

Influence of Temperature on The Yield and Characteristic of Bio Oil from Pyrolysis of Pine Sap

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Abstract. The purpose of this work is to investigate the influence of temperature on the yield and characteristic of bio oil produced from pyrolysis of pine sap. The batch pyrolysis processes were conducted in an electric furnace at various temperature ranging from 350°C to 450°C. In each experiment, about 1 kg sample was pyrolyzed to obtain bio oil under inert environment by flowing nitrogen gas at 0.4 lpm. The produced bio oils were then characterized to obtain their physical and chemical properties. The result exhibited that the bio oil yield increased as the pyrolysis temperature increases. The highest yield of bio oil of 23.03 wt.% was achieved at 450°C. At this condition, the bio oil had specific gravity of 0.998, degree of acidity (pH) of 3.83, heating value of 5673.05 cal/g, and viscosity of 1.97 mm²/s. The bio oil composed of hydrocarbon component with carbon chain of C₁₀–C₂₁. It was found that more than 70 wt.% bio oil occupied by hydrocarbon fuel of >C₁₄ that could be categorized as biodiesel fuel. In the meantime, bio oil produced at 350°C composed of hydrocarbon with carbon chain of C₁₀ only that could be utilized as gasoline fuel.

1. Introduction

Energy needs in Indonesia, especially in the fields of transportation, industry and households continue to increase in line with economic and population growth. Based on the data from the state electricity company, most of Indonesia's energy needs are still supplied by fossil energy. Petroleum still ranks highest, which is 51.66%. The second level is natural gas that occupy about 28.57%. The rest is supplied from oil energy at 15.34% and renewable energy 4.43% [1]. Ironically, conventional energy sources in the form of fossil energy, which is the main energy source in Indonesia, have increasingly limited reserves. This encourages efforts to find alternative energy as a substitute for fossil energy as an energy supply.

One of the alternative energies is biomass, both in the form of products and waste. In Indonesia, biomass is a very important natural resource with various primary products as fiber, wood, oil, foodstuffs and so on, besides being used for primary purposes biomass is also used as an energy source (fuel). Biomass is the only source of carbon that can be renewed and also be processed into good gas, liquid and solid fuels [2].

Pyrolysis is an irregular decomposition process of organic materials caused by the heating process without the presence of air [3]. This process produces organic vapors, pyrolysis gases, and charcoal where the organic vapors produced contain carbon monoxide (CO), methane (CH₄), carbon dioxide



(CO₂), tar and water (H₂O). Organic vapor is then condensed into liquid that is known as bio-oil. Several parameters that affect the product of pyrolysis are temperature, moisture or water content, type of material, carrier gas flow rate, residence time, particle size of the sample, and type of pyrolysis [4],[5]. The temperature affects the product to be produced because the decomposition reaction of the chemical bond in the material occurs due to high temperature heating. Pyrolysis temperature plays an important role in the process of bio oil production, both the yield and composition of bio oil [6]. Unlike other alcohol-based fuels, pine oil is an oxygen-containing fuel obtained from pine sap. Pine oil is a renewable energy that has a higher heating value, viscosity, and boiling point than diesel [7]. A previous study also found that by mixing pine oil with diesel fuel, HC and CO content can be reduced by 30% and 65%, respectively. Nevertheless, in order to obtain good pine oils for fuel application, information about the properties of pine oil produced at different pyrolysis temperatures is necessary to be evaluated. Some important physical and chemical properties of bio oil that commonly considered for fuel application are viscosity, specific gravity, heating value, and chemical composition.

Based on the description above, this study focused on the investigation of the effect of temperatures on the yield and characteristic of bio oil produced from pyrolysis of pine sap.

2. Materials and Methods

2.1. Materials

Pine sap (mercury) originating from several pine trees in Central Java Indonesia was used as the feedstock. It was obtained from Perum. Perhutani of Central Java Regional Division. Nitrogen gas with a purity of 99.99% was also used as a carrier gas during the experiment to ensure there is no oxygen in the system and to carry the vapor product into the condenser.

2.2. Experimental Setup

Figure 1 shows the schematic diagram of the experimental setup. The electrically-heated pyrolysis reactor constructed from stainless steel 340 with a thickness of 2 mm, a diameter of 100 mm, and a height of 500 mm was used in this work. The inside and wall temperatures of the reactor were monitored by using K-type thermocouples. The cooling system consisted of a 300 mm length of Liebig condenser and a 250 ml glass pot for collecting the condensed bio oil.

