The Chemical Composition and Physical Properties of the Light and Heavy Tar Resulted from Coconut Shell Pyrolysis

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ABSTRACT

The tar resulted from pyrolysis of coconut shell is a waste. It is important to be clarified their chemical composition and physical properties in order to find out their feasibility as source of a fuel. This research was resulted two immiscible organic fractions, and these were further determined their physical properties such as water composition by using ASTM D-95 methods, ash composition (ASTM D-482), flash point C.O.C (ASTM D-92), kinematics of viscosity (ASTM D-445), and caloric valued using bomb calorimetric. In addition, tar composition was determined by gas chromatography-mass spectrometry (GCMS). The result provided oil which was categorized as light and heavy bio-oils. The light bio-oil has specific gravity 0.99, ash content 0.01%, kinematics viscosity 25.5 cSt, flash point <27 ^oC, pH 3 and heating value 10304 kcal/kg. On the other hand, heavy bio-oils gave specific gravity 1.13, ash 0.46%, kinematics viscosity 185 cSt, flash point 134 ^oC, pH 2.5 and heating value 6210 kcal/kg. Moreover, the light bio-oil contained 79 compounds which was composed of phenol 16.4%, hydrocarbon 12.4%, phenolic 27.6%, other oxygenated compounds 53.6%, and acetic acid 3%, meanwhile the heavy bio-oils contained of 18 compounds which was consisted of phenol 31.2%, lauric acid 6.0%, phenolic 27.6%, and other oxygenated compounds 35.3%, respectively. With this result, it was clarify that these bio-oils could not be used directly as a fuel for motor nor diesel machinery.

Key words: tar composition, physical properties of fuel, coconut shell, pyrolysis

INTRODUCTION

The technology of pyrolysis has been used by local community since a long time ago, and conventionally has been applied to produce a solid carbon. Recently, this method has paid many attentions for development such as by using condensation to afford liquid smoke besides the solid carbon. The physical properties and composition of this liquid smoke depend on the type of biomass, methods and the pyrolysis conditions such as temperature, leaving time of steam, rate of increasing temperature pyrolysis. The conventional pyrolysis, usually applied temperature is roughly 500 ^oC, leaving time of the steam between 5 and 30 minute, and using atmospheric pressure. The steam did not directly flow out such as in quick pyrolysis. This condition is able to initiate the reaction further within each steam component to provide a solid carbon and liquid smoke [1].

Coconut shell usually contains 32% of hemicellulose, 14% cellulose, and 46% lignin. Pyrolysis of it can provide the decomposition of these components with different rate on applied of a range temperature. The different of reactivity from each component cause competition during decomposition process [2]. The process-condition optimum for a slow pyrolysis of coconut shell using constant fire was at 550 ^oC, heating rate 60 ^oC per minute, and provided liquid smoke maximum 45% [3]. The resulted chemical composition of liquid smoke was a mixture, mostly contained water, carboxylic acids, carbohydrate, and the derivative of lignin. In addition, the oils resulted also slightly acidic, viscous, reactive, and thermally unstable. Their chemical composition and physical properties was much different to the petroleum based-oils. This result, in order to direct application as motor fuel still requires specifics attentions and further research.

The standard as a fuel usually following the American Society for Testing and Material (ASTM) grade, and the standard of fuel resulted from biomass pyrolysis until recent time was not determined yet. Because the variation composition and physical properties of the liquid smoke, and also the pyrolysis methods still under going development. As consequence, application this liquid smoke resulted from biomass pyrolysis still require along study to find out a standard and properties as a fuel [4].

Pyrolysis of coconut shell by local community usually was conducted at 350 ^oC under atmosphere pressure and afforded solid carbon, liquid fraction or liquid smoke, organical fraction (tar), and gas. Economically, the solid carbon produced usually could be convert to afford activated carbon and bricket. Meanwhile liquid smoke commonly used as a food preservant, and increase latex acidity. The gas resulted could also be recycle directly as fuel for pyrolysis. But, tar product has no further application.

