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Improvement of Rubberwood Manufacturing Process by Utilization of Thermal Treatment of Wood Residues

Hiroaki Habaki[1], Saori Mitani[2], Rizafizah Othaman[3], Ryuichi Egashira[4]
[1,4]Dept. of International Development Engg., Graduate School of Science and Engineering, Tokyo Institute of Technology, Japan
[2,3]Dept. of International Transdisciplinary Science and Engg., School of Environment and Science, Tokyo Institute of Technology, Japan
([1]hhabaki@tse.ens.titech.ac.jp, [3]rizafizah@ukm.edu.my, [4]regashir@tse.ens.titech.ac.jp)

Abstract- The sawmilling process in the rubberwood manufacturing process has been studied and the thermal treatment of the rubberwood residue was designed to be incorporated in the process. The thermal treatment of the rubberwood sawdust aimed to prepare the off-gas, pyroligneous acid and activated carbon to use in the process as a heat source, preservative agent and adsorbent for wastewater treatment, respectively. Firstly, the thermal treatment of the sawdust was experimentally conducted to analyze the off-gas and some combustible components, such as hydrogen, carbon monoxide and methane, were measured. Hydrogen had a major contribution to show relatively high heating value of the off-gas. The yield of off-gas increased with the treatment temperature and the heating value of the off-gas increased with the temperature mainly due to the increment of hydrogen yield. The suggested process was roughly evaluated with the simple balances of material and energy. The prepared pyroligneous acid and activated carbon were sufficient for the preservation and wastewater treatment in the process and the suggested process could make all residues desterilized in the process. When the treatment temperature was 1079K, the obtained off-gas could provide the lower heating value to meet the heat requirements of both thermal treatment and preservation operations.

Keywords- *Rubberwood Manufacturing Process, Rubberwood Residue Utilization, Thermal Treatment*

I. INTRODUCTION

Rubber tree (*Hevea Brasiliensis*) has been widely planted in South Asia for latex production. After the end of the latex-producing cycle, some of the old trees were used as heat source and the rests were left decayed. Then, the effective utilization of the trees has been developed to produce high-end furniture from environmentally friendly wood resource. The hewed out trees were firstly processed to logs and timbers, and the furniture was manufactured. [1]. Although the most part of the old trees are effectively utilized, various forms of wood residues (WR) are still generated as byproducts to cause the serious environmental issues [2, 3]. For the effective utilization of the WR, the modified sawmilling process was suggested, as illustrated in Fig. 1 [4]. The feed logs are cut using band saws into timbers and sent to the Preservation and drying operation. Then the treated timbers are molded to prepare furniture products. At the current Preservation and drying operation, the preservative agents used contained harmful compounds such as boric acid, borax pentahydrate and so on [5-7], and the spent preservative agents are discharged as wastewater without any treatment, causing aquatic and soil contaminations around ambient environments [3, 7]. The suggested process incorporated the pyrolysis operation to treat with the wood residue. The operation should convert the WR into the pyroligneous acid (PA), activated carbon (AC) and off-gas to be utilized in the process as the preservative agent, adsorbent to treat with wastewater and the heat source in the process, respectively [4]. The thermal treatment of biomass has been studied over a long period and the utilization of the products has been also well discussed. The AC was prepared from various kinds of carbon source, such as wood, rice husk, bagasse, oil palm shell waste, walnut and so on., to be utilized generally for the wastewater treatment in order to remove organic [8-11] or metal compounds [12, 13]. The PA has antimicrobial or sterilizing activities to be used as preservative agents [14-16]. Another liquid product of tar has been reported on its application potency as the bio-oil fuel [18, 19]. The utilization of the off-gas from biomass pyrolysis has been intensively discussed and many studies on biosyngas and GTL have been reported [20-23]. In our previous study, the saw dust was thermally treated to obtain the PA and AC under the various experimental conditions. The off-gas from the pyrolysis of biomass contained flammable or combustible components, such as hydrogen, methane and other hydrocarbon components and the effective utilization of off-gas might be expected to make the sawmilling process more efficient from an energy expenditure viewpoint.

This study aims to enhance the process efficiency by incorporating pyrolysis of RW residues to produce the AC, PA and off-gas. The characteristics of the AC and PA have been reported in previous study [4]. Then, the off-gas from the pyrolysis of rubberwood sawdust was mainly characterized in this study, and the process efficiency would be discussed in terms of material and energy balances at each operation based on the simple process flow.

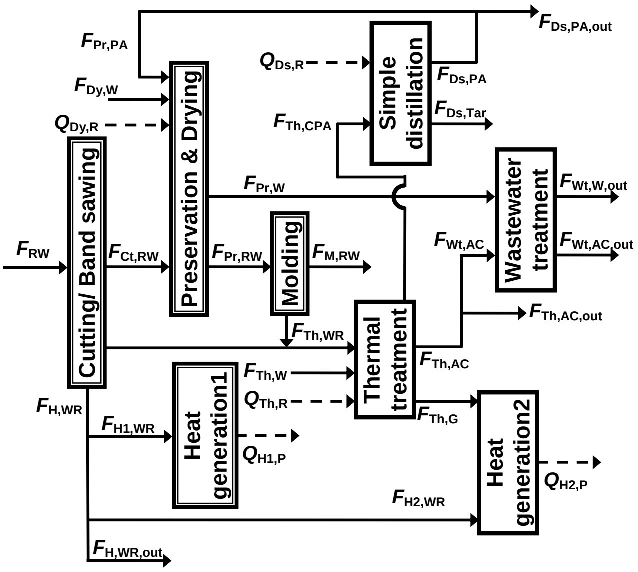

Figure 1. Conceptual process flow diagram of suggested sawmilling process in rubberwood furniture manufacturing, operations presented by double line: conventional operations, operations by single line: operations incorporated in suggested process

II. PYROLYSIS OF RUBBER SAW DUST

A. Experimental

The feed rubberwood sample was provided from RW manufacturing company in Malaysia in the form of saw dust, just same as that used in our previous study [4]. The feed RW saw dust was screened by a commercial sieve (1.7×10^{-3}m apertures, purchased from Tokyo Screen Co.) and was dried in desiccator with silica-gel for at least a day before the thermal treatment.

