Pyrolysis-GC/MS study of fast growing wood *Macaranga gigantea*

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**Abstract.** Py-GC/MS study on fast growing wood *Macaranga gigantea* at different temperatures has been conducted. The pyrolysis yields and chemical compounds obtained based on the pyrograms of the biomass by Py-GC analyses were compared with those obtained from batch pyrolysis experiments under similar conditions. Results show that the pyrolysis yields of *Macaranga gigantea* from Py-GC/MS analyses and batch reactor experiments at 300-450 °C were generally similar, ranging from 35 to 65%. Pyrolysis of the woody biomass with both techniques produced compounds which are mostly derived from pyrolysis, thermal degradation, or volatilization of lignin and cellulose/hemicellulose.

1. **Introduction**

Pyrolysis gas chromatography-mass spectrometry (Py-GC/MS) is a suitable method in providing structural information of samples which contain high boiling point components that cannot be eluted in ordinary GC-MS columns [1]. Results from Py-GC/MS can be used to identify individual components of an organic substance or changes to an organic matrix, to determine the origin particular kinds of organic matter and to be used as a guideline to design the operation condition of larger scale pyrolysis experiments [2-4]. Our previous works demonstrated that Py-GC/MS was very helpful to thoroughly study the behavior of major constituent in wood (e.g. lignin, cellulose) during pyrolysis at different temperatures [5].

*Macaranga gigantea* (or merkubung, tutup gede, simbar kubang, sangkubang, serkubung, maweneng, mahaweneng, kagurangen, same and tula-tula) is a softwood species that has strong adaptability and is easily found in disturbed forest ecosystem. This woody plant has a fast growth rate (pioneers). It is so abundant that it is usually viewed as weeds that are not worth keeping. On the other hand, *Macaranga gigantea* can be considered having great potential as a feedstock for biofuel production because it has high concentrations of lignin (28%) and cellulose (63%) with a low moisture content of 41.99% [6]. However, pyrolysis studies on the woody biomass as a renewable energy source are very limited. Therefore, it is worthwhile to study the characteristics of products obtained from pyrolysis of *Macaranga gigantea* using Py-GC/MS to understand the behavior of major precursors in *Macaranga gigantea* over pyrolysis. The pyrolysis yields resulted from Py-GC/MS analyses and those from batch pyrolysis experiments under similar conditions were compared.
2. Materials and methods

2.1. Materials
Macaranga gigantea samples were collected from Mulawarman University Education Forest located at Bukit Soeharto, Kutai Kertanegara, East Kalimantan, Indonesia. The samples were chipped, air dried and then crushed to 100 mesh. Chemicals used in the project were sulfuric acid, ethanol, benzene, sodium hydroxide, potassium dichromate solution, ferrous ammonium sulfate solution, phenanthroline-ferrous sulfate, sodium chlorite, acetic acid, and argon gas. All chemicals were used without further purification.

2.2. Sample characterization
The moisture content and ash content of the wood samples were analysed using the ASTM method D3173 – 11 and the ASTM method D 3174-12, respectively. The Klason lignin content was determined by the TAPPI standard method [7]. The α-cellulose contents was determined according to the TAPPI standard method [8]. The elemental composition of the wood (C, H, O, N, S) sample was also characterised. The C, H and N contents were analysed using LECO-CHN 628 analyser while the S content was analysed using Kaiyuan 5E-IRS II with oxygen as a carrier gas.