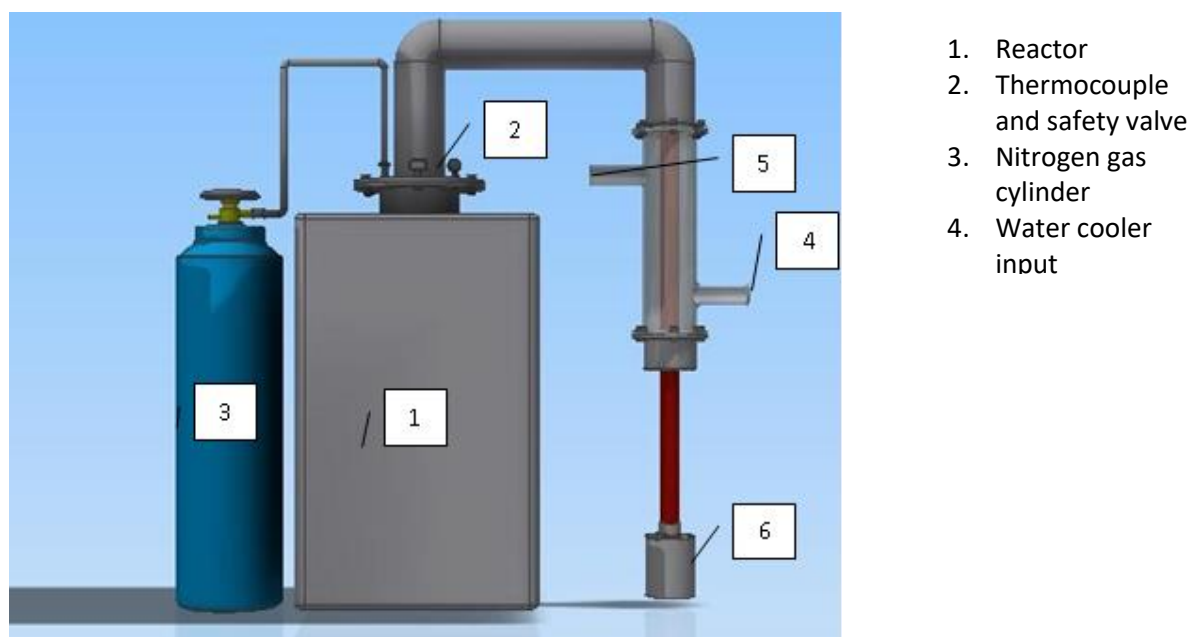


Figure 1. Schematic representation of the pyrolysis experimental setup

2.3. Pyrolysis Experimental Procedure

In each experimental run, about 0.4 lpm high purity nitrogen gas was supplied into the reactor and others equipment for ensuring inert environment and for sweeping the vapor product from the pyrolysis reactor into the condenser.

The experiments were initially performed by put about 1 kg of pine sap into the reactor and then heated to a predetermined pyrolysis temperature. The pyrolysis reactor was designed and operated in batch processes. In this study, the sample was treated at several pyrolysis temperatures ranging from 350°C to 450°C. During the process, the bio oil products were collected in the collector. There are two types of bio oil samples for each pyrolysis temperature, namely bio oil collected before reaching the specified pyrolysis temperature, called sample A, and bio oil collected after reaching the specified pyrolysis temperature until the completion of pyrolysis process, called sample B. Both types of bio oil were then subjected to determine the specific gravity, heating value, viscosity, acidity (pH), and chemical composition.

3. Results and Discussion

3.1. Yield of Products

The yield of solid, liquid and gas products (% by weight) as a result of the pyrolysis process of pine sap at various temperatures are presented in Figure 2. As shown in the figure, the rate of the decomposition reaction increased with the increase of temperature. This condition caused the increase of the rate of chain breaking of the compounds in the material. A greater amount of water and volatile compounds evaporated rapidly as the temperature increases resulting in the increase of liquid products. The obtained results are in line with a previous study reported by Anis et. al [8] and Kim et. al [9] whose found that the yields of liquid and gas products increase as the temperature rises.

