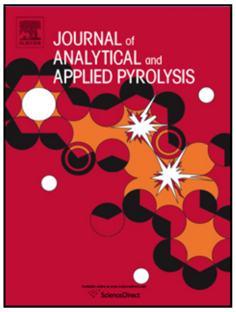

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Characterisation and Py-GC/MS analysis of *Imperata Cylindrica* as potential biomass for bio-oil production in Brunei Darussalam

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Highlights

- Characterisation and Py-GC/MS were conducted to evaluate the bioenergy potential of *I. Cylindrica*.
- *Imperata Cylindrica* has a calorific value of 18.39 MJ/kg, with low ash content of 2.97% and high volatile content of 72.01%.
- Py-GC/MS analysis revealed abundant furanic compounds, guaiacyl lignin, p-hydroxyphenyl lignin, syringyl lignin, aromatic hydrocarbons, ketonic compounds, organic acids and miscellaneous hydrocarbons.
- *Imperata Cylindrica* is a potential feedstock for value-added platform chemicals and energy production.
- The highest bio-oil yield from the pyrolysis of *Imperata Cylindrica* was 37.16% at 500°C

Abstract

Bio-oil production from renewable sources has been seen as suitable alternative to supply future energy demand. Perennials grasses are currently being developed as a suitable second-generation biofuel feedstock. It has advantages such as rapid growth rate, easy to grow, minimal maintenance and utilise marginal land without competing with food supply. Taking into account of the various challenges attributed to the transformation of second-generation biomass for energy production, this work systematically looks at the ecological perspective and the availability for bioenergy production from *Imperata Cylindrica* in Brunei Darussalam. Biomass characterisation was carried out to determine the properties and energy content, meanwhile py-GC/MS study was conducted to identify building blocks of value-added chemical from *I.Cylindrica*. The physicochemical properties of feedstock was thoroughly evaluated using thermogravimetric analysis, proximate analysis, elemental analysis, compositional analysis, calorific value, and analytical pyrolysis interfaced with gas chromatograph (Py-GC/MS). Characterisation results indicate that *Imperata Cylindrica* has a calorific value of 18.39 MJ/kg, with low ash content and high percentage of volatile matter. Py-GC/MS analysis revealed the presence of furfural, 2,3-dihydrobenzofuran, 4-vinylguaiacol, propenylguaiacol, guaiacol and 4-ethylphenol. The fixed-bed pyrolysis experiment of *imperata cylindrica* showed that the yield of bio-oil increases with the increase of temperature and it reached a peak of 37.16% at 500°C. These results show that *Imperata Cylindrica* is suitable as feedstock for bio-oil production via pyrolysis process.

Keywords: *Biomass; Pyrolysis; Py-GC/MS; Thermogravimetric analysis; Biofuel*

1. **Introduction**

Brunei Darussalam is a country located in Southeast Asia, on the north of Borneo Island between 4°N and 5.8°N latitude and 114.6°E and 115.4°E longitude with a land area of 5765 km^2 (576500 ha). Energy sector in Brunei heavily rely on the production of oil and gas, having one of the highest carbon footprint contributors at 22.1 metric tons of CO_2 per capita [1]. Despite relying on the production of oil and gas, Brunei Darussalam is blessed with rich natural vegetation and biodiversity, which is considering to diversifying its energy resources, and following the global trend in search of alternative energy sources such as biomass. Several studies has been started to explore potential renewable energy resources in Brunei Darussalam, such as rice husks [2], Acacia tree species [3], wood residues and municipal solid waste [4]. The broad diversity of biomass has resulted in the increased research and development of technologies to produce feasible energy and chemicals from biomass. *Imperata cylindrica* or cogongrass as perennial grasses is one of the potential biomass for bioenergy production. Garrity et. al have estimated 4% of total land in Asia which are covered by *Imperata cylindrica* [5]. Currently, there is no study for *Imperata cylindrica* as potential biomass in Brunei Darussalam. Based on Garrity et. al estimation, a general reasonable calculation estimates of the area for *Imperata cylindrica* in Brunei Darussalam to be 23,060 ha.

Imperata cylindrica is a species of grass in the family Poaceae, and known as one of the most important weed in the world. There are nine species of genus *imperata* worldwide and widely distributed to east and Southeast Asia, India, Micronesia, Melanesia, Australia, and eastern and southern Africa [6]. It can grow in height of 30 - 200 cm and a leaf width of about 2 cm. The leaf blades will begin to appear at ground level, possess finely serrate sharp margins and are hairy at the base. The young leaves appear light green while older leaves appear orange-brown to brown colour [7]. Reproduction system of *Imperata cylindrica* are can be formed from rhizome fragments as small as 0.1 gram by reproduced asexually and also can be formed through sexual by flowering and seed production [8]. *Imperata cylindrica* is best adapted and thrives to full sun with an optimum temperature of 30 ºC [9]. It has the ability to grow on a wide range of soil types without special nutrient treatment and can be found in a wide range of habitats, grassland, cultivated annual crops, plantations, abandoned farm land, road and railway embankments, pine and hardwood forests, recreational areas and deforested areas [6]. The weather condition and habitat in Brunei Darussalam can be considered optimum, in which *Imperata cylindrica* as a C_4 plant will have an advantage over a C_3 plant. *Imperata cylindrica* belong to C_4 perennial grass and assimilates CO_2 via the C_4 photosynthetic pathway [10]. The C_4 photosynthetic pathway will convert energy from sunlight to chemical energy and used to produce organic compounds that are the building blocks of biomass [11]. A high efficiency of CO_2 fixation into biomass is one of important factor in the selection of energy crops. C_4 photosynthesis is the most efficient form of photosynthesis due to their photorespiration-suppressing modifications have ability to maximizing the CO_2 fixation than C_3 photosynthesis plant [12–15]. Comparison yields of photosynthetic pathway among perennial grasses are presented in table 1.

Imperata cylindrica or cogongrass is one of the perennial grasses which is very widespread in tropical and subtropical regions in Asia spanning about 35 million ha [5]. Range of its applications are used for roofing traditional houses (51 %), medicinal plant (13 %), animal feed (22 %) and erosion control (8 %) [22,23]. For many decades, *Imperata cylindrica* has been an invasive weed to farmers, which has a potential to become a source of energy crop. Effective utilisation of perennial grasses as raw materials for bioenergy and biofuel have advantages such as efficient, fast growing, relatively easy to harvest and process, less maintenance and can be an important contribution to the reduction of anthropogenic CO_2 emissions [17]. Investigation and research on *Imperata cylindrica* as bioenergy is comparatively recent and still needs development. Several literatures has investigated about characterization and its exploitation as potential biomass. Kamaroddin et. al. [24] investigated fuel properties of *Imperata Cylindrica,* Promdee & Vitidsant [25] investigated bio-oil synthesis by pyrolysis of *Imperata Cylindrica*, and pyrolytic characteristics and kinetic studies were investigated by Li et. al. [26] and Oladokun et. al. [27].