The conditions of the thermal treatment of RW are listed in Table 1 and the schematic diagram of the used apparatus is illustrated as Fig. 2. The apparatus was just same as used in the previous study. The feed RW was thermally treated in a stainless steel tube (I.D. 3.84×10^{-2}m×0.7m) with a commercial cylindrical electric furnace under various conditions to obtain the AC, CPA and off-gas. The specified amount of RW saw dust was set in the sample holder and placed at the center of the tubular reactor. The thermocouple of NiCr-Constantan was used to measure the temperature of the tubular reactor inside. The sensing portion of the thermocouple was fixed at the center of the reactor and just above the feed RW. Before heating the apparatus only nitrogen gas was introduced for 10 minutes to replace air inside of the reactor and the furnace was started to be heated. The heating rate in the reactor was adjusted at 0.4 $\mathrm{K{\cdot}min^{-1}}$ from room temperature up to the specified temperature. When the temperature attained 473K, the steam was started to be introduced into the reactor. For the introduction of steam, deionized water was directly supplied to the tubular reactor to generate steam inside of the reactor. The steam flow rate was controlled with a micro plunger pump (LC10-ADVP, Shimazu Corp.) by adjusting the deionized water flow rate. Nitrogen was kept flowing during the thermal treatment as an inert carrier gas. The gas flowing out of the reactor was sent to the iced bath to obtain condensable liquid as CPA. The obtained CPA was purified into PA by simple distillation up to 413K, in the same procedure as given in the previous study. Non-condensable gases, i.e. off-gases, were periodically sampled by syringe to analyze by gas chromatograph. The flow rates of off-gas gases were calculated based on the flow rate of nitrogen gas, which was assumed to be constant before and after passing through the reactor. The mass fraction of water in the off-gas was estimated with the assumption that the off-gas should be saturated with water at the temperate of the iced bath. The mass fractions of other components were determined by analysis of the off-gas by gas chromatograph.

TABLE I. EXPERIMENTAL CONDITIONS OF THERMAL TREATMENT OF RUBBERWOOD SAWDUST

Feed	rubberwood sawdust
Atmospheric gas	steam
Treatment temperature, T_{Th} [K]	697 – 1097
Holding time, t_{Th} [h]	1 – 2

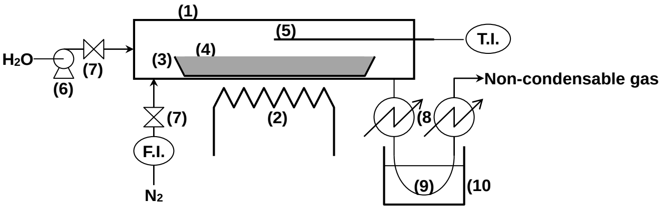

Figure 2. Experimental apparatus for thermal treatment of rubberwood sawdust, (1)tubular reactor, (2)electric tubular furnace, (3)sample holder, (4)feed/solid product, (5)thermocouple, (6)micro-plunger pump,(7)valves, (8)condensers, (9)liquid product trap, (10)iced bath, F.I.: flow rate indicator, T.I: temperature indicator

The ultimate analysis of the feed RW sawdust was conducted with CHN corder (MT-6, Yanako). The obtained off-gas was analyzed by gas chromatograph (GC18AMT, Shimazu) with TCD and the micropacked column (MICROPACKED ST, Shinwa Chemical Industries Ltd.) was used. The obtained PA was analyzed by gas chromatograph (GC-14B, Shimadzu Corp.) with FID and the capillary column (Shimadzu Hicap-CBP20) was used. The mass fractions of water in the solutions were determined by Karl Fischer titrator (758 KFD Titrino from Methrohm).

B. *Results and Discussion*

According to the result of the elemental analysis of the feed RW, the mass fractions of carbon, oxygen, hydrogen and nitrogen were 0.46, 0.46, 0.059 and 0.0017, respectively. The moisture was measured as 0.102 in mass fraction. This composition was almost the same as the result in the previous study. The lower heating value of the rubberwood was estimated as 1.50×10^4 $\mathrm{kJ \cdot kg\text{-}wood^{-1}}$ with the following equation [24],

$$\begin{aligned}\gamma_{\mathrm{WR}} &= 33904980 \cdot x_{\mathrm{RW,C}} + 119713880 \cdot x_{\mathrm{RW,H}} \\ &\quad - 17789650 \cdot x_{\mathrm{RW,O}} + 10464500 \cdot x_{\mathrm{RW,S}}\end{aligned} \tag{1}$$

where $x_{\mathrm{RW,C}}$, $x_{\mathrm{RW,H}}$, $x_{\mathrm{RW,O}}$ and $x_{\mathrm{RW,S}}$ mean the mass fractions of carbon, hydrogen, oxygen and sulfur in the feed RW.

The yields of AC, CPA and off-gas, Y_{AC}, Y_{CPA} and Y_{gas}, were defined with the following equations,

$$Y_{\mathrm{AC}} = W_{\mathrm{AC}} / W_{\mathrm{RW}} \tag{2}$$

$$Y_{\mathrm{CPA}} = W_{\mathrm{CPA}} \cdot \left(1 - x_{\mathrm{CPA,W}}\right) / W_{\mathrm{RW}} \tag{3}$$

$$Y_{\mathrm{gas}} = \left(W_{\mathrm{gas}} - W_{\mathrm{gas,W}}\right) / W_{\mathrm{RW}} \tag{4}$$

where W_{AC}, W_{RW}, W_{CPA}, W_{gas}, $W_{\mathrm{gas,W}}$ and $x_{\mathrm{CPA,W}}$ mean the masses of AC, feed sawdust, CPA, off-gas and water in off-gas, and the mass fraction of water in CPA, respectively. The W_{gas} was estimated from the mass balance equation,

$$W_{\mathrm{RW}} + W_{\mathrm{SW}} = W_{\mathrm{AC}} + W_{\mathrm{CPA}} + W_{\mathrm{gas}} \tag{5}$$

where W_{SW} means the mass of water introduced into the reactor. $W_{\mathrm{W,gas}}$ was estimated with the assumption that the obtained gas from the iced bath was saturated with water at the temperature of ice bath. The yield of PA relative to the feed sawdust was defined as the following equation,

$$Y_{\mathrm{PA}} = W_{\mathrm{PA}} \cdot \left(1 - x_{\mathrm{PA,W}}\right) / W_{\mathrm{RW}} \tag{6}$$

where $x_{\mathrm{PA,W}}$ means the mass fraction of water in PA. The mass fractions of acetic acid, methanol, syringol, cresol, guaiacol and phenol in PA were determined by GC analysis of PA. In this study the obtained CPAs were not analyzed with GC because CPA contained tar fraction in high level and some components must be inappropriate for GC analysis. The mass fraction of water was decided with the aquameter. Then, it was assumed that all components measured in PA were contained in CPA and all amounts of the components measured in PA were completely recovered from CPA to PA by the simple distillation. Then with the mass balance equations the mass fractions of the components mentioned above in CPA were decided.

$$x_{\mathrm{CPA},i} = \left(W_{\mathrm{PA}} / W_{\mathrm{CPA}}\right) \cdot x_{\mathrm{PA},i} \tag{7}$$

Here $x_{\mathrm{CPA},i}$ and $x_{\mathrm{PA},i}$ mean the mass fractions of component *i* in CPA and PA, respectively. Figs. 2 and 3 show the yields of AC, CPA and PA relative to the unit mass of feed sawdust, and mass fraction of component *i* in PA, respectively. For the comparison, the data in the previous study [4] were shown in this figure. The Y_{AC} decreased with an increase in the thermal treatment temperature and they were almost same as the previous results. Y_{CPA} and Y_{PA} were almost constant with the treatment temperature. The effects of treatment time on the yields were also so small. At T=897 K both of Y_{CPA} and Y_{PA} were little smaller than those of the previous results and in the process evaluation the values of Y_{CPA} and Y_{PA} measured in this study would be employed. The obtained PA contained the wood preservative components in relatively high concentrations, such as acetic acid, methanol, syringol, guaiacol, cresols and phenol. The mass fractions of some components in PA were almost the same as those presented in the previous study and the mass fractions of acetic acid were much smaller in this study than those in previous study. The actual reason explaining this reduction could not be determined. The used feed saw dust might have changed during the storage, causing the difference in the compositions of PA.

