

Pyrolysis and Characterization of the Products for Recycle of Rubberwood Residues

Student ID#: 02M18316

Name: LIM, KEAN GIAP

Supervisor: EGASHIRA, RYUICHI

ゴム樹材残材のリサイクルのための熱分解および生成物のキャラクタリゼーション

林 建業

元素分析および熱分析によりゴム樹材およびその熱分解について明らかにした。これに基づいたゴム樹材の乾留及びこれに続く単蒸留により、粗木酢液、純木酢液、などの種々の転換物を作成した。これらの分析により、ゴム樹材残材のリサイクルの可能性を示した。さらにゴム樹材加工プロセス内でのリサイクルの一例として、得られた純木酢液によるゴム樹材の抗菌・防腐を試みた。分析の結果と併せて、この純木酢液が防腐性能を有することを示した。

1, Introduction

In Southeast Asian Countries, rubberwood (*Heavea brasiliensis*) furniture is one of the important products for exportation. Various forms of residues are discharged from the process of rubberwood manufacturing. At those countries, the wood residues are illegally disposed and burned at isolated country sites or dumping sites. In Malaysia, about 4×10^5 ton/year of rubberwood residues were evolved[1]. These disposal methods do cause environmental problems, such as accidental forest fire, emission of CO₂, soil contamination by toxic preservatives etc. Besides, the issue of wood preservative has also been paid attention because of the toxicity of present wood preservative products. Tanjore et al. has stated the Pentachlorophenol, one of the substances of wood preservative, is highly toxic, easily diffuse into environment and cause illness to people who handled it[2].

Meanwhile, wood can be precursor of various kinds of useful chemical substances, e.g., activated carbon, pyrolygneous acid (PA) and fuel offgas. The PA has been reported as a potentiality of protecting wood from decay fungi [3,4]. A simple material balance calculation of wood residues conversion and recycle of previous research showed that PA derived from rubberwood residues could be used as a substitute for the ordinary toxic wood preservatives in wood process[1].

In this study, in aiming to tackle mentioned problems in Southeast Asian Countries, a better understanding of decomposition behavior of rubberwood; the effects of temperature on the yields and characteristic of products; and the potential of wood preservation is a priority assignment, since it has not yet been investigate. In this study, the thermal analysis was conducted to obtain thermochemical fundamental information of decomposition of rubberwood. Subsequently, the pyrolysis of the rubberwood was studied experimentally to yield char and crude pyrolygneous acid(CPA). The PA obtained from CPA by simple distillation was then tested for the effectiveness of antifungus. Yielded char, CPA, PA and WT were characterized.

2, Elemental and Thermal Analyses of Rubberwood

2.1, Experimental

Rubberwood sawdust from wood manufacturing factory of Malaysia was used as raw material for the experiments. The raw material of rubberwood sawdust was grinded to 250 μ m prior to experiment. TG and DTA measurements were conducted simultaneously in TG8120 thermobalance (Rigaku Corporation).

The experiments were carried out under inert helium atmosphere with a constant flow rate of 100ml/min. The mass of material, 20 mg, was distributed all over the volume of platinum crucible. Five different heating rates were used: 2, 20, 35, 50, 100 °C/min. The maximum heating temperature was 850 °C.

2.2, Results and Discussion

The result of the ultimate analysis is shown in **Table 2.1**. The moisture content was calculated by drying the material for 24 Hr. at 105°C drying oven, 1 Hr. cooling in desiccator. The result reported here is based on the dried sawdust.

The DTG curves are shown in **Figure 2.1**. From the DTG curves, the decomposition of rubberwood takes place vigorously at temperature 240-420°C. Within this temperature range, two peaks were observed. The first peak shows decomposition of hemicellulose. This constituent has been reported degrade around 245°C[5]. The second peak is due to decomposition of cellulose and lignin. The mainly decomposition at this range is cellulose [5].

The DTA curve of $\beta=20^\circ\text{C}/\text{min}$ is shown in **Figure 2.2**. The endothermic peak near to 100°C is caused by dehydration of free water of the sample. The cellulose exothermic peak was observed near 400°C. The later peak is due to decomposition of lignin. This observation is same as reported phenomena of different wood [6].

