Slow Pyrolysis Of *Imperata Cylindrica* In a Fixed Bed Reactor

K.Azduwin, M.J.M.Ridzuan, S.M. Hafis and T.Amran T.A

***Abstract*—** Slow pyrolysis of *Imperata Cylindrica* has been conducted in a fixed bed reactor to determine the effect of temperature and particle sizes towards the product yield. The characterization of the *Imperata Cylindrica* has been analysed using several instruments such as Thermogravimetric Analysis (TGA), Carbon Hidrogen Nitrogen Sulfur and Oxygen (CHNS/O) analyzer, Bomb Calorimeter, and several analytical methods. Pyrolysis experiments were performed at temperature between 450- 600 °C, and particle sizes of 0.25-1.00 mm with constant nitrogen flow rate of 100 $cm^3 min^{-1}$ and heating rate of 22 ºC . min^{-1} (slow mode). The highest liquid oil yield obtained was 20.88 % at temperature 500 °C, with particle size of 0.5-1.0 mm, and heating rate of 22 ºC . min^{-1}. The obtained yield of liquid, solid and gas from pyrolysis were found in the range of 3.25-20.88 %, 22.63-30.50 % and 49.13-74.13 % respectively at different pyrolysis conditions. Liquid bio-oil produced from the pyrolysis of *Imperata Cylindrica* shows high water content in the range of 58.09-72.74 % which was checked using Karl Fisher Titration. From Gas Chromatography-Mass Spectrometry (GC-MS), the chemical components present in the liquid oil from pyrolysis of *Imperata cylindrica* include acids, phenols, ketones, aldehydes, ethers, and some species of aromatics.

***Keywords*—** Biomass, Fixed bed reactor, Imperata Cylindrica, Slow pyrolysis.

I. INTRODUCTION

Slow pyrolysis is often related to the production of charcoal while fast pyrolysis was related with production of bio-oil. Slow pyrolysis of biomass will produce high content of charcoal [1]. Researches in the world are more focusing on fast pyrolysis since it was the promising routes in producing bio-oil and this have cause neglecting of conventional (slow) pyrolysis process although slow pyrolysis also permits in producing solid, liquid, and gaseous yields in considerable portions [2].

The product from pyrolysis is highly dependent on the feedstock and the process conditions employed the pyrolysed liquid which known as bio-oil and it can yields up to 70–75 wt% from wood [3].

However, bio-oils are still considered as low quality liquid fuels compared to petroleum based fuel, due to its poor properties such as complex multiphase structures, low heating values, high contents of water, oxygen, solids and ash, high surface tension and viscosity, have instable chemical and thermal, pH values is low (acidic) , and also poor ignition and combustion properties. Although bio-oils are lacking in some properties compared to petroleum fuel, it does have some specialty in lubricate properties. Furthermore, bio-oils are more environmental friendly since they are biodegradable and less toxic as well. The challenge of research today is to develop bio-oils as commercialized liquid fuels to compete with existing petroleum fuels.

Some factors might affect the chemical composition of bio-oil such as biomass feedstock type, pyrolysis parameters (residence time, pressure, temperature, gaseous environment heating rate), pre-treatment process, and also condensation and vapour filtration (condensing method and medium, filter type, cooling rate). Hence, the different use of biomass feedstock and different reactor configuration will give different results among them. As a result, the fuel properties of different bio-oils usually vary in wide ranges.

II. METHODOLOGY

A.Biomass Feedstock

The biomass material used as a feedstock for this experiment is *Imperata Cylindrica* or cogon grass (lalang). To ensure the consistency of the results obtain, one batch of lalang was prepared together and it was plucked from UTM compound area. The plants were initially cut into small pieces and then it was dry in the oven for 48 hours at 100 ºC .The sample was then crushed before it was sieved to a smaller size. The characterization of *Imperata Cylindrica* was shown in Table I. In this study, proximate analysis of the *Imperata Cylindrica* was performed using the thermogravimetric analysis (TGA) TGA/SDTA851 for determination of its moisture content, volatile matter, fixed carbon and ashes. The elemental analyses of *Imperata Cylindrica* were determined using a Perkin Elmer CHNS/O Analyzer. Extractives, hemicelluloses, lignin and cellulose concentration of *Imperata Cylindrica* are based on the experimental procedure [4].