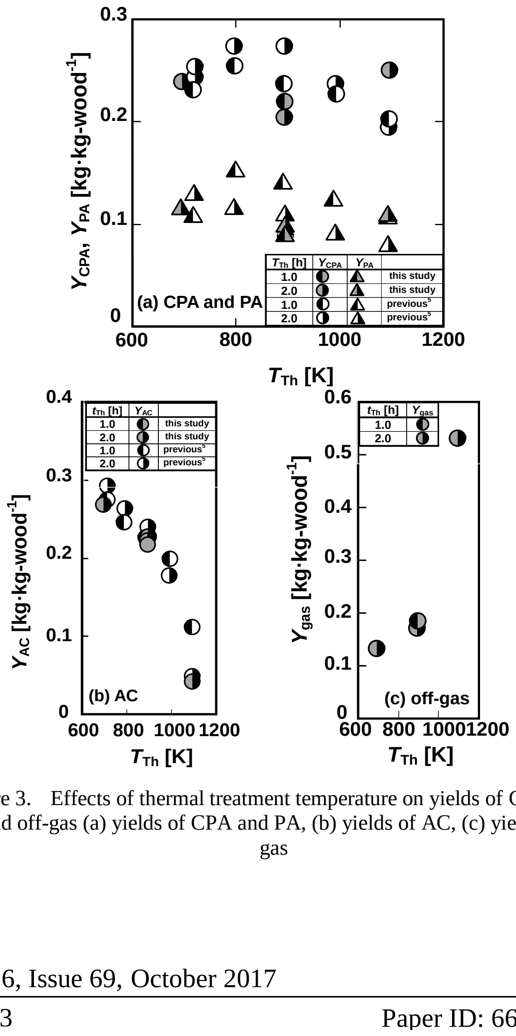

Figure 3. Effects of thermal treatment temperature on yields of CPA, PA, AC and off-gas (a) yields of CPA and PA, (b) yields of AC, (c) yields of off-gas

Fig. 4 shows the time changes of the flow rates of combustible components in the off-gas, such as hydrogen, carbon monoxide and methane.

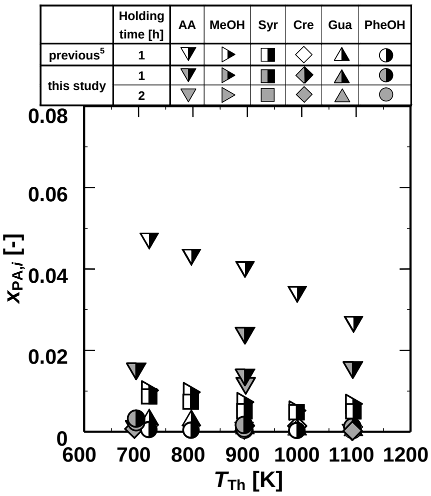

Figure 4. Effects of T_{Th} on component i in PA

For any case the combustible components started to be generated from around 450K and the flow rates of hydrogen were larger than those of carbon monoxide or methane. The higher treatment temperature could make the gas flow rates of carbon monoxide and hydrogen larger and the flow rate of hydrogen at 1097K was so large. This might be caused by the water-gas-shift reaction and the reaction would be dominant in the range of T>900K.

$$CO + H_2O \rightleftarrows CO_2 + H_2$$
$$C(s) + H_2O \rightleftarrows CO + H_2$$

This reactions are exothermic under ordinary pressure and at T>873K. In the range of higher temperature Boudouard reaction might occur to generate carbon monoxide.

$$C + CO_2 \rightarrow 2CO$$

On the other hand, the effects of the temperature on methane generation were little during the initial 1 hour operation. After 1.5 hours, the methane flow rates suddenly increased and the flow rate became larger when the temperature was at 697K. According to the work done by Herguido *et al.* (1992) [25], methane generation is basically independent of the equilibrium conditions of water-shift reaction. Methane should be generated by the following exothermic reactions,

$$C(s) + 2H_2 \rightleftarrows CH_4$$
$$CO + 3H_2 \rightleftarrows CH_4 + H_2O$$

The equilibrium constants of these reactions should decrease with an increase in the temperature, causing a decline of the methane flow rate as the treatment temperature increased. For most cases the gas flow rates attained the maximum values at around 1 hour operation and they decreased with time. Figs 6 and 7 show the masses of the obtained components in the off-gas, such as hydrogen, carbon monoxide, methane and carbon dioxide. The obtained mass of each component was estimated by the integration of the gas flow rate along the treatment time, shown in Fig. 5. The yields of the combustible gases became larger with the treatment temperature except for methane and the hydrogen yield drastically increased from 897K to 1097K. The reactions of methane generation might be insensitive to the treatment temperature under the studied conditions. The effects of the operation time were so little and one hour operation must be appropriate for the thermal treatment. The lower heating values of the obtained off-gas were estimated as follows, 1.26×10^3 kJ·kg-wood^{-1} at T_{Th}=697K, 2.63×10^3 kJ kg-wood^{-1} at T_{Th}=897K and 1.57×10^4 kJ kg-wood^{-1} at T_{Th}=1097K for t_{Th}=1 h. When t_{Th}=2h, the lower heating value was estimated as 2.47×10^3 kJ kg-wood^{-1} at T_{Th}=897K. The used parameters are listed in Table 2.

TABLE II. LIST OF PROPERTIES OF COMPONENTS IN PROCESS SIMULATION

	Specific heat [kJ·kg^{-1} K^{-1}]	Enthalpy formation [kJ kg^{-1}]	Latent heat [kJ kg^{-1}]
water(l) 4.23	-1.59×10^4	2.26×10^3	
methanol(g)	1.38	-6.26×10^3	-
methanol(l)	2.53	-7.45×10^3	1.13×10^3
acetic acid(g)	1.11	-7.20×10^3	-
acetic acid(l)	2.04	-8.01×10^3	8.70×10^2
phenol(g)	1.10(300K) 2.26(800K)	-1.50×10^3	-
phenol(l)	1.30(273K) 2.38(373K)	-1.63×10^3	4.75×10^2
phenol(s)	-	-1.75×10^3	-
cellulose(s)	1.21	-5.92×10^3	-
Enthalpies of formations of components in ofF-gas [kJ kg^{-1}]			
	673 K	873 K	1073 K
hydrogen(g)	5.43×10^3	8.37×10^3	1.14×10^4
carbon monoxide(g)	-3.55×10^3	-3.32×10^3	-3.08×10^3
carbon dioxide(g)	-8.57×10^3	-8.34×10^3	-8.09×10^3
methane(g)	-3.60×10^3	-2.83×10^3	-1.95×10^3

