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Study of Pyrolysis of Ulin Wood Residues

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Abstract. As abundant resources, ulin wood residues could be converted into bioenergy through pyrolysis process. To detail analysis, the pyrolyzer reactor was connected to micro GC for online gas analysis. By comparing to other biomass e.g. pinewood and low-grade coal, the ulin wood residues exhibited similar result when the pyrolysis process started around 400 °C. The char product decreased as elevated temperature due to gasification process. Based on the gas analysis, this pyrolysis produced a gas product which predominant composed of CO. The SEM analysis also showed that the pyrolysis treatment resulted in fine char with nanopores particles. Hence, the reactivity of the solid product would be increased significantly. Therefore, the ulin wood residues could be other alternatives as a renewable energy source through pyrolysis process.

INTRODUCTION

Nowadays, the world is facing energy crisis which is the stock of the fossil fuel reducing. In Indonesia, the stock of crude oil is around 4.3 billion barrel that is 0.3% stock of world's crude oil. Whereas, the using of oil in Indonesia reaches 356 million barrel per year. It is predicted that stock of the crude oil in Indonesia will run out in 12 years. This matter motivated every element to develop renewable energy resources such as biofuel, biomass, geothermal, water, wind, ocean wave, sunlight, and tides which have not been optimized. One of the potential renewable energy sources is biomass. The examples of biomass are wood and logging residues, crops and the waste, the organic portion of municipal solid waste, animal wastes, municipal biosolids (sewage), waste from food industries, and aquatic plants and algae [1]. As an agricultural country, Indonesia has a large potential of biomass. Biomass can be converted to bioenergy. According to Ministry of Energy and Mineral Resources of the Republic of Indonesia, the potency of bioenergy from biomass residue is around 49,810 MW. Until now, the using of bioenergy only reached about 1,618 MW or 3.25% from the total potency of biomass. The largest biomass that has been converted into bioenergy were a residue of palm, cornstalks, and husks. Whereas, there are still many residue biomass that can be converted into bioenergy. According to study done by ZREU at the year 2000, the main source of the biomass is from rice plant residues, which is the energy potency is 150 GJ/year, rambung wood and rubber wood is 120 GJ/year, sugar residues is 78 GJ/year, palm residues is 67 GJ/year, and plywood and veneer production, ulinwood, coconut residues are around 20 GJ/year. Unlike fossil fuel, biomass does not have to reach million years so biomass is potential material that can be used to change the using of fossil fuel. Biomass can produce many products such as liquid fuels (ethanol, biodiesel, methanol, vegetable oil, and pyrolysis oil), gaseous fuels (biogas, producer gas, and syngas), solid fuels (charcoal and coke). These products of biomass conversion can be used for many aspects, like chemical industries, energy industries, transport industries, and environmental industries. Gasification and pyrolysis are methods to convert biomass into those useful products. These methods are thermochemical conversion. But pyrolysis is a base of the thermochemical conversion of carbonaceous material [2]. Pyrolysis is a thermochemical decomposition by combusting the carbonaceous material without oxygen. Pyrolysis process is one of reaction step

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of the gasification process. During pyrolysis, large components of hydrocarbon molecules are broken down into simpler or smaller components of hydrocarbon. From this process of decomposition, can be divided into three phase of products (gas, liquid, and solid). The gas products consist of condensable gases (vapor) and non-condensable gases (primary gas). Condensable gases made of heavier molecules and condense caused by cooling and will add to the liquid product, while non-condensable gases do not condense by cooling. These gases consist of lower molecules gases (CO, CO_2, CH_4, C_2H_6, and C_2H_4). The solid product is char. It contains almost 85% carbon, but it may also contain oxygen and hydrogen. The liquid product is known as tar, bio-oil, or biocrude. It is a black tarry fluid that consists of phenolic homolog compounds. These products of pyrolysis process can be used for energy.

In Indonesia, biomass from forestry sector has a large potency, where the area of forest in Indonesia is quite large, for about 52.3% of the area of Indonesia. But, the rate of deforestation has reached 610,375.92 ha per year. This matter is causing some environment problems. Ulin wood is one of forestry product in Indonesia that has been decreased due to over-exploitation. Ulin wood is one of the largest plants in Indonesia, but it grows slowly. It included hardwood which usually used to building construction, bridge construction, and shipping. It is also known as ironwood. In Indonesia, it grows in Kalimantan and Sumatra. The residual of ulin wood can be converted into bioenergy so we can recycle it. This matter can help a little with environmental problems. To convert ulin wood residues into bioenergy, we can use pyrolysis process. Pyrolysis characteristic depends on few factors, including pyrolysis temperature, pressure, residence time, and heating rate. In this study, we observed about the influence of pyrolysis temperature to pyrolysis products from ulin wood residues. The characteristics of wood pyrolysis is according to the spesies of hardwood and softwood [3]. To know about characteristic pyrolysis from another source of carbonaceous material, pine wood as softwood, and sub-bituminous coal as a non-renewable energy source were also investigated using TGA (Thermogravimetric analysis).