Thermochemical and biochemical processes are the two main process technologies for conversion of biomass. In recent years, there has been an increasing focus on using thermochemical technologies which convert biomass to valuable fuels and chemicals. The major thermochemical of biomass conversion techniques are combustion, gasification and pyrolysis. Among the thermo-chemical processes, pyrolysis has received special attention, as it can convert biomass directly into solid, liquid (bio-oil) and gaseous products by thermal decomposition of biomass in the absence of oxygen [28,29]. Biomass pyrolysis is a very complex series of reaction, which depends on many different variables, such as feedstock, moisture content, residence time and temperature. In the effort to produce bio-oil with desirable properties, biomass characterisation analyses and pyrolysis GC/MS are suitable techniques to achieve this. Basic understanding of the pyrolysis characteristics of the main lignocellulosic biomass building blocks is the basis and essentially important for biomass thermochemical conversion to valuable products [30,31]. Biomass characterisation and analytical pyrolysis combined with gas chromatography-mass spectrometry (Py–GC/MS) is a tool to identify and evaluate volatile fragments that evolved. Py-GC/MS offers advantages such as the small quantities of sample required, high repeatability and rapidness [32,33].

For perennial grass, the amount of total cell wall fraction is about 80% of the plant dry weight and is composed of primarily of cellulose, hemicellulose and lignin. Grass plants are typically characterised by loosely bound fibres and has a lower proportion of lignin, unlike wood biomass which are characterised by slow growth and composed of strong bound fibres with hard external surface. Lignin is a cross-linked amorphous copolymer incorporate from random polymerization of three primary components p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units. Cellulose and hemicellulose are polysaccharides that have more than 2 monosaccharides structures linked together covalently by glycosidic linkages. Cellulose is a polysaccharide consisted of linear polymer of D-glucose units linked to each other via β-1,4-glycosidic bonds. Hemicellulose is a heteropolysaccharide containing many different sugar monomers (primarily xylose, mannose, galactose, and arabinose) [34–36]. Proportions to determine these properties are based on varying amounts of cellulose, hemicellulose, lignin and extractives as main building blocks biomass. In addition, grasses contain non-cell wall carbohydrates, such as sucrose, fructose, glucose and starch [11,37,38]. Consequently, the difference in proportions of biomass building blocks will contribute to distribution of chemical compositions in liquid product from thermal degradation product of biomass and also significantly contribute to the amount of oxygenated compounds, complex organic, viscous, and acidic mixture [34,39].

Promdee and Vitidsant has studied the pyrolysis oil identification of *Imperata cylindrica* from Thailand and around 25 components were detected in the bio-oil samples [40]. Table 2 show several literatures which have reported the identification of platform chemicals from pyrolysis of grasses (Switchgrass, Napier grass, Reed canary grass, *Imperata Cylindrica*).

There are no thorough study available on the bioenergy production from *Imperata cylindrica* in Brunei Darussalam. This paper discusses the resource utilisation of *Imperata cylindrica* for potential biomass and bio-oil production in Brunei Darussalam via pyrolysis in terms of characterisation and identification of value-added chemicals. A review of prior potential description of *I.cylindrica* as bio-energy crops in Brunei Darussalam and experimental investigation in term of characterisation, identification valuable products via Py-GC/MS and bio-oil synthesis via fixed bed pyrolysis are presented. This will encourage the usage of underutilised feedstock sources such as perennial grass for bioenergy utilisation.

2. **Experimental**

2.1. **Biomass preparation and characterisation**

The *Imperata cylindrica* sample used in experiment was obtained from a field in Muara, Brunei Darussalam. The samples were ground and sieved to small particles sizes with a range of 0.125 mm – 0.25 mm and then dried at 45°C for 24 hours. Ultimate analysis was performed using a CE Instruments Flash EA 1112 Series CHNS-O analyser (Thermo Quest Italy). Proximate analysis determines the moisture content, ash content, volatile matter and fixed carbon according to the standard test method ASTM D3173, ASTM D3174, ASTM D3175 respectively. Elemental compositions (C, H, N, O, and S) are obtained on a dry basis. Higher heating value (HHV) for all samples was determined using a bomb calorimeter according to the ASTM D2015 standard test method. To ensure the reproducibility and repeatability of the data, the experiments were repeated five times. The experiment HHV value was compared by correlations using data obtained from elemental analysis developed by Ozyuguran et.al below [47]:

$$HHV = 0.2791N + 0.3984C + 0.4030H - 1.8644S - 0.03153O \qquad \text{Eq. (1)}$$

Compositional analysis of biomass samples was performed by conventional NREL methods. To obtain the amount of extractives, 100 mL distillate water is added for 1 g of free moisture in the sample and then heated at 105 °C for 2 h. The samples was filtered and washed with distillate water and dried at 105 °C for 12 hours. The weight difference before and after hydrolysis is calculated as the amount of extractives. 100 mL of 0.5 M H_2SO_4 solution was added to the sample residue and heated at temperature 105 °C for 2 h. The mixture was filtered and washed with distilled water until the pH is neutral and then the samples were dried at 105 °C for 12 hours. The difference between the sample weight before and after treatment with 0.5 M H_2SO_4 is calculated as the hemicellulose content. In addition, 10 mL of 72% H_2SO_4 was added and kept for 4 hours at room temperature. 100 mL distilled water was added and heated at temperature 105 °C for 2 hr. The mixture was filtered and washed with distillate water until the pH is neutral. The residue was dried at 105 °C for 12 hours. The weight difference of the residue between the before and after treatment with 72% H_2SO_4 corresponds to the cellulose content. Consequently, the residue was heated at 600 °C for 2 hours. The lignin content corresponds to the difference between the weight of ash and the weight of residue. The percentage extractives, hemicellulose, cellulose and lignin is based on moisture and ash-free basis.

2.2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out with an automated Perkin Elmer Pyris 1 TGA thermogravimetric analyser. Samples were heated at a heating rate of 25 °C/min from 40 °C to 900 °C under nitrogen atmosphere with a flow rate of 20 mL/min.

2.3. Py-GC/MS analysis

The samples were dried, ground and sieved to particles size with a range of 0.125 mm – 0.25 mm prior to Py-GC/MS analysis. CDS 5200 micro pyrolyser close-coupled to a PerkinElmer Clarus 680 gas chromatograph and Clarus 600S mass spectrometer with heating rate 20 °C/ms. Separation was carried out using a PerkinElmer Elite-1701 column (cross-bond, 14% cyanopropylphenyl and 85% dimethyl polysiloxane; 30 m, 0.25 mm inner diameter, and 0.25 mm film thickness). The GC oven was held at 45 °C for 5 min, then heated at 5 °C/min to 250 °C, and held at this temperature for 5 min.

