



Pyrolysis-Gc/Ms Analysis of Fast Growing Wood *Macaranga* Species

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ABSTRACTS

Py-GC/MS analysis of six different species of fast growing *Macaranga* wood has been studied. Flash pyrolysis was conducted at different temperatures (250-850 °C) under a flow of helium followed by GC/MS analysis of the products. The total pyrolysis yields of the six different species of *Macaranga* were mostly between 40 and 90% within the range of pyrolysis temperature applied. Pyrolysis of the woody biomass produced compounds which are mostly derived from thermal degradation or volatilization of lignin and cellulose/hemicellulose, the original major constituents of the biomass. The Py-GC/MS technique indicated that *M. gigantea* was the most potential species for biofuel production and the optimum pyrolysis temperature to produce high yields of bio-oil was 450 °C.

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1. INTRODUCTION

The contribution of fossil fuels to the increasing world burden of greenhouse gases has encouraged investigation of renewable sources as providers of liquid fuel (biofuel). Wood, consisting mainly of lignin, cellulose and hemicellulose, is such a source and biofuel production by wood pyrolysis is a relatively economic and environmentally friendly method of utilizing wood as an energy source (Heidari et al., 2019). However, the characteristics of wood are highly variable and it would be useful to have a method of rapidly assessing the relative biofuel yield and yields of major compounds (biofuel quality) of different wood species as a function of variables such as temperature.

Pyrolysis gas chromatography - mass spectrometry (Py-GC/MS) is an analytical method to investigate samples containing non-volatile or high boiling point components and high polarity compounds that cannot be analyzed using conventional GC-MS techniques. It has been found that the overall yield and product distribution among broad chemical classes were similar for *Pinus radiata* and grape marc pyrolysed in a Py-GC/MS system (Subagyono et al., 2016b) and in a short residence time flow reactor (Subagyono et al., 2015a). Likewise, product distribution for pinewood pyrolysis in a Py-GC/MS system was generally similar to that for the same wood pyrolysed in a short residence time fluidized bed reactor (Zmiewski et al., 2015). Finally, the conversions in several different classes of fast pyrolysis reactors have been found to be similar (Bridgwater, 2012). Thus, for wood and similar biomass, Py-GC/MS results are a guide to what would be expected in a wide range of short residence time reactors.

East Kalimantan, an Indonesian province, has almost 15 million hectares of forest mostly primary and secondary dryland forests (or tropical dryland forests) (Kiswanto et al., 2018), with at least 6,000 endemic species of plants, including species of

Macaranga (Amirta et al., 2016b), which belong to the major group angiosperms and family Euphorbiaceae. Native species of *Macaranga* also occur in southern Asia, Africa, Australia and the South Pacific (Webster, 1994). These woody plants have a fast growth rate and they are usually considered as weeds, but *Macaranga* plants are a potential biofuel feedstock, because the wood contains high concentrations of lignin and cellulose with a low moisture content (Amirta et al., 2016a).

Six different species of *Macaranga* with different lignin and cellulose contents have been used as feedstock for bioethanol production (Amirta et al., 2016a) but not investigated for pyrolysis bio-oil production. The yield and nature of the oil from wood are highly variable, as will be shown in this study, and if the oil potential of closely related wood species is to be surveyed economically, it is necessary to find a method of rapidly and cheaply comparing the yield and quality of the oil from different wood species as a function of important variables such as temperature. To date, cheap, rapid methods have not been adopted, and this paper proposes Py-GC-MS as a suitable method and exemplifies its use. It is not sufficient to identify the products. They must also be graded according to how useful they would be in a practical application of bio-oil; this is an important feature of this new method of identifying which of a group of species and which conditions give the best combination for producing as high a yield as possible of good quality bio-oil, easily upgraded to a useful product. Previous studies of Py-GC/MS of closely related species had different aims. Galetta et al. (2014) pyrolysed samples of three *Eucalyptus* species from various locations at one temperature and looked at the yields of a few compounds to calculate the guaiacyl/syringyl ratio in the lignin and assess the pulping potential of the samples. Gerber et al. (2016) analysed a large number of genotypes of *Arabidopsis* in order to study how closely the different types were related

to each other. Ohra-aho *et al.* (2018) concentrated on the yields of a few pyrolysis products to establish a method of determining the proportions of different sugars in the carbohydrate component of wood and pulps from 18 *Eucalyptus* species. No study of closely related species concentrated on their relative potential for production of bio-oil with respect to its yield and composition. Our previous work demonstrated that the products of Py-GC-MS from a range of types of biomass gave a good approximation to the composition of the pyrolysis oil for short-residence-time pyrolysis, where the effects of secondary reactions are reduced (Compare Subagyono *et al.*, 2016a and Subagyono *et al.*, 2016b). Py-GC-MS only requires small amounts of sample and thus permits a rapid survey of the effects of temperature and biomass source on the yield and composition of the bio-oil. Even small differences in biomass composition, such as occur in species from the same genus, give observable differences in bio-oil composition (Gerber *et al.*, 2016; Ohra-aho *et al.*, 2018). Such small differences may be important in deciding which species to exploit for bio-oil production and what would be the best pyrolysis temperature to use. Therefore, it is worthwhile to study the characteristics of the products obtained from pyrolysis of *Macaranga* species, differing in characteristics such as lignin and cellulose content, using Py-GC/MS, to provide information on the potential values of the pyrolysis products as liquid fuel. (Galetta *et al.*, 2014)

In this paper, we report the results obtained from Py-GC/MS of six different species of Indonesian *Macaranga*. The pyrolysis yield and relative abundance of different classes of identified compounds at different temperatures were determined. The compounds were graded as 'desirable' or 'undesirable' depending on their usefulness in practical applications of the oil. Flash pyrolysis was conducted at a range of

temperatures between 250 and 850 °C to investigate the change in behaviour of the lignocellulosic biomass during pyrolysis, in order to determine the species and temperature which give the highest production of compounds that could be treated to give useful fuels.