2.3. Py GC-MS procedures
Pyrolysis GC-MS was carried out on a Chemical Data Systems (CDS) Pyroprobe 5200 connected to a GC-MS (Agilent 6850 GC and 5790 MSD) with a method described in our previous paper [5]. Pyrolysis was conducted at different temperatures (300, 350, 450 °C). Each sample (~20 mg) was analysed in duplicate and a fresh sample was used for each temperature and the duplicate experiment. The weights of each sample before and after the pyrolysis experiment were recorded to calculate the pyrolysis yields. MSD ChemStation software was used to process all pyrolysis-chromatograms (pyrograms). Peaks observed in the pyrograms were matched with the compounds listed in the library provided by the software. Only peaks with >90% matching quality with the library were marked. The pyrolysis yields and the chemical compounds based on Py-GC/MS analyses and those obtained from batch pyrolysis experiments under similar conditions were compared. For the batch pyrolysis experiments, 250 g of wood samples were used and the reaction time was 30 mins. The reaction time was started after the chosen pyrolysis temperatures (300, 350, 400 °C) were reached. Details of the batch experiments are presented elsewhere [9]. The biocrude oil produced was analysed by Gas Chromatography-Mass Spectrometry (GC/MS-QP2010S SHIMADZU, GC column: Abdel 5SMS, column oven temperature 40 °C, injection temperature 310 °C). The mass spectrometer was operated in an electron impact (EI) mode at 70 eV.

3. Results and discussions
3.1. Characterisation of Macaranga gigantea
The chemical composition, ash content, moisture content and the elemental composition of Macaranga gigantea are presented in Table 1. The wood samples had low nitrogen and sulphur content, because the major original constituent of wood (lignin, cellulose and hemicellulose) were low in both elements. The high carbon and oxygen content were in correspondence with the high lignin, cellulose and hemicellulose content in the wood. The high oxygen content however can lead to production of oxygenated compounds [10-12] in the pyrolysis products which may reduce the quality of the pyrolysis oil.
Table 1. Physical and chemical characteristics of *Macaranga gigantea*

| Lignin<sup>a</sup> | α-Cellulose<sup>a</sup> | Moisture content<sup>a</sup> | Ash content<sup>a</sup> | C<sup>b</sup> | H<sup>b</sup> | O<sup>b</sup>* | N<sup>b</sup> | S<sup>b</sup> |
|-------------------|------------------------|-----------------------------|-----------------------|-------|-------|--------|-------|-------|
| Value (%)         | 27.6±0.7               | 63.0±0.1                    | 10.68                 | 0.64  | 45.29 | 5.18   | 49.27 | 0.10  | 0.16  |

<sup>a</sup> wt%; <sup>b</sup> air dried basis; * by difference

3.2. Pyrolysis yields

The total product yields from Py-GC/MS and batch experiments were used to evaluate the change in the yields of individual pyrolysis products with temperature (Figure 1). The total pyrolysis yields of *Macaranga gigantea* resulted from both methods at various pyrolysis temperature were similar, ranging from 35 to 65%, except for the case at 300°C, at which the yield from the batch experiment is considerably higher than that based on the Py-GC/MS results. This may be due to the longer reaction time used in the batch reactor pyrolysis system. The increase in pyrolysis temperature resulted in higher pyrolysis yields. The increase in pyrolysis yields can be related to the different thermal degradation condition of the original constituents in the wood, namely lignin and cellulose. Cellulose starts to decompose at 280 °C until 300-350 °C, while lignin starts to decompose at 300-350 °C until 400-450 °C [13].

![Figure 1. Total pyrolysis yields of Macaranga gigantea](image)

3.3. Pyrolysis product

In the pyrogram of the pyrolysis product, there were almost 100 compounds detected (Table 2), while in the chromatogram of the pyrolysis product only 40 compounds were observed (results not shown). However, it is important to note that the difference in the number of compounds detected was also partly due to different pyrolysis system used. The major compounds in the pyrolysis products were acetic acid, hydroxy acetaldehyde, phenols, vanillin, isoeugenol, syringaldehyde and other oxygen containing compounds (Figure 2). Vanillin, isoeugenol isomers, acetovanillone, homovanillic acid, coniferyl alcohol, and syringaldehyde were pyrolysis products of lignin, which is one of the major components in *Macaranga gigantea*. These lignin derived compounds were also observed from pyrolysis of different types of wood lignin [14, 15]. Pyrolysis of different building blocks of lignin (p-coumaryl alcohol, coniferyl alcohol, and synapyl alcohol) also produced phenol and its derivatives [15, 16].
16]. In the pyrograms, compounds derived from cellulose and hemicellulose were also detected. Thermal degradation of xylose [17] or dehydration of 2-furanmethanol [18] produced furfural. Hydroxyl acetaldehyde, acetic acid related compounds, furans and its derivatives, some ketones and aldehydes were produced from pyrolysis or thermal degradation of cellulose/hemicellulose [19, 20].

