Effect of temperature on bio-oil characteristics in pyrolysis of *Sunan* candlenut olicake

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Abstract—This study aims to determine the effect of temperature on the characteristics of bio-oil on the pyrolysis of *Sunan* candlenut oilcake (SCO). SCO is the waste that arises from the compression of the *Sunan* candlenut seeds in the biodiesel production process, which can be converted into bio-oil as a raw material for bio-fuel. Furthermore, to obtain bio-oil, SCO was pyrolyzed in a fixed bed reactor and the temperature varied at 250,350, 450, 550, and 650 ºC to find the best conditions. The bio-oil was tested for the properties of the hydrocarbon compounds contained using gas chromatography-mass spectrometry (GC-MS) and then compared. The results show that the percentage of hydrocarbons increases with increasing temperature. The bio-oil from the pyrolysis of SCO contains more than 70% hydrocarbon compounds at temperatures above 450 ºC. Aromatic hydrocarbon increases with increasing temperature and are stable from 550 ºC. Based on the results, it can be stated that the pyrolysis of SCO with the aim of obtaining bio-oil with optimum hydrocarbons content can be carried out at temperature intervals of 450 to 550 ºC.

Index Terms— pyrolysis fixed bed, Sunan candlenut, hydrocarbon, GC-MS.

I. INTRODUCTION

The world is fast becoming a global village due to the increasing daily requirement of energy by all populations across the world while the earth in its form cannot change. The need for energy and its related services to satisfy human social and economic development, welfare, and health is increasing. Returning to renewables to help mitigate climate change is an excellent approach that needs to be sustainable in order to meet the energy demand of future generations. This study reviewed the opportunities associated with renewable energy sources which include the use of abundant biomass.

Research on the conversion of biomass into biofuels has been going on for a long time, which is already in the third generation [1]. First-generation biofuels with ethanol products are produced by fermenting sugars extracted from plants and starch contained in corn kernels or other starchy crops. Second-generation biofuels are generally produced using two approaches, namely biochemical and thermochemical using lignocellulosic biomass as raw materials [2], agricultural waste [3], urban waste [4], residues of food production or inedible biomass such as grass [5] and trees specifically grown for energy production [6]. This second generation of biofuels aims to reduce the competition between humans and machines, as happened in the first generation. The third generation of biofuels will later draw attention to microbes and microalgae, which are considered viable alternative energy sources [7, 8].

The most widely available main source of bioenergy is oil palm plantations [9]. In terms of economies of scale, this plant is very economical, as shown by the large number of these plants being in various regions in Indonesia. However, the result of this oil palm plant is edible oil, which is a staple food for the Indonesian population. When used as bioenergy, it will disrupt the price stability and the availability of edible oil in the market. Therefore, the development of bioenergy producing plants focuses as much as possible on non-food plants.

Previously, the Jatropha plant was developed, but since it is a shrub, it cannot be used as a conservation plant at the same time. As a megadiversity country, Indonesia has several plants that have the potential to produce bioenergy, as well as conservation plants, one of which is *Sunan* Candlenut *(Reutealis Trisperma (Blanco) Airy Shaw)*. *Sunan* candlenut is toxic and therefore it cannot be consumed as a vegetable candlenut. According to Pranowo [10], *Sunan* candlenut fruit is composed of 2-4 seeds consisting of 62-68% coir or fruit skin, 11-16% seed coat or shell, and 16-27% kernel. This kernel contains more crude oil, which is above 50%, and is the raw material for biodiesel through the esterification process.

In the *Sunan* candlenut biodiesel production, the crude oil production stage is carried out using a press of about 146 kg/cm2. At this stage, waste will be produced in the form of cake or kernel dregs, which contain an average

of 12.9% oil. The use of cake waste in small quantities is only limited to fertilizers, briquettes, and biogas. However, it must be handled on a large scale to avoid polluting the environment. Since it is part of the biomass, *Sunan* candlenut oilcake (SCO) can be converted into biofuel through a thermal conversion process, and one of the technologies that can be applied is pyrolysis.