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TABLE I
CHARACTERIZATION OF IMPERATA CYLINDRICA

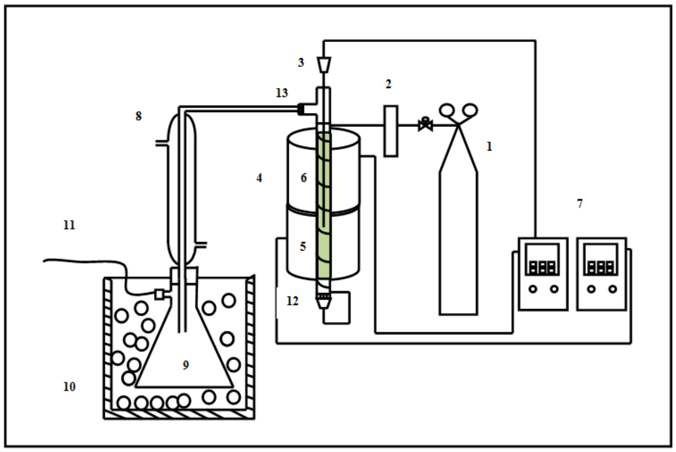
Analysis	Result
Proximate (wt. %)	
Moisture content	6.3
Volatile matter	69.7
Fixed carbon and Ash content	23.9
Ultimate (wt. %)	
Carbon	34.1
Hydrogen	6.6
Nitrogen	0.8
Oxygen	57.5
Analysis	Result
Sulfur (if any)	1.0
Component (wt. %)	
Extractives	11.2
Hemicellulose	27.6
Lignin	16.5
Cellulose	35.1
Heating value(MJ/kg, dry basis)	
HHV	16.5
LHV	14.2

B. Pyrolysis experimental

Fig. 1 shows the pyrolysis apparatus set up, the biomass sample is fed into stainless steel reactor tubing 0.43 m long with internal diameter of 9.2 mm. Two tube furnaces were used to heat the sample which control by two simultaneous PVX program controllers. Thermocouple was placed inside the reactor tubing to read the actual reaction temperature. After loading the sample, the reactor is closed and nitrogen gas was fed in to completely remove air in the system. The flow rate of the nitrogen gas was measured using rotameter. The nitrogen gas tubing is wind along the reactor tube to pre-heat the gas before it goes to the reaction system so that it does not cool down the reaction temperature. After air was completely removed from the system, the reaction can be run. As the temperature raise up, gases were produced and it was cooled using condenser and hence condensed the gas into liquid. The liquid product trapped in the liquid collector were collected while non condensed gas remains in the collector was cooled by the ice cube inside the ice tub to condense more gas into liquid. And the remaining non-condensable gas in the collector was released out of the system.

Before started, 8 gram of dried biomass sample with average diameter of 0.25 - 1 mm were fed in the reactor tube. After all connections were made, a nitrogen gas flow rate of 100 $cm^3 . min^{-1}$ was maintained and measured using rotameter. The heating rate was set constant at 22 ºC . min^{-1} while the hold time was constantly set for 3 minutes for each sample. The liquid oil were weighed after the pyrolysis, same goes with the solid produced which remains in the reactor tube. The gas produced was determined by material balance.

To see the effect of temperature towards product yield, the pyrolysis were initially run with four different temperatures from 450, 500, 550 and 600 ºC. The temperature at highest liquid yield in the first run was chosen as a constant parameter for the second run. In the second run, four different range of particle sizes of <0.25 mm, 0.2-0.3 mm, 0.3-0.5 mm and 0.5-1 mm were chosen as the variable parameters to see the effect of particle size on the yield by using highest liquid yield temperature which obtained in the first run.