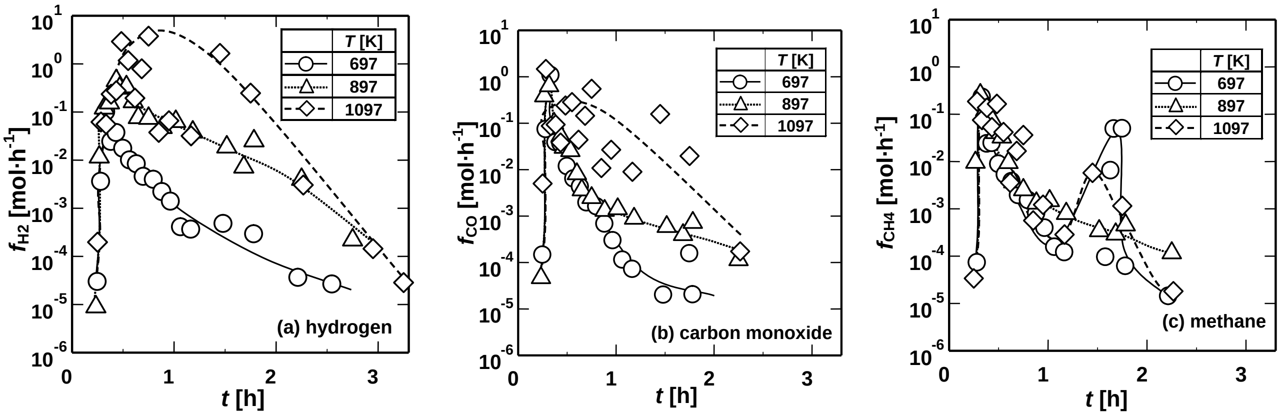

Figure 5. Time courses of flow rates of component *i* in off-gas (a) hydrogen, (b)carbon monoxide, (c) methane

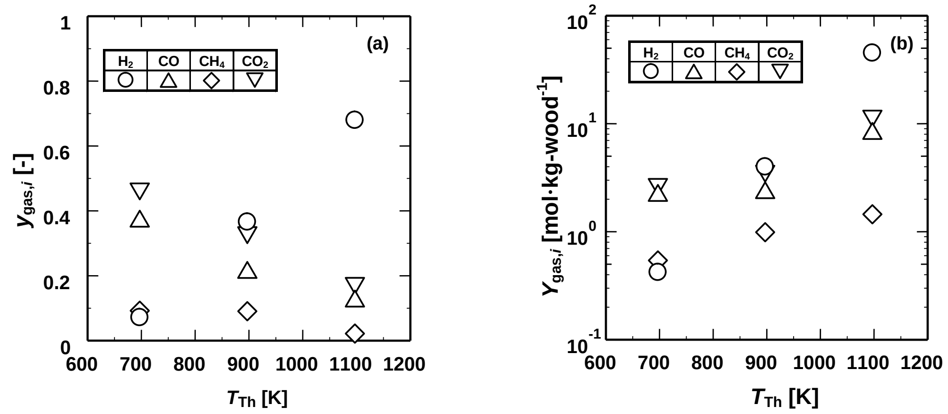

Figure 6. Effects of T_{Th} on molar fractions (a) and yields (b) of component *i* in off-gas (t_{Th}: 1 h)

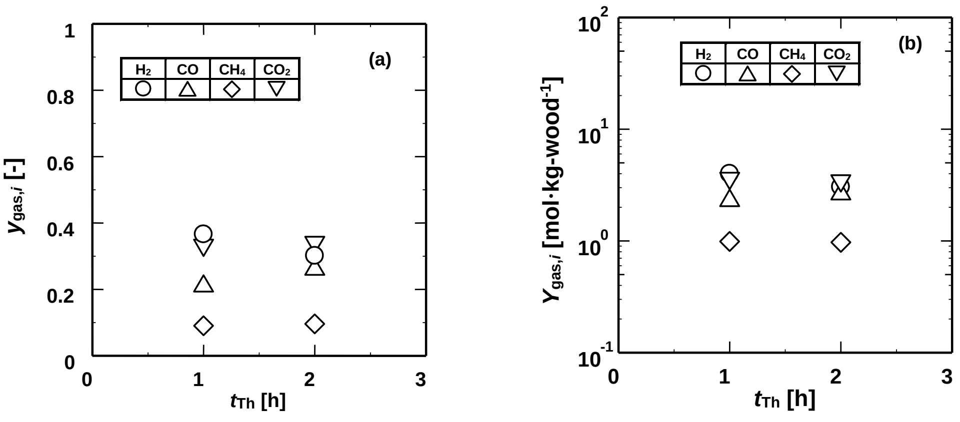

Figure 7. Effects of t_{Th} on molar fractions (a) and yields (b) of component *i* in off-gas (T_{Th}: 897 K)

III. SAWMILLING PROCESS

A. Process Description and Simulation

According to the suggested sawmilling process shown in Fig.1, the main material stream of the product furniture passed through the Cutting/Band sawing, Preservation & Drying, and Molding operations. Some part of the residuals from the Cutting/Band sawing and Molding operations, $F_{Th,WR}$, was sent to the Thermal treatment operation to obtain the AC, crude pyroligneous acid (CPA) and off-gas. Some other parts of the residues, $F_{H1,WR}$ and $F_{H2,WR}$, were utilized as a heat source at the Heat generation 1 and 2, and the other, $F_{H,WR,out}$, was discharged from the process. The CPA originally contained the phenolic compounds, which had the preservative effects. Then, it was distilled to separate into the PA and tar, and the obtained PA was utilized as a preservative agent at the Preservation & Drying operation. The wastewater from the operation was sent to the Wastewater treatment operation. At this operation the AC was utilized as adsorbent to remove the phenolic compounds in the wastewater down to the effluent standard.

The material balance equations around the Cutting/Band sawing operation are expressed as,

$$F_{\mathrm{Ct,RW}}=\alpha_{\mathrm{Ct,RW}}\,F_{\mathrm{RW}} \tag{8}$$

$$F_{\mathrm{Th,RW}}=\alpha_{\mathrm{Th,RW}}\,F_{\mathrm{RW}} \tag{9}$$

$$F_{\mathrm{H,RW}}=\alpha_{\mathrm{H,RW}}\,F_{\mathrm{RW}} \tag{10}$$

$$(\alpha_{\mathrm{Ct,RW}} + \alpha_{\mathrm{Th,RW}} + \alpha_{\mathrm{H,RW}} = 1)$$

The ratio of residue amount to be preserved relative to the amount of feed rubberwood, $\alpha_{\mathrm{Ct,RW}}$, was fixed as 0.2 [2]. The $F_{\mathrm{Th,WR}}$ stands for the wood flow rate to be thermally treated and the other wood flow rate, $F_{\mathrm{H,WR}}$, was the wood flow rate used as heat source at the Heat generation 1 and 2. The $\alpha_{\mathrm{Th,WR}}$ was influential on the process performance, and the effects on the mass and enthalpy balances at the operations would be evaluated.