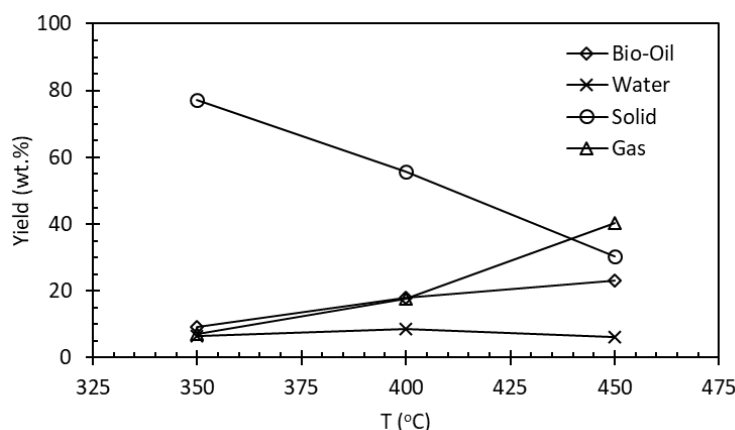


Figure 2. The yield of products from pyrolysis of pine sap as a function of pyrolysis temperature

3.2. Specific Gravity of Bio Oils

Figure 3 shows the specific gravity of bio oils. It could be observed that the specific gravity of bio oil from pyrolysis process of pine sap varied greatly ranging from 0.678 to 0.998. At a temperature of 400°C the specific gravity of bio oils was 0.843 for A sample and 0.886 for B sample, which is almost the same as the specific gravity of biodiesel fuel i.e. 0.815 - 0.860 and avtur fuel of 0.835. Nevertheless, these specific gravity of bio oils from pyrolysis process of pine sap were smaller than that of gasoline. This showed that bio oil generated by pyrolysis of pine sap can be utilized as a mixture of biodiesel or avtur fuel but cannot be used as a mixture of gasoline when viewed from the value of its specific gravity.

Based on the figure, the higher the pyrolysis temperature, the specific gravity of bio oils from pine pyrolysis was also higher. A higher pyrolysis temperature caused the decomposition of pine sap to be more intense. As a result, more smoke was formed, then condensed to become volatile. Volatile material

produced at higher pyrolysis temperatures has the highest specific gravity because the ratio of mass to volume was greater [6],[10].

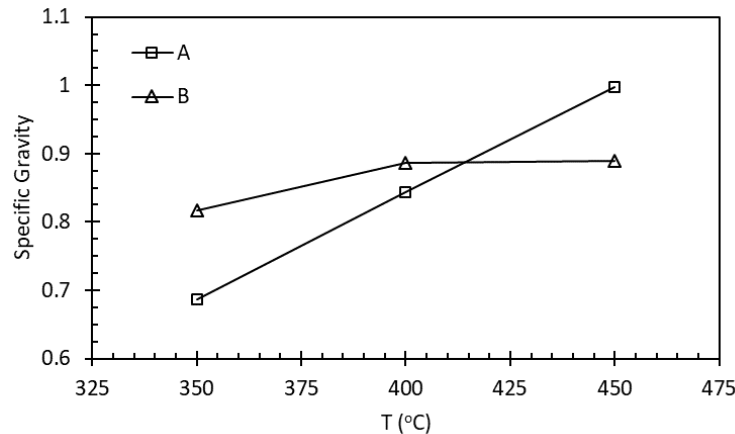


Figure 3. Specific gravity of bio oils from pyrolysis of pine sap as a function of pyrolysis temperature

3.3. Heating Value of Bio Oils

Figure 4 shows the heating value of bio oils at various pyrolysis temperatures. It could be observed that heating value of bio oils increased with the increase of temperature for both A and B bio oil samples. The biggest increase in the heating value of bio oil was obtained in B sample which was equivalent to 50.19%. This is due to bio oil produced at high temperatures tended to contain more hydrocarbons compounds which contribute to the calculation of the heating value of bio oil. It was found that the highest heating values of bio oils were obtained at 450°C of about 7,638.23 cal/g for A sample and of about 7,461.91 cal/g for B sample. These heating values of bio oil are comparable to diesel.

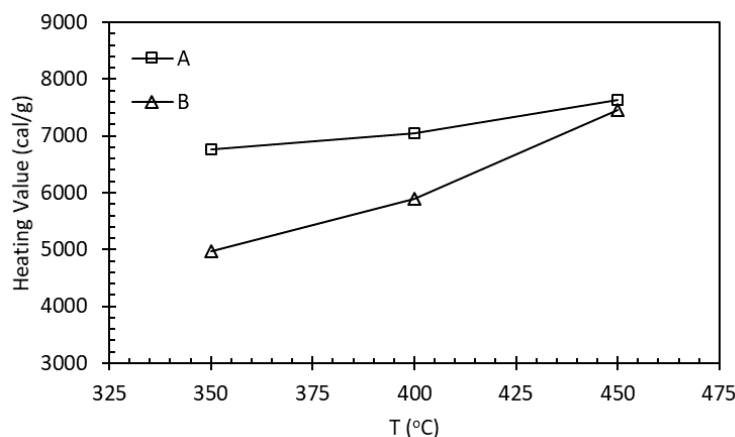


Figure 4. Heating value of bio oil from pyrolysis of pine sap as a function of pyrolysis temperature