Approximately 2 - 3 mg of samples were pyrolysed at three different temperature 400 °C, 500 °C, and 600 °C for 15 s, and then the gases products were purged by high purity helium (99.9995%) into gas chromatograph via a transfer line preheated at 270 ◦C. The flow rate of the carrier gas was 50 ml/min with a split ratio of 50:1. The inlet temperature was 230 °C. The pyrograms was analysed using the Automated Mass spectra Deconvolution and Identification System by NIST (AMDIS). The volatile fragments were analysed by comparison with the results in literature and by fitting with mass spectra from NIST spectral libraries. Quantitative calculations were carried out by calculating percentage areas for each component pyrolysis product. The calculations results were used to compare and interpret the experiment results.

2.4 Pyrolysis yield studies

The pyrolysis of *Imperata Cylindrica* was performed in a stainless steel fixed bed reactor (2.68 cm i.d. and 50 cm length) inserted in a horizontal tube furnace (Carbolite Gero 300 - 3000 Electrical Furnaces). The fixed bed reactor is heated by the furnace, which has a temperature controller unit. The reactor inlet side had been installed a thermocouple to monitor temperature inside reactor and a connector for N_2 sweeping gas inlet. The nitrogen gas (99.9995% of purity N_2) flow is controlled by a flow meter and the pyrolysis vapour from the reactor is swept through the condenser. The transition tube together with the reactor head is lagged to minimised condensation of pyrolysis vapours. The condenser utilises a water-ice mixture maintained between 10 to 15 °C.

The reactor was filled with 25 g of sample for all experiments. Pyrolysis was conducted at three temperatures; 400, 500 and 600 ºC and the temperature of the reactor was raised at 25 ºC/min to the final temperatures of pyrolysis and the heating rate was kept consistent for all experiments. The pyrolysis process was run until no bio-oil was collected, taking about 40 – 60 min after the final temperature was reached. The final products of char left inside the reactor and the bio-oil from condenser were collected in Erlenmeyer flask. The product of gas from pyrolysis was calculated based on mass balance of biomass feed. Figure 1 shows the schematic diagram of the experimental set up used in this work.

3. Results and discussion

3.1. **Proximate and ultimate analysis**

The results of proximate analysis, HHV and ultimate analysis of samples are listed in Table 3 which is compared with various samples in literatures [2,27,40,41,48]. *I. Cylindrica* has a volatile content of 72.01% which can be considered as a desirable feedstock for energy production via pyrolysis process and indicate high liquid yield production. The ash content is lower as compared to rice husk (14.83%) [2], elephant grass (8.26%) [48] and switchgrass (4.5 – 10.5 %) [17]. The elephant grass in reference showed high ash content but has similar volatile matter as *I. Cylindrica.* Several literatures have reported that elephant grass has a higher content of phosphorus and potassium than other perennial grasses, and a higher mineral content in elephant grass increased ash content in spite of the similar volatile matter with *I. Cylindrica* [48–50]. High mineral contents means high ash content. In biomass conversion processes, this will have an adverse effect on the bio-oil productivity, and can cause fouling, erosion and slagging during pyrolysis. The ultimate analysis results showed a low N and S content, which is desirable due to lower toxic NO_x and SO_x emission during conversion processes.

The H/C and O/C ratios of experimental results and solid fuels from various literatures [2,44,48,51–61] are compared in the Van Krevelen diagram in Figure 2 below. It can be seen that biomasses have larger O/C and H/C ratios compared to coals. IC experimental result (H/C = 1.53; O/C = 0.83) are located in the region of biomass which has the lowest H/C and O/C ratios as compared to elephant grass, rice husk, cassava rhizome, cassava bagasse, and sugarcane bagasse. O/C and H/C ratios illustrate energy contents of biomass based on oxygen-carbon and hydrogen-carbon bonds contained in the materials. Lower O/C and H/C ratios indicated higher energy content of the biomass and located the biomass nearer towards coal, which is used as reference solid fuel [11].

The higher heating value (HHV) value obtained from experiment (18.39 MJ/kg) has similar value with HHV from correlation (18.47 MJ/kg). The HHV on dry basis shows that *I.cylindrica* has a higher calorific value when compared with other biomass such as cassava bagasse with 15.27 MJ/kg [61], sugarcane bagasse with 16.10 MJ/kg [61], elephant grass with 15.77 MJ/kg [48] and rice husk with 17.34 MJ/kg. The heating value obtained experimentally is slightly higher as compared to literatures. Several literatures [27,62] reported HHV values of *I.cylindrica* with 17.03 MJ/kg and 16.50 MJ/kg with O/C and H/C ratio of around 2.3 and 1.3 respectively, which suggest that higher O/C and H/C ratios in biomass corresponds to a reduction in their heating values. Huang et. al. mentioned that the HHV value increases with the increase in C and H contents, but decreases with an increase of N content [63]. Sheng and Azevedo have reported that the HHV decreases with an increase in ash content and a trend exists between the HHV and volatile content [64].

The compositional analysis of *I.cylindrica* from table 1 shows that it has 12.49% extractives, 44.49% cellulose, 25.13% hemicelluloses and 17.89 % lignin. *I.cylindrica* shows a lower lignin % content as compared to rice husk [2] and elephant grass [48]. Difference in the compositional analysis between of *I.cylindrica* of experimental and *I.cylindrica* of literature will generate a variance of pyrolysis chemicals products.

3.2. Thermal decomposition characteristics

The results of TGA/DTG in temperature range of 40 °C to 900 °C at a heating rate of 25 °C/min is presented in figure 3. The TGA/DTG curve can be described into three stages: moisture removal, main devolatilisation and continuous small degradation. During the initial stage, the moisture content in the biomass is removed at the range 40 °C – 105 °C. In the second stage, the main degradation occurs and the maximum volatile evolved between 105 °C to 500 °C. The peak of degradation rate is 21.82 %/min and the temperature corresponding to the peak of degradation rate is 352.59 °C. In the third stage, a smaller weight loss observed above 500 °C is corresponding to the devolatilisation of heavier chemical structures, which can also be observed during the previous thermal decomposition. The final temperature is 900 °C which gives the residual weight 21.11 %.

Table 4 summarises the characteristic properties of *I.cylindrica* as a result from derivative the DTG in figure 4. T_{onset} was calculated by linear extrapolation the slope of $\left(\frac{-dm}{dt}\right)$ in correspondence with the first local maximum in $\left(\frac{-d^2m}{dt^2}\right)$ curve and down to the minimum level of the $\left(\frac{-dm}{dt}\right)$ axis which describes the starting of hemicellulose decomposition (T_{onset} = 260.8 °C) [65]. The temperature appropriate to the maximum of hemicellulose degradation rate, $\left(\frac{-dm}{dt}\right)_{sh}$ (13.082 %/min) is characterised by $T_{shoulder}$ (300.29 °C). The peak temperature (T_{peak} = 352.59 °C) was obtained by

$\left(\frac{-dm}{dt}\right)_{peak}$ (21.821 %/min) corresponds to the maximum of cellulose decomposition rate which useful for evaluating the reactivity [66]. The end of cellulose degradation and the further decomposition dominated by lignin and tar or char, is identified by T_{offset}. T_{offset} (382.59 °C) was calculated by linear extrapolation of the slope $\left(\frac{-dm}{dt}\right)$ corresponding with the first local minimum in $\left(\frac{-d^2m}{dt^2}\right)$ curve and down to the minimum level of the $\left(\frac{-dm}{dt}\right)$ axis. Higher temperatures than the T_{offset} corresponds to a secondary devolatilisation which occurs with a smaller weight loss.