The parameters need to establish the kinetic equation for the thermal decomposition of the samples was defined as follows.

In this study, the thermal reaction of wood assumed as solid state reaction, thus, the reaction equation was defined as,

$$\frac{dX}{dt} = k(1 - X) \quad (2.1)$$

Here, X is the conversion, and was defined as,

$$X = \frac{W_0 - W}{W_0 - W_f} \quad (2.2)$$

The rate constant, k can be expressed according to the Arrhenius equation, that is:

$$k = A e^{-\frac{E}{RT}} \quad (2.3)$$

The heating rate was expressed as $dT/dt=\beta$. Substitute equation 3.4 to equation 3.2, following equation can be obtained.

$$\ln\left(\frac{dX}{dt}\right) = \ln\left(\beta \frac{dX}{dT}\right) = \ln[A(1-X)] - \frac{E}{RT} \quad (2.4)$$

By plotting $\ln(dX/dt)$ vs. T^{-1} at specified X obtained by different β result a straight line. Apparent activation energy, E can be obtained by taking mean value of each straight line.

The value for the kinetic parameter at wood decomposition temperature range was obtained at same conversion ($X=0.2, 0.3, 0.4, 0.5$ and 0.6). The results are shown in **Figure 2.3**. The obtained apparent activation energy, E was 160 kJ/mol. This value was within the range reported for various type of wood[7,8].

Table 2.1: Characters of rubberwood sawdust

Moisture content	[-]	0.1020
Ash	[wt%](m.f)	1.50
Element	[wt%](m. f.)	
C	46.79	
O	44.20	
H	5.89	
N	0.31	

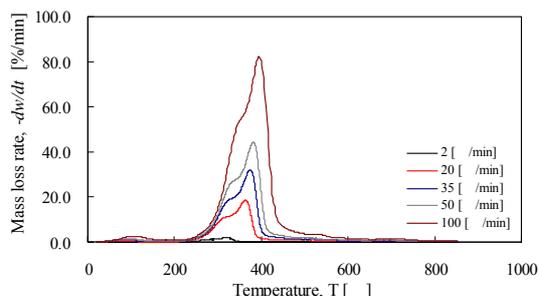


Figure 2.1: Influence of heating rate on DTG curve.

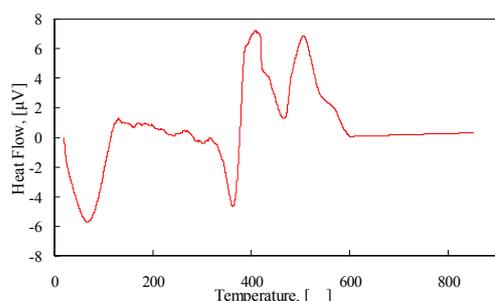


Figure 2.2: DTA curve of decomposition of rubberwood

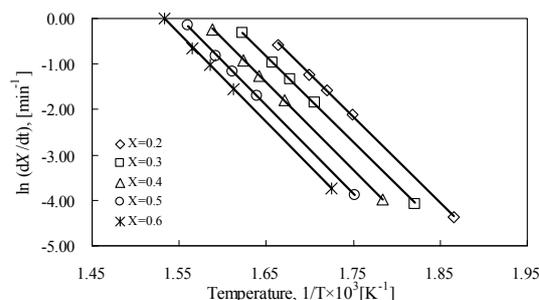


Figure 2.3: Evaluation of thermal decomposition of rubberwood by differential method

3, Pyrolysis of Rubberwood

3.1, Experimental

A schematic of the apparatus is shown in **Figure 3.1(i)**. The feed rubberwood sawdust was pyrolyzed in the N_2 atmosphere by the electric tube furnace. The flow rate of N_2 was 0.5 L/min (s.t.p.). Pyrolysis temperature was varied in the range of 200~1,000 °C. The offgas was condensed to obtain CPA by two condensers.

