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Characterization of Rubber Shell Liquid Smoke at Various Pyrolysis Temperatures and the Application to Latex Coagulant

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ABSTRACT
Rubber commodities in East Kalimantan have a significant growth area. From 2008 to 2017, the rubber plantation area's growth averaged 3.79%, with rubber production growth up to 4.88% per year. In addition to producing rubber latex, which is the main product of rubber trees, it also produced many rubber shells. With the vast achievement of rubber plantation area in East Kalimantan, the rubber shells production will increase as well so that it has the potential to become untapped waste. The test results of the chemical content of rubber shells taken from smallholder plantations in the Marang Kayu area contain high halo cellulose and alpha-cellulose levels, about 76.7% and 44.267 so that it has the potential to be processed into liquid smoke. Research has been carried out on rubber shell liquid smokes manufacture using a pyrolysis process with various temperatures of 250-300ºC, 300-350ºC, 350-400ºC and 400-425ºC. The highest liquid smoke rendement is at pyrolysis temperatures of 300-350ºC, maximum decomposition process of cellulose and lignin content happened from rubber shells. The highest acid content test on liquid smoke by titrimetric was shown at the pyrolysis temperature of 350-400ºC, about 12%. Identification of the chemical content of liquid smoke using GCMS was obtained with the highest content in acid products and their derivatives, with an area of acetic acid of 54.43%. Liquid smoke of rubber shells formed has a pH of 3.4 so that it can be used as a latex coagulant and produce rubber quality of SIR 5 sheets according to SNI 1903-2011.

Keywords: *Rubber Shell, Pyrolysis, Liquid Smoke, GCMS*

1. INTRODUCTION

Rubber commodities in East Kalimantan have a significant growth area. During the 2008-2017 periods, rubber plantation's width area grew up to 3.79 % on averagely, with the growth of rubber production averaged 4.88 % per year. In 2017 the rubber planting area reached 115.160 Ha, with total production up to 63.510 tons approximately. (East Kalimantan's Provincial Agriculture Department, 2018). In addition to producing the rubber latexs that are their main product, Rubber trees also produce plentiful rubber shells. Due to rubber plantation growth in East Kalimantan, rubber shells' production is increasing as well so it has potentially become untapped waste.

Liquid smoke is a liquid mixture from smoke dispersion colloids in the water, which was the condensation products containing few components formed due to pyrolysis of organic material, such as cellulose, hemicellulose and lignin. During pyrolysis, cellulose will produce carbonyl and acetic acid along with its homologous, lignin will produce phenol and tar, and hemicellulose will produce furfural, furan and carboxylic acid [1]. The manufacture of liquid smoke from rubber shells with a pyrolysis temperature of 200ºC produces liquid smoke with a pH of 2,495 and an acid content of 13.71% acid [2]. Various agricultural product has biomass waste contain specific chemical and physics properties that produce different liquid smoke quality. Therefore, an application is crucial to analyze the liquid smoke component in various biomass waste [3].

The liquid smoke utilization of rubber shells was hoped to replace formic acid that was usually used as coagulant latex. Formic acid is an expensive and hard to get coagulant chemical. Therefore, it was needed to

indentify and characterize the quality of liquid smoke from the rubber shells in various temperature processes that could be used as coagulant latex to increase the value of rubber shells waste and increase environmentally friendly use material.

2. METHODOLOGY

2.1. Research Material

Rubber shells and latex obtained from CV Nursery Marang Kayu Kutai Kartanegara

2.2. Tools

Pyrolysis tank, oven, glassware, furnace, stove, scale, pH meter, measuring cups, rubber grinding tool, coagulation container, GCMS

2.3. Method

Rubber shells are dried up under the sun until dry (water content ± 10-15%). The rubber shell is scaled before being entered into the pyrolysis tool. Next heats up the temperature 250-300ºC, 300-350ºC, 350-400ºC, 400-450ºC. When the pyrolysis tool is heated up, the condenser is watered with ±25ºC to cooling down the formed. During the pyrolysis process, the temperature and time are measured. The formed liquid smoke is paced into Erlenmeyer and measured its volume to know the amount of rendement production. Liquid smoke is identified by using GCMS Methods.