2. MATERIALS AND METHODS

2.1. Sample preparation and characterisation.

Six species of *Macaranga*, namely *M. hypoleuca*, *M. gigantea*, *M. motleyana*, *M. tanarius*, *M. winkleri*, and *M. pearsonii* (30-40 years old), were collected from Mulawarman University Education Forest located at Bukit Soeharto, Kutai Kertanegara, East Kalimantan, Indonesia. The trunks of *Macaranga* samples were chipped, air dried and then crushed to pass a 100 mesh. For comparison, a gymnosperm species, *Pinus radiata* (30-40 years old), was used. The *Pinus radiata* sample was supplied by Australian Bluegum Plantations Pty Ltd through Greening Australia and was harvested in the Green Triangle Region, South East Australia. The wood sample was chipped, dried at 75 °C under N₂ and then crushed to <1.4 mm.

Moisture content, volatile matter, fixed carbon and ash content of the above wood samples were determined by the testing laboratory of PT. Jasa Mutu Mineral, Indonesia using the ASTM method. The lignin and α -cellulose (referred to as cellulose below) contents were determined using the TAPPI standard method (Amirta *et al.*, 2016a; Amirta *et al.*, 2016b). Elemental analyses were carried out by PT. Geoservices, Balikpapan, Indonesia for C, H, N and S for the wood samples. The C, H and N contents were analysed using an LECO-CHN 628 analyser, while the S content was analysed using a Kaiyuan 5E-IRS II Infrared Sulfur Analyser with oxygen as a carrier gas. Heating values of the wood samples were calculated using the Dulong formula (Heating value = $0.3383C + 1.4428(H-O/8) + 0.0942S$).

2.2. Py/GC-MS procedures.

Pyrolysis GC-MS was conducted using the method described in our previous paper (Subagyono *et al.*, 2016b). A Chemical Data Systems (CDS) Pyroprobe 5200 linked to a GC-MS (Agilent 6850 GC and 5790 MSD) was used. Each sample (0.15-0.20 mg) was accurately weighed and inserted into a quartz tube plugged at each end with quartz wool. The tube was then pushed into the platinum heating coil of the Pyroprobe. The coil was heated under helium for 1 sec at 100 °C, then the temperature was raised at 10 °C/msec from 100 °C to a chosen temperature in the range 250-850 °C and held at the final temperature for 15 sec. The pyrolysis products were transferred in a flow of helium (1.0 mL/min) through a transfer line held at 320 °C to the GC-MS. An Agilent HP-5MS GC capillary column, 30 m long, 0.25 mm internal diameter with a film thickness of 0.25µm was used, with helium flowing at 1.0 mL/min. The inlet temperature for GC was 320 °C. The GC temperature program was: 3 min at 30 °C, then the temperature was raised at 8 °C/min to 305 °C and kept at 305 °C for 10 min. At the GC inlet, a split ratio of 50:1 was applied. The mass spectrometer was operated in electron impact mode at 70 eV, the ion source temperature being 230 °C. The mass range (m/z) scanned was 29-450 amu (m/z).

Each sample was also weighed after its pyrolysis run to enable calculation of pyrolysis yields. The pyrogram obtained from each run was processed using the Agilent MSD ChemStation software. The peaks were assigned based on library identification using the mass spectra of the compounds, combined with a judgement based on the literature of the likelihood of the compound being formed during wood pyrolysis (Hatcher *et al.*, 1989; Hatcher *et al.*, 1990; Obst, 1983; Pastorova *et al.*, 1994; Pouwels and Boon, 1990; Pouwels *et al.*, 1989; Ralph and Hatfield, 1991). The total pyrolysis yield and the relative concentration (RC) of an individual compound (also referred to below as “concentration”) are calculated as follows:

$$\begin{aligned} \text{Total pyrolysis yield (\%)} \\ = 100\% \\ - \left(\frac{\text{weight of residue after pyrolysis}}{\text{weight of original sample}} \times 100\% \right) \quad (1) \end{aligned}$$

$$\begin{aligned} \text{Relative concentration of compound (\%)} \\ = \frac{\text{RP of compound} \times \text{total pyrolysis yield}}{100} \quad (2) \end{aligned}$$

Where *RP* is the peak area of the compound in the total ion chromatogram as a percentage of the area of all the peaks in the total ion chromatograms. Most studies only give *RP*, which does not permit an assessment of the actual yields of the compounds and therefore cannot follow yield changes e.g., as a function of temperature. *RC* will in general be greater than the actual concentration, particularly at higher pyrolysis temperatures, because yields of gases not detected by the GC are not taken into account. However, comparisons with conventional pyrolysis experiments (Subagyono *et al.*, 2015; Subagyono *et al.* 2014; Subagyono *et al.*, 2016) suggest that this error will be relatively small at the lower temperatures.

3. RESULTS AND DISCUSSION

3.1. Characteristics of the wood samples.

Lignin, holocellulose and cellulose contents of the different species of *Macaranga* are presented in Table 1. The lower lignin content of *M.hypoleuca* and *M.gigantea* would be expected to lead to higher yields of gases and liquids (Burhenne *et al.*, 2013).

The moisture contents of the six different species of *Macaranga* ranged from 11 to 16% (Table 2), with that of *M. winkleri* being considerably higher than the others, a disadvantage for oil production. The low (<2.2%) ash yield is advantageous for biofuel production, since, in general, minerals tend to reduce biofuel yield and increase char and gas yields (Syamsudin *et al.*, 2016). The higher ash yields of *M. tanarius* and *M. pearsonii* would make them inferior in this respect for biofuel production. The elemental compositions of the six species of *Macaranga* were similar (Table 3). All had low N and S contents. The high O content was as would be expected from the high lignin, cellulose and hemicellulose contents in the wood. The high

contents of O lead to substantial contents of oxygen-containing compounds, such as phenols, cresols, carboxylic acids, esters, aldehydes and ketones (Compare Subagyono *et al.*, 2015a; Subagyono *et al.*, 2016a,b) in the pyrolysis products, which lower the quality of the pyrolysis oil.