The heating value of a fuel is equal to the absolute combustion enthalpy value where the high heating value of the fuel is influenced by the high volatile matter content which usually burns longer. High fuel heating value is not only influenced by high volatile matter and fixed carbon content, but also by low ash and moisture content in the fuel [11- 13].

3.4. Viscosity of Bio Oils

Figure 5 shows the viscosity of bio oils at various pyrolysis temperatures. The viscosity of bio oils from pyrolysis process of pine sap increased with increasing temperature. It was found that the highest viscosity of bio oil was obtained at 450°C of about 1.966 mm²/s and the lowest viscosity of bio oil at

350°C of about 1.128 mm²/s. In general, the viscosity of various pyrolysis oils is influenced by various factors including the type of raw material, pyrolysis temperature, water content in pyrolysis oil, and the pyrolysis process used [14, 15].

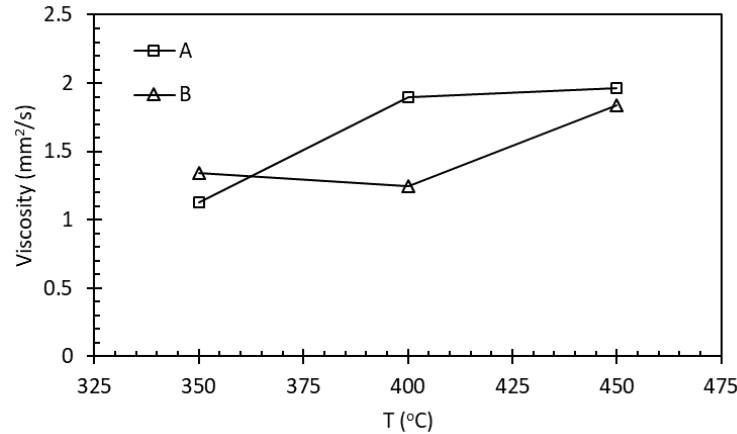


Figure 5. Viscosity of bio oil from pyrolysis of pine sap as a function of pyrolysis temperature

Figure 5 also indicates that the value of the viscosity of bio oils from pyrolysis of pine sap varied greatly between 1.1 mm²/s to 1.9 mm²/s. It was found that viscosity of bio oils from pyrolysis of pine sap was comparable than the viscosity of diesel and avtur fuels. This shows that for bio oil produced at higher pyrolysis temperature of 450°C, it can be directly applied in diesel engine without further purification or as a mixture of diesel and aviation fuels. In the meantime, for bio oil of pine sap produced at lower pyrolysis temperature of 350°C, it can be utilized as a mixture of gasoline fuel.

3.5. Degree of Acidity (pH) of Bio Oils

Figure 6 shows the degree of acidity (pH) of bio oil particularly the B sample of bio oil at various pyrolysis temperatures. It could be seen that the bio oil pH increased as the increase of pyrolysis temperature. This identifies that the higher the temperature process, the pH of bio oil tended to close to neutral condition. In this work, the highest bio oil pH produced from pyrolysis of pine sap was obtained at 450°C of about 3.83. It should be noted that the value of acidity (pH) is influenced by the temperature and type of raw material [15].