3.3. Analytical py-GC/MS

Fig. 5 shows the typical pyrograms from py-GC/MS of *I.Cylindrica* at temperature 400 °C, 500 °C and 600 °C, and the corresponding identified compounds are listed in Table 5. The percentage peak areas correspond to the relative yields of the products among all of the identified components. The products are identified to group ten major platform components namely furan compounds, guaiacyl lignin, p-hydroxyphenyl lignin, syringyl lignin, aromatic hydrocarbons, ketone compounds, organic acids, cycloalkenes, ester and miscellaneous hydrocarbon [34,35,49,67–72]. A summary of percentage of major platform group components is presented in table 6. Previous studies have reported that furanic compounds, aromatic hydrocarbons, esters, cycloalkenes, ketonic compounds, acids and miscellaneous hydrocarbon can be generated from pyrolysis of polysaccharides (hemicellulose and cellulose) [35,68–70,73–76]. Pyrolysis of lignin produces guaiacyl lignin, p-hydroxyphenyl lignin, syringyl lignin, aromatic hydrocarbons and miscellaneous hydrocarbon [34,68,69,74,77,78]. Temperature is one of the important variables affecting the lignocellulosic biomass products distribution.

The results shown in table 5 indicate that the main components of furanic compound were dominated by 2,3-dihydrobenzofuran, furfural and 2-furanmethanol, where 2,3-dihydrobenzofuran gave highest yield in comparison to other furan compounds at all temperatures. The other furanic compounds detected were 3-Methylfuran, 5-Methylfurfural and 2,5-Dimethylfuran. The dehydration reaction of cellulose and hemicelluloses during pyrolysis will form furanic compounds [79] . In comparison with the pyrolysis products at 400 ºC and 500 ºC, the highest percentage peak furanic compound products were found at 600 ºC, which agrees with the study by Liaw et al. and Lu et. al. [80,81]. The chemical derivatives from furanic compounds are value-added chemicals which are widely used as organic solvents or reagents for the production food additives, fuel additives and other products [82,83].

Aromatic hydrocarbon and cycloalkenes from py-GC/MS were detected at all temperatures. The chemicals detected from aromatic hydrocarbon products were toluene, ethylbenzene, p-xylene, styrene, propylbenzene, benzene-acetaldehyde and indanone. The results obtained were relatively close with previous work from pyrolysis of switchgrass by Imam and Capareda [41] . The yields of toluene and indanone are observed to give a maximum percentage peak area of 3.01 % and 3.00 %, respectively at an elevated temperature of 600 ºC. The cycloalkenes detected were cyclopentadiene, 2-Methyl-2-cyclopenten-1-one, 2-Hydroxy-2-cyclopenten-1-one, 3-Methyl-2-cyclopenten-1-one, 2,3-Dimethyl-2-cyclopenten-1-one and 2-Hydroxy-3-methyl-2-cyclopenten-1-one. Cyclopentadiene gave the optimum result amongst all of the other cycloalkenes compounds. Cyclopentadiene is a precursor to cyclopentene, which is used for the production of specialty polymers, synthesis of metallocene compounds, and synthesis of organic photoelectric materials [84].

Guaiacyl Lignin (Guaiacol, 4-Vinylguaiacol, Propenylguaiacol, Isovanillin, Guaiacylacetone, 2-Methoxy-4-methylphenol, 4-Ethyl-2-methoxyphenol and 2-Methoxy-4-propenylphenol) were produced in significant amounts. A similar results of significant amounts has been shown by Promdee and Vitidsant [40]. In comparison with Promdee and Vitidsant work, the feedstock in this work has high polysacharide composition, resulting in various chemical compounds obtained. Maximum peak of 4-Vinylguaiacol (22.14 %) was obtained at 400 ºC, and guaiacol, propenylguaiacol, 2-Methoxy-4-methylphenol and 4-Ethyl-2-methoxyphenol gave results of 8.8 %, 3.97 %, 2.32% and 5.26% at 400 ºC respectively.

The main products of p-hydroxyphenyl lignin were 2-Methylphenol, p-Cresol, 2,4-Dimethylphenol and 4-Ethylphenol. 2-Methylphenol, p-cresol, and 4-ethylphenol were the predominant p-hydroxyphenyl-type, which gave a higher peak area percentage. 2-Methylphenol and 4-Ethylphenol gave optimum peak area percentage of 3.73 % and 4.95 % respectively at 600 ºC. While, for p-cresol gave optimum peak area percentage of 3.00 % at 500 ºC.

The main products from syringyl lignin consists of 1,2,4-Trimethoxybenzene, 2,6-Dimethoxyphenol and 2,6-Dimethoxy-4-allylphenol. The peak for the organic acids and ester was detected as n-hexadecanoic acid, methyl hexadecanoate and acetic acid. n-Hexadecanoic acid and methyl hexadecanoate are value-added chemicals which widely used as organic solvents or reagents for the production food additives, fuel additives and other products soaps, cosmetics, and industrial mold release agents [85].

The identified peaks detected which belongs to ketonic compounds were 1-hydroxy-2-butanone, 2,3-Pentanedione and 1-(3,4-Dimethoxyphenyl)ethanone and for miscellaneous hydrocarbon compounds were (2E)-3,7,11,15-Tetramethyl-2-hexadecen-1-ol, 5-tert-Butylpyrogallol and hexadecane. Hexadecane gave a significant peak area at 400 °C. Previous studies have found that the hexadecane content in the pyrolysis of switchgrass is 8.5 % at temperature range of 400 °C to 600 °C [41] and sorghum between 7.9 % - 9.3 % at temperature range 550 °C to 650 °C [67].

The highest % peak area of the group components are from guaiacol lignin with 45.27% at 400 °C and reduced to 36.96% at 600 °C. Although the compositional analysis of IC contains about 70% of cellulose and hemicellulose as compared to lignin, the degradation products from lignin is significantly high. This may be due to the synergistic effects of the interactions between the three basic components of biomass. Zhang et al. concluded that cellulose promotes an increase in lignin-derived phenolic products, and that when the cellulose content is higher and the hemicellulose content is lower, the production of guaiacols and syringols will be enhanced [86]. Furthermore, other researchers have mentioned that the secondary reactions from the degradation of cellulose produces phenolic compounds [87–89]. For the lignin-derived compounds, the trend shows that for an increase in the pyrolysis temperature, the guaiacyl lignin and syringyl lignin decreases, while the p-hydroxyphenyl lignin and the aromatic hydrocarbon increases. Finally, it is worth noting that the peak areas of the gas chromatogram only reflect the signal strength detected by the FID detector. It cannot represent the absolute percentage of each detected compound without a quantification analysis.