3.2. Py-GC MS

Firstly, *M. winkleri*, which had the lowest pyrolysis yield at 300 °C, had the equal lowest cellulose content and the equal lowest ash-free holocellulose (cellulose+hemicellulose) content among the six species (Table 1). Since hemicellulose decomposes to volatile compounds at 200-260 °C and cellulose at 240-350 °C (Mohan *et al.*, 2006), the low pyrolysis yield at 300 °C for this species may be due to the

low concentration of cellulose and relatively low concentration of hemicellulose. Secondly, at 850 °C the pyrolysis yield for *M. gigantea* was about 5 wt% lower than for the other five species, and this species had the highest hemicellulose content and consequently the lowest cellulose+lignin content of the six species. Perhaps this combination resulted in more polymerization and hence a reduction in yield. However, in general, the pyrolysis yields are not related in any simple way to the concentrations of the wood components or the elemental analysis. There is no substitute for an experimental determination of the pyrolysis yields.

Table 1. Chemical composition of *Macaranga* species (Mean±SD*)

Species	Chemical composition (%)**		
	Lignin	Holocellulose	α-Cellulose
<i>M. hypoleuca</i> ^a	27.6±0.2	73.0±0.8	68.8±0.5
<i>M. gigantea</i> ^a	27.6±0.7	71.0±0.3	63.0±0.1
<i>M. motleyana</i> ^a	30.8±0.4	72.2±1.7	65.4±0.3
<i>M. winkleri</i> ^a	28.7±0.9	69.7±0.2	63.2±0.9
<i>M. pearsonii</i> ^a	32.9±1.1	70.7±0.2	67.4±1.1
<i>M. tanarius</i> ^b	30.4±0.3	69.3±0.3	65.5±0.1
<i>P. radiata</i> ^c	26.7±0.0	70.9±0.4	68.4±0.7

*SD – standard deviation of duplicates, **Wt% dry basis (db) a the data were taken from Amirta *et al* (2016b), ^b the data were taken from Amirta *et al* (2016a), ^c the data were taken from Subagyono *et al.* (2015a)

Table 2. Proximate analysis result of *Macaranga* species and *P. radiata**

	Moisture content (%)	Ash content (%)	Fixed Carbon (%)	Volatile matter (%)
<i>M. hypoleuca</i>	11.68±0.06	0.70±0.04	15.02±0.14	84.28±0.05
<i>M. gigantea</i>	11.96±0.00	0.72±0.02	16.16±0.06	83.13±0.04
<i>M. motleyana</i>	12.42±0.06	0.85±0.04	16.62±0.23	82.53±0.13
<i>M. tanarius</i>	13.35±0.11	2.19±0.04	15.37±0.20	82.44±0.06
<i>M. winkleri</i>	16.24±0.07	1.96±0.00	14.75±0.15	83.28±0.08
<i>M. pearsonii</i>	13.58±0.04	0.74±0.01	16.89±0.13	82.37±0.08
<i>P. radiata</i> **	4.2±0.1	0.50±0.02		

* Wt% dried basis (db), ** the data were taken from Subagyono *et al.* (2015a)

Table 3. Elemental composition of *Macaranga* species

Species	C* (%)	H* (%)	O** (%)	N* (%)	S* (%)	Heating value (MJ/kg)
<i>M. hypoleuca</i>	49.8±0.1	5.7±0.0	43.6±0.1	0.1±0.0	0.1	15.1
<i>M. gigantea</i>	50.7±0.2	5.8±0.1	42.4±0.3	0.1±0.0	0.2	15.7
<i>M. motleyana</i>	50.8±0.2	5.9±0.1	42.3±0.3	0.1±0.0	0.1	15.7
<i>M. tanarius</i>	50.9±0.2	5.9±0.0	40.7±0.2	0.1±0.0	0.2	15.8
<i>M. winkleri</i>	51.6±0.2	6.0±0.0	40.2±0.2	0.1±0.0	0.1	15.7
<i>M. pearsonii</i>	51.0±0.1	5.8±0.1	42.3±0.2	0.1±0.0	0.1	15.4
<i>P. radiata</i> ***	47.3±0.2	6.2±0.0	46.1±0.3	<0.30	<0.40	16.6

* Wt% dried basis (db), ** Wt% dried basis (db) calculated by difference, *** the data were taken from Subagyono et al. (2015a)

The total pyrolysis yields of *Pinus radiata* in 350-750 °C were 38-93% (Subagyono et al., 2016b) compared to 43-92% for *Macaranga* species **Figure 1**. The higher inorganic content (ash yield) of some of the *Macaranga* species may include components that catalyse repolymerization and hence reduce pyrolysis yields at higher temperatures (Subagyono et al., 2014). **Figure 2** shows the pyrograms for *M. gigantea* and *M. winkleri* obtained at different pyrolysis temperatures. The pyrograms of the other species were similar. The compounds identified in the pyrograms are listed in Table 4. The compounds identified in the pyrograms of the six different species of *Macaranga* were similar **Figure 2** but there were differences in concentration between species (especially at the lower temperatures); this may be due to the different composition of the original constituents in the wood (lignin, cellulose, hemicellulose). The products identified in the pyrograms were mainly derived from lignin, cellulose and hemicellulose. As pyrolysis temperature increased, lower boiling-point (smaller-molecular-weight) compounds showed more intense, distinguishable peaks in the pyrograms. Thus, pyrolysis at higher temperature would lead to a more useful bio-oil, with less need for further treatment.