EXPERIMENT

The sample of tar was afforded from direct pyrolysis of coconut shell (150 kg), conditions: 250 – 300 ^oC, 5-6 h pyrolysis, at atmosphere pressure. Smoke resulted was condensed and further distillated to afford two layers product. After left overnight, this layer afforded upper layer (liquid smoke) and bottom organic layer (light tar), and residue as a heavy tar.

Figure 1. The home-scale convensional apparatus for pyrolysis: 1. Convensional furnace with wood as fuel; 2. Reactor; 3. Smoke flow pipe; 4. Tar condensed collecting; 5. Condenser; 6. Liquid smoke collecting.

Determination physical properties and chemical composition

The light and heavy tar was determined their physical properties, including water content (ASTM D-95), ash content (ASTM D-482), flash point C.O.C (ASTM D-95), kinematics viscosity (ASTM D-445), calor value (bomb calorymetry). Chemical composition was determined with GCMS (Shimadzu QP2010S, column Rtx-5MS, 30 meter, internal diameter 0.25 mm, carrier gas helium, oven 70 ^oC, injection temperature 310 ^oC, pressure 13.7 kPa, total flow 40.0 mL/min, colomn flow 0.50 mL/min, purge flow 3,0 mL/min and split ratio 72.9).

RESULT AND DISCUSSION

Physical properties of light and heavy tar

The physical properties of tar as a fuel were determined using the methods for analysis of petroleum oil according to the recommendation of Oasmaa and Peacocke (2010) [9]. Result for determination of light and heavy tar was presented in Table 1.

Table 1. Physical properties of tar from coconut shell pyrolysis

Parameter	Light tar	Heavy tar	Range [5]	
			Min.	Max.
Ash, % wt	0.01	0.46	-	0.10
Water, % vol.	7	24	-	1.0
Kinematics viscosity, cSt	25.5	185	-	180
Flash point, ^oC	< 25	134	60	-
Density	0.99	1.13	-	0.991
pH	3	2,5	-	-
Calor value, kkal/kg	10304	6210	10.000	-

The ash content of heavy tar indicated higher than the value of the light tar (Table 1), and this result also much higher than the maximum ash content which was recommended by Directorate General of Oils and Gas (Dirjend MIGAS) in Indonesia [5]. The ash content reported for coconut shell itself was 0.9% [6]. The higher content of ash in liquid fuel may causes precipitation of waste in the burning system. Furthermore, the water content both from light and heavy tar indicated much higher that that allowed in the standard of fuels. The higher water content may be caused by the humidity of source coconut shell and reaction product of dehydration during the pyrolysis. From the result, water content ranged from 15 to 30%, and depended on the type and conditions of raw material of coconut shell and pyrolysis process [7].

Viscosity can be determined as the ability of a liquid flowing. Table 1 display the heavy tar viscosity was slightly higher to the maximum value for standard of oil as a fuel. The determination of bio-oil as a light, light-medium, medium, and heavy bio-oils was based on their physical properties such as kinematics viscosity (cSt). Their value was 1.9-3.4, 5.5-24, 17-100, and 100-638, respectively [8]. According this classification, the light tar could be categorized as light bio-oil, and the heavy tar as a heavy bio-oil.

The flash point of a fuel indicated the lowest temperature of a fuel could be burnt and giving quick flash in a flame. The value of flash point for light tar showed below 25 ^oC (Table 1). This result indicated the chemical composition of light tar was mostly volatile compounds and easily to be burnt such as hydrocarbon and alcoholic compound with low molecular weight. On the other hand, the heavy tar gave much higher a flash point and over to the minimum value of the standard as a fuel.

The Chemical Composition of the Light and Heavy Tar

Pyrolysis process afforded three liquids, a water (polar) and two organic layers (light and heavy tar). High content of water and lignin from source of coconut shell could separate these layers [9]. The result for chemical analysis of the light (Figure 1 and Table 2) and heavy tar (Figure 2 and Table 3) was presented as a chromatogram. The light tar contained minimum 79 compounds detected, and the heavy tar indicated 18 compounds.