The pyrolysis conversion process is one of the promising technologies as biomass can be converted into syngas, bio-oil, and bio-char. Syngas and bio-oil have a thermal value and can be used as alternative energy, bio-oil can also be upgraded into fuel for diesel engines [11].

During pyrolysis, large biomass molecules are broken down into relatively smaller and lighter sizes through reactions such as depolymerization, dehydration, decarboxylation, deoxygenation, oligomerization, and aromatization. The number and ratio of these fractions are influenced by many factors, such as heating rate, pyrolysis temperature, biomass composition, and catalyst effect [12]. Biomass is formed from the main elements in the form of carbon, hydrogen, oxygen, nitrogen, and sulfur. During pyrolysis, carbon binds other atoms into smaller molecules with various bond chain models. Carbon and hydrogen atoms are bonded to each other through covalent bonds to form hydrocarbons [13].

Based on the atomic arrangement, hydrocarbon compounds are categorized into two groups, namely aliphatic and aromatic hydrocarbons. Aliphatic hydrocarbons are organic compounds made up of carbon and hydrogen atoms that are arranged in straight chains, branched structures, or non-aromatic ring structures. Aromatic hydrocarbons are compounds, which consist of carbon and hydrogen atoms in a ring structure with delocalized pi electrons. The main difference is that aliphatic has a high carbon to hydrogen ratio, while aromatics have a low carbon to hydrogen ratio. Aliphatic hydrocarbons can be found in three types, alkanes, alkenes, and alkynes [14], these compounds can be found in crude oil and natural gas. Aromatic hydrocarbons are named because of their pleasant aroma and characteristic of petroleum products. The dominant compounds of the aromatic group include benzene, toluene, and xylene (BTX) [15].

In this study, the characteristics of the bio-oil produced by fixed bed pyrolysis at temperatures of 250, 350, 450, 550, and 650 ºC were observed by examining its composition using Gas Chromatography-Mass Spectrum (GC-MS) test and comparing the hydrocarbon characteristics of each treatment. This study aims to determine the optimum temperature for pyrolysis.

II. MATERIALS AND METHODS

The material prepared for this study was *Sunan* candlenut seeds pressed with a strength of 146 kN to remove the oil and leave the *Sunan* candlenut dregs. The pulp was then crushed and sieved with a mesh size of 35 followed by drying in an electric oven at 110 ºC for 3 hours to obtain uniform grain size and moisture content. To determine the content of C, H, N, S, and O, a final analysis test was conducted using CHN Elementary Leco type 628 add-on, the results are shown in Table 1.

TABLE 1.
Ultimate analysis of *Sunan* candlenut oilcake (SCO)

Physical property	$(wt.\%)$ $^{db.}$
C	59.10
H	8.33
N	2.72
S	0.32
O ^{a}	25.80

$^{db.}$ *dry base.*
^{a} *by difference.*

Pyrolysis tests were performed using a laboratory-scale fixed bed reactor. The reactor is similar to a furnace with electricity as the heat source, connected to a shell, and a cubic condenser as a coolant to convert steam into condensate. At the end of the outlet, there is an isolation box for 5 bottles of bio-oil containers. The isolation box has a gas outlet pipe, the end of which is immersed in water to avoid oxygen contamination.