Pyrolysis of lignin produced vanillin, isoeugenol isomers, coniferyl alcohol, eugenol, acetovanillone and homovanillic acid. These compounds have also been observed from pyrolysis of different types of wood lignin, including pine lignin (Saiz-Jimenez and de

Leeuw, 1984; Wagner et al., 2011). The phenolic compounds were pyrolysis products of different building blocks of lignin, p-coumaryl alcohol, coniferyl alcohol, and synapyl alcohol (Kleinert and Barth, 2008; Wagner et al., 2011). For example, alkyl-phenols are p-hydroxyphenyl units (Kristensen et al., 2009) derived from p-coumaryl alcohol, whilst methoxy-phenols are guaiacyl units (Kristensen et al., 2009) derived from coniferyl alcohol. The dimethoxyphenol and syringyl alcohol, comes from syringyl groups expected to be present in hardwood lignin. Decomposition of phenol produced 1,3-cyclopentadiene (Mulholland et al., 2000). Pyrolysis of carbohydrate (e.g. D-glucose) may also produce 1,3-cyclopentadiene (Paine lii et al., 2018).

Compounds derived from cellulose/hemicellulose were also observed in the pyrograms. Furfural is a thermal degradation product of xylose (Xing et al., 2011), or is formed via dehydration of 2-furanmethanol (Aho et al., 2008). Furans, furfurals, hydroxyacetaldehyde, acetic acid, ketones and aldehydes were products derived from cellulose and hemicellulose (Aho et al., 2008; Jackson, 2013; Lu et al., 2016; Shi et al., 2012) that may be formed via degradation or decomposition of cellulose to form (1) small molecular products or (2) low-degree oligomers (Liu et al., 2014).

In particular, hydroxyacetaldehyde can also be produced from pyrolytic fragmentation (ring scission) of holocellulose (Lu et al., 2016). Ketonization of hydroxyacetone derived from cellulose or propanal (Jackson, 2013; Liu et al.,

2014) gives 3-pentanone. Small molecular weight oxygenates, such as hydroxyacetaldehyde and 1-hydroxypropanone **Table 4** could have been produced from condensed-phase secondary pyrolysis of cellulose derived levoglucosan (Liu *et al.*, 2014) or from fragmentation of the levoglucosan ring and subsequent reactions (Shen *et al.*, 2015). The same compounds are also pyrolysis products of hemicellulose (Shen *et al.*, 2015). Some ketones, aldehydes and acetic acid related compounds were also pyrolysis products of cellulose/hemicellulose (Jones *et al.*, 2010; Mullen and Boateng, 2008). Lignin also produces small amounts of acetic acid (Carrier *et al.*, 2017), but most of the acetic acid comes from the cellulose and hemicellulose. The relative peak area (RP) of the major compounds (RP>1%) identified in the pyrograms of *M. gigantea* were calculated and are presented in **Table 5**. The individual RP **Table 5** for other *Macaranga* species had similar trends so they are not shown.

As can be seen in **Tables 5 and 6**, the peak areas and concentrations of lignin derived products such as phenols, vanillin, isoeugenol and acetovanillone increased slightly with increasing pyrolysis temperature up to 550 °C. Comparisons can be made with other studies on wood pyrolysis. For fast pyrolysis of wood from *Eucalyptus* trunks in a fluidized-bed reactor, the peak yield of small lignin-derived compounds occurred at only 400-425 °C (Jiang *et al.*, 2010). However, for wood pyrolysed under Py-GC conditions, peak yields of small lignin-derived molecules were at higher temperatures, 550 °C for pine unstated species (Thangalazhy-Gopakumar *et al.*, 2011), 600 °C for poplar (hardwood) and 650 °C for *P. radiata* **Table 6**. Thus the *Macaranga* value is within the range found for other woods. The pyrolysis of polymerized coniferyl alcohol (G-

type lignin) probably formed isoeugenol and vanillin (Wagner *et al.*, 2011). At lower temperatures (<350 °C), guaiacol derivatives were formed, such as 2,6-dimethoxy-phenol, 2-methoxy-4-(2-propenyl)-phenol, 2-methoxy-4-propyl-phenol. The low concentrations of some low boiling point compounds in the pyrograms may be due to the thermal behaviour of lignin. The main process of thermal degradation of lignin occurs around 400 °C, forming aromatic hydrocarbons and phenolic –OH groups (Brebú and Vasile, 2010). This is in contrast to what was observed for the fast pyrolysis of isolated lignins, where the maximum yield of phenolic compounds was at 700 °C, rather than near 500 °C (Hu *et al.*, 2018). Above 550 °C, the yields of nearly all the identified lignin-derived products (except 1,2-benzendiol) tended to decline with increasing temperature, leading to an overall decline in the total yield of identified lignin-derived compounds.

The cellulose/hemicellulose polymers broke down to small-molecular-weight bio-oil-type compounds in 350-450 °C, and higher pyrolysis temperatures either did not lead to further breakdown to unidentified low-molecular-weight non-condensable gases, or any such breakdown was compensated by the depolymerisation of cellulose/hemicellulose-derived polymers or larger molecules at higher temperature, for example, secondary pyrolysis of levoglucosan (Liu *et al.*, 2014). In contrast, some studies have suggested that primary monomeric phenols formed in lignin fast pyrolysis can oligomerize (Anca-Couce, 2016; Bai *et al.*, 2014). It is important to note that at lower temperatures (<350 °C), the concentrations of some pyrolysis products appearing early in the pyrograms (<10 mins) were very low (<0.5%).

