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PHENOLIC COMPONENTS OF THE TAR FRACTION FROM PYROLYSIS OF RUBBERWOOD

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HALIMAHTON MANSOR, KHOO, K.C. & NOR AZAH MOHD. ALI. 1991. Phenolic components of the tar fraction from pyrolysis of rubberwood. Tars collected as by-products of pyrolysis of rubberwood (*Hevea brasieliensis* Muell.) at several intrinsic temperatures were studied. The tars were distilled into six fractions such as a low boiling fraction (b.p. below 170° *C*), high boiling fractions (170-210° *C*, 210-235° *C*, 235-270° *C*, 270-315° *C*) and pitch. Increasing the intrinsic temperature above 250° *C* increased the amount of the high-boiling fraction and pitch. The highest yield of the high-boiling fraction (76%) based on the weight of tar was obtained at intrinsic temperature of 500° *C*. The fraction which came out at 270-315° *C* was only obtained at intrinsic temperature > 700° *C*. There was a significant change in the quantity of the weak acid (phenolic compounds) and neutral portions in the high boiling fraction with intrinsic temperature. The highest amount of weak acids was obtained at intrinsic temperature of between 500 to 700° *C*. Syringol was found to be the major phenolic component, followed by guaiacol and other phenols such as the xylenols, cresols, catechol and resorcinol.

Key words: Pyrolysis - rubberwood - wood tar - intrinsic temperature - fractional distillation - phenolic constituents

Introduction

Pyrolysis is a process involving thermal degradation of wood to produce char, tar, liquid and gaseous products (Klar 1925). Historically, charcoal was widely used as fuel, wood acid as a source of vinegar and chemical intermediates, wood spirit as solvents for dyes and wood tar as a main source of creosote. Stiff competition from coal distillation and synthetic chemical industries resulted in the decline in the use of biomass for these materials. However, with the depleting supply of fossil fuels, plant resources, which are renewable, are becoming increasingly more important. Recently, more interest is shown on liquid fuels since they are easy to handle, store and transport, and readily used in many heat and power applications (Bridgewater 1990).

Among the thermochemical conversion technologies of biomass, pyrolysis gives a very flexible and economical means by which a wide variety of liquid products can be derived in addition to fuel gas, charcoal and a range of potentially valuable chemicals (Bridgewater 1990).

Traditionally, rubberwood has been used as fuel either in the form of firewood or as charcoal. However, the increasing demand of rubberwood sawn timber, has forced charcoal manufacturers to use the less valuable parts of the tree, such as branchwood and off-cuts. Besides the use of these materials as fuel and for charcoal production, another effective means of using this biomass residue is distillation for the production of pyroligneous acids, wood spirits and wood tars which possess many potential uses. At present, only a small number of these uses are exploited since not many detailed studies have been done on the chemical characterisation of these by-products. In fact, in Malaysia, charcoal manufacturers are unaware of the potential uses of the by-products from their charcoal kilns, hence these substances are just entirely removed and ignored.

This paper reports part of the work conducted on the pyrolysis of rubberwood (*Hevea brasiliensis*) with respect to the amounts and components of the tars from the pyrolysis run at several intrinsic temperatures, with special attention being given to the phenolic constituents.

Materials and methods

Rubberwood (25 *kg*) was pyrolysed in a steel retort in the absence of air. The vapour was condensed and the non-condensible gases were piped back into the retort furnace. The mixture of the by-products collected was fractionally distilled to separate the wood spirit and pyroligneous acid fractions from the heavier wood tar fraction. The tar was then removed for analysis.

Fractionation of tar

Tar (100 *g*) from each pyrolysis run was fractional distilled according to ASTM D246-84 (ASTM 1984). The distillate fractions were then weighed before further analysis.

Fractionation of high-boiling fractions

This was conducted according to the method of Yatagai *et al.* (1986).

Separation and identification of phenolic constituents in the high-boiling fractions

Gas chromatography (GC) was performed on a Shimadzu gas chromatograph model GC-9A equipped with flame ionisation detector (FID) and a CR-3A Chromatopac data processer. The column used was a 25 *m* long and 0.24 *mm* i.d. glass capillary coated with PEG 20 *M*. GC was run at 60°*C* for 30 *min*, then programmed from 60 to 175°*C* at $5°C\ min^{-1}$, with N as a carrier gas at a flow rate of 0.6 $ml\ min^{-1}$.

