed differences among treatments. The analysis was performed with SPSS software version 24.0 (IBM Corporation, Armonk, NY, USA).

3. Results and Discussion

3.1. Characteristics of pine cone biomass

The proximate and ultimate analyses are summarized in Table 1. The results showed that the cellulose and lignin content of pine cones were 38.5% and 36.4%, respectively. These percentages are comparable to those found in various lignocellulose materials, including softwoods, hardwoods, and non-woody plant biomass, typically consisting of 35-55% cellulose, 20-40% hemicellulose, and 10-25% lignin (Boutaieb et al., 2020; Gulsoy and Ozturk, 2016; Nanda et al., 2017). The volatile matter of pine cones used in this study was 79.22%. In pyrolysis processes, the high amount of lignin in pine cones compared to other lignocellulose materials can be considered a superior advantage for biofuel production (Boutaieb et al., 2020). It has been well-studied that lignin is difficult to be decomposed during the pyrolysis with a catalyst and/or enzyme, therefore, lignin is being explored as a precursor to producing bio-oil (liquid biofuel). However, the lignin heating value is relatively higher than others (cellulose and hemicellulose) because of its higher carbon content, so it can be a good solid fuel/char.

3.2. Thermal gravimetric analysis (TGA)

Figure 3 illustrates a thermal gravimetric analysis (TGA) conducted on pine cone biomass. The TGA curve reveals the presence of three distinct phases of decomposition reactions within the pine cone. In the initial phase, an initial weight loss of approximately 4% occurs between 50-100 °C, which can be attributed to the moisture content and the volatiles released from the pine cone biomass. Following this, between 100-120 °C, a slight reduction in the pine cone's weight is observed, primarily due to the elimination of bound water (Boutaieb et al., 2020).

Table 1. Chemical compositions, proximate and ultimate analysis of pine cone.

Characteristics	Value
Cellulose	38.5
Lignin	36.4
Proximate analysis (%)	
Moisture content	9.0
Ash	0.9
*Fixed carbon	11.88
Volatile matter (VS)	78.22
Ultimate analysis (%)	
Carbon (C)	55.3
Hydrogen (H)	5.44
Nitrogen (N)	0.21
Sulfur (S)	0
*Oxygen (O)	39.05

* Measure by difference (Fixed carbon% =100- (%moisture+ %volatile matters+ %ash content)

** Measure by difference (O% =100- (%C+ %N+ %H+ %S))

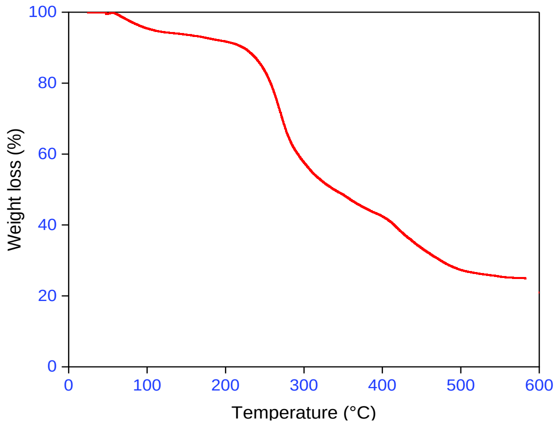

Figure 3. TGA measurement curves of raw material.

During the second phase, occurring within the temperature range of 250-350 °C, the most significant weight reduction of pine cones, amounting to 45%, was noted. This weight loss is attributed to decomposing the primary chemical constituents, namely cellulose and hemicelluloses, which are known to break down at elevated temperatures. Lignin decomposition is the third phase in the formation of lignocellulose materials and takes place at 500-600°C (Boutaieb et al., 2020; Dawood et al., 2017; Jeong et al., 2019; Nanda et al., 2017; Yang et al., 2007).