Description:

1. Nitrogen bottle	7. Power Controller
2. Rotameter	8. Condenser
3. Thermocouple	9. Liquid Collector
4. Electric Heater	10. Ice bath Tub
5. Reactor Tube	11. Gas release
6. Biomass Sample	12 &13. Mesh sieve

Fig. 1 Pyrolysis experimental set-up

III. RESULT AND DISCUSSION

As can be seen in Fig. 2 for the effect of temperature, the conversion efficiency increased from 69.50 % to 76.31 % when the final pyrolysis temperature was raised from 450 to 600 ºC. The results shows that the liquid yield increases from 4.5 to 10.13 % when the temperature is increased from 450 to 500 °C then decreases to 8.31 % when the temperature is further increased to 600 °C. The gas yield decreased from 65.00 to 61.63 % when the pyrolysis temperature is increased from 400 to 500 °C, but increased to 68 % when the temperature is further increased to 600 °C. The decrease of liquid yield and rapid increase of gas yield are observed at higher temperature, this is due to secondary cracking of the pyrolysis liquid occurred in to gaseous product at higher temperature.

Secondary tar destruction may lead to the decrease in the oil yield or increase in the gas yield and conversion at higher temperatures [5]. The solid yield significantly decreases from 30.50 to 23.69 % with the same temperature rising. The decrease in the solid yield as the temperature increased due to the increasing primary decomposition of the sample at higher temperature. The oil yield reached maximum value at temperature 500 ºC about 10.13 %. And due to that, this temperature is used in the second run for pyrolysis of Imperata Cylindrica.

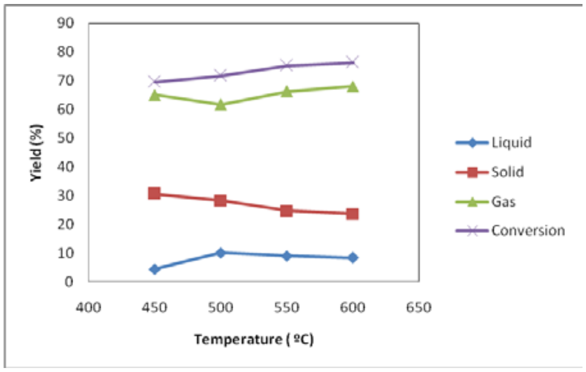


Fig. 2 Effect of temperature on slow pyrolysis of Imperata Cylindrica

For the second run, four particle size of <0.25 mm, 0.25-0.3 mm, 0.3-0.5 mm and 0.5-1 mm were selected and the pyrolysis experiments were conducted at the highest liquid yield temperature obtained in the previous experiment which is 500 ºC with a constant heating rate of 22 ºC . min^{-1} and sweeping gas velocity of 100 $cm^3.min^{-1}$. As can be seen in Fig. 3, the conversion efficiency was decreased with larger particle size because larger particles will heat up more slowly compared to small particle, so the average particle temperatures is lower and hence affect the product yield. It can be seen that char and liquid yield is increased as the particle size is increased from 0.25 mm to1.00 mm but gas yield was decreased.

The longer residence time of the volatiles in the reactor has lead to the decreases of liquid yield as the particle size decreased because when using smaller particles, it will favour the hydrocarbons cracking [6]. The maximum pyrolysis oil yield obtained was 20.88 % with a particle size of 0.5-1.0 mm. It was shown that when the particle size is increased, the solid yield also increased. This is due to the greater temperature gradient in the particles, so that at a set time the inside temperature of the particle is lower than the surface, which perhaps gives rise to the solid yields. At lower particle size ranges, more residence time of volatiles inside the reactor results in the heavier molecules (tar) cracking in to lower molecules and thus lead to rise of gaseous product. The study found that solid and liquid yield increases from 22.63 to 30.00 % and 3.25 to 20.88 % respectively and gas yield decreases from 74.13 to 49.13 % when the particle size is increased from 0.25 to 1.00 mm.