METHODS

The experiment apparatus consist of pyrolyzer which was connected to micro-GC to analyze the gas product. The system is the batch. Before the experiment started, micro-GC was set to bake out for about 1 h. Then Indonesian ulin wood as the biomass was fed into the pyrolyzer and the experiment was set as shown in Fig. 1. The proximate and ultimate analysis of ulin wood compared to other sources are shown in Table 1.

TABLE 1. Proximate and ultimate analysis of ulin wood, pine wood, and sub-bituminous coal

Sample	Proximate analysis			Ultimate analysis			
	FC	Volatile	Ash	C	H	N	O
Ulin wood	22.83	74.32	2.85	49.28	5.64	0.3	44.78
Pine wood	15.49	81.27	3.24	46.69	5.89	0.0	47.42
Sub bittuminous coal	49.0	48.4	2.6	58.37	5.12	0.85	35.66

The N_2 gas was flown along the pyrolyzer for about 1 hour before the experiment started. The N_2 flow is 100 ml/min. While waiting for the purging, thimber filter was set and winded by ribbon heater. The temperature of the ribbon heater was set at about 110 °C and kept constant. The cold trap was set by adding ethanol within temperature at the range -70 °C until -77 °C by adding N_2 liquid to ensure tar condensation [4]. Then pipeline of gas was connected between timber filter, cold trap and gas bag to the micro-GC. Set point of the pyrolyzer was 300 °C. After the pyrolyzer was purged, then the experiment can be started. The valve of the gas bag was opened when the temperature of the pyrolyzer reached the set point. The reaction time is 30 min. After 30 min, the pyrolyzer was switched off and gas product kept to be collected for about 20 min and then the valve was closed. Experiments were repeated by changing the temperature of reaction 400 °C, 500 °C, 600 °C, and 700 °C. The pyrolysis produced char, tar, and gas. Char was collected in SUS mesh. Gases were collected in the gas bag. Tar was collected at the bottom of the pyrolyzer then were trapped in the timber filter and cold trap.

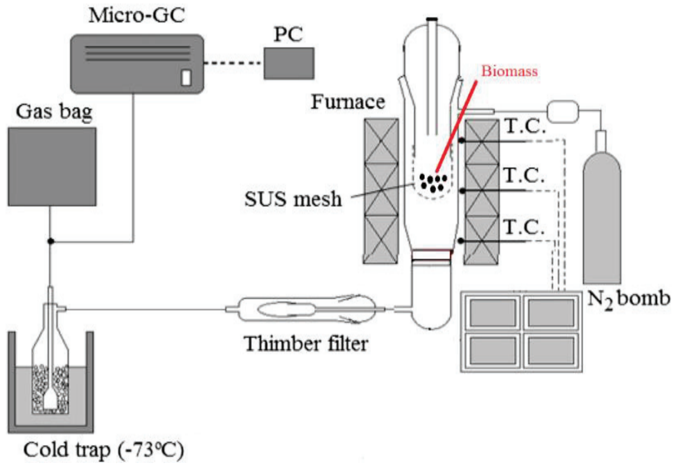

FIGURE 1. Experimental apparatus for pyrolysis

RESULTS AND DISCUSSION

TGA Analysis

Combusting of biomass without the presence of oxygen and at a certain heating rate to a maximum temperature required is a pyrolysis process. Basically, pyrolysis of biomass is in the temperature range 300-650 °C. Pyrolysis can be divided into two kinds, slow pyrolysis and fast pyrolysis. Slow pyrolysis is a pyrolysis process that the residence time of vapor is on minutes or longer. This type of process mainly produces char. Usually, the range of temperature is 400-500 °C in a well-insulated reactor. Fast pyrolysis is a pyrolysis process that has short vapor residence times [5]. This type of process mainly produces tar or bio-oil and gas. To determine the pyrolysis characteristic of ulin wood, we using TGA (Thermogravimetric analysis). We also compared it with another biomass and non-biomass source such as pine wood and sub-bituminous coal. Figure 2 shows the compared profiles of the weight fraction and derivative weight curve of the pine wood, sub-bituminous coal, and ulin wood.