Results and discussion

Fractionation of tar

The rubberwood tars from all of the runs at the corresponding intrinsic temperatures (temperature measured in the centre of the retort) were distilled under atmospheric pressure into six fractions, namely, the low boiling fraction collected below 170°*C*, the high boiling fractions which distilled at 170 to 210°*C*, 210 to 235°*C*, 235 to 270°*C*, 270 to 315°*C*, and the residue or pitch. Table 1 shows the percentages of the low-boiling, high-boiling fractions and pitch in the tars at each intrinsic temperature. In general, a low intrinsic temperature (250°*C*) gave a tar containing a very high amount of the low-boiling fraction and very low yields of the high boiling fraction and pitch. Increasing intrinsic temperature resulted in an increase in the amounts of the high-boiling portion and the pitch. It has been established that during pyrolysis, the hemicellulose of the wood is broken down at 200 to 260°*C*, followed by cellulose at 240 to 350°*C* and lastly lignin at 280 to 500°*C* (Goldstein 1978). From Table 1, it can be concluded that pyrolysis of rubberwood at a retort temperature of around 500°*C*, would produce the highest yield of the high-boiling fraction. The results in Table 1 follow quite closely the general behaviour of wood pyrolysis which yields at 250 to 300°*C* and 300 to 400°*C* maximum amounts of condensible pyroligneous products and condensible tar respectively (Goldstein 1978).

Table 1. Compositions of rubberwood tar obtained at several intrinsic temperatures

Intrinsic temperature (°*C*)	Low boiling fractions	High boiling fractions	Pitch	High boiling fraction		
				Weak acids	Strong acids	Neutral
250	92.3	1.8	5.9	1.0	0.1	0.7
450	31.3	23.7	45.0	8.1	0.2	15.4
500	7.5	75.7	16.8	32.0	1.7	42.0
700	19.7	51.6	28.7	30.0	1.1	19.9
800	12.0	33.3	54.7	15.0	2.3	16.0

Values in percent based on weight of tar; Low boiling fraction - up to 170°*C*; High boiling fraction - 170 to 315°*C*

The percentage fractional compositions of the high-boiling fractions of the tar obtained at the respective intrinsic temperatures are shown in Table 2. The amount of fraction 170 to 210°*C* ranged from 2 to 9%; that of fraction 210 to 235°*C* ranged from 4 to 13%, of fraction 235 to 270°*C* from 4 to 59% and of fraction 270 to 315°*C* from 13 to 17%. At the lowest intrinsic temperature, 250°*C*, only the fraction 170 to 210°*C* could be obtained, while fraction 270 to 315°*C* was only obtained at intrinsic temperature greater than 700°*C*. The highest amounts of fractions 210 to 235°*C* and 235 to 270°*C* were produced at intrinsic temperature of 500°*C*. On the other hand, the maximum amount of fraction 270 to 315°*C* was obtained at intrinsic temperature of 800°*C*, while that for fraction 170 to 210°*C* at intrinsic temperature of 450°*C*.

Table 3. Components of phenolic fraction of the high boiling portion (values in percent based on phenolic fraction)

Intrinsic temperature (°C)	Guaiacol	2,6-xylenol	Creosol	o-cresol/ phen	4-ethyl guaiacol	p-cresol	m-cresol	2,3-xylenol	3,5-xylenol	3,4-xylenol	Syringol	catechol	resorcinol
	RT (27.4)	RT (28.6)	RT (29.6)	RT (30.8)	RT (31.3)	RT (32.4)	RT (32.5)	RT (33.8)	RT (34.4)	RT (35.4)	RT (36.7)	RT (37.9)	RT (39.1)
250	10.5	t	t	10.4	t	t	22.0	t	t	13.4	14.3	t	29.4
450	4.0	2.1	1.4	8.9	3.0	9.2	10.3	1.3	4.4	5.0	25.8	t	24.5
500	12.6	0.2	8.8	7.1	8.2	10.0	7.8	0.7	3.2	1.3	32.2	t	7.9
700	16.6	1.8	7.9	13.5	9.0	5.3	10.7	1.4	3.3	0.4	21.0	0.3	8.8
800	9.5	1.8	6.9	7.4	9.3	8.9	6.1	2.4	4.9	1.0	22.1	6.7	12.6
PT	10.3	0.6	16.2	9.6	9.0	17.9	4.8	2.4	9.4	4.9	11.2	1.6	2.1

RT - retention time; PT - Pine tar; t - < 0.2

Table 2. Fractional compositions of the high boiling fractions of rubberwood tar obtained at various intrinsic temperatures*