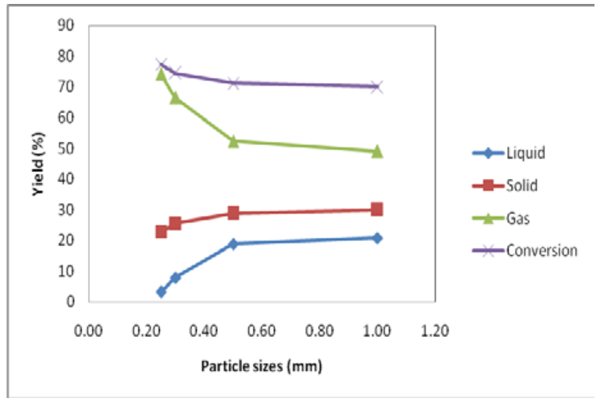


Fig. 3 Effect of particle size on slow pyrolysis of Imperata Cylindrica

IV. BIO-OIL ANALYSIS

A. Water Content

The water content in the bio-oil was analyzed by Karl-Fischer titration according to ASTM D 1744. The existence of water in the bio-oil is unavoidable, which is due to moisture in the raw material. In general, the water content of bio-oil is usually in the range of 30-35 wt % [7], and it is hard to remove from bio-oil resulting from the certain solubility of bio-oil and water. The existence of water has both negative and positive effects on the storage and utilization of bio-oils. On the one hand, it will lessen heating values in combustion, and may cause phase separation in storage. On the other hand, it is beneficial to reduce viscosity and facilitate atomization.

As seen in Fig. 4 and 5, water content for most of the liquid oil sample was in the range of 58.09-72.74 wt. %. And it can be seen that for the effect of temperature, the water content was decrease as the temperature rise up but at 600 ºC the water content was suddenly increase. This might because longer residence time in the process has caused secondary cracking of volatile occurred and thus will form some hydrates compound at this state which can contributes to higher content of water at higher temperature. For the effect of particle size, the water content was inconsistent, this might because of the gap of the particle size for each sample are not the same, and thus affect the trend of the graph. At larger size it possess the higher water content which is about ~72.74 wt. % might because of the distribution of the particle size was inconsistent besides the heat does not reach at the core of the particle size due to larger size. And this has caused higher water content in the bio-oil produced.