3.3. Effect of pyrolysis temperature on the yield of the products

The fraction yields of pine cone pyrolysis (bio-oil, bio-char, and gas) are shown in different temperatures in Figure 4. Increasing the temperature from 500-850 °C reduces the yield of char from 29.6% to 18.3%, which is due to secondary decomposition and volatile matter loss at higher pyrolysis process temperatures (Boutaieb et al., 2020; Dawood et al., 2017). Additionally, the findings indicated that increasing the temperature resulted in an upsurge in gas production, escalating from 33.9% to 45.5%. Concurrently, an indirect relationship was observed with bio-oil production, reaching its peak yield at 600 °C (38.3%) but subsequently declining. This decline is associated with the secondary cracking of pyrolysis vapors at higher pyrolysis temperatures (Mangut et al., 2006), and it shows that at high temperatures, there is a decrease in bio-oil yield, which is due to the increase in the gas yield. Furthermore, high temperatures are linked to a notable advantage in facilitating free radical recombination reactions, leading to a subsequent rise in the formation of biochar (Durak, 2015). These results are consistent with those reported earlier (Demirbas, 2007; Durak, 2015; Encinar et al., 2009). The product yield of pine cone biomass in pyrolysis is consistent with that of previous reports (Table 2).

3.4. Characteristics of bio-oil

Table 3 shows the physical and chemical characteristics of pine cone bio-oil at 600 °C. The proximate analysis indicates that the bio-oil has a relatively high density of 0.992 g/cm^3, which is comparable to conventional liquid fuels. The bio-oil density was 0.992 g/cm^3, which is more than heavy oil (0.855 g/cm^3) (Jambeiro et al., 2018). The water content of 10% is moderate, suggesting the presence of some aqueous phase components, which can affect combustion efficiency and storage stability. The low ash content (0.19%) signifies minimal inorganic impurities, making the bio-oil suitable for energy applications. The acidic pH (3.4) reflects the presence of organic acids, which is typical for bio-oils derived from pyrolysis and may necessitate upgrading for certain applications. The pH of bio-oil was found to be 3.4, higher than that of palm shell residue (Ghorbannezhad et al., 2020), sugarcane bagasse (Islam et al., 2010), rice straw bio-oil (Islam et al., 2002), and is similar to pine needles bio-oil (Varma and Mondal, 2018). The ultimate analysis reveals that the bio-oil contains 57.1% carbon, 6.77% hydrogen, and 29.6% oxygen, with negligible nitrogen (0.32%), resulting in an H/C ratio of 1.41 and an O/C ratio of 0.38. These values are indicative of a partially oxygenated hydrocarbon, characteristic of pyrolysis bio-oils, and suggest that upgrading processes such as hydrodeoxygenation may be required to improve fuel quality. The empirical formula ($CH_{1.41}N_{0.38}O_{0.004}$) further illustrates the chemical composition. Additionally, the calorific value of 23.74 MJ/kg demonstrates the energy potential of the bio-oil, making it a promising candidate for energy recovery. Overall, these characteristics position bio-oil as a viable intermediate product for biofuel production or chemical feedstock applications, albeit with potential requirements for bio-refinery.

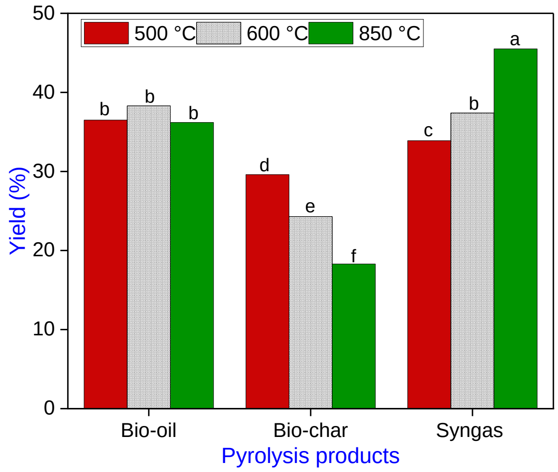

Figure 4. Effect of pyrolysis temperature on the product yield.