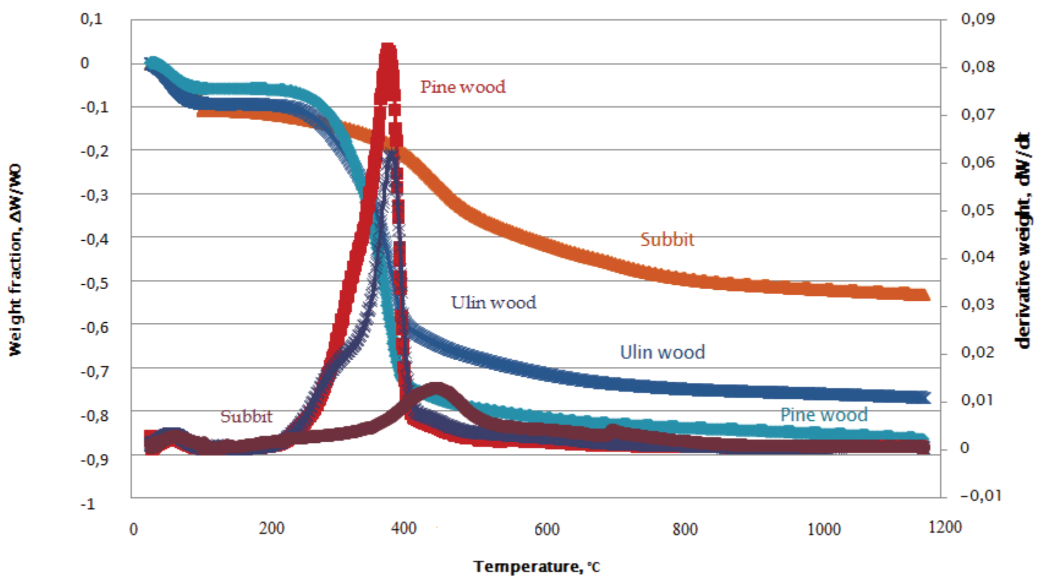

FIGURE 2. TGA profiles for pine wood, sub-bituminous coal and ulin wood

TGA experiments runs for about small sample for about 5-10 mg [6]. The TGA ran for small sample to decrease the consequence of the secondary reaction [6]. For this experiment, the sample was measured for 10 mg and the gas N_2 flow was 100 ml/min. The condition was set for three conditions, first heating up from 25 – 125 °C, then linear for about 30 min, then heating up again to 1200 °C. The heating rate was 50 K/min.

The weight fraction of all solid sources was decreased as the increasing of the temperature. The derivative weight of pine wood and ulin wood has similarity that the highest derivative weight is around temperature 350 °C. The derivative weight of the sub-bituminous coal has similar trend as low-grade coal and high-grade coal because coal has carbon as the dominant component. The loss of weight of all solid source is small at temperature 200 °C due to moisture evaporation. From all of the solid sources, sub-bituminous coal has the lowest weight loss because of high fixed carbon, then followed by ulin wood and the highest is pine wood. For ulin wood, thermal decomposition began at temperature 300 °C. Char oxidation began at 800 °C. So, for pyrolysis of ulin wood we decided to observe the pyrolysis characteristics at temperature 300 °C, 400 °C, 500 °C, 600 °C, and 700 °C.