![Py-GC/MS 450 °C](image)

**Figure 2.** A pyrogram of pyrolysis product at 450 °C and a chromatogram of pyrolysis product at 400 °C (1= acetone, 2= 2-furancarboxaldehyde, 3= 4-methoxy-phenol, 4=2-methoxy-4-methyl-phenol, 5=2,3-dimethoxytoluene, 6= 2,6-dimethoxy-phenol, 7= eugenol, 8=1,2,3-trimethoxy-5-methyl-benzene, 9= 2,6-dimethoxy-4-(2-propenyl)-phenol, 10=3-pentanone, 11=acetic acid, 12=butanedial, 13=2-hydroxy-2-cyclopenten-1-one, 14=phenol, 15=pentanal, 16=2-methoxy-4-methyl-phenol, 17=2-methoxy-4-vinyl-phenol, 18=1-methoxy-4-(1-propenyl)-benzene, 19=2-methoxy-4-propyl-phenol, 20=2,6-dimethyl-3-methoxymethyl-p-benzoquin, 21=2,6-dimethoxy-4-(2-propenyl)-phenol, 22=4-hydroxy-2-methoxycinnamaldehyde, 23=3,5-dimethoxybenzaldehyde, 24=3-hydroxybenzaldehyde 2,4-dinitrophenylhydrazone)