3.4 mass balance of bench scale pyrolysis experiment

The product yield from the fixed bed pyrolysis of IC and comparison from literatures can be found in table 7 below. As the temperature increases, the char yield decreases and the gas and bio-oil yield increases. The bio-oil yield peaks at 500°C with 37.16%, and will reduce down slightly at higher temperature. This is due to the secondary cracking of bio-oil to gases at higher temperatures, as reported in other literatures [25,41,62,90]. Although the products has not been fully characterised yet, the trends can be understood from the degradation of the three basic components of biomass.

The decomposition of cellulose forms activated cellulose and then undergoes two parallel pathways of depolymerisation process which produces anhydrosugars and derivatives, furans and cyclopentanones, and fragmentation process which produces linear carbonyls, linear alcohols and linear esters. The bio-oil from lignin pyrolysis mainly consists of polycyclic aromatic hydrocarbons and phenolic compounds, xylan oil mainly consists of acids, furfurals [80].

Bio-char yield from IC pyrolysis decreased from 34 % to 27 % as temperature is increased from 400 to 600 ºC respectively, which showed a similar trend reported by Imam and Capareda [41]. The investigation had reported char yield from lignin pyrolysis is the highest, and that from cellulose and hemicellulose the lowest. The lignin structures are natural amorphous polymer consisting of three aromatic alcohols, namely p-hydroxyphenyl, guaiacyl, and syringyl [91–93]. Sharma et al. [94] has showed that the chars lost both hydroxyl and aliphatic groups with an increase in temperature, and the increase in aromatic character above 450 ºC resulting in an aromatic carbon content at high temperatures. Aromatic monomers showed good thermal stability, which led to a higher char yield from lignin compared to cellulose and hemicellulose.

Generally, the gas product increase with an increase in temperature, reported as shown from 31.44 % to 35.96 % for 400 to 600 °C. This is due to an increased release of volatile matter and secondary decomposition of bio-oil which as temperature is increased [93,75].

4. Conclusion

Various characterisation analyses, TGA and Py–GC/MS of *Imperata cylindrica* has been performed to investigate the characterisation and analysis of value-added chemicals from pyrolysis of *Imperata cylindrica*. The products generated from Py-GC/MS are abundant with furanic compounds, guaiacyl lignin, p-hydroxyphenyl lignin, syringyl lignin, aromatic hydrocarbons, ketonic compounds, organic acid compounds and miscellaneous hydrocarbons. The temperature at 500 °C has shown a good result in terms of the optimum amount of components detected and the percentage peak area. Furfural, 2,3-dihydrobenzofuran, 4-Vinylguaiacol, propenylguaiacol, guaiacol and 4-ethylphenol has shown a higher peak area percentage and has potential as value-added platform chemicals from Imperata cylindrica bio-oil. The fixed-bed pyrolysis of *Imperata cylindrica* showed that the yield of bio-oil peaks at 500°C with 37.16%.

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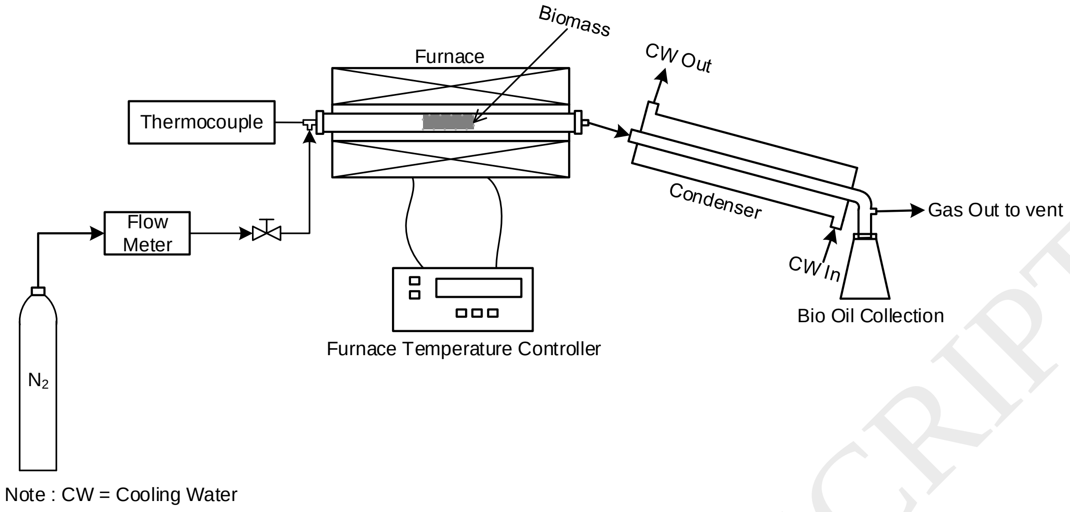

Fig. 1. Schematic diagram of the fixed bed pyrolysis setup

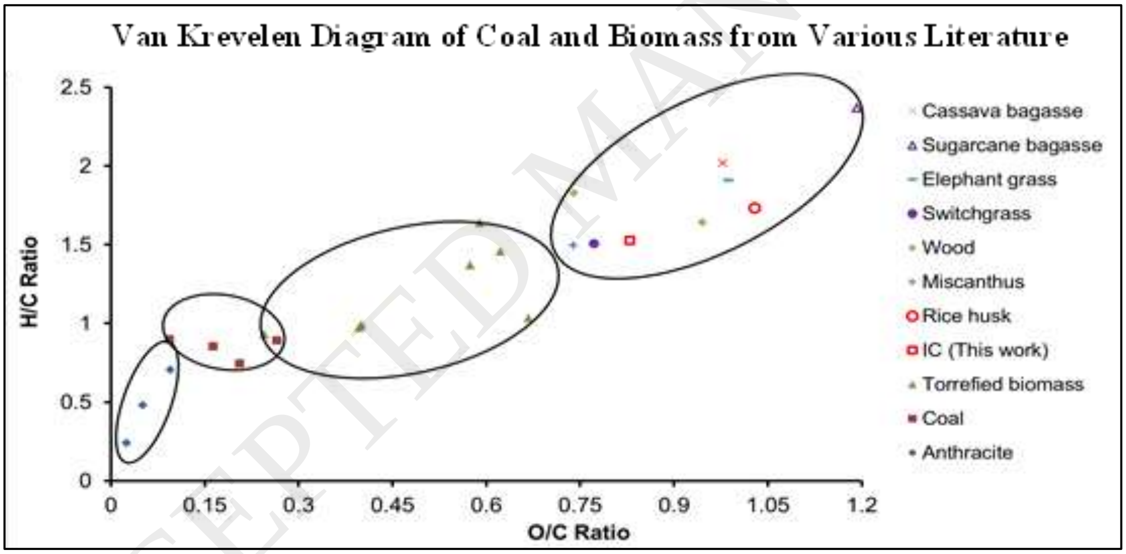

Fig. 2. Van Krevelen diagram for coal and various biomass (Anthracite [51,52], Indonesian Coal [53–55], Torrefied biomass [56,57], Rice husk [2], Miscanthus [58], Switchgrass [44], Wood [59], Cassava rhizome [60], Elephant grass [48], Sugarcane bagasse [61], Cassava bagasse [61], *I.cylindrica*)