For the section of products characterization, elemental analysis was conducted to the obtained char. Identification of components of CPA was carried out by using gas chromatography (GC). Shimadzu Hicap-CBP20 capillary column (ID 0.22mm×25m) and Shinwa HR-1 capillary column (ID 0.22mm×25m) were attached to GC equipment(Shidmazu Corporation). The detector model for both GC is flame ionization detector (FID). The water content of CPA was analyzed by using Karl Fischer (Model 756 Titrino, Methrom-Shibata Co., Ltd.). The pH of CPA was determined by using glass electrode pH meter (TOA Electronic Ltd.).

3.2, Results and Discussion

The yield of each product fraction was expressed as,

$$Y_i = \frac{W_i}{W_0} \quad (3.1)$$

The yield of interested components was defined as,

$$y_i = x_i \cdot Y_{CPA} \quad (3.3)$$

The yield of each product is shown in **Figure 3.2**. As temperature increases, the char yield decreased, as a result the

devolatilization reactions become successively more favored. The decomposition of char occurred actively between 230~430°C. For the temperatures above 530°C, the yield of char tends to become constant at 0.24. Contrary, the yield of non-condensable gas(G) and CPA has increased by increasing the pyrolysis temperature. The yield of CPA above 430°C tends to become constant at yield of 0.52. The yield of G becomes constant above 530°C. This implied that decomposition of rubberwood above 430°C enhance only the yield of G.

The result of elemental composition of char obtained from various pyrolysis temperatures is shown in **Figure 3.3**. The carbon content increased with increasing the temperature. Oxygen content took the opposite tendency. This showed the bond of oxygen dissociated from substances of wood. Meanwhile, the O/C ratio decreased with increasing pyrolysis temperature. This implied the progress of carbonization of sample is high at higher temperature range.

The pH value of yielded CPA is shown in **Figure 3.4**. The result has indicated no effect of pyrolysis temperature on pH value of CPA. As expected, the pH value is nearly constant at 2.5. As a fact, compositions of CPA showed high value of acetic acid. Meanwhile, the composition of CPA in this study was different from previous study[1].

The yield of components of CPA is shown in **Figures 3.4** and **3.5**. As pyrolysis temperature increase, the yield of interested component also increased. Two temperature groups of constant yield of component can be observed. One is constant above 330°C, that is acetic acid, methanol, acetone, guaiacol and syringol. The other is constant above 430°C, that is water, phenol, o-cresol, m-cresol and p-cresol. This grouping is almost same as reported by literature where oxygenates will appear around 400°C and phenolic compound around 500°C by flash pyrolysis[9].

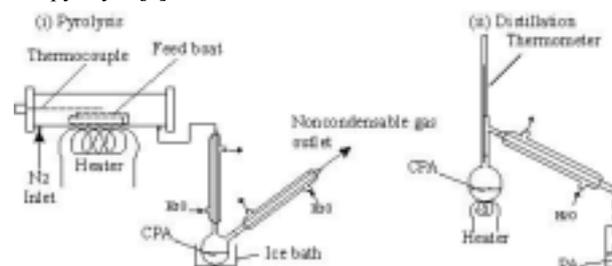


Figure 3.1: Schematic diagram of experimental apparatus.

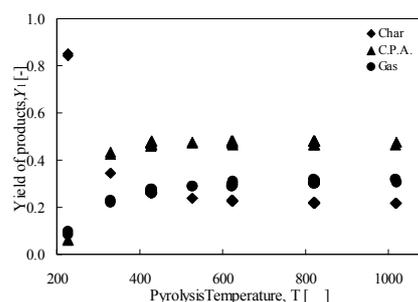


Figure 3.2: Effect of temperature on the yield of products.