**Table 2.** List of major compounds detected in the pyrograms of *Macaranga gigantea*

| Compound                  | RT (min) | The percent relative peak area | Batch products |
|---------------------------|----------|-------------------------------|---------------|
|                           |          | 300 °C | 350 °C | 450 °C |                     |
| hydroxy acetaldehyde      | 1.875    | 0.13  | 1.11  | 16.34 | √                    |
| 3-pentanone               | 2.092    | 0.37  | 0.35  | 1.39  | √                    |
| methoxy acetic acid       | 2.158    | 0.87  | 0.48  | 0.03  |                     |
| acetic acid               | 2.394    | 0.84  | 9.07  | 1.34  | √                    |
| 1-hydroxy-2-propanone     | 2.733    | 0.84  | 0.02  | 8.78  | √                    |
| dimethyl-furan            | 3.468    | 0.07  | 0.21  | 0.35  |                     |
| methyl isobutyrate        | 3.958    | 0.05  | 0.19  | 0.15  |                     |
| Compound                              | RT (min) | The percent relative peak area at 300 °C | 350 °C | 450 °C | Batch products |
|--------------------------------------|----------|----------------------------------------|--------|--------|----------------|
| 3-penten-2-one                       | 4.156    | 0.00                                   | 0.18   | 0.33   |                |
| 4-cyclopropyl-1-butene               | 4.392    | 0.00                                   | 1.57   | 0.97   |                |
| acetic acid, methyl ester            | 4.853    | 0.03                                   | 2.08   | 4.78   |                |
| butanedial                           | 5.061    | 0.00                                   | 0.03   | 2.26   |                |
| pyruvic acid, methyl ester           | 5.306    | 0.05                                   | 1.14   | 5.16   |                |
| thiophene                            | 5.447    | 0.11                                   | 0.24   | 0.57   |                |
| furfural                             | 6.248    | 0.70                                   | 0.88   | 1.27   |                |
| 2-butanone                           | 6.87     | 0.00                                   | 0.02   | 0.68   | √              |
| acetol acetate                       | 7.2      | 0.06                                   | 0.13   | 0.35   |                |
| phenol                               | 7.389    | 0.05                                   | 0.03   | 0.06   | √              |
| butyrolactone                        | 8.143    | 0.06                                   | 0.02   | 0.14   |                |
| furanone                             | 8.18     | 0.11                                   | 0.25   | 1.85   |                |
| furfuryl alcohol                     | 8.18     | 0.35                                   | 0.25   | 1.85   | √              |
| 2-hydroxy-2-cyclopenten-1-one        | 8.416    | 0.08                                   | 0.39   | 2.53   |                |
| 4-methyl-5H-furan-2-one              | 9.613    | 0.05                                   | 0.02   | 0.19   |                |
| 3-methyl hydantoin                   | 9.999    | 5.42                                   | 3.84   | 1.11   |                |
| methyl-cyclopentene                  | 10.357   | 0.34                                   | 0.26   | 0.35   |                |
| 4-methyl-5H-furan-2-one              | 11.026   | 0.10                                   | 0.05   | 0.22   |                |
| 2-methoxy-phenol                     | 11.884   | 1.41                                   | 0.50   | 2.30   | √              |
| pentanal                             | 11.997   | 7.35                                   | 10.87  | 2.25   |                |
| 3-hydroxy-2-methyl-4H-pyran-4-one,   | 12.393   | 0.17                                   | 0.08   | 0.16   |                |
| 3-methyl-2,4(3H,5H)-furandione        | 12.6     | 0.25                                   | 0.32   | 0.43   |                |
| 2,4-dimethyl-phenol                  | 13.053   | 0.06                                   | 0.06   | 0.01   | √              |
| 2-methoxy-4-methyl-phenol            | 13.873   | 0.48                                   | 0.72   | 1.44   | √              |
| 3-methoxy-1,2-benzenediol            | 15.154   | 0.05                                   | 0.06   | 0.37   | √              |
| 4-ethyl-2-methoxy-phenol             | 15.409   | 0.14                                   | 0.25   | 0.53   | √              |
| 2-(2-propenyl)-phenol                | 15.635   | 0.04                                   | 0.05   | 0.01   |                |
| 2-methoxy-4-vinylphenol              | 16.031   | 4.85                                   | 6.03   | 3.91   |                |
| 3-phenyl-2-propenal                  | 16.653   | 0.03                                   | 0.05   | 0.07   |                |
| 1-methoxy-4-(1-propenyl)benzene      | 16.521   | 0.04                                   | 0.02   | 0.02   |                |
| 2,6-dimethoxy-phenol                 | 16.653   | 1.63                                   | 2.30   | 2.03   | √              |
| 2-methoxy-4-(2-propenyl)-phenol      | 16.747   | 0.19                                   | 0.18   | 0.16   |                |
| 3-isopropylbenzaldehyde              | 16.917   | 0.10                                   | 0.10   | 0.01   |                |
| 5-methoxy benzofuran                 | 17.105   | 0.00                                   | 0.02   | 0.02   |                |
| vanillin                             | 17.473   | 2.55                                   | 2.02   | 1.36   | √              |
| 2-methoxy-4-(1-propenyl)-phenol      | 17.576   | 0.28                                   | 0.30   | 0.37   |                |
| isoeugenol                           | 18.246   | 4.00                                   | 3.85   | 2.68   | √              |
| 2-methoxy-4-propyl-phenol            | 18.415   | 1.27                                   | 1.08   | 1.14   |                |
| 2-ethyl-1,4-benzodioxin              | 18.698   | 12.20                                  | 5.96   | 0.99   |                |
| 1-(2,4,6-trimethylphenyl)-ethanone    | 18.802   | 1.38                                   | 0.98   | 0.48   |                |
| acetovanillone                       | 18.849   | 1.53                                   | 1.39   | 1.13   |                |
4. Conclusions
The pyrolysis yields of *Macaranga gigantea* with Py-GC/MS and batch pyrolysis were generally similar. Pyrolysis of *Macaranga gigantea* gave 35-65% yield at different pyrolysis temperatures and conditions. Pyrolysis of the wood samples produced compounds that were mostly derived from pyrolysis or thermal degradation of lignin and cellulose/hemicellulose.

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