The experimental stage is shown in Figure 1. 500 grams of SCO are added to the reactor, then 1 L/minute of inert nitrogen gas is exhaled for 5 minutes. The furnace which has been set at a temperature of 250 ºC is switched on and held for 15 minutes.
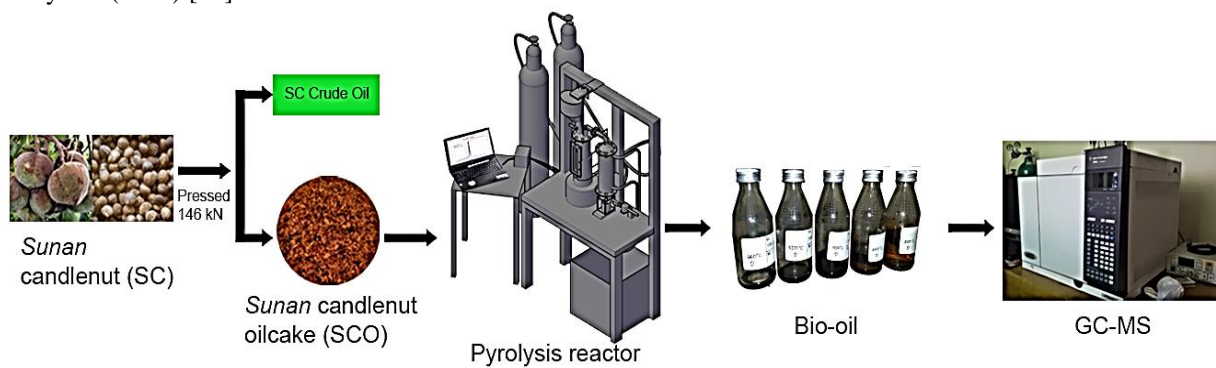

Fig. 1. Experiment scheme

The bio-oil produced at this stage is collected in the first bottle. Furthermore, the second bottle is placed at the end of the outlet, and the furnace is set at a temperature of 350 ºC after being held for 15 minutes. The same steps were conducted for temperatures of 450, 550, and 650 ºC.

Five samples of bio-oil experimental results were then analyzed using gas chromatography-mass spectrometry (GC-MS), which consists of GC Agilent 7890B chromatography and Agilent 5977B-MSD spectrometer. The column used in the chromatography was HP-5 MS UI and the carrier gas was Helium with a sweep speed of 1.3 mL/min. The heating program is set to 70 °C in 3 minutes, then heats the column at an incline of 10 °C/min until it reaches 290 °C, and hold for 2 minutes. The identification of compounds was automatically carried out by comparing the mass spectra with the NIST-14 MS library. The MS scan range is m/z 40-350, with a frequency of 4.5 scans/sec. The gain factor is 1.0 and the EM (Electron Multiplier) is 1780 Volts, and the MS source and quadrupole temperature are 230 °C and 150 °C, respectively.

III. RESULT AND DISCUSSION

3.1 Effect of temperature on the relative content of different compounds in bio-oil

The spectrum in the diagram of GC-MS test results for each bio-oil shows many peaks, and it shows the number of compounds detected with various % area values. The bio-oil produced by pyrolysis at a temperature of 250 ºC contains 24 types of compounds, while at temperatures of 350, 450, 550, and 650 ºC there are 34, 14, 26, and 30 types of compounds, respectively. Figure 2 shows the spectrum of the compounds contained in the pyrolysis bio-oil at a temperature of 450 ºC. Changes in the number of types of compounds in each bio-oil did not show a significant correlation with temperature. The pyrolysis of biomass occurs in stages [16], from a temperature of 250 to 450 ºC, the first stage of biomass pyrolysis decomposes the volatile fraction by leaving tar. At this stage, acid compounds, esters, and phenols are more dominantly formed [17]. These 3 compounds, especially acids, have many types of bond chains formed by oxygen atoms. Acid compounds at this stage have long chains such as oleic acid ($C_{18}H_{34}O_2$) and 9-octadecenoic ($C_{28}H_{44}O_4$). In Table 1 it can be seen that SCO has an oxygen content of 25.80%, which encourages the formation of these 3 compounds at low temperatures.

In the second stage from 450 to 650 ºC, the sticky tar is broken down into condensate and ash by pyrolysis. At this stage, hydrocarbon compounds tend to form with the main bonds of carbon and hydrogen atoms, although acidic compounds exist, but only limited types with short chains such as n-hexadecanoic acid ($C_{16}H_{32}O_2$). The bio-oil produced at a temperature of 450 ºC has the least variety of compounds, which explains why the end of the first phase and the beginning of the second phase of pyrolysis occur at this temperature.