Coconut shell was composed mostly with lignin and then cellulose and hemicellulose. Pyrolysis decomposed these compounds. Hemicellulose will decompose at temperature 200-260 ^oC, cellulose in 240-350 ^oC, and lignin between temperature 280 and 500 ^oC. The heavy tar mostly contained an oxygenate compounds and phenolic with phenol as the higher component (Table 2 and 3). This was dominantly a result of lignin decomposition. The heavy tar was a water-immiscible organic fraction, which mostly was a reaction product of a heavy lignin pyrolysis [9]. Moreover, the more dominant of phenol compound in both fractions exposed that phenol separation was not only because its boiling point, but its interactive properties with the other composed components or create an azeotropic mixture and could be evaporated in broad boiling points. Because of this phenol compounds contained in both fraction resulted more acidic. The only sharp different of both fractions was their flash point, which was the light tar much easy to be burnt compare to the heavy tar. This was described by more volatile chemical composition of light tar such as hydrocarbon compounds and low-weight of alcohol compounds.

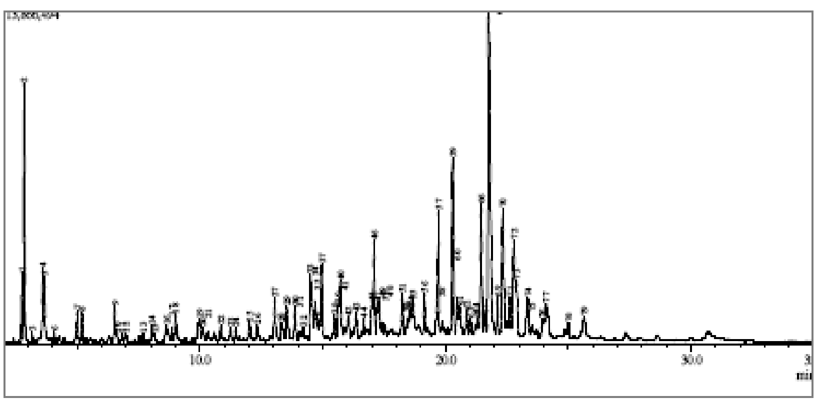

Figure 2. GCMS chromatogram of light tar

Table 2. Chemical composition of light tar

Compounds	Molecular Weight (MW)	%	Compounds	Molecular Weight (MW)	%
Propanone	58	1.01	Propanoic acid	74	0.39
Methyl acetate	74	5	Unknown	136	0.72
Oxolane	72	0.16	2,3-Dimethyl-2-cyclopentanone	110	0.71
Methyl propanoate	88	1.45	Acetylfurane	110	0.35