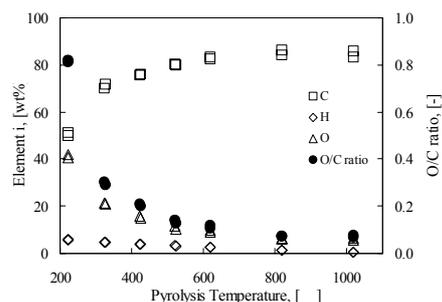


Figure 3.3: Elemental analysis of char obtained at various pyrolysis temperatures

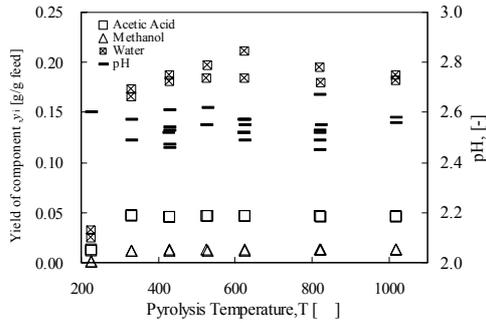


Figure 3.4: Effect of temperature on pH and component yield of CPA

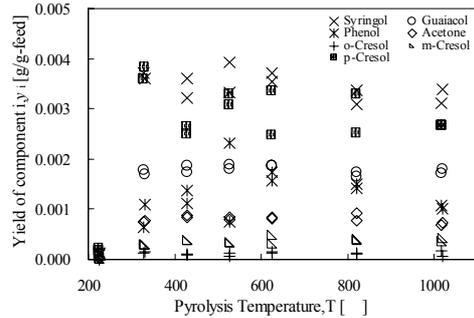


Figure 3.5: Effect of temperature on component yield of CPA

4, Simple Distillation of CPA

4.1, Experimental

The CPA was separated into PA as a distillate and wood tar (WT) as a still residue by simple distillation. WT should be separate in the reason of quality and handling at other process of wood manufacturing. The schematic diagram of instrument is shown in **Figure 3.1(ii)**. The operation was terminated at 120°C. Characterizations of PA and WT were carried out by the same analysis method described in 3.1.

4.2, Results and Discussion

The yield of products in simple distillation was defined as,

$$y_i = \frac{W_i}{W_{CPA}} \quad (I=PA,WT) \quad (4.1)$$

The yield of PA and WT relative to the sawdust was expressed as,

$$\langle Y_i \rangle = \frac{W_i}{W_0} \quad (4.2)$$

The yields of PA and WT from CPA, Y_i are shown in **Figure 4.1**. The yield of PA was constant at 0.5 with CPA yielded above 430°C. The yield of PA based on the sawdust, $\langle Y_i \rangle$ was about 0.24. The yield of PA in this study was quite smaller than previous value[1], due to the different characteristic of used PA as mentioned in 3.2.

The pH value of yielded PA is shown in **Figure 4.1**. The pH of each PA took almost the same value of 2. PA was more acidic than CPA. The yields of components in PA are shown in **Figure 4.2**. The acetic acid, methanol, acetone and water were higher than 0.6. Phenolic compounds were also identified in PA. This suggested that the PA could be used as a preservative.

5, Antifungus & Wood Preservation of PA

5.1, Experimental

The PA used here was obtained by distillation of CPA yielded at 400, 600, and 800°C. The decay fungus used was *Fomitopsis palustris* (Berk. et Curt.) Gilbn. & Ryv., FFPRI 0507 as brown rotter and *Trametes versicolor* (L.:Fr.) Pilát FFPRI 1030. as white rotter.

Antifungus Each PA material was diluted by ion-exchange water to make 2, 4, and 20-folds of concentration dilution. Petri

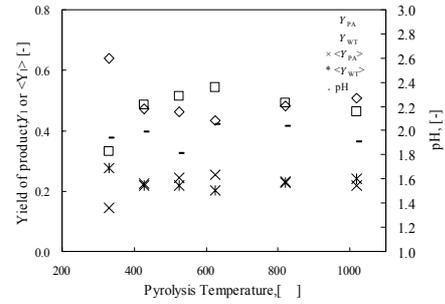


Figure 4.1: Yield of distillation products and pH of PA

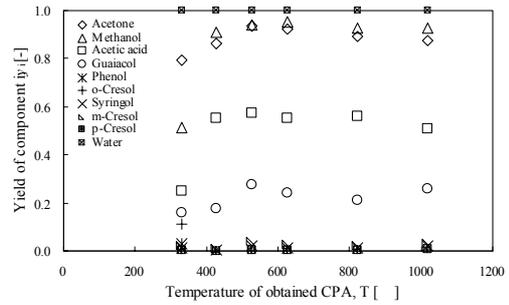


Figure 4.2: Yield of distillate components

dishes (ID 90×15mm) were filled with 20ml potato dextrose agar (PDA) and 1ml of each concentration of PA dilution was added uniformly to PDA. The fungus was inoculated to the center of prepared Petri dish. The Petri dish was placed upside-down in dark place for 6 and 12 days incubation. Incubation temperature was 27°C. The state of growth was visually inspected and the growth inhibition was evaluated by measuring the diameter of growth colony.