The material balance equations around the Thermal treatment and Simple distillation operations are expressed as,

$$F_{\mathrm{Th,W}}=\beta_{\mathrm{Ct,RW}}\,F_{\mathrm{Th,RW}} \tag{11}$$

$$F_{\mathrm{Th,G}}=\alpha_{\mathrm{Th,G}}\,F_{\mathrm{Th,RW}} \tag{12}$$

$$F_{\mathrm{Th,AC}}=\alpha_{\mathrm{Th,AC}}\,F_{\mathrm{Th,WR}} \tag{13}$$

$$F_{\mathrm{Th,CPA}}=\alpha_{\mathrm{Th,CPA}}\,F_{\mathrm{Th,WR}} \tag{14}$$

$$F_{\mathrm{Ds,Tar}}=\alpha_{\mathrm{Ds,Tar}}\,F_{\mathrm{Th,CPA}} \tag{15}$$

$$F_{\mathrm{Ds,PA}}=\alpha_{\mathrm{Ds,PA}}\,F_{\mathrm{Th,CPA}} \tag{16}$$

The $F_{\mathrm{Th,W}}$ expresses the water flow rate at this operation used as the atmospheric gas at the thermal treatment, determined based on the experimental results in this study. The $\alpha_{\mathrm{Th,G}}$, $\alpha_{\mathrm{Th,AC}}$, $\alpha_{\mathrm{Th,CPA}}$, $\alpha_{\mathrm{Ds,Tar}}$, and $\alpha_{\mathrm{Ds,PA}}$, showing the yields of off-gas, AC, CPA, tar and PA, and the compositions in CPA and PA would be also decided based on the experimental results.

The material balance equations around the Preservation/Drying and Molding operations are expressed as,

$$F_{\mathrm{Pr,PA}}=\beta_{\mathrm{Pr,PA}}\,F_{\mathrm{Ct,RW}} \tag{17}$$

$$F_{\mathrm{M,RW}}=F_{\mathrm{Pr,RW}} \tag{18}$$

$$F_{\mathrm{Pr,W}}= F_{\mathrm{Pr,PA}}+F_{\mathrm{Dy,W}} \tag{19}$$

$$F_{\mathrm{Dy,W}}=\beta_{\mathrm{Dy,W}}\,F_{\mathrm{Ct,RW}} \tag{20}$$

$$F_{\mathrm{M,RW}}=\alpha_{\mathrm{M,RW}}\,F_{\mathrm{Pr,RW}} \tag{21}$$

The amount of PA required for preservation was fixed as $\beta_{\mathrm{Pr,PA}}=0.167$ kg·kg-wood^{-1} [16]. The flow rate of wastewater from the preservation operation, $F_{\mathrm{Pr,W}}$, was determined by the summation of the flow rates of the PA required for preservation, $F_{\mathrm{Pr,PA}}$, and steam flow rate for drying, $F_{\mathrm{Dy,W}}$. The amount of steam required for the drying operation was fixed as $\beta_{\mathrm{Dy,W}} = 0.63$ kg-steam kg-wood^{-1}. The yield of molded rubberwood was fixed as $\alpha_{\mathrm{M,RW}}=0.78$ [2].

The material balance equations around the Wastewater treatment operation are expressed as,

$$F_{\mathrm{Wt,AC}}=\beta_{\mathrm{Wt,AC}}\,F_{\mathrm{Pr,W}} \tag{22}$$

$$F_{\mathrm{Wt,W,out}}=F_{\mathrm{Pr,W}} \tag{23}$$

$$F_{\mathrm{Wt,AC,out}}= F_{\mathrm{Wt,AC}} \tag{24}$$

The flow rate of the AC required for the operation, $F_{\mathrm{Wt,AC}}$, was dependent on the temperature at the Thermal treatment operation which was the most influential on the adsorbabilities [4] and $F_{\mathrm{Wt,AC}}$ was estimated according to the following method. The contaminant in wastewater was assumed to be only phenol and to be removed by the AC. The adsorbed amount of phenol on the AC after the Wastewater treatment would be in equilibrium with the phenol concentration in the initial wastewater and the constants of phenol adsorption isotherms were cited from the previous study [4]. Then the required amount of AC per unit mass flow rate of the wastewater, $\beta_{\mathrm{Wt,AC}}$ was determined.

The heat flow rate required in the process was generated at the Heat generation 1 and 2. The heat requirements at the Preservation & Drying operation and at the Thermal treatment and Simple distillation operations were generated at the Heat generation 1 and 2, respectively. The mass flow ratio of wood to be preserved relative to feed wood, $\alpha_{\mathrm{Ct,RW}}$, was fixed as 0.2, and the heat flow rate from the Heat generation 1 was fixed. The heat flow rate from the Heat generation 2 was dependent on the mass flow rate of residue to be thermally treated and the treatment temperature at the Thermal treatment. The following equations are expressing the enthalpy balances around the mentioned operations. At Heat generation 1 and 2,

$$Q_{\mathrm{H1,P}}=\gamma_{\mathrm{WR}}\,F_{\mathrm{H1,WR}} \tag{25}$$

$$Q_{\mathrm{H1,P}}=Q_{\mathrm{Dy,R}} \tag{26}$$

$$Q_{\mathrm{H2,P}}=Q_{\mathrm{Th,R}}+Q_{\mathrm{Ds,R}}=\gamma_{\mathrm{WR}}\,F_{\mathrm{H2,WR}}+\gamma_{\mathrm{Th,G}}\,F_{\mathrm{H2,G}} \tag{27}$$

At Thermal treatment and Simple distillation operations,

$$Q_{\mathrm{Th,R}}+Q_{\mathrm{Ds,R}}=\gamma_{\mathrm{ThDs}}\,F_{\mathrm{Th,WR}} \tag{28}$$

At Preservation & Drying operation,

$$Q_{\mathrm{Ds,R}}=\gamma_{\mathrm{Dy,W}}\,F_{\mathrm{Ct,RW}} \tag{29}$$

At the Thermal treatment and Simple distillation operations, the required heat flow rates were estimated by the temperatures of materials and the standard enthalpy changes of formations. The temperatures of the materials entering and exiting the Thermal treatment operation were set at 298K and the temperatures of the thermal treatment, respectively. The RW was pyrolyzed with water to make AC, CPA and off-gas. At the Simple distillation operation, the CPA at 298K was introduced and the PA and tar were obtained as vapor and liquid at the operating temperature. It was assumed that the PA contained water, methanol, acetic acid and phenol. The concentrations of water, methanol and acetic acid in the PA were determined based on the experimental results and the other component in the PA was assumed to be phenol. It was also assumed that the obtained tar should be pure phenol, and all components of methanol, acetic acid and water in CPA could be recovered into PA by the Simple distillation operation. Then the compositions of CPA were determined with the material balances. The compositions in PA were determined based on the experimental results. The used RW and AC were assumed to be cellulose and graphite. With these conditions and assumptions, the values of γ_{ThDs}, the heat required for the Thermal treatment and Simple distillation operations relative to amount of the RW to be thermally treated, were estimated. The required heat for the Preserved & Drying operation, $Q_{\mathrm{Ds,R}}$, was estimated from the amount of steam required for drying treatment of the preserved wood, as $\gamma_{\mathrm{Dy,W}}=2.66\times10^{3}$ kJ kg-wood^{-1} [2]. The suggested process as shown in Fig. 1 would be simulated in terms of material and heat flows within the process. The conditions of each operation and compositions of the modeled CPA and PA used in the simulation are listed in Tables 3 and 4, respectively. The ratio of residue amount to be thermally treated relative to F_{RW}, $\alpha_{\mathrm{Th,WR}}$, was changed and the effects on the material and heat flows in the process were simulated. The detailed simulation results about the flow rates of wood streams around the Cutting/Band sawing, Thermal treatment and Simple distillation operations are shown in Appendix.