Table 2. Comparison of present bio-oil and other pyrolysis oils.

Biomass	Reactor type	Temperature (°C)	Bio-oil yield (%)	Ref.
Pine cone	Fixed bed	600	38.3	Present study
Pine needles	Semi-batch	550	43.76	Varma and Mondal (2018)
Sesame stalk	Reactor–furnace system	550	25	Gogoi et al (2020)
Sugarcane bagasse	Fixed bed	400-600	45-55	Gonçalves et al (2017)
Mixed wood sawdust	Fluidized bed	600	25-30	Suriapparao and Vinu (2018)
Sugarcane bagasse	Semi batch reactor	350-650	30-40	Varma and Mondal (2017)

Table 3. Characteristics of bio-oil at 600 °C.

Characteristics	Value
Proximate analysis	
Density (g/cm^3)	0.992
Water content (%)	10
Ash content (%)	0.19
pH	3.4
Ultimate analysis (%)	
Carbon (C)	57.1
Hydrogen (H)	6.77
Nitrogen (N)	0.32
Oxygen (O)	29.6
H/C	1.41
O/C	0.38
N/C	0.004
Empirical formula	$CH_{1.41}N_{0.38}O_{0.004}$
Calorific value (MJ/kg)	23.74

The results showed that more than 20 compounds have been determined in the bio-oil and selected from these compounds with more probability with the main peaks. Complex nature of the bio-oil chemicals as well as the library limitations of information, it is not feasible to separate the peaks. Figure 5 shows the range of GC/MS, and Table 4 shows the list of bio-oil components, which have the maximum percentage with their compound name, peak area, retention time, and chemical formula. The most main compounds in bio-oil are Pyridazino; oxide; Maltol; 3-Methylcyclopentane-1,2-dione; Guaiacyl acetone and 2-Vinyl-9-[3-deoxy-β-d-ribofuranosyl] with their relative composition of 14.8, 8.85, 6.89, 13.4 and 4.12 %, respectively. The retention times and peak areas indicate the presence of a diverse range of organic compounds with varying functional groups, reflecting the complex nature of the pyrolysis-derived bio-oil. Key identified compounds include nitrogen-containing species such as pyridine (3.06%) and picoline (5.16%), which can contribute to the bio-oil's basicity and potential applications in the chemical industry. Oxygenated compounds like furfuryl alcohol (2.35%) and hydroxymethylfurfural (2.27%) indicate the partial degradation of cellulose and hemicellulose components, making these intermediates valuable for fine chemicals or biofuel production. Phenolic compounds such as phenol (1.39%) and pyrocatechol (2.29%) are present, which contribute to the bio-oil's high reactivity and potential use in polymer production or as antioxidants. The presence of guaiacyl derivatives such as guaiacyl acetone (13.4%) and acetoguaiacone (3.13%) highlights the influence of lignin decomposition, offering the potential for high-value aromatic chemicals. Maltol (8.85%) and 4-hydroxy-2-methoxycinnamaldehyde (7.26%) demonstrate the presence of flavor or fragrance precursors, indicating applications beyond energy production. Additionally, the detection of higher molecular weight compounds like vanillin lactoside and melezitose suggests the incomplete decomposition of polysaccharides. Overall, the composition of the bio-oil reflects a balance between low molecular weight volatiles and higher molecular weight compounds. These results are comparable with data obtained from comprehensive literature (Ghorbannezhad, Dehghani Firouzabadi, et al., 2018; Ghorbannezhad, Firouzabadi, et al., 2018; Varma and Mondal, 2018).

