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Fast Pyrolysis of Agricultural Residues from Cassava Plantation for Bio-oil Production

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Abstract: Fast pyrolysis experiments have been conducted on cassava rhizome and stalk for producing bio-oil. The purpose of this work was to determine the thermochemical characteristics and pyrolysis behaviour of agricultural residues from cassava plantation and investigate the optimum process conditions for maximising bio-oil yield. Proximate, ultimate and heating value analyses were carried out on the samples. Microscale pyrolysis reactor coupled with gas chromatography and mass spectrometry (Py-GC/MS) was used for studying the effects of temperatures and alkali metal contents on pyrolysis products. Results showed that cassava residues contain high volatile contents (78-80 wt%, dry basis), very low nitrogen (0.7-1.3 wt%, dry ash-free basis) and sulphur (<0.1 wt%) contents with a medium heating value (LHV ~18 MJ kg^{-1}), suggesting that an environmentally friendly bio-fuel could be produced via thermochemical conversion processing like fast pyrolysis. Results from Py-GC/MS showed that both cassava stalk and rhizome reached their highest liquid yields at pyrolysis temperature of 500 °C and pyrolysis of cassava rhizome gave higher yields of virtually all liquid-range compounds compared to cassava stalk. Furthermore, alkali metals seem to have an adverse effect on bio-oil yield. The addition of ash led to the decrease in the yields, while the reduction of alkali metals by water washing showed an increase in the yields of almost all compounds.

Keywords: Agricultural Residues, Cassava Stalk, Cassava Rhizome, Pyrolysis, Thermochemical Characterisation

Introduction

Biomass as a source of sustainable energy is widely accepted for its potential to satisfy environmental concerns over the use of fossil energy. It provides the only source of renewable liquid, gaseous and solid fuels [1]. For energy production, biomass can be either applied directly by combustion or transformed by conversion processes. One of the promising conversion processes for liquid fuel production is fast pyrolysis. This involves heating biomass rapidly (high heating rate) at a high temperature in the absence of oxygen to produce the pyrolysis vapour. The evolved vapour is then cooled down to room temperature to obtain pyrolysis liquid product, which is called "bio-oil". The non-condensable gases and the solid residue bio-char are valuable by-products which can be used as a heating source. The process conditions of fast pyrolysis are normally selected in order to obtain the highest liquid yields. Apart from the process parameters, the characteristics of biomass feedstocks also play an important role on the pyrolysis end products.

In this work, agricultural residues from cassava plantation, namely cassava stalk and cassava rhizome, were chosen as biomass feedstocks since they are available in large quantity in many tropical countries like Brazil, Thailand, Nigeria and Indonesia. Currently, the main product of cassava plantation, the tuber, is getting more important for its use as feedstock for bio-ethanol production. In this work we propose an alternative way of managing the residues by transforming the low energy density solid biomass into a liquid biooil that can be readily stored and transported. The bio-oil produced can be used as a fuel and for the production of chemicals. An overview of applications of bio-oil can be found inliterature [2].

The thermochemical characterization of cassava stalk and rhizome was carried out in this work. The biomass samples were pyrolysed using an analytical pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) technique in order to investigate the effects of reaction temperature and ash contents on pyrolysis liquid yields.

Methodology

Biomass feedstock

Agricultural wastes from cassava plantation, cassava stalk and rhizome, from Nakhon Ratchasima province in Thailand was used as feedstock in this study.