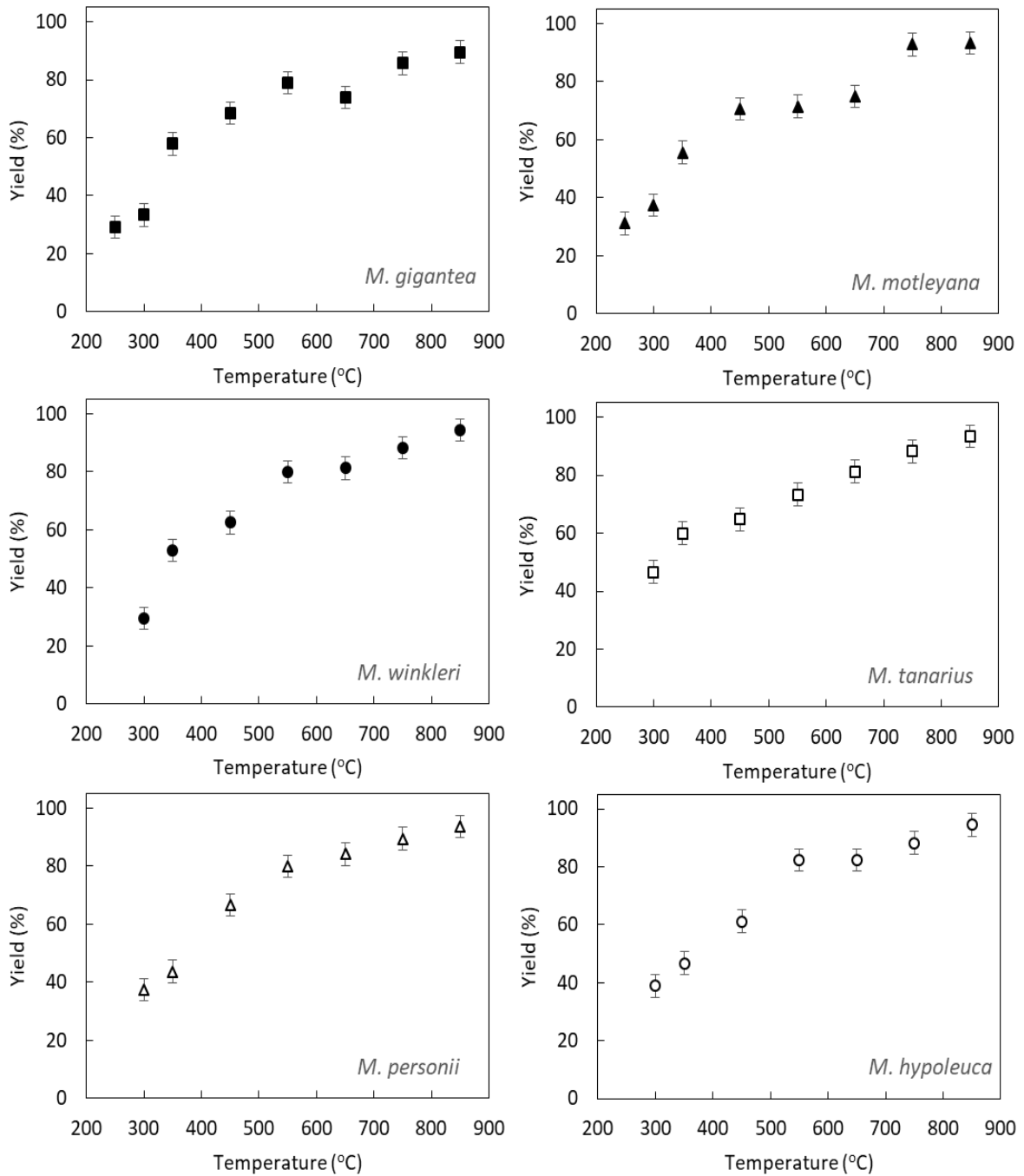


Figure 1. Total pyrolysis yields (%) of *Macaranga* species at different pyrolysis temperatures