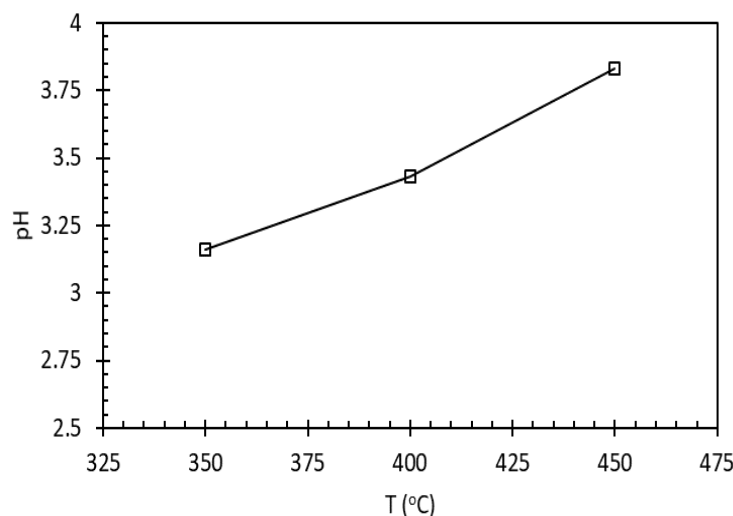


Figure 6. Acidity (pH) of bio oil as a function of temperature

3.6. Chemical Composition of Bio Oils

Chemical compositions of bio oil particularly the B sample of bio oil at various temperatures of pyrolysis are tabulated in Tables 1 to 3. Compositions of bio oil was analyzed by using a Gas Chromatography–Mass Spectrometry (GC-MS) analyzer. At a temperature of 350°C, the bio oil was dominated by the C₁₀ bond of hydrocarbon compounds while at higher temperatures of 400°C and 450°C, the bio oil was dominated by the C₁₀–C₂₁ bonds of hydrocarbon compounds. This result indicated that the higher the temperature of pyrolysis, the more bio oil compounds produced. It was found that at a temperature of 450°C, there were 21 peaks of compounds in which Methyl pimar was found to be the largest compound in bio oil with 19.66%. Meanwhile at a lower temperature of 350°C, there are only 10 peaks of compounds with α -Pinene of 31.82% as the major compound in bio oil. These results proved that the bio oil is mainly composed of lighter hydrocarbon components.

Table 1. Chemical composition of bio oil produced at 350°C

No	Compound	Molecular Formula	% Area
1	1R- α -Pinene	C ₁₀ H ₁₆	31.82
2	Camphene	C ₁₀ H ₁₆	6.41
3	Bicyclo[3.1.1]heptane, 6,6-dimethyl-2-methylene-, (1S)-	C ₁₀ H ₁₆	1.49
4	Bicyclo[3.1.0]hexane, 6-isopropylidene-1-methyl-	C ₁₀ H ₁₆	1.57
5	3-Carene	C ₁₀ H ₁₆	14.79
6	1,3-Cyclohexadiene, 1-methyl-4-(1-methylethyl)-	C ₁₀ H ₁₆	3.49
7	Cyclohexene, 1-methyl-4-(1-methylethenyl)-, (S)-	C ₁₀ H ₁₆	28.57
8	1,4-Cyclohexadiene, 1-methyl-4-(1-methylethyl)-	C ₁₀ H ₁₆	3.08
9	Terpinolen	C ₁₀ H ₁₆	5.66
10	2,4,6-Octatriene, 2,6-dimethyl-, (E,Z)-	C ₁₀ H ₁₆	3.14

Table 2. Chemical composition of bio oil produced at 400°C

No	Compound	Molecular Formula	% Area
1	1,3-Cyclohexadiene, 1,3,5,5-tetramethyl-	C ₁₀ H ₁₆	10.54
2	α -Pinene	C ₁₀ H ₁₆	1.38
3	Camphene	C ₁₀ H ₁₆	1.44
4	1,3,6-Octatriene, 3,7-dimethyl-	C ₁₀ H ₁₆	9.20
5	Cyclohexene, 1-methyl-4-(1-methylethylidene)-	C ₁₀ H ₁₆	8.27
6	Cyclohexene, 1-methyl-4-	C ₁₀ H ₁₆	39.25
7	1,4-Cyclohexadiene, 1-methyl-4-(1-methylethyl)-	C ₁₀ H ₁₆	2.43
8	2,4,6-Octatriene, 2,6-dimethyl-, (E,Z)-	C ₁₀ H ₁₆	14.48
9	7-Acetyl-6-ethyl-1,1,4,4-tetramethyltetralin	C ₁₈ H ₂₆ O	3.30
10	Methyl pimar-7-en-18-oate #	C ₂₁ H ₃₄ O ₂	6.90
11	Methyl abietate	C ₂₁ H ₃₄ O ₂	2.81