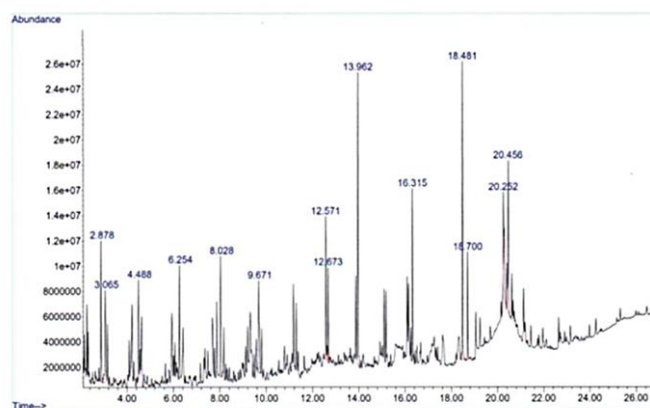Based on their composition, these compounds can be

Fig. 2. GC-MS oil subfraction of SCO pyrolysis at 450 °C

grouped relatively into 10 types, and this is performed to facilitate the analysis. These groups include Aldehydes, ketones, esters, acids, furans, phenols, N-containing compounds, aliphatic hydrocarbons, aromatic hydrocarbons, and anhydrous sugars [18]. Table 2 shows the group of compounds detected by GC-MS.

TABLE 2.
Relative content of different compounds in GC–MS of bio-oils from pyrolysis of SCO by various temperature

Compositions	Relative content (% area)				
	250 ºC	350 ºC	450 ºC	550 ºC	650 ºC
Aldehydes	nd.	nd.	nd.	nd.	nd.
Ketones	1.4	nd.	nd.	nd.	nd.
Esters	7.08	4.75	5.04	2.69	2.39
Acids	57.49	35.73	nd.	9.74	7.08
Furans	nd.	nd.	nd.	nd.	nd.
Phenols	5.29	4.31	nd.	nd.	nd.
N-containing compounds	18.08	18.73	24.88	14.47	13.09
Aliphatic hydrocarbons	6.67	33.14	62.65	57.71	62.14
Aromatics hydrocarbons	3.99	3.34	7.44	15.39	15.29
Anhydrous sugars	nd.	nd.	nd.	nd.	nd.

nd. Not detected

The percentage of oxygenate compounds such as esters, acids, and phenols tends to decrease with increasing temperature. In the first stage of pyrolysis at temperatures of 250 and 350 ºC, the acid compounds even reached 57.49 and 35.73%, respectively. Meanwhile, nitrogen-based compounds increased in the first stage of pyrolysis and decreased in the second stage of pyrolysis. Based on the nitrogen content of SCO, as shown in Table 1, 2.72% is relatively low, and therefore the high percentage of nitrogen-based compounds is caused by the process of blowing inert nitrogen gas into the reactor, which aims to reduce the presence of oxygen as a condition for the pyrolysis process [19]. For this reason, the design of the pyrolysis reactor should be considered with a minimum of free space. Meanwhile, anhydrous sugars, furans, and aldehydes were not detected, while only 1.4% of ketones were detected. These 4 compounds are formed at low temperatures below 170 ºC [20] and since they are carbonyl, they will combine with the water fraction separated from the oil fraction, as shown in Figure 3, while only the oil fraction is detected by

GC-MS.