Intrinsic temperature (°*C*)	High boiling fractions			
	170-210°*C*	210-235°*C*	235-270°*C*	270-315°*C*
250	1.8	-	-	-
450	8.8	11.1	3.8	-
500	4.3	12.7	58.7	-
700	7.7	6.9	23.9	13.1
800	3.5	3.6	9.4	16.8

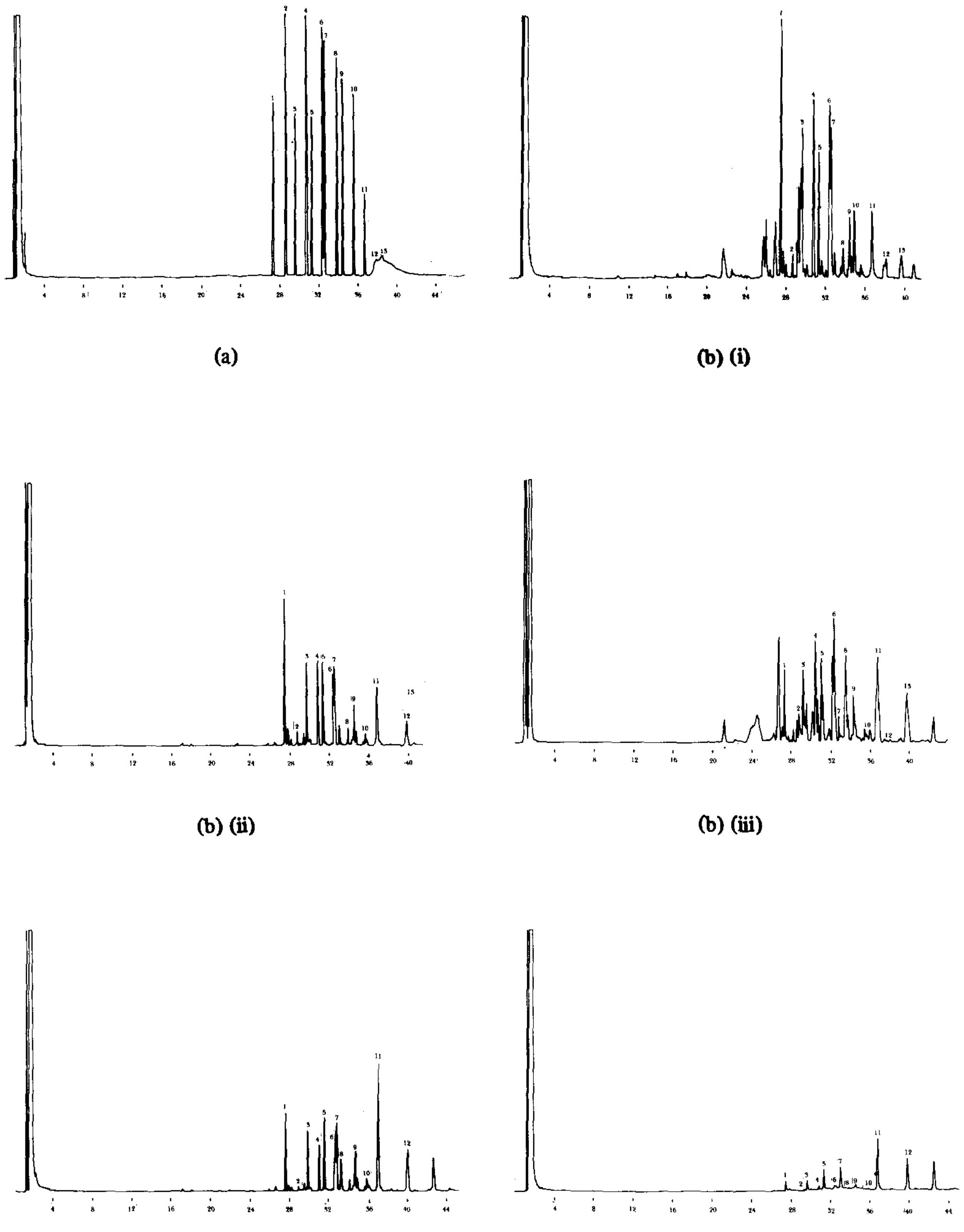
* Based on weight of tar in percent

High-boiling fraction

The high boiling fractions of the tars were separated into strong acids, weak acids (phenols) and neutrals. The results are shown in Table 1. At the range of the intrinsic temperatures indicated, the content of strong acids was very small, in the range of 0.1 to 2.3% with respect to the weight of tar. These results are not surprising since most of the strong acids, namely acetic acid, are present in the pyroligneous acid or aqueous fraction of the pyrolysis process. However, the content of weak acids varied significantly with the change of intrinsic temperature increasing from 250°*C* to reach a maximum at between 500 to 700°*C*, and then decreasing with further increase in intrinsic temperature. The same trend was also observed for the content of the neutral portion. The weak acid fraction mainly contains phenolic substances derived from the breakdown of lignin in the wood (Goldstein 1978). As mentioned earlier, lignin degradation occurs at about 280 to 500°*C* thus explaining for the high weak acid content (32.0%) at the intrinsic temperature of 500°*C* (Table 1). The marked decrease in the content of the weak acids after 500 to 700°*C* may be due to the decomposition of these substances at higher temperatures. The high-boiling fractions at the various intrinsic temperatures were made up of almost equal proportions of weak acids and neutrals except at intrinsic temperature of 450°*C* where the amount of neutrals was approximately twice that of weak acids and at 700°*C* where the proportion of neutrals was approximately half. The amount of the neutral fraction was about the same throughout except at intrinsic temperatures of 250 and 500°*C*. Further study on the content of the neutral fractions is still in progress.

Identification and proportion of phenolic components

The phenolic compounds in the weak acid portions of the high-boiling fractions were separated by gas chromatography (GC). They were identified by GC retention time of 14 standard samples, namely guaiacol, 2,6-xylenol, creosol, o-cresol, phenol, 4-ethyl guaiacol, p-cresol, m-cresol, 2,3-xylenol, 3,5-xylenol, 3,4-xylenol, syringol, catechol and resorcinol (Figure 1). The phenolic contents in the rubberwood tars at the various intrinsic temperatures were



(a) (b) (i)

(b) (ii) (b) (iii)

(b) (iv) (b) (v)

Figure 1. a. Gas chromatograph for the standard phenols.**b.** Gas chromatograms for the weak acid fractions at intrinsic temperature of 800°C: i) b.p. up to 170°C; ii) b.p. 170-210°C; iii) b.p. 210-235°C; iv) b.p. 235-270°C; v) b.p. 270-315°C (1: guaiacol; 2: 2,6-xylenol; 3: creosol; 4: o-cresol/phenol; 5: 4-ethylguaiacol; 6: p-cresol; 7: m-cresol; 8: 2,3-xylenol; 9: 3,5-xylenol; 10: 3,4-xylenol; 11: syringol; 12: catechol; 13: resorcinol)