Table 3. Chemical composition of bio oil produced at 450°C

No	Composition	Molecular Formula	% Area
1	1,3-Cyclohexadiene, 1,3,5,5-tetramethyl-	C ₁₀ H ₁₆	1.05
2	α -Pinene	C ₁₀ H ₁₆	0.86
3	Camphene	C ₁₀ H ₁₆	1.08
4	1,3-Cyclohexadiene, 1,3,5,5-tetramethyl-	C ₁₀ H ₁₆	3.12
5	3-Carene	C ₁₀ H ₁₆	3.66
6	Cyclohexene, 1-methyl-4-(1-methylethenyl)-, (S)-	C ₁₀ H ₁₆	14.73
7	Cyclohexene, 1-methyl-4-(1-methylethylidene)-	C ₁₀ H ₁₆	1.96
8	2,4,6-Octatriene, 2,6-dimethyl-, (E,Z)	C ₁₀ H ₁₆	2.37
9	Naphthalene, 1,2,3,4-tetrahydro-1,1,6-trimethyl-	C ₁₃ H ₁₈	1.07
10	Androst-2,16-diene	C ₁₉ H ₂₈	3.23
11	Methyl pimar-7-en-18-oate	C ₂₁ H ₃₄ O ₂	19.66
12	Phenanthrene, 7-ethenyl-1,2,3,4,4a,4b,5,6,7,8,10, 10a - dodecahydro-4a,7-dimethyl-1-methylene-, [4aS-(4a α ,4a β ,7 β ,10a β)]-	C ₁₉ H ₂₈	2.35
13	Androstan-17-one, 3-ethyl-3-hydroxy-, (5 α)-	C ₂₁ H ₃₄ O ₂	2.40
14	7-Acetyl-6-ethyl-1,1,4,4-tetramethyltetralin	C ₁₈ H ₂₆ O	10.95
15	Methyl abietate	C ₂₁ H ₃₂ O ₂	9.60
16	Androst-2,16-diene	C ₁₉ H ₂₈	3.28
17	1-(Hydroxymethyl) - 4a-methyl-7-vinyl -1,4,4a,4b,5,6,7,8, 10,10a-decahydro-3(2H)-phenanthrenone #	C ₁₈ H ₂₆ O ₂	1.81
18	10,18-Bisnorabieta-8,11,13-triene	C ₁₈ H ₂₆	3.10
19	Pimaric acid	C ₂₀ H ₃₀ O ₂	7.48
20	Dehydroabietic acid	C ₂₀ H ₂₈ O ₂	2.84
21	Abietic acid	C ₂₀ H ₃₀ O ₂	3.39

Table 4 shows bio oil fraction composition based on the carbon atoms number in the bio oil compounds. These bio oil fraction refer to general fuel fraction including gasoline, kerosene, diesel, biodiesel, and heavy fuel fractions. Gasoline fraction is composed of hydrocarbon compounds with carbon atoms ranging from C₅ to C₁₀ [16]. Gasoline is one type of fuel oil for internal combustion engines application. Compared to others fuel from hydrocarbon compounds, gasoline has a small number of carbon atoms. Besides gasoline fraction, there is a fraction of diesel from the bio oil achieved from pyrolysis process of pine sap. Diesel is hydrocarbon fuel used for diesel engines. Diesel has a number of carbon atoms ranging from C₁₀ to C₁₅. The bio oil contained also heavy fuels fractions. Heavy fuels are heating fuels with carbon atoms of C₁₈ to C₂₅ [16].

Table 4. Bio oil fraction composition at different pyrolysis temperature

Number of Carbon Atoms	Bio oil Fraction Composition (%)			Fuel Fraction
	350°C	400°C	450°C	
C ₅ -C ₁₀	100	86.99	28.83	Gasoline
C ₁₁ -C ₁₂	-	-	-	Kerosene
C ₁₀ -C ₁₅	-	-	1.07	Diesel
C ₁₄ -C ₂₄	-	13.01	70.09	Biodiesel
C ₁₈ -C ₂₅	-	13.01	70.09	Heavy Fuel

4. Conclusion

Pine sap feedstock was successfully pyrolyzed using an electrically-heated reactor to produce bio oils. The greater the temperature of pyrolysis process, the higher the yield of bio oils was obtained. Chemical compounds of bio oils became vary at high temperature processes making its specific gravity, heating value, viscosity, and degree of acidity (pH) values increased considerably. The results showed that only C₁₀ carbon atom structures were produced at a lower pyrolysis temperature of 350°C that is totally gasoline fraction. In the meantime, at a higher pyrolysis temperature of 450°C, the produced bio oil contained more hydrocarbon components and is dominated by the C₁₈–C₂₁ carbon atom structures indicating the bio oil has the characteristics of biodiesel fraction. The relatively high gasoline and biodiesel fractions composition illustrates that bio oil generated from pyrolysis process of pine sap has the potential as a source of hydrocarbon fuels.

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