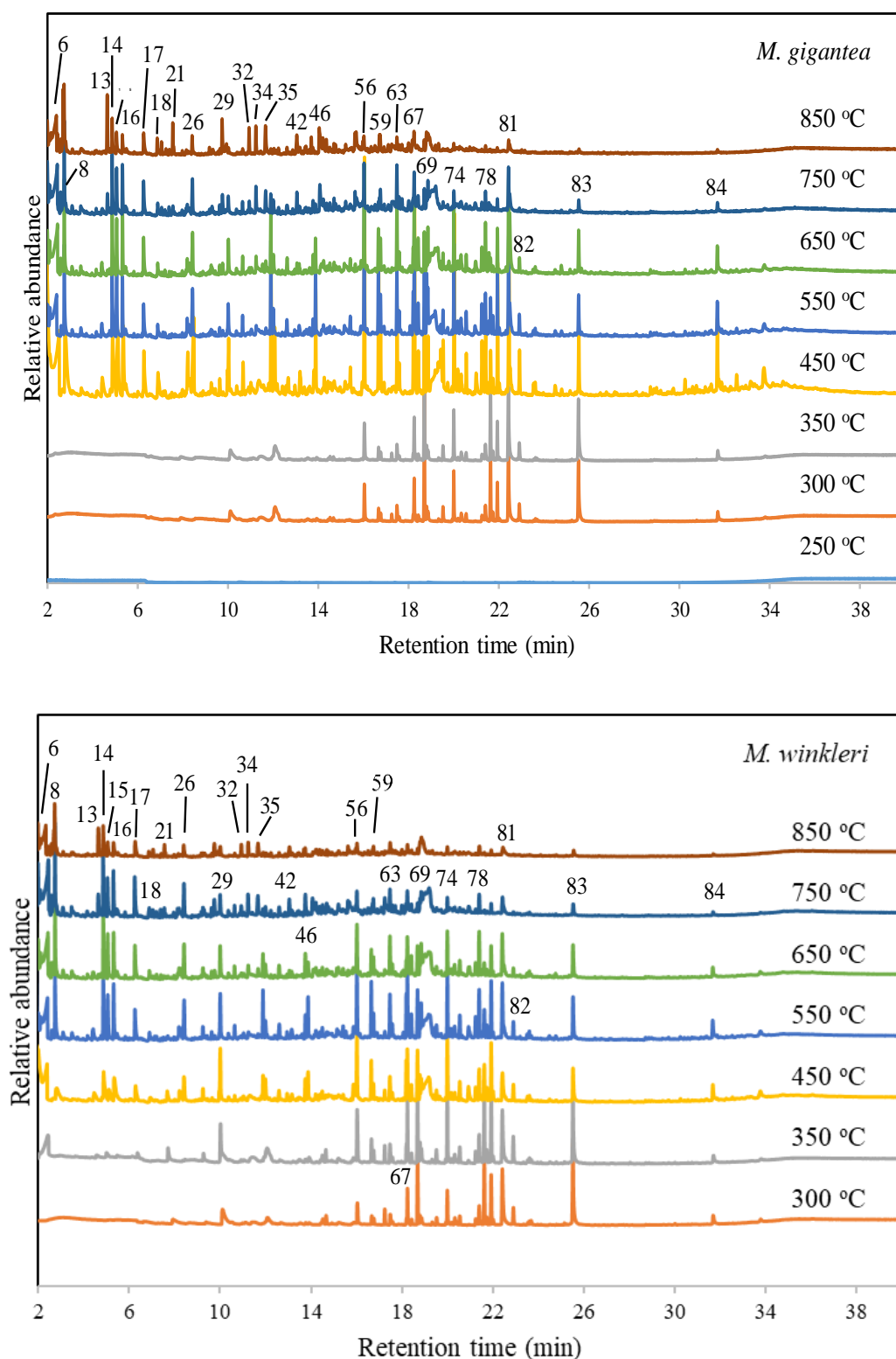


Figure 2. Pyrograms of *M. gigantea* and *M. winkleri* at different pyrolysis temperatures (numbers refer to Table 4)

Table 4. List of major compounds identified in the pyrograms of *Macaranga* species

No.	Compounds	Retention Time (min)	m/z	No.	Compounds	Retention Time (min)	m/z
1	1,3-cyclopentadiene	1.74	32, 44, 66	24	furanone	8.18	55, 84
2	2-propen-1-ol	1.77	39, 57	25	furfuryl alcohol	8.18	55, 70, 84
3	hydroxy acetaldehyde	1.87	31, 60	26	2-hydroxy-2-cyclopenten-1-one	8.41	55, 98
4	3-pentanone	2.09	29, 57, 86	27	acetophenone	9.17	55, 77, 105
5	methoxy acetic acid	2.15	45, 60, 82	28	5-methyl-2-furfural	9.29	53, 96, 110
6	acetic acid	2.39	43, 60	29	phenol	9.75	66, 94
7	2-butenal	2.58	41, 70	30	4-hydroxy-5,6-dihydro-(2H)-pyran-2-one	9.99	58, 114
8	1-hydroxy-2-propanone	2.73	43, 74	31	2-hydroxy-3-methylcyclopent-2-enone	10.64	55, 69, 112
9	dimethyl furan	3.46	86, 96	32	indene	10.93	39, 63, 89, 116
10	isobutyric acid, methyl ester	3.95	43, 102	33	4-methyl-5H-furan-2-one	11.02	41, 69, 98
11	3-penten-2-one	4.15	41, 69, 84	34	2-methyl-phenol	11.24	77, 90, 108
12	4-cyclopropyl-1-butene	4.39	55, 81, 96	35	3-methyl-phenol	11.67	77, 107
13	methyl-benzene	4.64	39, 65, 91	36	2-methoxy-phenol	11.88	81, 109, 124
14	acetic acid, methyl ester	4.85	43, 73	37	pentanal	11.99	44, 57
15	butanedial	5.06	29, 58	38	2,6-dimethyl-phenol	12.23	77, 107, 122
16	pyruvic acid. methyl ester	5.30	43, 102	39	3-hydroxy-2-methyl-4h-pyran-4-one	12.39	71, 97, 126
17	Furfural	6.24	39, 82, 96	40	3-methyl-2,4(3H,5H)-furan-2-one	12.60	56, 84, 114
18	ethyl-benzene	6.86	51, 91, 106	41	2,3-dimethyl-phenol	12.86	107, 122
19	1,3-dimethyl-benzene	7.05	91, 106	42	2,4-dimethyl-phenol	13.05	91, 107, 122
20	acetol acetate	7.20	43, 86	43	3-hydroxy-4-methylbenzaldehyde	13.18	42, 107, 136
21	styrene	7.54	78, 96, 104	44	4-ethyl-phenol	13.42	107, 122,
22	2-methyl-2-cyclopenten-1-one	7.96	53, 67, 96	45	2-methoxy-4-methyl-phenol	13.87	95, 123, 138
23	butyrolactone	8.14	42, 56, 86	46	1,2-benzenediol	14.17	64, 110
48	3-(1-methylethyl)-phenol	14.51	43, 110, 121	47	2,3-dihydro-benzofuran	14.39	91, 110, 120
49	4-ethyl-3-methyl-phenol	14.70	121, 136	63	vanillin	17.47	81, 123, 151
				64	2-methoxy-4-(1-propenyl)-phenol	17.57	77, 164