3.5. Characteristics of bio-char

The effect of temperature on the characteristics of different bio-chars is provided in Table 5. As the temperature increases from 500 °C to 850 °C, there is a noticeable decrease in moisture content, from 1.3% to 1.11%, indicating the removal of water. The volatile matter content drops substantially from 25.36% at 500 °C to 6.98% at 850°C, reflecting the increased carbonization and the reduction of lighter organic compounds at higher temperatures. Concurrently, the fixed carbon content rises from 72.88% to 89.34%, which enhances the energy density of the biochar. The ash content also increases with temperature, from 0.46% to 2.57%, possibly due to the concentration of inorganic materials during pyrolysis. The ultimate analysis shows a clear increase in carbon content (from 74.5% to 93.6%) and a decrease in hydrogen (from 2.99% to 1.44%) and oxygen (from 22.26% to 4.72%) as the temperature increases, which is consistent with the higher degree of carbonization and the reduction of oxygenated compounds. This is further supported by the H/C and O/C ratios, which decrease with higher temperatures, indicating a more carbon-rich, hydrophobic, and oxygen-depleted biochar. The calorific value of the biochar increases from 25.5 MJ/kg at 500 °C to 32.89 MJ/kg at 850 °C, reflecting the enhanced energy content due to the higher fixed carbon and lower volatile matter at higher pyrolysis temperatures. Low H/C ratios can be related to higher carbonation and aromaticity at higher temperatures. The lowest values of H/C and O/C indicate the stability of the biochar and the highest potential for carbon decomposition (Boutaieb et al., 2020).

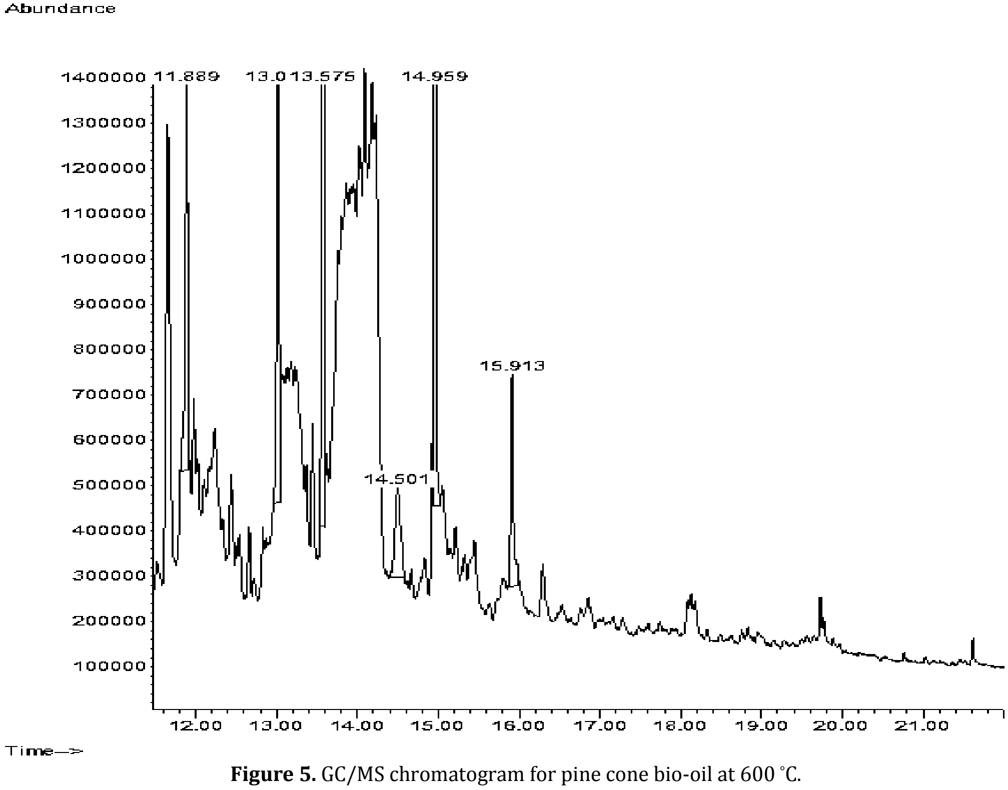

Figure 5. GC/MS chromatogram for pine cone bio-oil at 600 °C.