Fig. 3. Appearance of oil and water fraction

3.2 Effect of temperature on hydrocarbons content in bio-oil

The hydrocarbon compounds contained in the bio-oil during the pyrolysis of SCO at different temperatures are shown in Table 3. Based on the group of hydrocarbons, at a temperature of 250 ºC, there were 6 types of hydrocarbon compounds with 4 aliphatic (6.67%) and 2 aromatics (3.99%). At a temperature of 350 ºC, 15 hydrocarbon compounds were detected with 14 aliphatics (33.14%) and 1 aromatic (3.34%), at a temperature of 450 ºC there were 9 hydrocarbon compounds with 8 aliphatics (62.65%) and 1 aromatic (7.44%), at a temperature of 550 ºC. there are 16 hydrocarbon compounds with 13 aliphatics (58.16%) and 3 aromatics (15.39), while at a temperature of 650 ºC there were 19 hydrocarbon compounds, including 15 aliphatics (62.14) and 4 aromatics (15.29%). The compounds contained in all bio-oils are mainly aliphatic hydrocarbon with a higher percentage than aromatics. This is related to the high carbon content in SCO while the hydrogen is low, and therefore it tends to form a straight (aliphatic) carbon chain. The percentage of hydrocarbons increases with increasing temperature, this is due to the decomposition of carbon, which requires higher activation energy [16].
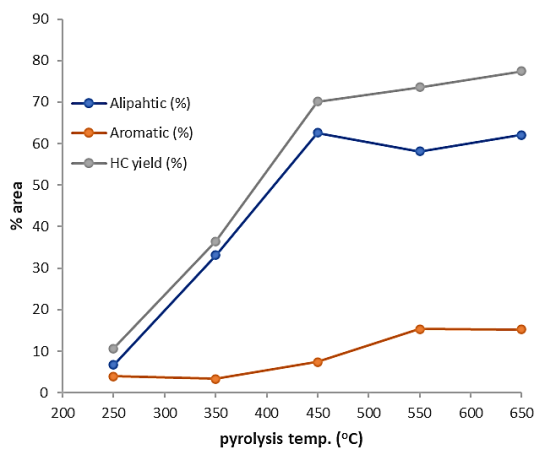

Fig. 4. Graph of hydrocarbon composition in bio-oil at increasing pyrolysis temperature

TABLE 3.
Hydrocarbon compounds in bio-oil resulting from SCO pyrolysis at various temperatures