Thermochemical characterization methods

Proximate analysis was performed on the biomass samples for the determination of moisture, volatile, ash and fixed carbon contents. The ASTM standard test methods for measuring moisture, volatile and ash contents are ASTM E1756-01, E872-82 and E1755-01, respectively. The fixed carbon contents were calculated by difference. Ultimate analysis was performed in order to determine the basic elemental composition of the biomass samples. Carbon, hydrogen, nitrogen and sulphur contents were measured, while oxygen contents were calculated by difference. The instruments used were CE- 440 and Carlo-Erba elemental analysers, which are based on combustion methods. The instrumental accuracy is ±0.3% absolute and the detection limit for sulphur determination is <0.1%. The higher heating values (HHV) of the samples were determined by bomb calorific experiment according to the ASTM D2015 standard test method. The lower heating values (LHV) of biomass samples were calculated according to Eq. (1) [3].

$$\mathbf{LHV_{dry}\ (MJ\ kg^{-1}) = HHV_{dry} - 2.442(8.936H/100)} \qquad \mathbf{(1)}$$

Where H is the weight percentage of hydrogen on dry basis

Analytical pyrolysis gas chromatography-mass spectrometry (Py-GC/MS)

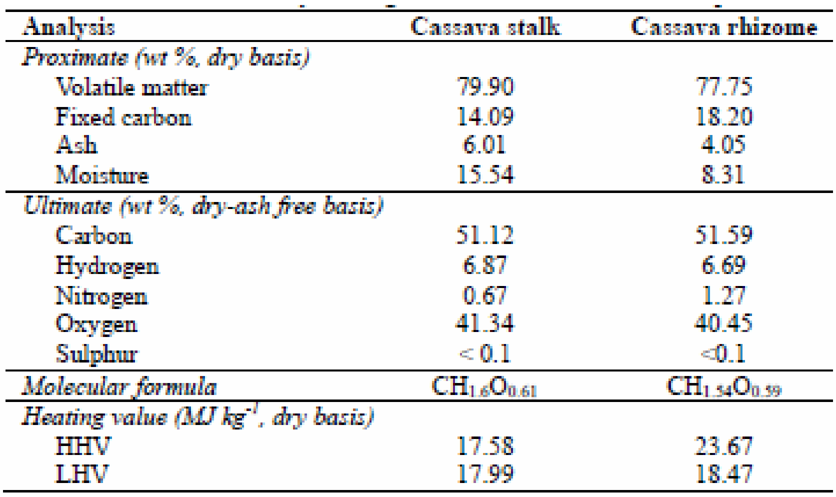
Pyrolysis experiments were carried out using a pyrolysis autosampler CDS AS-2500 with pyroprobe CDS 2000. Approximately 0.5 mg of sample was placed in a quartz tube along with a quartz filler rod. The pyroprobe programme was at 400-600 °C for 0.01 second at the heating rate of 3000 °C/second and hold for 10 seconds. PerkinElmer AutoSystem XL Gas Chromatograph was used to separate the pyrolysis vapours. The column used was PP 1701 60m x 25 µm with a 0.025 µm film thickness. Helium at a velocity of 38 cm/s was used as a carrier gas and the split injection ration was 1:125. In addition, the oven programme began at 45 °C for 4 minutes and then heated at heating rate of 4 °C/min to 240 °C. The injector and detector temperature was set at 280 °C. The separated compounds were then analysed using a PerkinElmer Turbomass Gold Mass Spectrometer with Electron Impact (EI) mode. The mass spectra were obtained at the ionisation energy of 70 eV from m/z 28 to 600 with the speed of 1.0 second/decade. Identification of chromatographic peaks from pyrolysis GC/MS experiments was carried out by comparing the mass ions (m/z) of each peak with NIST mass spectral database. Three experimental runs were performed per sample and the averaged values were used for analysis

Results and Discussion

Thermochemical characterization of biomass samples

Table 1 summarises the main thermochemical characteristics of cassava stalk and rhizome. The volatile matter and fixed carbon contents of the samples are similar to those of wood, while the ash contents are similar to that of straw (4-6% [4]) and higher than that of wood (approximately 1% [4]). The high ash contents imply the high alkali metal contents in the biomass. Alkali metals, especially K and Na, are known to have a catalytic impact on pyrolysis of biomass leading to a lower liquid yield and higher gas yield [5]. Therefore, one would expect that the quantity of the liquid product produced from pyrolysis of cassava residues would be in the same range as that of straw and less than that of wood.