TABLE III. CONDITIONS IN PROCESS SIMULATION

T_{Th}	[K]	697	897	1097
$\alpha_{\mathrm{Th,AC}}$	[kg-AC kg-wood^{-1}]	2.45×10^{-1}	2.03×10^{-1}	3.70×10^{-2}
$\alpha_{\mathrm{Th,CPA}}$	[kg-CPA kg-wood^{-1}]	1.82	1.70	1.24
$\alpha_{\mathrm{Th,G}}$	[kg-off-gas kg-wood^{-1}]	1.96×10^{-1}	2.57×10^{-1}	8.99×10^{-1}
$\alpha_{\mathrm{Ds,PA}}$	[kg-PA kg-CPA^{-1}]	9.37×10^{-1}	9.16×10^{-1}	8.97×10^{-1}
$\alpha_{\mathrm{Ds,Tar}}$	[kg-Tar kg-wood^{-1}]	6.28×10^{-2}	8.40×10^{-2}	1.03×10^{-1}
$\beta_{\mathrm{Wt,AC}}$	[kg-AC kg-water^{-1}]	3.83×10^{-1}	4.49×10^{-2}	2.46×10^{-2}
$\beta_{\mathrm{Th,W}}$	[kg-water kg-wood^{-1}]	1.14	1.25	1.24
$\gamma_{\mathrm{Th,G}}$	[kJ kg-wood^{-1}]	1.26×10^{3}	2.63×10^{3}	1.57×10^{4}
γ_{ThDs}	[kJ kg-wood^{-1}]	7.68×10^{3}	9.11×10^{3}	1.13×10^{4}
lower heating value of off-gas	[kJ kg-wood^{-1}]	1.26×10^{3}	2.63×10^{3}	1.57×104

TABLE IV. COMPOSITIONS OF MODEL CPA AND PA

$x_{\mathrm{CPA},i}$	MeOH	AA	PheOH	W
T_{Th}=697K	3.80×10^{-4}	1.06×10^{-2}	1.16×10^{-1}	8.73×10^{-1}
T_{Th}=897K	3.87×10^{-4}	1.34×10^{-2}	1.24×10^{-1}	8.61×10^{-1}
T_{Th}=1097K	5.75×10^{-4}	1.37×10^{-2}	1.68×10^{-1}	8.17×10^{-1}
$x_{\mathrm{PA},i}$				
T_{Th}=697K	4.06×10^{-4}	1.14×10^{-2}	5.56×10^{-2}	9.33×10^{-1}
T_{Th}=897K	4.10×10^{-4}	1.42×10^{-2}	4.98×10^{-2}	9.36×10^{-1}
T_{Th}=1097K	6.41×10^{-4}	1.53×10^{-2}	7.50×10^{-2}	9.09×10^{-1}

B. Results and Discussion

The products from each operation generally increased with $\alpha_{\mathrm{Th,WR}}$, as expressed by Eqs. (8-16), the flow rate of the main stream for product, $F_{\mathrm{Ct,RW}}$, was fix constant. As mentioned in the experimental results, the flow rate of off-gas, $F_{\mathrm{Th,G}}$, increased with T_{Th}, the flow rate of AC, $F_{\mathrm{Th,AC}}$, decreased with an increase in T_{Th}, and the flow rates of CPA and PA, $F_{\mathrm{Th,CPA}}$ and $F_{\mathrm{Th,PA}}$, were the highest at 897K, respectively. The enthalpies required for the Drying, Thermal treatment and Simple distillation operations are shown in Fig. 8. The enthalpies required for the Thermal treatment and Simple distillation operations, $Q_{\mathrm{Th,R}}+Q_{\mathrm{Ds,R}}$, increased with $\alpha_{\mathrm{Th,RW}}$ mainly because of the increment of $Q_{\mathrm{Th,R}}$. The enthalpy required for the Preservation & Drying operation, $Q_{\mathrm{Dy,R}}$, was constant and independent of $\alpha_{\mathrm{Th,RW}}$. As can be seen, $Q_{\mathrm{Th,R}}+Q_{\mathrm{Ds,R}}$ was much larger than $Q_{\mathrm{Th,R}}$ in the larger range of $\alpha_{\mathrm{Th,RW}}$ and the Thermal treatment and Simple distillation operations were found to be the most energy intensive operation in this process.

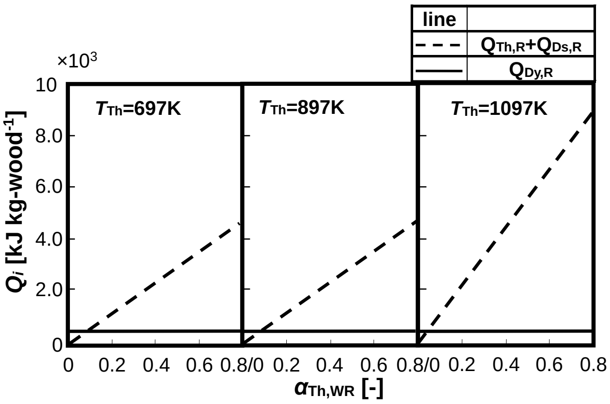

Figure 8. Effects of $\alpha_{\mathrm{Th,WR}}$ on required heats for Drying, Thermal treatment and Simple distillation operations

Fig. 9 shows the effects of $\alpha_{\mathrm{Th,RW}}$ on the flow rates of wood residues around the Heat generation 1 and 2. When T_{Th}=697K or 897K, in the range of high $\alpha_{\mathrm{Th,RW}}$ all residue could be treated and $F_{\mathrm{H,WR,out}}$ could be made 0. For this condition $Q_{\mathrm{Th,R}}$ was much larger than $Q_{\mathrm{Dy,R}}$ and most of the residue should be consumed at the Heat generation 2 as heat source. On the other hand, when T_{Th}=1079K, $F_{\mathrm{H,WR,out}}$ could be at any time made 0. The ratios of the heating values of off-gas relative to the heats required for the Thermal treatment and Preservation & Drying operation, $H_{\mathrm{gas}}/(Q_{\mathrm{Th,R}}+Q_{\mathrm{Dy,R}})$, were estimated as 0.164 at T_{Th}=697K, 0.289 at T_{Th}=897K and 1.39 at T_{Th}=1097K, respectively. This means that when T_{Th}=697K or T_{Th}=897K, the wood residue should be used as the heat source at the Heat generation 2 and other heat sources should be necessary to consume up the all wood residue. When T_{Th}=1097K $Q_{\mathrm{Th,R}}$ and $Q_{\mathrm{Dy,R}}$ could be met only by the heat recovered from the obtained off-gas. Therefore all residue could be thermally treated without any heat source from outside of the process, and both of $F_{\mathrm{H,WR,out}}$ and $F_{\mathrm{H2,WR}}$ could be also made 0.