Pyrolysis Temp. (ºC)	Compounds	Formula	Aliphatic (%)	Aromatic (%)	HC yield (%)
250	1-tetradecene	$C_{14}H_{28}$	1.47		
	pentadecane	$C_{15}H_{32}$	2.91		
	8-heptadecene	$C_{17}H_{34}$	0.92		
	heptadecene	$C_{17}H_{36}$	1.37		
	toluene	C_7H_8		1.34	
	naphthalene	$C_{10}H_8$		2.65	
	total		*6.67*	*3.99*	*10.66*
350	1-heptene	C_7H_{14}	2.36		
	heptane	C_7H_{14}	1.61		
	1-octene	C_8H_{16}	3.01		
	octene	C_8H_{18}	1.58		
	1-nonene	C_9H_{18}	1.86		
	nonene	C_9H_{18}	1.87		
	1-undecene	$C_{11}H_{22}$	1.88		
	1-dodecene	$C_{12}H_{24}$	0.3		
	1-tetradecene	$C_{14}H_{28}$	2.97		
	pentadecane	$C_{15}H_{32}$	5.95		
	hexadecane	$C_{17}H_{36}$	0.85		
	8-heptadecene	$C_{17}H_{34}$	4.71		
	heptadecane	$C_{18}H_{34}$	2.34		
	1-decene	$C_{10}H_{20}$	1.85		
	toluene	C_7H_8		3.34	
	total		*33.14*	*3.34*	*36.48*
450	1-octene	C_8H_{16}	6.07		
	1-nonene	C_9H_{18}	4.86		
	1-decene	$C_{10}H_{20}$	5.25		
	1-undecene	$C_{11}H_{22}$	6.81		
	1-dodecene	$C_{12}H_{24}$	6.56		
	1-tetradecene	$C_{14}H_{26}$	10.8		
	pentadecane	$C_{15}H_{32}$	14.65		
	heptadecane	$C_{16}H_{34}$	7.65		
	toluene	C_7H_8		7.44	
	total		*62.65*	*7.44*	*70.09*
550	1-octene	C_8H_{16}	3.64		
	1-nonene	C_9H_{18}	4.1		
	1-decene	$C_{10}H_{20}$	3.76		
	decane	$C_{10}H_{22}$	4.34		
	1-undecene	$C_{11}H_{22}$	4.55		
	1-dodecene	$C_{12}H_{24}$	4.84		
	1-tridecene	$C_{13}H_{26}$	4.73		
	1-tetradecene	$C_{14}H_{26}$	6.59		
	pentadecane	$C_{15}H_{32}$	10.5		
	cetene	$C_{16}H_{32}$	1.96		
	hexadecane	$C_{17}H_{36}$	1.7		
	8-heptadecene	$C_{17}H_{34}$	3.49		
	heptadecane	$C_{18}H_{34}$	3.96		
	toluene	C_7H_8		5.08	
	p-xylene	C_8H_{10}		3.38	
	benzene, 1, 3-dimethyl-	C_8H_{10}		6.93	
	total		*58.16*	*15.39*	*73.55*
650	1-hexene	C_6H_{12}	1.67		
	cis-1-butyl-2-methylcyclopropane	C_8H_{16}	4.23		
	octane	C_8H_{18}	2		
	1-nonene	C_9H_{18}	4.1		
	1-octene, 3, 7-dimethyl-	$C_{10}H_{20}$	3.6		
	decane	$C_{10}H_{20}$	3.82		
	1-undecene	$C_{11}H_{22}$	4.48		
	1-dodecene	$C_{12}H_{24}$	4.51		
	1-tridecene	$C_{13}H_{26}$	4.65		
	1-tetradecene	$C_{14}H_{26}$	6.28		
	pentadecane	$C_{15}H_{32}$	9.38		
	cetene	$C_{16}H_{32}$	2.15		
	hexadecane	$C_{17}H_{36}$	1.62		
	8-heptadecene	$C_{17}H_{34}$	5.99		
	heptadecane	$C_{16}H_{34}$	3.66		
	benzene	C_6H_6		1.66	
	toluene	C_7H_8		4.87	
	benzene, 1, 3-dimethyl-	C_8H_{10}		4.35	
	o-xylene	C_8H_{10}		4.41	
	total		*62.14*	*15.29*	*77.43*

As shown in Figure 4, at temperatures of 450, 550, and 650 ºC respectively, 70.09, 73.55, and 77.43%, this indicates a great potential for SCO as a raw material for biodiesel. The percentage of aromatics increased significantly from a temperature of 450 ºC, but the composition was stable at higher temperatures. Considering the energy required, it can be stated that the interval of 450 to 550 ºC is the optimum temperature for the pyrolysis of SCO.

IV. CONCLUSION

Research on the effect of temperature on the characteristics of hydrocarbon compounds in bio-oil due to the pyrolysis of SCO was carried out with the following conclusions:

- The waste generated by the esterification process in the production of biodiesel from Sunan candlenut biomass is possibly used as raw material for biofuel through the pyrolysis process to bio-oil. The results of the GC-MS test show that bio-oil contains a relatively high amount of hydrocarbon compounds, which are the main requirement as raw material for biofuels.
- The hydrocarbons in bio-oil increase with increasing pyrolysis temperature and reach values above 70% at pyrolysis temperatures above 450 ºC, it can be stated that the increase in temperature affects the increase in the percentage of hydrocarbons in the pyrolysis of the SCO.
- Aromatic hydrocarbon compounds, the main characteristics of biofuels increase from a temperature of 450 oC and then stabilize as the temperature increases. By considering energy requirements, the optimum SCO pyrolysis can be accomplished at temperature intervals of 450 to 550 ºC.

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