Table 1 Results of the analysis of agricultural wastes from cassava plantation



Analysis	Cassava stalk	Cassava rhizome
Proximate (wt %, dry basis)		
Volatile matter	79.90	77.75
Fixed carbon	14.09	18.20
Ash	6.01	4.05
Moisture	15.54	8.31
Ultimate (wt %, dry-ash free basis)		
Carbon	51.12	51.59
Hydrogen	6.87	6.69
Nitrogen	0.67	1.27
Oxygen	41.34	40.45
Sulphur	< 0.1	<0.1
Molecular formula	$CH_{1.6}O_{0.61}$	$CH_{1.54}O_{0.59}$
Heating value (MJ kg^{-1}, dry basis)		
HHV	17.58	23.67
LHV	17.99	18.47

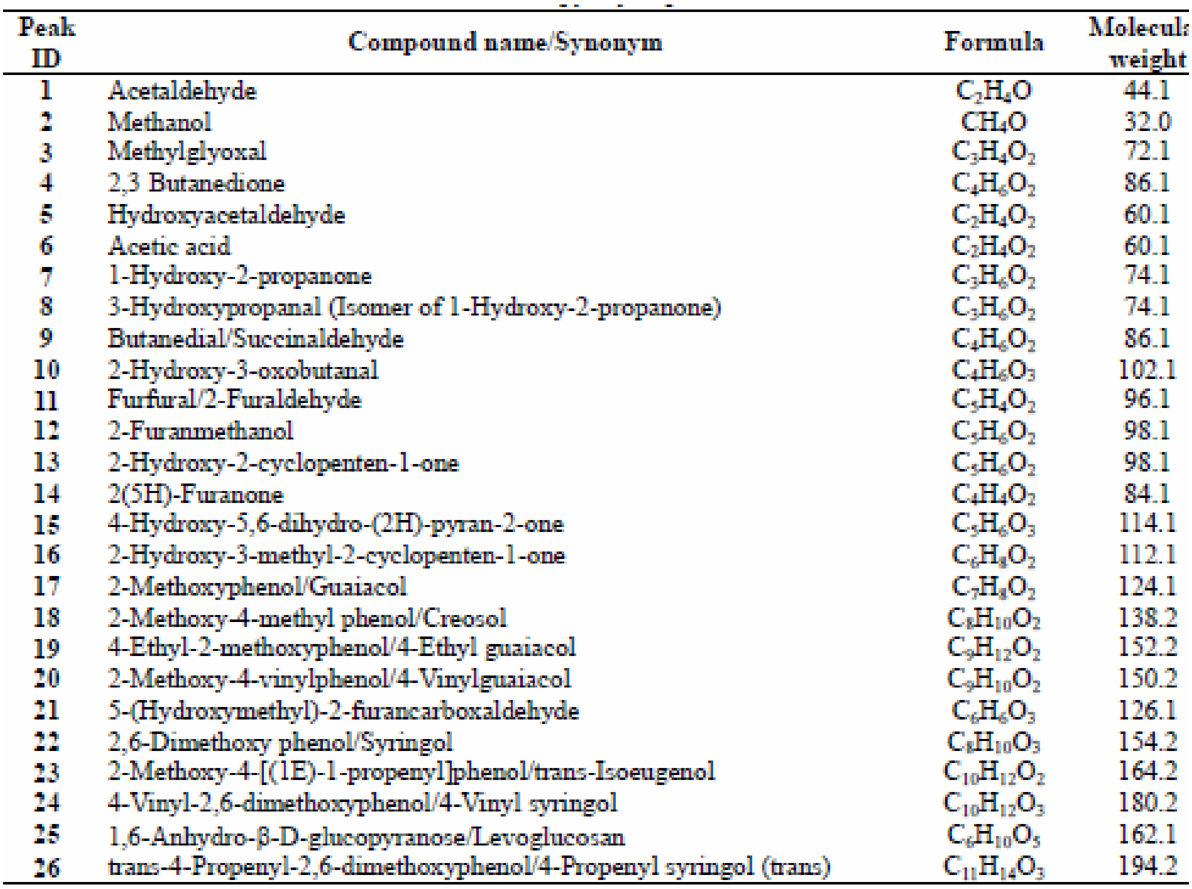
Ultimate analysis results of the samples are very similar to those of wood. The oxygen content of biomass is significantly high. This leads to the oxygenated pyrolysis liquid products and the much lower heating values than those of fossil fuels. Accordingly, removal of oxygenated species during or after the pyrolysis reactions is necessary to obtain a higher fuel grade product. Furthermore, the cassava rhizome contains very low amounts of nitrogen and sulphur compared with coal, which contains 1.4 and 1.7 wt% of nitrogen and sulphur, repectively. If the biomass itself or the pyrolysis products derived from the biomass are burnt for energy, the amounts of nitrogen oxides and sulphur oxides given off will be much lower than when burning fossil fuels. It is therefore beneficial to the environment when using biomass for energy production. The heating values of the agricultural residues are lower than those of fossil fuels. This is mainly because of the high oxygen content. When comparing between feedstocks, one can see that the rhizome has a higher heating value than the stalk. This is actually due to the lower oxygen and ash content of the rhizome. Hence cassava rhizome may be a slightly better feedstock for thermochemical conversion processes like fast pyrolysis.