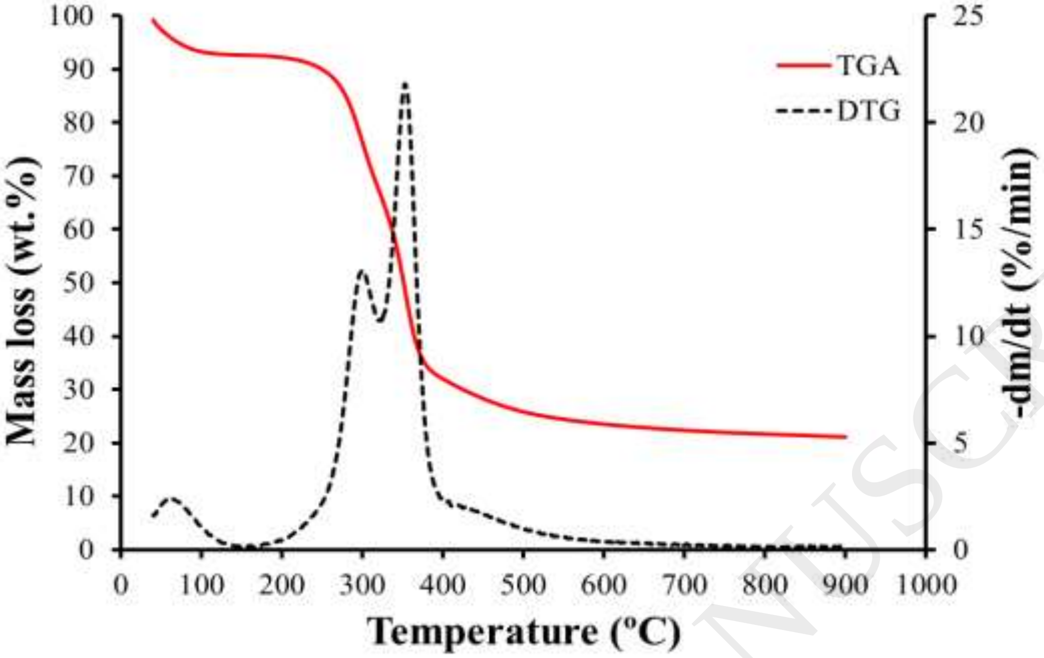

Fig. 3. TGA and DTG curve of *I.cylindrica*

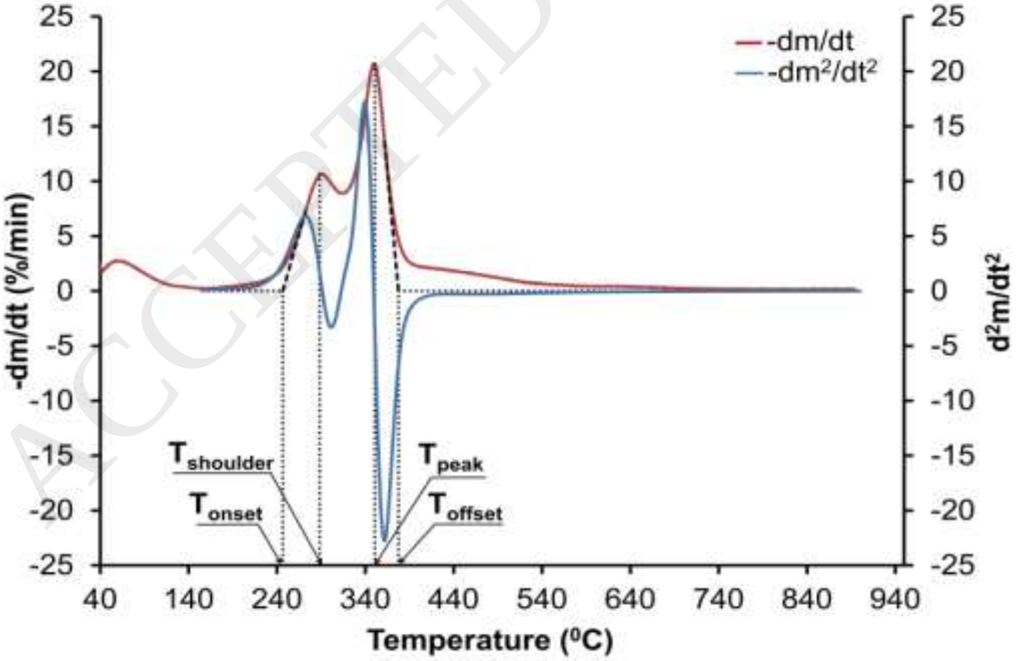

Fig. 4. Characteristic of temperature zone by using derivative DTG

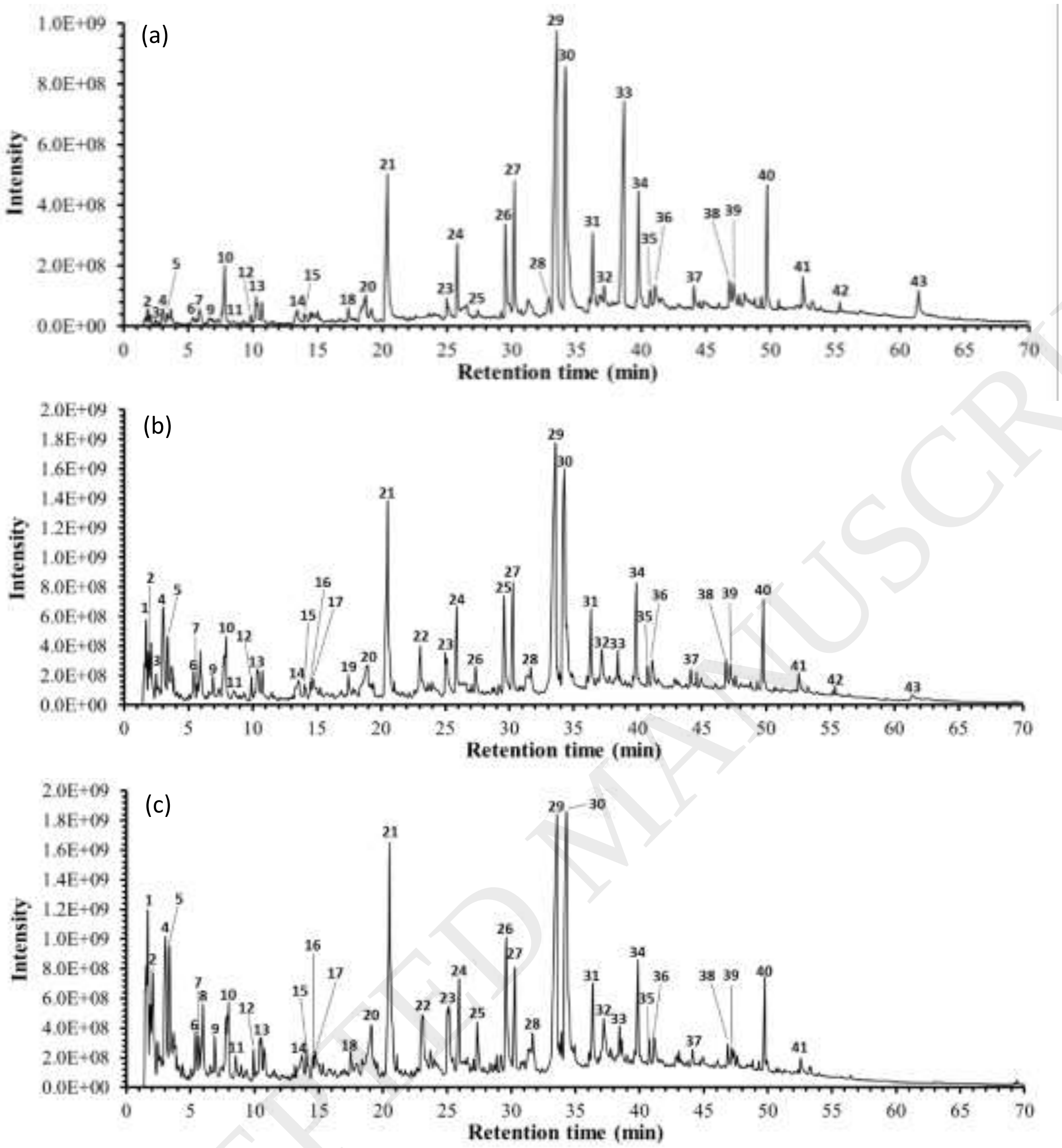

Fig. 5. Chromatogram of the pyrolysis GC/MS of Imperata cylindrica at temperature (a) 400 °C, (b) 500 °C and (c) 600 °C

Table 1. Comparison yields of perennial grasses C_3 and C_4 photosynthetic pathway

Species	**Photo-synthetic pathway**	**Yields (tDMha^{-1}yr^{-1})**	**Reference**
Napiergrass	C_4	22.0 – 31.0	[16]
Switchgrass	C_4	0.9 – 34.6	[17]
Smooth bromegrass	C_3	3.3 – 6.7	[17]
Miscanthus sp	C_4	5 – 44	[18]
Reed canary grass	C_3	1.6 – 12.2	[17]
Imperata Cylindrica	C_4	11.5 – 20	[19–21]

Table 2. Platform chemicals that could be obtained via pyrolysis of grasses species [40–46]

Platform Chemicals	**Possible Derivatives**
Acetic acid	Acetic anhydride, Ethyl acetate, Vinyl acetate, Terephtalic acid
Furfural	Furan, Tetrahydrofuran, Furfuryl alcohol, Maleic anhydride, 2-(5H)-Furanone, Methyl furan, 2-Hydroxymethyl-5-vinyl furan, Maleic acid, Levulinic acid, Tetrahydrofurfuryl alcohol
1,4-Butanediol	Tetrahydrofuran, Adipic acid, γ-Butyrolactone,
Levoglucosan	5-Hydroxymethylfufural, Furfural, Acetic acid, 1,6-Anhydro-beta-D-glucofuranosa, 1,4:3,6-dianhydro-α-D-glucopyranose
5-Hydroxymethylfufural	2,5-Furan dicarboxylic acid, 5-Hydroxymethyl-furoic acid, Furandialdehyde, 2,5-Dihydroxymethylfuran, 2,5-Dihydroxymethyltetrahydrofuran
Benzene	Styrene, Phenol, Cumene, Cyclohexane, Cyclohexanone
Toluene	Benzoic acid, Dinitrotoluene, Toluene diisocyanate, Diaminotoluene
Xylene	Terephthalic acid, Isophthalic acid
Phenol	Cyclohexanone, Cyclohexanol, Bisphenol A, Nitrophenols
