Improvement of Rubberwood Process Using the Thermally Treated Products from Wood Residue

Student ID#:04M18110   Name:KONISHI, Shunsuke   Supervisor:EGASHIRA, Ryuichi

1. Introduction:

In Southeast Asia Countries, various forms of residues are discharged from the process of rubberwood manufacturing. In this process, a portion of wood residues are being thrown away to isolated country site and are burned illegally. These disposal methods do cause environmental problems, such as accidental forest burning, release of hazardous gases, and soil contamination by toxic preservatives. Besides, the issue of wood preservative has also been paid attention because of the toxicity of present wood preservative products. These problems are considerably serious in these countries.

Wood can be thermally decomposed into useful materials such as pyroligneous acid (PA), char and fuel off-gas. PA from wood can be used as a substitute for the ordinary toxic wood preservative[1,2,4]. The char was studied to have a high adsorption capacity to remove unfavorable components from waste water[3,5]. Off-gas contains some flammable gases such as, H_2, CO, CH_4.

In this study, we are trying to improve the existing rubberwood process. Thermal decomposition of rubberwood was conducted to obtain the useful products. The yield and characteristic of the products were estimated. We proposed a rubberwood process in which the products is utilized as a preservative, adsorbent and gas energy. The balance of heat energy as well as material balance in the whole process was estimated based on the experimental data.

2. Thermal treatment of rubberwood and characterization of the products:

2.1, Experimental

Thermal treatment

Rubberwood sawdust was treated thermally to obtain crude pyroligneous acid (CPA), char, and off-gas in the various conditions. **Table 2.1** shows the experimental conditions, specified temperature, steam flow rate and holding time at specified temperature. The CPA was distilled into PA and tar at 413K. The apparatus of thermal treatment and distillation are figured in **Figure 2.1**.

Characterization of the products

The CPA, PA and off-gas were analyzed by GC to know the concentration of main components. Elementary analysis of the char and rubberwood were also conducted. Preservative efficiency of PA was estimated by comparing the composition of phenolic compounds in PA with that in the previous preservative. Phenols are known to have the preservative effect. The calorific value of the gas, char and wood were calculated from enthalpy difference between before and after burning.

Adsorption

The char produced at 700K was used in the adsorption experiment. The char was mixed with various concentrations of aqueous phenol and the mixtures were put in the agitator at 303K for 120 hours enough for the adsorption equilibrium. After the adsorption experiment, the aqueous phenols were separated from the char by the filtration. The initial and separated phenol solutions were analyzed by GC. The adsorption mass of phenol on the unit mass of the char was estimated.

Table 2.1   Experimental condition in the thermal treatment

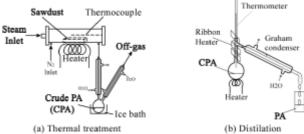| Run No	Experimental condition
A-700	700K, 0.03m³-steam/h, hold time 1hour
A-900	900K, 0.03m³-steam/h, hold time 1hour
A-1092	1092K, 0.03m³-steam/h, hold time 1hour
A-1292	1292K, 0.03m³-steam/h, hold time 1hour
B-700	700K, 0.03m³-steam/h, hold time0.5hour
B-900	900K, 0.03m³-steam/h, hold time 0.5hour
B-1092	1092K, 0.03m³-steam/h, hold time 0.5hour
B-1292	1292K, 0.03m³-steam/h, hold time0.5hour
C-1092	1092K, 0.015m³-steam/h, hold time 1hour
C-1292	1292K, 0.015m³-steam/h, hold time 1hour