3. RESULTS AND DISCUSSION

Research results are conducted by using several steps. The following results are obtained:

3.1. The Content of Rubber Shells

Rubber shell as raw material from Marangkayu Kutai Kartanegara is tested, it showed in Table 1.

Table 1. Rubber Shells test

Parameter Uji	Hasil Uji
Haloselulosa	76.7%
Alfa selulosa	44.267%
Kadar abu	23.25%
Kadar air	10.57%
Karbon terikat	0.353%

Rubber Shells containing high halo cellulose and alfa cellulose; 76.7% and 44.267% respectively, ash content 23.25%, and water content 10.57%, where rubber shells have been dried up for three days. During the process of pyrolysis, the cellulose will produce carbonyl and acetic acid with its homologous. Biomass pyrolysis produces methanol rendement from methoxyl groups such as uranic acid and methyl ester and the other decomposition of the plant material, acetic acid component, from the acetyl group on hemicellulose [4].

3.2. Liquid Smoke Rendement

Rendement is the parameter to estimate the amount of raw material in producing products and know the processing efficiency rate. In this research, 20 kg of rubber shells obtained rendement ± 30.6 % with leftover charcoal, about 43%. Meanwhile, the amount of liquid smoke rendement obtained in each temperature process could be seen in Figure 1**.**

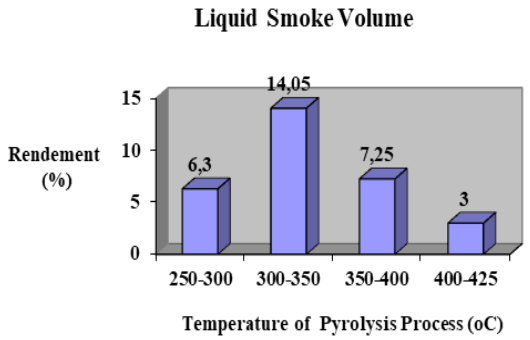

Figure 1 Liquid smoke of rubber shells' result.

Figure 1 shows the average result of liquid smoke obtained from shells pyrolysis process has yield as following results: temperature range 250-300ºC rendement's amount: 6.3%; temperature range 300-350ºC rendement's amount: 14.05%; temperature range 350-400ºC rendement's amount: 7.25% and temperature range 400-425ºC rendement's amount 3%. Liquid smoke of rubber shells obtained the most at pyrolisis range 300-350ºC with rendement's amount: 14.05% amount. According to [5], the result is the condensation result of rubber shells' pyrolysis process obtained the most at temperature 300oC for 3 hours duration. According to [6], liquid smoke of bamboo's rendement obtaining from pyrolysis reaching 61.34%, liquid smoke of pine wood 49.60 % and liquid smoke of teak wood 43.78 %. The amount of liquid smoke rendement produced by the pyrolysis process depends on the type of the chosen raw material [7]. According to [8], the liquid smoke composition is influenced by the temperature and pyrolysis time. The yield will increase according to the increase in pyrolysis time. The more raw materials, the longer it takes for the decomposition process. However, there was a decrease in yield with increasing time. This is due to the high temperature and long time, causing a greater loss of weight. This happens because the temperature of the water in the condenser increases so that the smoke is not condensed optimally.

The decomposition of rubber shells contents' time show in Figure 2.

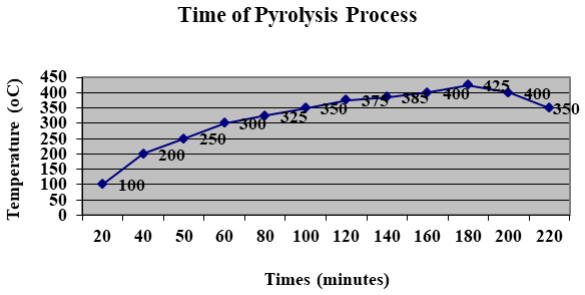

Figure 2 Time of Pyrolysis process.