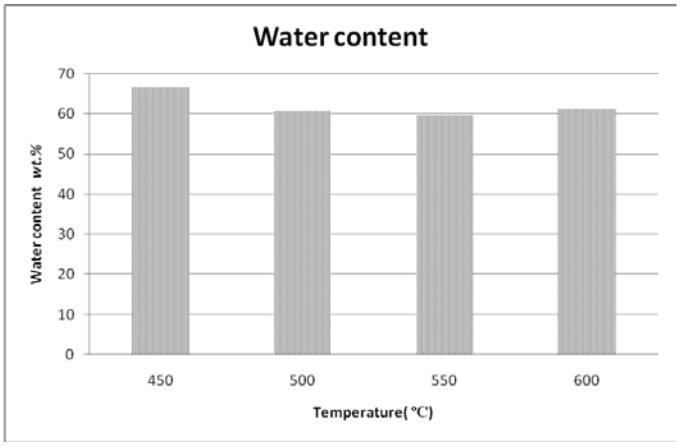


Fig. 4 Water content of liquid oil for different pyrolysis temperature

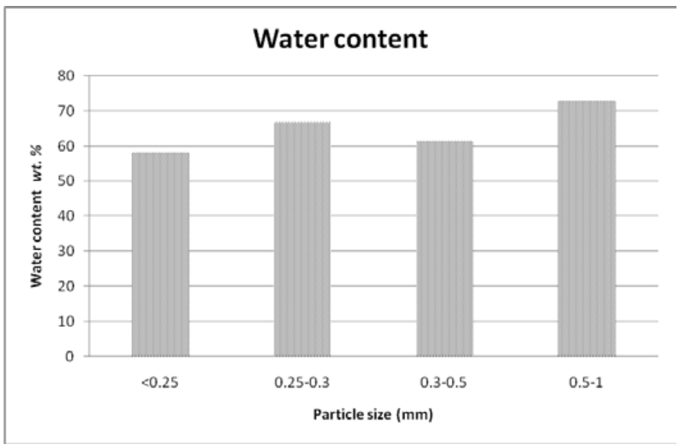


Fig. 5 Water content of liquid oil for different particle size

B.GC-MS

GC–MS analysis was carried out in order to get an idea of the nature and type of organic compounds in the pyrolysis liquid products. Over 60 components were detected in the bio-oil samples but only the major peaks were selected. The major functional group that presents in *Imperata Cylindrica* liquid oil are Carboxylic acids with higher proportion of 40.51 % (Table II). And this has shown that pyrolysed liquid oil from *Imperata cylindrica* was acidic due to the presence of high content of acids.

It was shown that pyrolysis liquid products are really complex and might be composed of hundreds of organic compounds. The chemical components presence in the pyrolysis liquid products mainly composed of acids, phenols, ketones, aldehydes, ethers, and some species of aromatics based on the pyrolysis of woods [8]. The biopolymer textures of the biomass itself such as cellulose and hemicelluloses is the reason of the presence of these aromatic and oxygenated compounds.

TABLE II
FUNCTIONAL GROUP PRESENTS IN *IMPERATA CYLINDRICA* LIQUID OIL

Functional group	Higher proportion (%)
Carboxylic acid	40.51
Alcohol	32.40
Alcohol,Amine	29.05
Aldehyde	28.64
Carboxylic acid,Ester	23.36
Ketone,Alkyne	20.10
Phenol	16.87
Carboxylic acid,Alcohol	15.00
Carboxylic acid,Ester,Alcohol	13.05
Hydrocarbon	12.00
Ketone	7.04
Ketone,Alcohol	4.08
Alcohol,Ester	6.98

V.CONCLUSION

In this study, pyrolysis of *Imperata Cylindrica* or ‘Lalang’ grass was investigated in a slow mode pyrolysis in a batch reactor system under various conditions. Overall, the highest oil yield obtained was about 20.88 % with sweeping N_2 gas of 100 $cm^3.min^{-1}$, temperature 500 ºC, heating rate of 22 ºC min^{-1} and particle size 0.5-1.0 mm. 500 ºC was suggested as the best temperature for decomposition of *Imperata Cylindrica* in producing more liquid oil yield in this study. The conversion efficiency was decreased with larger particle size. Larger particle size results in more amounts of liquid and solid yield and resulting less amount of gas yield compared to small particle size. For the effect of temperature, slow pyrolysis of *Imperata Cylindrica* results in higher gas yield in the range of 60-70 %. In a slow pyrolysis *Imperata Cylindrica* for the effect of particle size, it produce more gas in the range of ~50-75 % followed by solid ~20-30 % and liquid ~3-20 %.

Liquid bio-oil produced from the slow pyrolysis of *Imperata Cylindrica* contains a large amount of water in the range of 58.09-72.74 %. From GC–MS analysis, it shows that pyrolysis liquid products are really complex and may be composed of hundreds of organic compounds. The major functional group that presents in *Imperata Cylindrica* liquid oil are carboxylic acids with higher proportion of 40.51 % reflected that liquid oil of *Imperata cylindrica* was acidic due to the presence of high content of acids. The other chemical components present in the liquid oil from pyrolysis of *Imperata cylindrica* include acids, phenols, ketones, aldehydes, ethers, and some species of aromatics.

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