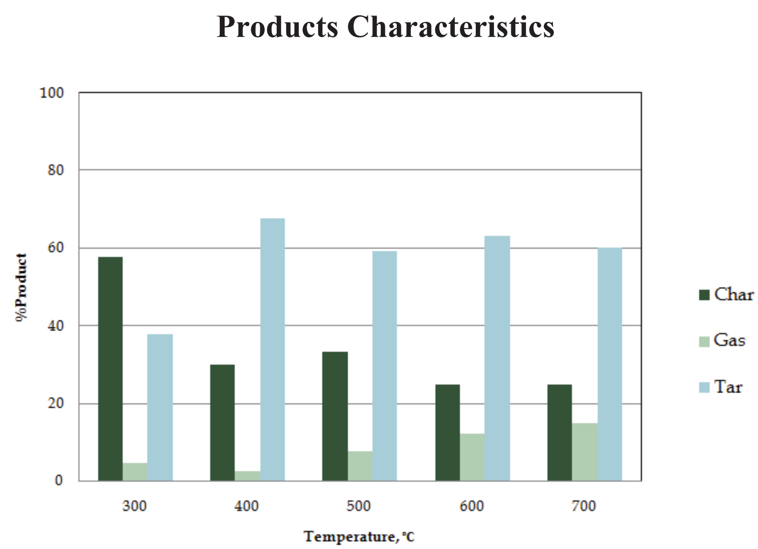

FIGURE 3. Total mass products of pyrolysis of ulin wood residues

Figure 3 shows the total mass products (char, gas, and tar) of ulin wood residues. Di Blasi *et al*. studied about pyrolysis of wood chip suggested that as the increasing of temperature, solid product initially decreasing because of competition among producing char and devolatilization [7]. The characteristics of devolatilization is based on the temperature reaction [8]. Along with higher temperature, the solid product tend to be constant due to the variation of wood degradation temperature. In the case of ulin wood, the trend seems to be as same as Di Blasi. The char yield is decreasing from temperature 300 °C and tends to become constant start from temperature 400 °C until 700 °C. But at temperature 500 °C, the char yield is higher than char at temperature 400 °C. This may be due to the heating while pyrolysis process so the char still higher than gas and liquid product.

Figure 4 shows about comparison SEM (Scanning Electron Microscopic) image among raw ulin wood residues before pyrolysis process and char products after pyrolysis process. E. Cetin *et al*. studied about char morphology of radiata pine, spotted gum, and sugar cane with the effect of heating rate and pressure by SEM analysis [9]. According to SEM images, the morphology of char changed after the pyrolysis process. From the SEM images on Fig.4, it is seen that raw ulin wood there are no visible pores while char products have visible pores. Char product pyrolysis at temperature 300 °C has pores within size 0.0167 mm. Char product pyrolysis at temperature 500 °C has pores within size 0.011 mm. While char product pyrolysis at temperature 700 °C has pores within size 0.0071 mm.

Table 2 shows the elemental analysis of char products pyrolysis. The contain of carbon is the highest among the other components at each sample of char. At higher temperature, the tar is mainly produced, so the carbon content in char is high. At higher temperature the carbon and nitrogen content are increasing while the hydrogen and oxygen content are decreasing.

From Di Blasi's studies, liquid yield tends to be increasing due to temperature increasing until maximum yield then will decreasing due to much higher temperature. So there is an optimum temperature to produce a liquid product in the pyrolysis process. In this pyrolysis of ulin wood residues, the optimum temperature to produce a liquid product is 400 °C. The study of Di Blasi *et al*. for wood chip has the optimum temperature to produce liquid 500 °C [2].

Meanwhile, the gas yield will be increasing due to temperature increasing [2]. At higher temperature, the gas yield will be higher. In pyrolysis of ulin wood residues, the highest gas yield is at temperature 700 °C. But there is an anomaly at the temperature 400 °C. At this temperature, the gas yield is lower than gas yield at temperature 300 °C.