Figure 2.1 Schematic diagram of experimental apparatus

2.2, Results and Discussion

Thermal treatment

The yield of each product in the thermal treatment was expressed as,

$$Y_i = \frac{W_i}{W_{sawdust}} \qquad (2\text{-}1)$$

The yield of each product is shown in **Figure 2.2**. It was studied that char is completely produced around 600K and the produced char is gradually consumed by steam above 800K In this study, the char yield decreased with increasing the treatment temperature due to the high consumption of carbon by steam. No char remained in the thermal treatments at 1292K. The char was consumed more in the experiment A than the others due to the more steam provided. As for CPA, the yield was not influenced by the temperature. It is because the wood is

completely decomposed into CPA by 600K and in the higher temperature range, the yield of CPA does not change any more. The CPA is composed of the volatile components from the wood and the water from the feed steam. The yield of CPA is determined by not only feed wood but also feed steam mass. The yield of CPA was higher in the Experiment A than the others. It is because that more steam was provided in the apparatus and the unreacted steam was directly condensed to the CPA. Contrary, the yield of the off-gas increased with increasing temperature. In the range of higher temperature, more char and steam were reacted and more off-gas was produced. The produced gas contained many inflammable components such as, H_2 and CO above 1092K. The reactions are written below,

$$H_2O + C \rightarrow H_2 + CO \qquad (2\text{-}2)$$

$$H_2O + CO \rightarrow H_2 + CO_2 \qquad (2\text{-}3)$$

Distillation

The CPA produced at each thermal treatment condition was distilled around same temperature, 413K. The yield of each product in the distillation was expressed as,

$$Y_i = \frac{W_i}{W_{CPA}} \qquad (2\text{-}4)$$

The yield of interested components in the PA was defined as,

$$y_i = x_i \cdot Y_{PA} \qquad (2\text{-}5)$$

The yield of PA and tar is shown in **Figure 2.3**. It was very difficult to control the distillation temperature which influences strongly the yield of products. The higher distillation temperature, the higher yield of PA and the lower yield of tar. As a result, the yield varied in the distillation of each CPA due to the unstable distillation conditions. However, the variation range of PA yields was between 0.7~0.9 and these values were enough for a wood preservative.

The concentration of phenols in PA is shown in **Figure 2.4**. All the PA contained larger phenols, preservative components, than the previous PA which was confirmed to have preservative effect. The result indicated that all the PA of this study had high preservative effect and could be used as a preservative.

Adsorption capacity of the char

Figure 2.5 shows the adsorption isotherms of phenol by the char. The char treated with steam atmosphere at 700K was prepared in this study. The adsorption by the char of 1292K was not conducted because the char was not obtained in the thermal treatment as mentioned above. The adsorptions by the char of 900 and 1092K were conducted in the previous studies[1,3,5]. The amount of adsorption of phenol increased with increasing temperature of thermal treatment. It means that the char treated at higher temperature has higher adsorption capacity. The adsorption capacities of char with steam were somewhat smaller than that of the chars with CO_2. However, the char with steam above 873K had enough adsorption capacity for an adsorbent of waste water. The Langmuir isotherm equation was used to quantify the adsorption capacity of each char. Product of the adsorption coefficient and the maximum adsorption amount of char, K·q , represents the relative adsorption capacity in a dilute solution. **Table 2.2** shows K·q of each char and also the relative adsorption capacity on CO_2-1073 basis.

Heating value of Off-gas

Figure 2.6 shows the mass production of components in the Off-gas at left axis, and the heating value at right side. The off-gas mainly contained Hydrogen, Carbon oxide, Carbon dioxide and Methane. The flammable gas, Hydrogen and Carbon oxide, increased with treatment temperature due to the

active reactions of carbon and steam. These reactions were shown above at equation (2-2),(2-3). At higher temperature, these reactions were more active, and Hydrogen and Carbon oxide were produced more. These high production of flammable gases resulted in the increase of the heating value of Off-gas. At low temperature, 700 and 900K, the off-gas contained little flammable gas and had low heating value as a heat recovery for the thermal treatment. On the other hand, the off-gas produced at 1092 and 1292K had high heating value and these were useful for the heat recovery.
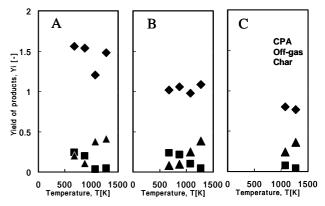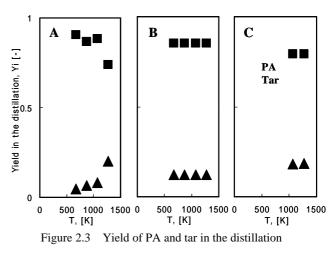