No.	Compounds	Retention Time (min)	m/z	No.	Compounds	Retention Time (min)	m/z
50	2,2'-bifuran	14.78	121, 134	65	2-allyl-4-methylphenol	17.71	133, 148
51	3-methoxy-1,2-benzenediol	15.15	97, 125, 140	66	3-(4-methylphenyl)-2-propyn-1-ol	18.01	115, 131, 146
52	4-ethyl-2-methoxyphenol	15.40	137, 152	67	isoeugenol	18.24	77, 136, 149, 164
53	2-(2-propenyl)-phenol	15.63	91, 134	68	2-methoxy-4-propylphenol	18.41	122, 137, 166
54	4-methyl-1,2-benzenediol	15.85	78, 110, 124	69	2-ethyl-1,4-benzodioxin	18.69	147, 162
55	ortho-methoxyacetophenone	15.85	124, 135, 150	70	1-(2,4,6-trimethylphenyl)-ethanone	18.8	91, 147, 162
56	2-methoxy-4-vinylphenol	16.03	77, 107, 135, 150	71	acetovanillone	18.84	123, 151, 166
57	3-phenyl-2-propenal	16.65	124, 132	72	levoglucosan	19.03	60, 73, 98, 162
58	1-methoxy-4-(1-propenyl)-benzene	16.52	133, 148	73	homovanilic acid	19.73	137, 180
59	2,6-dimethoxyphenol	16.65	139, 154	74	4-vinyl syringol	20.00	137, 165, 180
60	2-methoxy-4-(2-propenyl)-phenol	16.74	103, 131, 164	75	9H-fluorene	20.31	151, 180
61	3-isopropylbenzaldehyde	16.91	133, 148	82	syringyl acetone	22.91	137, 167, 210
62	5-methoxy-benzofuran	17.10	123, 133, 148	83	trans-sinapaldehyde	25.53	137, 165, 180, 208
				84	diguaiacyl-containing dimeric lignin products	31.68	272

These compounds include low boiling point compounds such as hydroxyacetaldehyde and some phenolic compounds. Higher pyrolysis temperatures facilitated secondary reactions and thus more compounds with low molecular weight were generated. The low concentrations of low boiling point compounds at lower temperatures were also observed in the pyrograms of *Pinus radiata* (Subagyono *et al.*, 2016b). The concentrations of furfural and furfuryl alcohol, derived from hemicellulose, did not change with pyrolysis temperature, perhaps because the hemicellulose polymers had

already been broken down at temperatures as low as 350 °C to produce these compounds.

Overall, therefore, the total yields of identified lignin-derived products peaked at 550 °C or below and fell at higher temperatures **Table 6**, whereas the total yields of identified small cellulose/hemicellulose derived products remained high to 750-850 °C **Table 6**. This has been found to be true for separated lignin and cellulose/hemicellulose from wood in many other cases (see above). Thus at 450 °C and above, the total concentrations of the identified products from cellulose and hemicellulose were

higher than those derived from lignin. This was partly due to the formation of low boiling point components from thermal degradation of cellulose and hemicellulose, such as acetic acid and hydroxyl acetaldehyde at higher temperatures.

Flash pyrolysis of *Macaranga* wood produced a large number of identified chemical compounds. The chemical substances in the pyrolysis products have some potential to be used for various applications, such as heat production, electricity production, and chemical production (Mohan *et al.*, 2006). For instance, the large fraction of phenolic compounds can be a potential feedstock for chemical production, such as adhesive or adhesive extender (Chum *et al.*, 1989; Jiang *et al.*, 2018) or phenolic resins (de Menezes *et al.*, 2017).

The bio-oil as a whole can be used as a fuel for heat and electricity production. However, it is important to note that the large number of oxygenated compounds in the products may result in a decrease in the heating value of the pyrolysis oil. Furthermore, the carboxylic acids, particularly acetic acid, will be corrosive and the aldehydes and alkenes will lead to instability and a tendency to polymerization (Lyu *et al.*, 2015; Zhang *et al.*, 2019). It would be desirable to choose species and reaction conditions such as temperature which would give the highest yields of bio-oil consistent with low concentrations of carboxylic acids, aldehydes and alkenes. Previous studies of the pyrolysis of closely related species have not clearly distinguished desirable from undesirable compounds see **Table 5**. In this respect this study is novel.

In this regard a Py-GC-MS study such as that of this paper can give valuable help. It can be argued that the yield of identified compounds would be a good indicator of the yield of useful bio-oil in fast pyrolysis, which has been considered as the best method of producing bio-oil (Mullen and Boateng, 2008). The larger molecules not eluted from the GC column

would require too much post-processing to be useful and the non-condensable gas and char will have different applications. Water will not be a useful product.

The total RC yield of cellulose and lignin derived identified products was highest at 550 °C and fell at higher temperatures see **Table 6**; the fall was probably greater than that indicated by the RC values, which will overestimate the oil yield at higher temperatures because of increased yields of non-condensable gas (see above). However, **Table 5** and the corresponding results for the other species indicate that the concentrations of acetic acid and hydroxylaldehyde were always high at temperatures of 550 °C and above, so that it would be desirable to keep the pyrolysis temperature less than 550 °C.

Since cellulose/hemicellulose gave more of the undesirable compounds than lignin, the best species and temperature would be those that gave maximum RC yield at below 550 °C, with a high lignin to cellulose ratio in the yields of identified products. These criteria lead to the choice of 450 °C as pyrolysis temperature and *M. gigantea* as the best species for bio-oil production. Even for these closely-related species, Py-GC/MS permits a clear distinction to be made as to which species would be best; the RC yields of lignin+cellulose-derived products varied from 46.6 to 54.2% at 450 °C and *M. gigantea* had a yield more than 2% greater than the next highest-yielding species. However, it is important to note that the optimum temperature using analytical pyrolysis under helium flow in a micro-reactor would not necessarily be the same as the optimum temperature in industrial wood processing facilities.