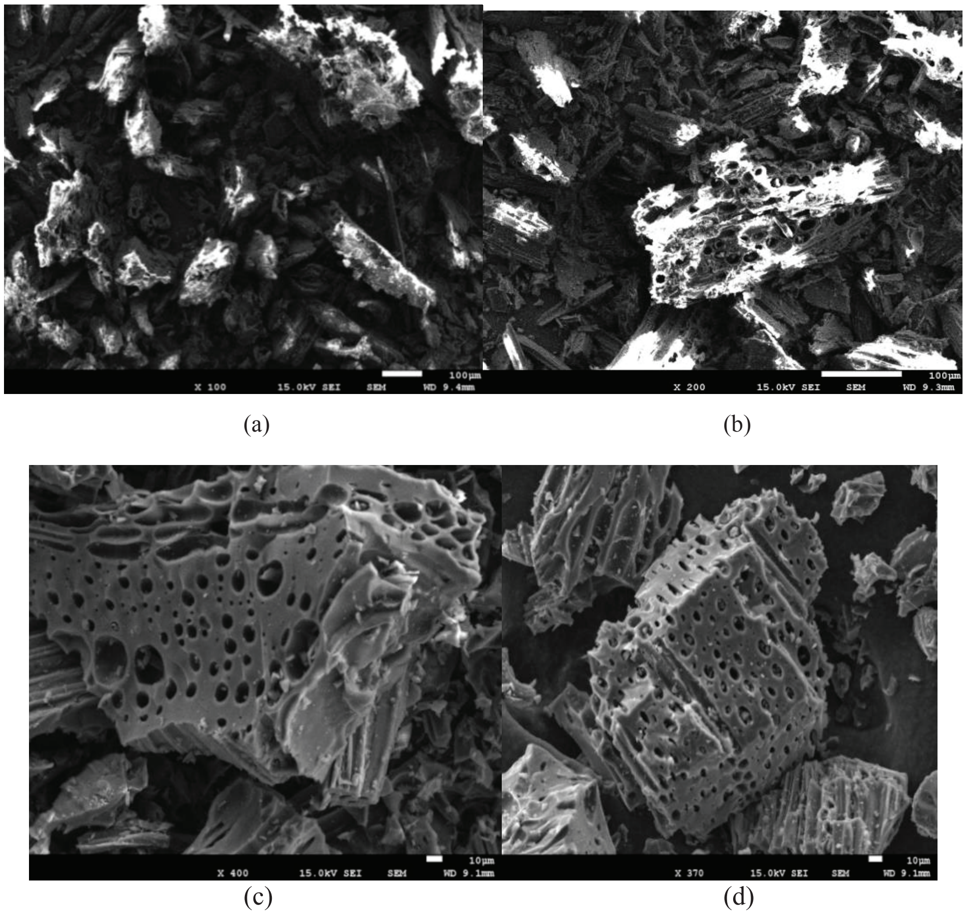

FIGURE 4. SEM images of char products: (a) ulin wood, (b) char at 300 °C, (c) char at 500 °C, (d) char at 700 °C

TABLE 2. Elemental analysis of char

Temperature (°C)	Mass sample (g)	Components			
		C (%)	H (%)	N (%)	O (%)
300	1.782	62.95	4.96	0.44	31.65
400	1.717	76.62	4.05	0.62	18.71
500	1.768	84.41	3.47	0.66	11.46
600	1.737	91.17	2.74	0.68	5.41
700	1.715	93.80	1.88	0.70	3.62

In this studies overall the gas yield has the lowest yield at each temperature reaction. The value of mean gas yield for each temperature reaction is about 8.35% of the total of the pyrolysis products. The composition of gas yield is shown in Fig. 5.

Figure 5 shows that the biggest three compositions of gas yield are CO, CO_2, and CH_4. Main gases produced at highest temperature [10]. These main gases producted at 700 °C. At low temperature is quite low but increasing significantly at a higher temperature, starts from temperature 600 °C and 700 °C. The composition of another hydrocarbon gases such as C_2H_6, C_3H_8, n-C_4H_{10}, i-C_4H_{10} is very low at every temperature pyrolysis. The trend of CO_2 gas is a little bit different from the other gases.

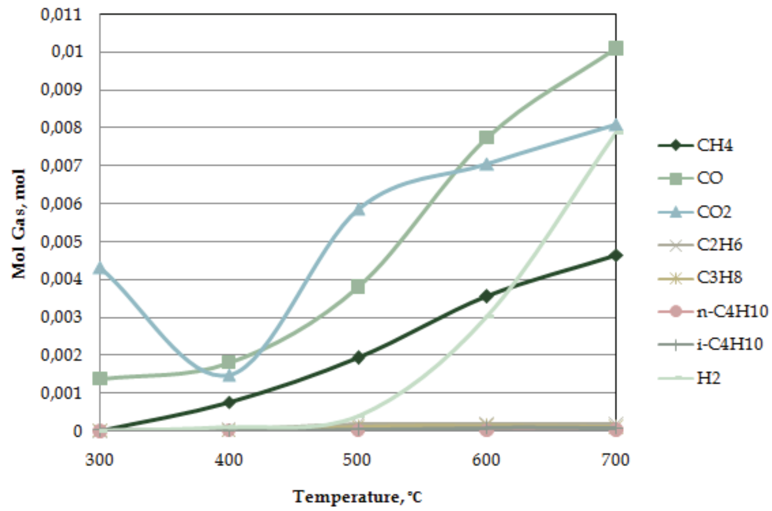

FIGURE 5. Gas compositions of the gas yield

CONCLUSION

Ulin wood residues as a biomass can be converted into bioenergy through pyrolysis process. Temperature influences the characteristics of pyrolysis products of ulin wood residues. The optimum temperature to produce a liquid product is 400 °C. The highest amount of char is at temperature 300 °C. The highest temperature pyrolysis produces char within the lowest pore size. Gas yield is the lowest amount of product pyrolysis. CO, CO_2, and CH_4 are the main composition of the gas yield at each temperature pyrolysis.

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