Guaiacyl	Propyl guaiacol, Eugenol, Iso-eugenol, Methoxyhydroxy phenyl glycol, Guaiacol, Creosol, Vanillin, Vanillic acid, Vanillyl alcohol, Coniferyl alcohol, Ferulic acid,
Syringyl	Syringeugenol, Syringol, Syringyl Creosol, Syringyl alcohol, Syringaldehyde,

Table 3. Proximate and ultimate analysis of experimental and literature characterisation data

Parameter	**Biomass**					
	This Experiment	**Literature**				
	IC	**IC** [27]	**IC** [40]	**EG** [48]	**SG** [41]	**RH** [2]
Proximate Analysis* (wt. %)						
Moisture	6.80	7.50	9.30	10.63	8.40	8.43
VM	72.01	76.58	64.30	72.54	84.20	68.25
FC	18.21[a]	15.09	16.10	19.20	11.90	16.92
Ash	2.97	0.83	10.30	8.26	3.90	14.83
Elemental Analysis* (wt. %)						
C	44.38	43.19	41.90	39.63	42.00	39.48
H	5.65	5.92	6.20	6.31	6.10	5.71
N	0.82	0.59	1.60	1.70	0.40	0.67
O	49.06[a]	50.17	39.80	52.16	47.40	21.10
S	0.09	0.14	0.19	0.20	0.10	< 0.10
O/C**	0.83	0.87	0.71	0.99	0.85	1.03
H/C**	1.53	1.64	1.78	1.91	1.74	1.74
Heating Value* (MJ/kg)						
HHV	18.39	17.03	-	15.77	19.8	17.34
$\text{HHV}_{\text{correlation}}$	18.47	17.91	18.03	16.79	17.62	17.36
Compositional Analysis* (wt. %)						
Hemicellulose	25.13	-	31.42	31.31	19.20	14.04
Cellulose	44.49	-	27.96	30.37	32.00	41.52
Lignin	17.89	-	39.45	26.02	18.80	33.67
Extractives	12.49	-	-	14.86	18.50	10.77

*based on dry basis, ** molar ratio

[a] by difference

VM = Volatile matter, FC = Fixed Carbon,

SG = Switchgrass, IC = Imperata cylindrica, RH = Rice husk, EG = Elephant grass

Table 4. Characteristic properties of *I.cylindrica* from TGA/DTG

Biomass	**T_{onset} (°C)**	**$T_{shoulder}$ (°C)**	$\left(\frac{-dm}{dt}\right)_{sh}$	$\left(\frac{-dm}{dt}\right)_{peak}$	**T_{peak} (°C)**	**T_{offset} (°C)**
IC	260.80	300.29	13.082	21.821	352.59	382.59

Table 5 Components identified in the py-GC/MS of *Imperata cylindrica* at temperature 400 °C, 500 °C and 600 °C