Preservation Undiluted and 2-folds diluted PA solutions were used. The experiment was carried out according to JWPS-FW-S.1[11]. Three rubberwood blocks (T:15mm, W:20mm, L:20mm) were used for each concentration of PA. The wood blocks were soaked in PA for 5 days in shaking incubator. Wood blocks were then transfer to culture box containing fungus to be exposed for 12 days at 27°C. Observation of the presence of fungus on wood surfaces and measuring of mass loss was carried out to evaluate the wood preservative effectiveness.

5.2, Results and Discussion

In the experiment of antifungus, the evaluation of growth inhibition index was defined as,

$$\alpha = \frac{d_0 - d_1}{d_0} \times 100 \quad (5.1)$$

Antifungus The result of 12 days antifungal test is shown in **Figure 5.1**. 2 and 4-folds of PA from either pyrolysis temperature solution did show fungus resistances with the growth inhibition index of 100%. The resistance was poor at 20-folds concentration of PA, especially the PA obtained by distillation of CPA yielded at 430°C. Since the component compositions of all PA are almost the same with one another, this may be affected by other components contained in PA, which are not identified in this study.

Preservation A wide colony of white fungus and tiny colony of brown fungus adhered at wood blocks was observed on the specimens without PA treated. Wood blocks treated with any dilution of PA showed no sign of fungus on the surfaces. This observation indicated PA has the potential of wood preservation. Evaluation by mass loss was indistinctness due to the period of incubation of wood blocks was not long enough.

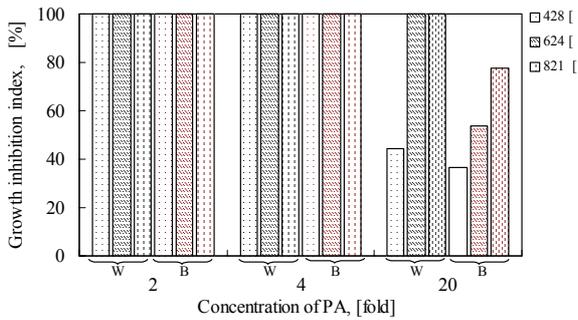


Figure 5.1: The effect of various PA on antifungal.
 W: *Trametes versicolor* B: *Fomitopsis palustris*

4, Conclusion

The mechanism of thermal decomposition of rubberwood was clarified by thermal analysis. The elemental analysis of rubberwood and characterization of various yielded products showed that rubberwood residues can be recycle. PA is suggested to be used as wood preservative in rubberwood manufacturing process. The result of PA component compositions, antifungal and preservation test has proved the possibilities. This was proposed as a way to solve environmental problem in Southeast Asian Countries.

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Nomenclature

W	Weight of sample or product	[g]
X	Conversion	[-]
T	Temperature	[°C]
t	Time	[s], [min]
k	Rate constant	[s ⁻¹]
β	Heating rate	[°C min ⁻¹]
E	Activation energy	[kJ mol ⁻¹]
A	Arrhenius constant	[s ⁻¹]
R	Gas constant	[J K ⁻¹ mol ⁻¹]
n	Reaction order	[-]
Y ₁	Yield of product	[-]
y _i	Yield of component	[-]
x _i	Composition of component	[-]
<Y _i >	Overall yield of product	[-]
α	Growth inhibition index	[%]
d	Diameter of colony	[cm]

<Subscripts>

0	Initial
l	CPA, Char, G, PA, WT
i	Component
l	Weight/diameter after desired days of incubation

Reference

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