Methyl propanoate	88	1.29	Methyl decanoate	186	0.97
Methyl isopropyl ketone	86	0.2	2-Methylcumarone	132	2.54
Ethylacetone	86	1.06	2-Methylcumarone	132	0.81
Methyl butanoate	102	0.71	Propoxybenzene	136	1.18
Toluol	92	0.89	Clorius	136	0.28
1-n-Decene	140	0.24	Unknown	124	0.23
Hexanone-(3)	100	0.26	2-Methylindanone	146	1.22
Acetylpropionyl	100	0.26	Unknown	246	0.2
Methyl valerate	116	0.2	4,7-Dimethylbenzofuran	146	0.53
Hexadecane	156	0.47	4,7-Dimethylbenzofuran	146	0.57
Methyl 2-butenoate	100	0.24	5,6-Dimethylindan	146	1.01
Ethyl benzene	106	0.86	Bicyclo[5.3.0]decapentaene	128	0.98
1,3-dimethyl benzene	106	1.27	Methyl dodecanoate	214	3.92
1,2 dimethyl benzene	106	0.91	Unknown	154	0.32
2-Methylcyclo-pentanone	98	0.37	Guajol	124	5.18
Dodecane	170	0.15	p-Creosol	138	0.91
2-Ethyltoluene	120	0.47	2-Methylnapthalene	142	0.64
1-Dodecene	168	0.4	2,6-Dimethylphenol	122	0.67
Benzo cyclobutane	104	0.3	2-Methylnapthalene	142	0.41
1,2,4-Trimethyl benzene	120	0.62	4-Ethylguaiacol	152	0.25
n- Tridecane,	184	0.61	p-Creosol	138	0.41
1-Methoxy benzene	108	1.39	p-Creosol	138	3.86
2-Methyl-2-cyclohexanone	110	0.93	1,4-Dimethoxy-2-methylbenzene	152	0.59
2-Methyl-2 cyclo-pent-1-enone	96	1.24	Phenol	174	16.4
Methyl caprilate	158	1	Methyl tetradecanoate	242	0.92
n-Heptadecane	240	0.27	4-Ethylguaiacol	152	4.9
2-Methyl-1-methoxy benzene	122	0.29	1-Hydroxy-2-ethylbenzene	122	1.75
Acetic acid	60	2.99	2,3-Xylenol	122	4
4-Methyl-1-methoxy benzene	122	1.01	m-Toluol	108	1.7
3-Methyl-1-methoxy benzene	122	0.62	2-Methoxy-4-propylphenol	166	1.53
2,3-Dimetil-2-cyclopent-1-enone	110	0.52	4-methyl-2-ethylphenol	136	0.27
Furane	96	1.84	1-Ethyl-4-methoxy benzene	136	0.83
Indane	116	0.51	Phlorol	122	1.94
Acetyl furane	110	1.03	Methyl hexadecanoate	270	0.31
Benzofurane	118	1.74	Syringol	154	0.86

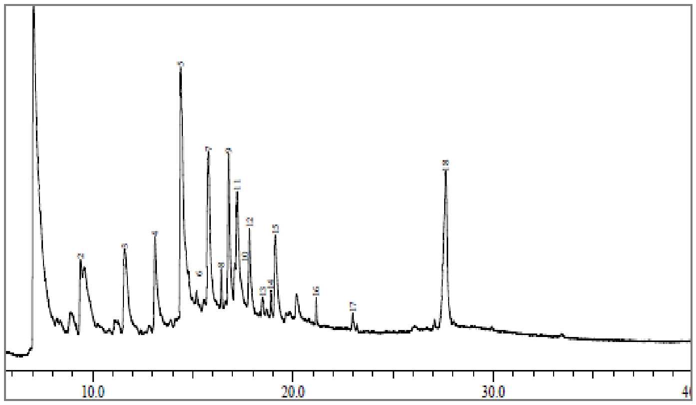

Figure 3. GCMS chromatogram of the heavy tar

Table 3. Chemical compisition of the heavy tar

Compounds	Molecular Weight (MW)	%	Compounds	Molecular weight (MW)	%
Benzenol	94	31.2	Dibenzylbutyrolactone	374	1.21
Guajol	124	1.62	Vulvic acid	200	5.96
p-Creosol	138	5.51	Unknown	226	2.72
4-Ethylguaiacol	152	3.90	Methoxyeugenol	194	0.55
Syringol	154	16.52	Methyl tetradecanoate	242	0.43
Methyl 4-methoxybenzoate	166	1.10	Methoxyeugenol	194	3.93
unknown	168	8.32	Methyl hexadecanoate	270	0.39
Methyl dodecanoate	214	0.73	Methyl cis-9-octadecenoate	296	0.16
1,2,3-Trimethoxy-5-methylbenzene	182	5.64	Isooctyl 2,4-dichloro-phenoxyacetate	332	10.04

CONCLUSION

Pyrolysis of the coconut shell provided two organic fractions, and categorized as a light and heavy tars. The light tar was easier to be burnt than the heavy tar, and both of them was a strong acidic. The GCMS analysis gave 79 compounds indicated in the light tar and it was composed of phenol (16.4%), hydrocarbons (12.4%), phenolic (27.6%), oxygenate compounds (53.6%), and acetic acid (3%). Meanwhile the heavy tar contained 18 compounds, which consisted of phenol (31.2%), lauric acid (6.0%), phenolic compound (27.6%) and the other oxygenate compounds (35.3%). However, both of these tars could not directly to be used as a fuel.

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