Micro-scale pyrolysis

Cassava stalk and rhizome samples were subjected to pyrolysis in a microscale reactor at three different temperatures, 400, 500 and 600 °C. The pyrolysis vapour products were then separated by gas chromatography (GC) and analysed by mass spectrometer (MS). The 26 liquid-range compounds identified from the chromatogram obtained are listed in Table 2. All the compounds have also been identified as biomass pyrolysis products by other researchers [6-7]. The pyrolysis products are mainly phenolics, ketones, aldehydes and alcohols. These compounds are typical of bio-oils produced from lignocellulosic materials [8].

One of the factors significantly influencing the pyrolysis products is the reaction temperature. Figs. 1 and 2 display the effect of temperatures on quantity of pyrolysis products derived from the agricultural wastes. It is obvious from the figures that at pyrolysis temperature of 500 °C all the liquid-range compounds reach their maximum level. The temperature of 400 °C seems to be too low for emitting compounds, whereas the temperature of 600 °C appears to be too high causing secondary thermal cracking which in turn leads to a reduction of liquid compounds and a production of gaseous products like CO, CO2 and light hydrocarbon gases.

Table 2 Identification of main pyrolysis products from cassava residues



Peak ID	Compound name/Synonym	Formula	Molecul weight
1	Acetaldehyde	C_2H_4O	44.1
2	Methanol	CH_4O	32.0
3	Methylglyoxal	$C_3H_4O_2$	72.1
4	2,3 Butanedione	$C_4H_6O_2$	86.1
5	Hydroxyacetaldehyde	$C_2H_4O_2$	60.1
6	Acetic acid	$C_2H_4O_2$	60.1
7	1-Hydroxy-2-propanone	$C_3H_6O_2$	74.1
8	3-Hydroxypropanal (Isomer of 1-Hydroxy-2-propanone)	$C_3H_6O_2$	74.1
9	Butanedial/Succinaldehyde	$C_4H_6O_2$	86.1
10	2-Hydroxy-3-oxobutanal	$C_4H_6O_3$	102.1
11	Furfural/2-Furaldehyde	$C_5H_4O_2$	96.1
12	2-Furanmethanol	$C_5H_6O_2$	98.1
13	2-Hydroxy-2-cyclopenten-1-one	$C_5H_6O_2$	98.1
14	2(5H)-Furanone	$C_4H_4O_2$	84.1
15	4-Hydroxy-5,6-dihydro-(2H)-pyran-2-one	$C_5H_6O_3$	114.1
16	2-Hydroxy-3-methyl-2-cyclopenten-1-one	$C_6H_8O_2$	112.1
17	2-Methoxyphenol/Guaiacol	$C_7H_8O_2$	124.1