Figure 2 shows that the pyrolysis process's total time is 200 minutes with shells' weight of about 20 kg. The longest time for the decomposition of rubber shells is 60 minutes with pyrolysis temperature at 350-400ºC. This condition shows the perfect decomposition reaction that happened from the rubber shells.

The maximum temperature is reached at 425ºC, after that it show to experience decreasing temperature and only obtain liquid smoke with lowest rendement about 3%. This happened both due to burned out rubber shells and turned to charcoal residue

3.3. Chemical Components Content of Rubber Shells' Liquid

Liquid smoke is tested using GC-MS to know the content of the chemical component in it. The test result of the various temperature against component can be seen as following:

Table 2. Liquid Smoke Components in the Temperature Pyrolysis Process at 250-300oC

No	% area	Liquid Smoke Components
1	24.88	Acetic acid (CAS) Ethylic acid
2	12.11	Anhydro Beta D-Glucopyranose
3	8.06	Acetic acid, propyl ester (CAS), n-Propyl acetate
4	7.89	2-Propanol (CAS) Isopropyl alcohol
5	5.78	2-Furancarboxaldehyde (CAS) Furfural
6	3.00	Butanal, 3-methyl- (CAS) 3-Methylbutanal
7	2.92	Phenol, 2,6-dimethoxy- (CAS) 2,6-Dimethoxyphenol
8	2.92	3(2H)-Pyridazinone, 4,5-dihydro-6-methyl- (CAS) 2,3,4,5-Tetrahydro-6-Methyl
9	2.73	Phenol, 2-methoxy- (CAS) Guaiacol
10	2.83	Propanoic acid, 2-methyl-, ethyl ester (CAS) Ethyl isobutyrate

Table 3. Liquid Smoke Components in the Temperature Pyrolysis Process at 300-350oC

No	% area	Liquid Smoke Components
1	23.60	Acetic acid (CAS) Ethylic acid
2	18.84	L-Serine (CAS) Serine, L-
3	10.26	Butanal, 3-hydroxy-(CAS) 3-Hydroxybutanal
4	5.30	2,5-Dimethoxybenzyl alcohol
5	4.88	Phenol, 2,6-dimethoxy- (CAS) 2,6-Dimethoxyphenol
6	3.95	1-Propanol, 2-methyl- (CAS)
7	3.25	2-Furancarboxaldehyde (CAS) Furfural
8	3.22	Cyclopentanone, 2-methyl- (CAS) 2- Methylcyclopentanone
9	3.18	Phenol (CAS) Izal

Table 4. Liquid Smoke Components in the Temperature Pyrolysis Process at 350-400oC

No	% area	Liquid Smoke Components
1	40.31	Acetic acid (CAS) Ethylic acid
2	7.89	1,6- Anhydro Beta D-Glucopyranose
3	6.63	Carbamic acid, phenyl ester (CAS) Phenyl carbamate
4	6.69	Acetic acid, pentyl ester (CAS) n-Amyl acetate
5	5.73	Butane, 2-methyl- (CAS) Isopentane
6	4.63	Acetic acid (CAS) Ethylic acid
7	2.80	Acetic acid (CAS) Ethylic acid
8	2.81	2,5-Dimethylcyclopentanone
9	2.36	Phenol, 2-methyl- (CAS) o-Cresol
10	2.18	Phenol, 3,5-dimethyl- (CAS) 3,5-Xylenol

Table 5. Liquid Smoke Components in the Temperature Pyrolysis Process at 400-425oC