compared to each other and also to that of a pine tar obtained commercially.

The contents of phenols in the tars from the rubberwood pyrolysis are shown in Table 3. The figures are based on the weight of the phenolic fraction at the corresponding intrinsic temperature. Among the phenols, syringol appears to be the major constituent, followed by guaiacol. On the other hand, the xylenols and catechol are present only in relatively small quantities. Under the GC condition employed, the retention times of o-cresol and phenol were very close together and hence it was not possible to quantify these two compounds separately. At 250°*C*, resorcinol and m-cresol were the major phenols, followed by syringol and the rest of the phenols. The content of syringol was markedly increased from 14% at 250°*C* to 26% at 450°*C* and 32% at 500°*C*. At higher intrinsic temperature > 500°*C*, the content of syringol was only slightly decreased.

Generally, at lower intrinsic temperature, the number of phenolic components was smaller than that at higher intrinsic temperature. This is not surprising since lignin breakdown only occurs between 280 and 500°*C*. The relatively high amount of syringol in these phenolic fractions is expected since it is already known that hardwood lignin is made up mainly of syringyl units while softwood lignin contains similar proportions of both syringyl and guaiacyl units, as reflected in the contents of these two phenols in the pine tar sample used for comparison (Table 3).

Conclusion

It is possible to convert by pyrolysis rubberwood as well as other wastewood into useful products the contents and amounts of which can be varied with temperature. The liquids produced from pyrolysis of rubberwood at various temperatures within the range of 250 to 800°*C* had different yields and compositions. Several phenolic compounds were identified, namely, syringol, guaiacol, 4-ethyl guaiacol, the xylenols, cresols, catechol, creosol and resorcinol in the high-boiling fractions (170 to 315°*C*). These phenols can be used as germicides, disinfectants and as raw material in the medical and chemical industries. Investigation into the by-products from kilns in the manufacture of charcoal in this country should be conducted to establish the potential uses of these by-products which at present are being discarded during the charcoal production. Charcoal is produced at a yield of not more than 28% from the local kilns. There is thus a loss of at least 72% wood substance in the form of the liquid, gaseous and tarry by-products which constitute an enormous amount of unutilised material as a potentially valuable resource for industry.

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