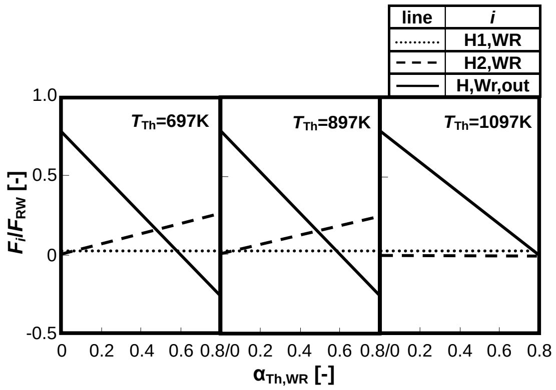

Figure 9. Effects of $\alpha_{Th,WR}$ on flow rates of wood residues around Heat generation1 and 2

Fig. 10 shows the effects of T_{Th} on the flow rates of AC and PA. With an increase in T_{Th}, F_{AC} and $F_{Ds,PA}$ increased and in the range of higher $\alpha_{Th,RW}$ F_{AC} and $F_{Ds,PA}$ were larger than the amounts of AC and PA required for the Wastewater treatment and Preservation operations, $F_{AC,Wt}$ and $F_{Pr,PA}$. When all residues should be treated, AC and PA should be excessive in this process and the destinations of these excessive products should be considered.

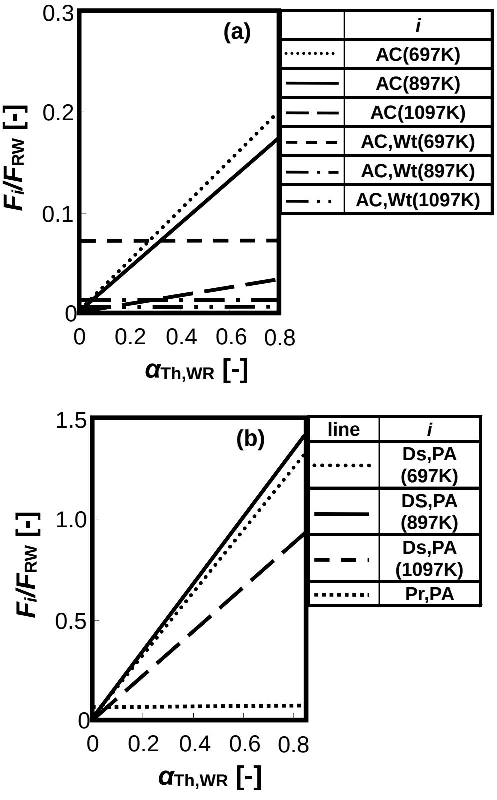

Figure 10. Effects of T_{Th} on mass flow rates of AC (a) and PA (a) around Wastewater treatment and Preservation and Drying operations

According to this assessment, at any temperature condition in the Thermal treatment operation, the suggested process could be operated for all residues to be consumed in the process and the improvement of the process efficiency could be also attained by effective utilization of the residues. However in this study the process was simply evaluated by the simple process model, based on the mass flow rates, the lower heating values and enthalpies of formations. The PA and AC were found to be excessive in the process and the utilization of tar was not discussed here. It was reported in recent research that PA and tar might have a possibility to be converted into bio-oil by blending the diesel oil fuel or heavy oils [21-23]. These products might bring substantial amounts of profits and be positively produced. For the excessive AC, the char has been generally used as heat sources for higher temperature. The prepared AC showed relatively low performance of adsorbability compared with the ordinary commercial AC and cannot be expected to be put on the market. The excessive AC and spent AC might be used in the process as better heat source. As discussed here, the major trends of the material and heat flows could be outlined and the recovery of off-gas from the Thermal treatment operation was found to be effective for the improvement of the rubberwood manufacturing process.

IV. CONCLUSIONS

The rubberwood manufacturing process has been studied for the amelioration, and the effective utilization of the wastes within the process was suggested to prepare the activated carbon, pyroligneous acid, and off-gas from the residues. In this study the off-gas from the thermal treatment was experimentally characterized and the utilization in the process was evaluated with the simple process model. The prepared activated carbon, pyroligneous acid and off-gas were utilized for the wastewater treatment as adsorbent, preservation of the logs as preservative agent and heat source, respectively. The analysis of the obtained off-gas showed that it contained some combustible gases, such as hydrogen, carbon monoxide and methane. The thermal treatment at higher temperature could enhance the hydrogen production, which was the main compound to decide the heating value of the off-gas. Then the suggested rubberwood manufacturing process was numerically simulated in terms of the material and energy balances. In any range of the thermal treatment temperature, all residues could be used up in the process and enough amounts of both pyroligneous acid and activated carbon could be produced. The amount of produced off-gas was also enough to utilize as the heat source. The off-gas generated at 1079K in the thermal treatment could provide the enthalpies required for the Thermal treatment, Simple distillation and Preservation operations. However this simulation was so simple to just show the outline of material and energy flow in the process. The utilization of the excessive products and byproducts should be necessary to be discussed. The further study must be crucial to for the design of more realistic operations in the suggested process.

Acknowledgement

The authors would like to acknowledge Hock Chuan Enterprise in Malaysia for proving the rubberwood sawdust.

Appendix

The specific heats, enthalpies of formation and latent heat used in the process simulation are listed in the Table 2. These values were estimated from the standard enthalpies of formations [26]. Fig. 11 shows the flow rates of rubberwood and products around the Cutting/Band sawing, Thermal treatment and Simple distillation operations. As mentioned in the experimental results, the flow rate of off-gas, $F_{\mathrm{Th,G}}$, increased with T_{Th}, the flow rate of AC, $F_{\mathrm{Th,AC}}$, decreased with an increase in T_{Th}, and the flow rates of CPA and PA, $F_{\mathrm{Th,CPA}}$ and $F_{\mathrm{Th,PA}}$, were the highest at 897K, respectively. The flow rate of tar, $F_{\mathrm{Ds,tar}}$, increased with $\alpha_{\mathrm{Th,RW}}$ and T_{Th}, as shown in Fig. 11(c).