No	% area	Liquid Smoke Components
1	36.10	Acetic acid (CAS) Ethylic acid
2	16.72	Phenol (CAS) Izal
3	6.29	Phenol, 2-methyl- (CAS) o-Cresol
4	6.32	Ethane, 1,1,1-triethoxy- (CAS) Triethyl orthoacetate
5	4.78	cis-1,3-Dideuterio-1,3-cyclohexandiamine
6	3.36	Phenol, 3,5-dimethyl- (CAS) 3,5-Xylenol
7	3.97	Phenol, 2-methyl- (CAS) o-Cresol
8	2.96	2-Propenoic acid, 2-methyl-, pentyl ester (CAS) n-Amyl methacrylate
9	2.37	Cyclopentanone, 2,5-dimethyl- (CAS) 2,5-Dimethyl cyclopentanone

The components of rubbers shells' liquid smoke in Table 2-5. The biggest component is acetic acid, and its derivatives at a temperature range 250-300ºC with amount 32.94%, temperature range at 300-350ºC counted for 23.6%, temperature range 350-400ºC as many as 54.43% and temperature range at 400-425ºC counted for 36.10%. Liquid smoke of rubber shells also contains 2-Propanol, Furfural, Butanal, Propanoic acid, L-Serine, Butanal and its derivates, Carbamic acid and its derivatives, butane and its derivatives, and phenol. According to [9], liquid smoke from palm oil shells contained 27 components and empty fruit bunches of 13 components, with the highest concentration of chemical components, were acetic acid and phenol. According to [10], the process of wood chemical decomposition at pyrolysis process happens gradually as follows at temperature range 100-150°C the only thing that happened is the evaporation of water molecules, at temperature 200-240°C, the decomposition of hemicellulose and cellulose become pyrolignate solution (organic acid with low boiling point such as; acetic acid, formiat, methanol, wood gas, wood gas (CO dan CO_2), and a few of ter). At temperature 240-400°C, depolymerization and bond breaking between C-O and C-C occurred. In this temperature range, cellulose has been degraded. Lignin started to decompose, and producing tar, pyrolignate solution and CO gas decreased, while CO, CH_4, and H_2 increased. At a temperature of more than 400°C, forming an aromatic layer occurred, and lignin is still decomposing til at temperature 500°C. The test result of acid content in rubber shell liquid using the titrimetric method shown in Table 6.

Table 6. The test result of acid content in rubber shell liquid

I (Temperature 250-300°C)	II (Temperature 300-350°C)	III (Temperature 350-400°C)	IV (Temperature 400- 425°C)
7.5%	10.5%	12%	7.5%

Table 6 show the temperature of 350-400oC obtained acid content of 12%.

The optimum condition acid content of liquid smoke from rubberwood at a temperature of 388.24°C obtained acid content of 16.64% [11]. Component of the commercial liquid smoke fractions was quantified as follows: acetic acid, carbonyls quantified as 2-butanone and phenols quantified as 2,6-dimethoxy phenol [12]. The acetic acid in liquid smoke has a high role as organic acids [13].

The liquid smoke pH value of rubber shell smoke's acidity is 3.4, which can coagulate the latex. The rubber sheet quality test is based on SNI 1903-2011. As shown in Table 7, the test result of rubber sheet quality met the quality requirements of SNI 1903-2011 and qualified as SIR 5.

Table 7. The test result of rubber sheet quality

Parameters	Results	SNI (Rubber Sheet) SIR 5
Po	47	Min 30
Pa	33	-
PRI	70	Min 70
Dirt Content,%	0.024	Max 0.05
Ash Content,%	0.41	Max 0.5
VM Content,%	0.55	Max 0.8
Nitrogen content,%	0.47	Max 0.6
Mooney viscosity	69.4	-

4. CONCLUSION

The highest component of rubber shells' liquid smoke is acetic acid and its derivatives. The highest liquid smoke rendement obtained pyrolysis temperature from 300 to 350°C; meanwhile, the highest acetic acid content in liquid smoke obtained pyrolysis temperature from 350-400oC with a width of 54.43%. Rubber shells' liquid smoke used as coagulant latex and can produce rubber sheet SIR 5 according to SNI 1903-2011.

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