Table 5. RP (%) of major compounds identified in the pyrograms of *M. gigantea*

No.	Compounds	Pyrolysis Temperature (°C)							Note*
		300	350	450	550	650	750	850	
Lignin derived products									
1	1,3-cyclopentadiene	0.0	0.0	0.1	0.2	0.2	0.6	2.1	D
2	phenol and its derivatives	14.3	15.3	13.6	14.0	11.1	7.7	10.2	D
3	1,2-benzenediol	0.0	0.0	0.5	0.6	2.4	5.0	6.2	D
4	vanillin	2.6	2.0	1.4	1.8	2.0	1.4	0.6	
5	isoeugenol	4.0	3.9	2.7	2.5	1.7	0.8	0.4	D
6	2-ethyl-1,4-benzodioxin	12.2	6.0	1.0	1.8	0.8	0.5	0.4	U
7	acetovanillone	1.5	1.4	1.1	1.5	1.5	0.9	0.4	U
8	homovanillic acid	3.3	2.8	1.2	0.0	0.8	0.4	0.2	U
9	4-vinyl syringol	5.7	7.1	3.3	2.6	1.8	0.6	0.3	D
10	9H-fluorene	1.9	1.2	0.7	1.0	0.9	0.5	0.3	U
11	2,4-diethoxybenzaldehyde	1.0	1.3	0.9	0.9	0.7	0.3	0.1	U
12	syringaldehyde	2.1	1.8	1.0	1.3	1.4	0.7	0.4	U
13	coniferyl alcohol	0.1	0.3	0.2	0.4	0.5	0.2	0.1	D
14	1-(3,5-dimethoxy-4-hydroxyphenyl)propyne	6.6	3.1	0.5	0.8	0.1	0.1	0.1	D
15	4-hydroxy-2-methoxycinnamaldehyde	7.6	4.3	1.5	1.8	1.7	1.0	0.5	U
16	trans-sinapaldehyde	7.6	4.1	0.9	1.0	1.0	0.4	0.2	U
17	diguaiacyl-containing dimeric lignin products	2.5	2.3	2.0	1.7	1.4	0.5	0.3	
Cellulose/hemicellulose derived products									
18	hydroxy acetaldehyde	0.1	1.1	16.3	13.4	13.0	13.2	12.1	U
19	methoxy-acetic acid	0.9	0.5	0.0	1.6	1.7	1.9	2.7	U
20	acetic acid	0.8	9.1	1.3	6.6	8.2	9.1	10.6	U
21	1-hydroxy-2-propanone	0.8	0.0	8.8	7.5	6.8	7.7	7.8	U
22	acetic acid, methyl ester	0.0	2.1	4.8	4.5	5.0	5.0	4.5	
23	butanedial	0.0	0.0	2.3	2.1	1.7	1.6	1.2	U
24	pyruvic acid, methyl ester	0.0	1.1	5.2	4.2	4.1	4.0	2.7	
25	furfural	0.7	0.9	1.3	1.3	1.4	1.4	1.4	D
26	furfuryl alcohol	0.4	0.2	1.8	1.4	1.2	1.0	0.5	D
27	2-hydroxy-2-cyclopenten-1-one	0.1	0.4	2.5	1.9	1.6	1.6	1.3	U
28	pentanal	7.4	10.9	2.2	1.0	0.7	0.6	0.3	U

*D= Desirable compounds (aromatic and aliphatic hydrocarbons, phenols, furans, alcohols) and U = Undesirable compounds (acids, aldehydes, ketones, polyaromatic hydrocarbons) in pyrolysis products

Table 6. RC (%) of major compound groups identified in the pyrograms of *Macaranga* species

Species	Lignin derived products						
	300 °C	350 °C	450 °C	550 °C	650 °C	750 °C	850 °C
<i>M. hypoleuca</i>	23.7	24.9	19.5	27.0	21.7	17.0	19.4
<i>M. gigantea</i>	24.4	32.9	22.4	26.7	22.2	18.5	20.3
<i>M. motleyana</i>	23.4	26.8	19.2	23.1	18.0	18.5	19.7
<i>M. tanarius</i>	28.5	26.2	17.3	21.8	18.4	15.6	18.0
<i>M. winkleri</i>	17.5	26.5	16.2	23.0	19.1	14.1	17.8
<i>M. pearsonii</i>	23.6	21.6	18.8	25.8	20.7	18.2	21.3
<i>Pinus Radiata</i>		11.2	26.5	35.2	42.7	34.9	

Species	Cellulose/hemicellulose derived products						
	300 °C	350 °C	450 °C	550 °C	650 °C	750 °C	850 °C
<i>M. hypoleuca</i>	4.0	10.9	29.2	36.9	38.3	46.2	41.6
<i>M. gigantea</i>	3.7	15.2	31.9	35.8	33.6	40.4	40.4
<i>M. motleyana</i>	5.5	18.7	35.8	32.1	36.3	45.5	44.8
<i>M. tanarius</i>	7.4	21.2	35.1	35.1	41.0	47.5	47.5
<i>M. winkleri</i>	2.5	13.4	27.3	39.4	40.6	45.9	50.1
<i>M. pearsonii</i>	2.4	11.7	29.7	36.3	38.1	40.0	37.6
<i>Pinus Radiata</i>		17.2	36.7	43.6	41.1	43.1	

4. CONCLUSION

Pyrolysis of the wood samples produced compounds that were mostly derived from thermal degradation of lignin and cellulose/hemicellulose. Py-GC/MS analysis provided comprehensive structural information about the *Macaranga* species through identification of a wide range of chemical compounds in their pyrolysis products. The differences in yields of identified bio-oil compounds between species was greater at lower temperature. Py-GC/MS provides a rapid small-sample method of finding the best conditions and species for maximum yield of higher-quality bio-oil. If the presence of undesirable compounds is to be kept to a minimum, it was found that the best temperature was 450 °C and the best of the six *Macaranga* species was *M. gigantea*. This procedure can be taken as a model of rapid surveys of the potentialities of species for bio-oil production by fast pyrolysis. Such rapid surveys are important when a group of sibling

uncultivated species, of limited usefulness except as bio-oil sources, are being considered for large-scale utilization. As far as can be ascertained, this is the first time Py-GC-MS has been used to discriminate between closely related species for the production of bio-oil, combined with the grading of the usefulness of the compounds produced.

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6. AUTHORS' NOTE

The authors declare that there is no conflict of interest regarding the publication of this article. Authors confirmed that the data and the paper are free of plagiarism

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