Peak ID	**Component**	**Formula**	**MW**	**Peak Area (%)**			**Group Classification**
				400 ºC	**500 ºC**	**600 ºC**	
1	Cyclopentadiene	C_5H_6	66	ND	1.60	2.67	Cycloalkenes
2	3-Methylfuran	C_5H_6O	82	0.81	1.33	1.61	Furan
3	2,5-Dimethylfuran	C_6H_8O	96	0.15	0.52	ND	Furan
4	Acetic acid	$C_2H_4O_2$	60	0.87	4.10	4.78	Organic Acid
5	Toluene	C_7H_8	92	0.31	1.68	3.01	Aromatics
6	Ethylbenzene	C_8H_{10}	106	0.41	0.72	1.23	Aromatics
7	p-Xylene	C_8H_{10}	106	0.06	0.32	0.95	Aromatics
8	1-Hydroxy-2-butanone	$C_4H_8O_2$	88	ND	1.66	2.33	Ketones
9	Styrene	C_8H_8	104	0.10	0.50	0.91	Aromatics
10	Furfural	$C_5H_4O_2$	96	2.00	3.72	4.08	Furans
11	Propylbenzene	C_9H_{12}	120	0.14	0.58	0.80	Aromatics
12	2-Methyl-2-cyclopenten-1-one	C_6H_8O	96	0.22	0.65	0.81	Cycloalkenes
13	2-Furanmethanol	$C_5H_6O_2$	98	1.43	1.18	0.22	Furans
14	2-Hydroxy-2-cyclopenten-1-one	$C_5H_6O_2$	98	1.11	0.53	0.87	Cycloalkenes
15	5-Methylfurfural	$C_6H_6O_2$	110	0.49	0.65	0.90	Furans
16	2,3-Pentanedione	$C_5H_8O_2$	100	ND	0.26	0.33	Ketones
17	3-Methyl-2-cyclopenten-1-one	C_6H_8O	96	ND	0.47	0.54	Cycloalkenes
18	Benzeneacetaldehyde	C_8H_8O	120	0.62	ND	0.04	Aromatics
19	2,3-Dimethyl-2-cyclopenten-1-one	$C_7H_{10}O$	110	ND	0.68	0.67	Cycloalkenes
20	2-Hydroxy-3-methyl-2-cyclopenten-1-one	$C_6H_8O_2$	112	0.49	1.58	0.32	Cycloalkenes
21	Guaiacol	$C_7H_8O_2$	124	8.80	11.56	10.77	G-Lignin
22	2-Methylphenol	C_7H_8O	108	ND	1.97	3.73	H-Lignin
23	p-Cresol	C_7H_8O	108	1.01	3.00	0.31	H-Lignin
24	2-Methoxy-4-methylphenol	$C_8H_{10}O_2$	138	2.32	3.00	2.68	G-Lignin
25	2,4-Dimethylphenol	$C_8H_{10}O$	122	0.31	1.01	1.52	H-Lignin
26	4-Ethylphenol	$C_8H_{10}O$	122	3.64	3.92	4.95	H-Lignin
27	4-Ethyl-2-methoxyphenol	$C_9H_{12}O_2$	152	5.26	4.20	3.28	G-Lignin
28	Indanone	C_9H_8O	132	1.01	2.56	3.00	Aromatics
29	4-Vinylguaiacol	$C_9H_{12}O_2$	150	22.14	17.82	13.93	G-Lignin
30	2,3-Dihydrobenzofuran	C_8H_8O	120	12.73	11.17	14.96	Furans
31	2,6-Dimethoxyphenol	$C_8H_{10}O_3$	154	2.86	2.66	2.31	S-Lignin
32	2-Methoxy-4-propenylphenol	$C_{10}H_{12}O_2$	164	0.70	1.62	2.14	G-Lignin

33	Hexadecane	$C_{16}H_{34}$	226	13.79	0.76	0.56	Misc
34	Propenylguaiacol	$C_{10}H_{12}O_2$	164	3.97	3.61	2.84	G-Lignin
35	1,2,4-Trimethoxybenzene	$C_9H_{12}O_3$	168	0.67	0.76	0.67	S-Lignin
36	Isovanillin	$C_8H_8O_3$	152	1.12	1.13	1.00	G-Lignin
37	5-tert-Butylpyrogallol	$C_{10}H_{14}O_3$	182	1.05	0.63	0.51	Misc.
38	1-(3,4-Dimethoxyphenyl)ethanone	$C_{10}H_{12}O_3$	180	0.88	0.80	0.62	Ketones
39	Guaiacylacetone	$C_{10}H_{12}O_3$	180	0.95	0.76	0.30	G-Lignin
40	(2E)-3,7,11,15-Tetramethyl-2-hexadecen-1-ol	$C_{20}H_{40}$	280	4.30	2.85	2.25	Misc.
41	2,6-Dimethoxy-4-allylphenol	$C_{11}H_{14}O_3$	194	1.51	0.80	0.57	S-Lignin
42	Methyl hexadecanoate	$C_{17}H_{34}O_2$	270	0.31	0.21	ND	Ester
43	n-Hexadecanoic acid	$C_{16}H_{32}O_2$	256	1.45	0.48	ND	Organic Acid

ND = Not detected, G-Lignin = Guaiacyl Lignin, H-Lignin = p-Hydroxyphenyl lignin, S-Lignin = Syringyl lignin, Misc. = Miscellaneous hydrocarbon.

Table 6. Percentage of major group components distribution of py-GC/MS *Imperata cylindrica* at elevated temperature

Group Component	**% Peak Area**		
	400 ºC	**500 ºC**	**600 ºC**
Furanic compound	17.62	18.57	21.76
Aromatic hydrocarbon	2.66	6.36	9.95
Cycloalkenes	1.82	5.51	5.88
Guaiacol lignin	45.27	43.70	36.96
P-hydroxyphenyl lignin	4.96	9.90	10.51
Syringyl lignin	5.04	4.22	3.55
Organic acid	2.31	4.58	4.78
Ketonic	0.88	2.72	3.28
Ester	0.31	0.21	0.00
Miscellaneous hydrocarbon	20.14	6.80	6.32

Table 7. Pyrolysis yield studies for Imperata cylindrica

Sample	Reactor Type	Pyrolysis Temperature (ºC)	Pyrolysis products yield (%)			Reference
			Liquid bio-oil	Solid char	Non-condensable gases	
Imperata Cylindrica	Fixed-bed	400	34.33	34.23	31.44	This work
		500	37.16	29.12	33.72	
		600	36.92	27.12	35.96	
Imperata Cylindrica	Fixed-bed	400	25.00	25.00	50.00	[25]
		500	33.67	14.33	52.00	
Cogongrass and Manillagrass	Twin screw (350 rpm)	400 - 550	53.56	27.35	19.09	[90]
Imperata Cylindrica	Fixed-bed	450 – 600	3.25 – 20.88	22.63 – 30.00	49.13 – 74.13	[62]