Table 4. Chemical compounds present in bio-oil at 600 °C detected by GC/MS.

Retention time (min.)	Peak area (%)	Compound name	Molecular formula
1.796	3.06	Pyridine	C_5H_5N
1.865	2.77	Propanal	C_3H_6O
2.196	5.16	Picoline	C_6H_7N
2.391	2.35	Furfuryl alcohol	$C_5H_6O_2$
3.174	3.45	Puranone	$C_4H_4O_2$
3.414	1.39	Phenol	C_6H_6O
4.128	14.8	Pyridazino; oxide	C_5H_5NO
5.180	6.89	3-Methylcyclopentane-1,2-dione	$C_6H_8O_2$
5.808	4.12	2-Vinyl-9-[3-deoxy-β-d-ribofuranosyl] hypoxanthine	$C_{12}H_{14}N_4O_4$
6.094	2.91	Methyl vinyl carbinol	C_4H_8O
6.357	8.85	Maltol	$C_6H_6O_3$
7.351	2.29	Pyrocatechol	$C_6H_6O_2$
7.683	2.27	Hydroxymethylfurfural	$C_6H_6O_3$
8.986	1	Homocatechol	$C_7H_8O_2$
9.478	2.25	Vanillin lactoside	$C_{20}H_{28}O_{13}$
9.900	3.13	Acetoguaiacone	$C_9H_{10}O_3$
11.889	13.4	Guaiacyl acetone	C_9H_9NO
13.021	2.06	Melezitose	$C_{18}H_{32}O_{16}$
13.575	2.91	Vanilacetic acid	$C_9H_{10}O_4$
14.501	7.26	4-Hydroxy-2-methoxycinnamaldehyde	$C_{10}H_{10}O_3$

Table 5. Characteristics of bio-chars.

Characteristics	Temperature (°C)		
	500	600	850
Proximate analysis (%)			
Moisture	1.3	0.82	1.11
Volatile matter	25.36	17.88	6.98
Ash content	0.46	1.36	2.57
*Fixed carbon	72.88	80.04	89.34
Ultimate analysis (%)			
Carbon (C)	74.5	85.8	93.6
Hydrogen (H)	2.99	2.32	1.44
Nitrogen (N)	0.25	0.26	0.24
**Oxygen (O)	22.26	11.92	4.72
H/C	0.47	0.32	0.18
O/C	0.22	0.104	0.037
N/C	0.002	0.002	0.002
Empirical formula	$CH_{0.47}N_{0.22}O_{0.002}$	$CH_{0.32}N_{0.104}O_{0.002}$	$CH_{0.18}N_{0.037}O_{0.002}$
Calorific value (MJ/kg)	25.5	30.12	32.89

* Measure by difference (Fixed carbon% =100- (%moisture+ %volatile matters+ %ash content)

** Measure by difference (O% =100- (%C+ %N+ %H+ %S))

4. Conclusions

The results indicate that increasing the pyrolysis temperature leads to a decrease in biochar yield and an increase in gas production, with bio-oil production peaking at 600°C before declining due to secondary cracking reactions at higher temperatures. Additionally, the chemical properties of the bio-oil show a high content of carbon and hydrogen, making it a suitable energy source or feedstock for the production of biofuels through advanced processes. Moreover, the cellulose and lignin content in pine cones underscores the high potential of this biomass for biofuel production, as lignin can serve as a precursor for producing high-value bio-oil. Overall, this research suggests that pyrolysis of pine cones could be a viable and sustainable option for producing biofuels and additives in the field of renewable energy.

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Competing interests

No competing financial interests or personal relationships are known to the authors that could have influenced this study.

Data availability statement

The data supporting the results of this study are available from the corresponding author upon reasonable request.

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