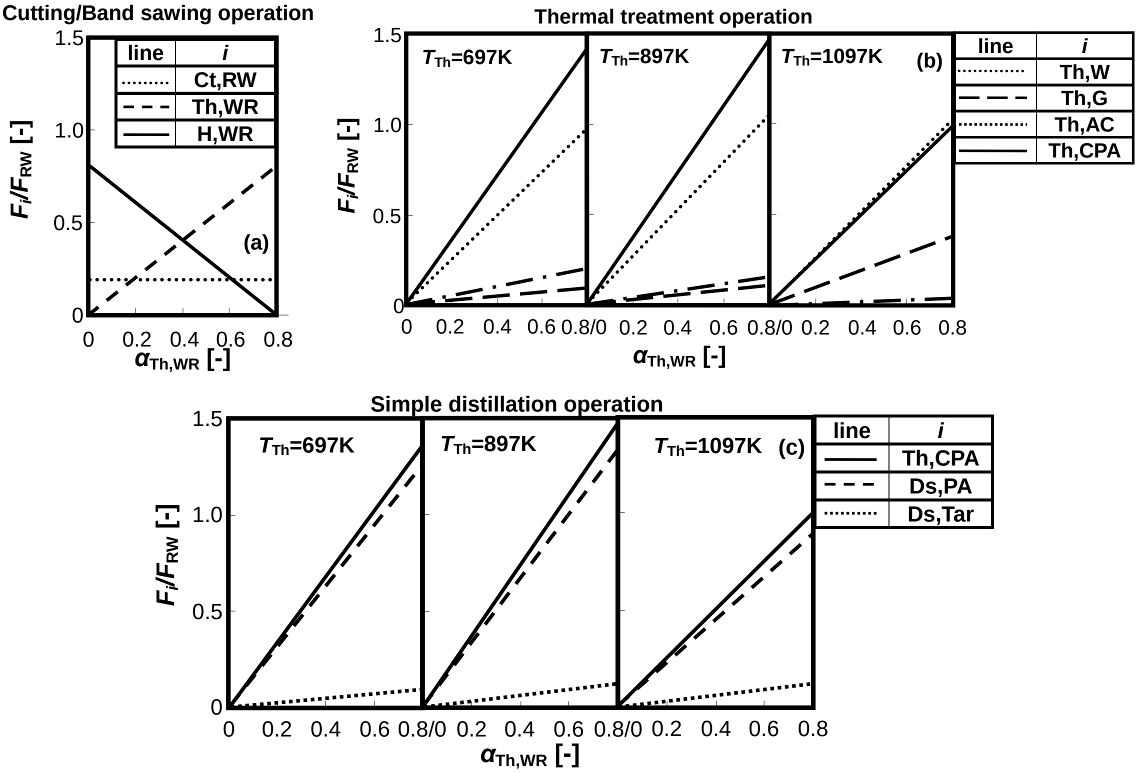

Figure 11. Effects of $\alpha_{\mathrm{Th,WR}}$ on mass flow rates around Cutting/Band sawing (a), Thermal treatment (b) and Simple distillation (c)

$F_{i,j}$ = flow rate of operation i into material j [kg h^{-1}]

f_i = flow rate of component i in off-gas [mol h^{-1}]

$Q_{j,\mathrm{P}}$ = heat flow generated at operation j based on feed rubberwood [kJ kg-wood^{-1}]

$Q_{j,\mathrm{R}}$ = heat flow required at operation j based on feed rubberwood [kJ kg-wood^{-1}]

T_{Th} = thermal treatment temperature [K]

t = time [h]

t_{Th} = holding time at thermal treatment temperature [h]

W_i = mass of material i [kg]

$x_{\mathrm{CPA},I}$ = mass fraction of component i in crude pyroligneous acid [–]

$x_{\mathrm{PA},I}$ = mass fraction of component i in pyroligneous acid [–]

$x_{\mathrm{RW},i}$ = mass fraction of component i in rubberwood [–]

Y_i = yield of material i based on feed rubberwood sawdust [kg kg-wood^{-1}]

$Y_{\mathrm{gas},i}$ = yield of component i in off-gas based on feed rubberwood sawdust [mol kg-wood^{-1}]

$y_{\mathrm{gas},i}$ = molar fraction of component i in off-gas [–]

$\alpha_{\mathrm{Ct,RW}}$ = ratio of wood residue amount to be preserved relative to feed rubberwood, as defined by Eq. (8) [–]

$\alpha_{\mathrm{Th,WR}}$ = ratio of wood residue amount to be thermally treated relative to feed rubberwood, as defined by Eq. (9) [–]

$\alpha_{H,WR}$ = ratio of wood residue amount to be used as heat source relative to feed rubberwood, as defined by Eq. (10) [–]

$\beta_{Th,W}$ = required amount of steam for Thermal treatment operation relative to rubberwood amount to be thermally treated, as defined by Eq.(11) [kg-water kg-wood^{-1}]

$\alpha_{Th,G}$ = yield of off-gas at Thermal treatment operation, as defined by Eq. (12) [kg-off-gas kg-wood^{-1}]

$\alpha_{Th,AC}$ = yield of activated carbon at Thermal treatment operation, as defined by Eq. (13) [kg-AC kg-wood^{-1}]

$\alpha_{Th,CPA}$ = yield of crude pyroligneous acid at Thermal treatment operation, as defined by Eq. (14) [kg-CPA kg-wood^{-1}]

$\alpha_{Ds,Tar}$ = yield of tar at Simple distillation operation, as defined by Eq. (15) [kg-off-gas kg-wood^{-1}]

$\alpha_{Ds,PA}$ = yield of pyroligneous acid at Simple distillation operation, as defined by Eq. (16) [kg-PA kg-CPA^{-1}]

$\beta_{Pr,PA}$ = required amount of pyroligneous acid for Preservation operation relative to rubberwood to be preserved, as defined by Eq. (17) [kg kg-wood^{-1}]

$\beta_{Dy,W}$ = required amount of steam for Drying operation relative to rubberwood to be dried, as defined by Eq. (20) [kg-steam kg-wood^{-1}]

$\alpha_{M,RW}$ = yield of molded rubberwood, as defined by Eq. (21) [–]

$\beta_{Wt,AC}$ = required amount of activated carbon relative to amount of wastewater at Wastewater treatment, as defined by Eq. (22) [kg-AC kg-water^{-1}]

γ_{WR} = lower heating value of rubberwood per unit mass of rubberwood [kJ kg-wood^{-1}]

$\gamma_{Th,G}$ = lower heating value of off-gas per unit mass of rubberwood [kJ kg-wood^{-1}]

γ_{ThDS} = heat required for thermal treatment and simple distillation per unit mass of rubberwood [kJ kg-wood^{-1}]

$\gamma_{Dy,W}$ = heat required for Drying operation per unit mass of rubberwood [kJ kg-wood^{-1}]

<Subscript>

AA: = acetic acid,

AC: = activated carbon,

C: = carbon,

Cre: = cresol

CH4: = methane,

CO: = carbon monoxide,

CPA: = crude pyroligneous acid,

Ct: = Cutting/Band sawing operation

Ds: = Simple distillation operation,

Exit: = exiting from process,

Gua: = guaiacol,

gas: = off-gas

H: = hydrogen

i: = component *i*, material *i*, heat flow *i* or operation *i*

M: = methanol,

O: = oxygen

out: = exiting operation

PheOH = phenol

PA: = pyroligneous acid

Pr: = Preservation & Drying operation

RW: = rubberwood

S: = sulfur

Syr: = syringol

Tar: = tar

Th: = thermal treatment operation

W: = water

WR: = wood residue

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