Figure 2.2 Yield of the products in the thermal treatment

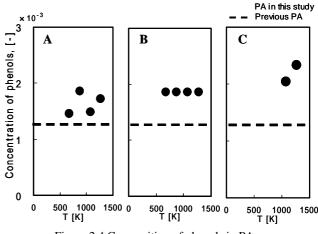Figure 2.3   Yield of PA and tar in the distillation
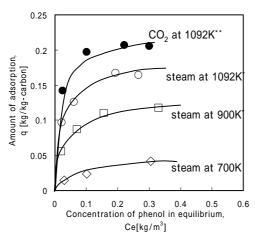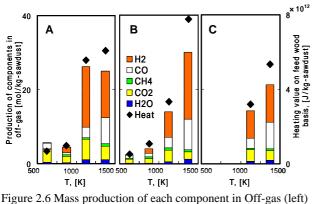

Figure 2.4 Composition of phenols in PA

Figure 2.5 Adsorption isotherms of phenol in the model solution

Table 2-2 Adsorption capacity of each char produced

	$q_8 \times K_L$ [m^3/kg-carbon]	Adsorption capacity [-]
CO_2-1092	20.3252	1
steam-1092	8.2645	0.4066
steam-900	4.5290	0.2228
steam-700	0.5293	0.0260

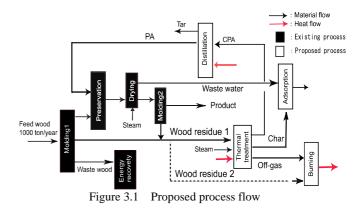Figure 2.6 Mass production of each component in Off-gas (left) and heating value of Off-gas (right)

3. Balance of material and heat in the process:

3.1, Proposed rubberwood process

We proposed an improved rubberwood process utilizing the thermal treated products, PA, char, and off-gas, from wood residue as shown in **Figure 3.1**. Some waste wood are burned to generate the heat for Drying. A portion of the remaining waste wood, wood residue1, is decomposed into the useful products in Thermal treatment. The other wood residue, wood residue2, is burned to recover the heat for the proposed process. After PA is put on the surface of wood product for preservation, it is washed out into the wastewater. This wastewater is contacted with the char adsorbing the phenols derived from PA. The Off-gas is also burned with wood residue2 in Burning and produces the heat for Thermal treatment and Distillation.

Figure 3.1 Proposed process flow

3.2, Calculation condition and assumptions

Feed wood of 1000 ton/year is provided to Molding1. It is molded into wood product, wood residue and waste wood. The wood product of 200 ton/year is treated with preservative by PA of constant rate, 33.4 ton/year. Flow rates of thermally decomposed products are calculated using the results of yield in the experimental section. The PA produced in Distillation are directly used as a preservative. All the PA components are assumed to be washed out into waste water during Drying. The flow of char requirement for adsorbent is determined from the results of adsorption experiment to meet the regulation of waste water. The flow of PA requirement for preservation is calculated from the reference data and it is constant, 33.4 ton/year. It is estimated the flow rate of required wood residue1 to obtain the requirement of PA and char. The flow of each material is defined as flow rate, ton/year.

The heat consumption in the thermal treatment was estimated from the difference between the enthalpy of inlet and outlet materials. The enthalpy of the inlet materials, sawdust and water, were calculated at room temperature and that of the outlet, Char, CPA and Gas, were calculated at the specified temperature of apparatus. We assumed the composition of each material, that the char was pure carbon, and CPA was composed of only water, acetic acid, methanol and phenol, and off-gas contained only H_2, CO, CO_2, CH_4 and H_2O. The same enthalpy calculation was conducted in the distillation. The flow of each heat is defined as heat flow, J/year.

3.3, Results and discussion

Figure 3.2 (a) shows the flow rates of the PA produced and preservative requirement against flow rate of wood residue1. The flow rate of the PA increased with wood residue1 and these were larger than that of requirement in all the cases. **Figure 3.2 (b)** shows the flow rates of the char produced and adsorbent requirement. The char treated at 900K were satisfied the requirement for the process at all the flow of wood residue1. The char treated at the other temperatures were less than the requirement at low flow of wood residue1. As the flow of wood rsidue1 increased, these char products increased and reached the requirement at a flow rate of wood residue1. **Figure 3.3** shows the minimum flow rate of wood residue1 at which the either PA or char meets the requirement The flow rate for char requirement was always larger than that for PA. We defined the residue1 flow for char as a required residue1 flow rate to meet both PA and char requirement.

Figure 3.4 shows the heat consumption in Thermal treatment and Distillation, and also heat recovery from off-gas and wood residue2 at the each defined residue1 flow. The heat consumption increased with increasing the defined residue1. When the residue was treated at 700K, the defined residue1 was high and then the heat consumption was also high. We estimated how much wood residue2 was burned for heat recovery. **Figure 3.5** shows the flow rate of the total required

wood residue, which is sum of the wood residue1 to obtain PA and char, and the wood residue2 to recover the heat. At the present process, wood residue is discharged at various flow rates. This flow rate depends on the situation. From the reference data, we estimated that the wood residue could be discharged from 66 to 374 ton/year. This range is shown as a red line in Figure 3.5. When the wood residue was treated at A-900, B-900, B-1092 and C-1092, the flow rates of the total required residue were below this range. The result means that in these conditions, the PA and char were satisfied the requirement and the heat is also recovered completely.

4. Conclusion :

We confirmed that the useful materials were produced by thermal treatment of wood. The PA had high preservative effect. The char had high adsorption capacity. The off-gas had high heating value and the heat recovery from off-gas was 10-40% of the heat consumption in the proposed process. The result of the process calculation showed that, when the wood residue was treated at 900 or 1092K, the total requirement of the residue was lowest. In these conditions, the useful products were obtained enough for the preservative and adsorbent, and the heat consumption for the proposed process was also recovered.
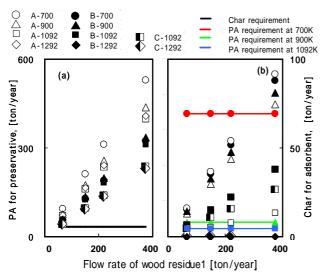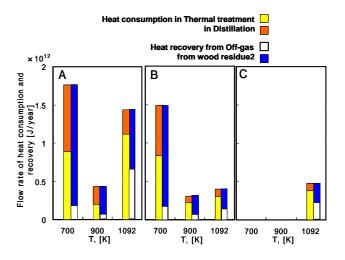

Figure 3.4   Flow rate of heat consumption and heat recovery at the defined flow rate of wood residue1

Figure 3.2   Flow rates of PA(a) and Char(b) against flow rate of wood residue1

Figure 3.5   Flow rate of the total required wood residue

Nomenclature

W	Mass of material	[g]
T	Specified temperature in the thermal treatment	[K]
Y_i	Yield of product	[-]
y_i	Yield of component	[-]
x_i	Composition of component	[-]
q	Amount of adsorption	[m^3/kg-carbon]
q	Saturated amount of adsorption	[m^3/kg-carbon]
Ce	Equilibrium concentration	[kg/m^3]
K_L	Langmuir adsorption coefficient	[m^3/kg]

References
[1] Sato, M., Bachelor thesis, Tokyo Institute of Technology, Japan, March (2005)
[2] Lim, K.G., Master thesis, Tokyo Institute of Technology, Japan, March (2004)
[3] Konishi, S., Bachelor thesis, Tokyo Institute of Technology, Japan, March (2004)
[4] Lim, K.G., et al.; RSCE 2004, ES-257 (2004 Bankok)
[5] Sato, M., et al.; SCEJ 70th annual meeting S117 (2005 Nagoya)

Figure 3.3   Flow rate of wood residue1 required for PA and char