18	2-Methoxy-4-methyl phenol/Creosol	$C_8H_{10}O_2$	138.2
19	4-Ethyl-2-methoxyphenol/4-Ethyl guaiacol	$C_9H_{12}O_2$	152.2
20	2-Methoxy-4-vinylphenol/4-Vinylguaiacol	$C_9H_{10}O_2$	150.2
21	5-(Hydroxymethyl)-2-furancarboxaldehyde	$C_6H_6O_3$	126.1
22	2,6-Dimethoxy phenol/Syringol	$C_8H_{10}O_3$	154.2
23	2-Methoxy-4-[(1E)-1-propenyl]phenol/trans-Isoeugenol	$C_{10}H_{12}O_2$	164.2
24	4-Vinyl-2,6-dimethoxyphenol/4-Vinyl syringol	$C_{10}H_{12}O_3$	180.2
25	1,6-Anhydro-β-D-glucopyranose/Levoglucosan	$C_6H_{10}O_5$	162.1
26	trans-4-Propenyl-2,6-dimethoxyphenol/4-Propenyl syringol (trans)	$C_{11}H_{14}O_3$	194.2

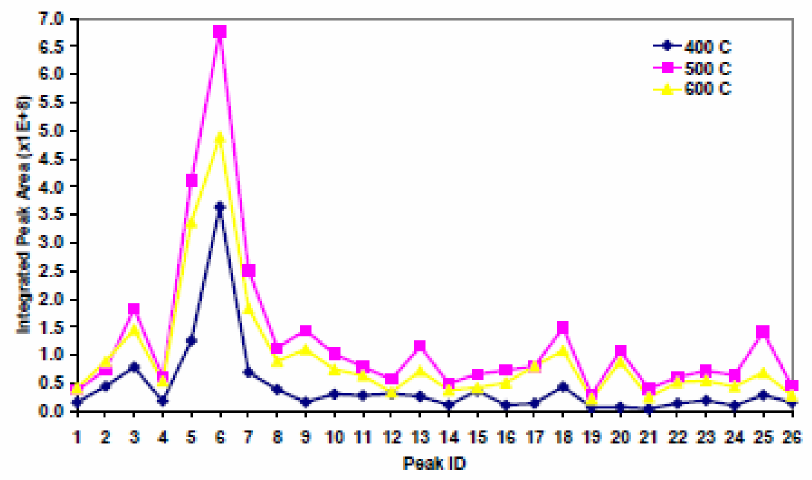


Fig. 1 Product yields from pyrolysis of cassava stalk at three different temperatures

Fig.3 compares the pyrolysis product yields of both feedstocks. It is apparent that the cassava rhizome gives higher amounts of liquid-range compounds compared to the stalk. This may be explained by the difference in ash contents as alkali metals in the ash can act as catalysts, reducing liquid products and promoting gaseous species. However, the difference between the feedstocks is less pronounced than the effect of temperatures as can be seen from Figs.1 and 2.

Since the inorganic metals present in biomass have an adverse effect on pyrolysis liquid yields, removal of these metals would increase the liquid yield. To prove this, two more experiments were carried out, one with water-washed cassava rhizome sample and the other one with the unwashed cassava rhizome plus some extra ash (25wt% of the biomass). The temperature set for both runs was 500 °C and results are shown by Fig.4. The waster-washed cassava rhizome sample gives the highest yields to almost all compounds, while the sample with the addition of ash results in the lowest yields to all compounds. This shows that de-mineralisation of biomass is advantageous to the production of liquid bio-oils. Therefore, it is suggested that the agricultural residues from cassava plantation should be subjected to washing by, for example, natural rain leaching prior to pyrolysis processing in order to maximize the pyrolysis liquid product.

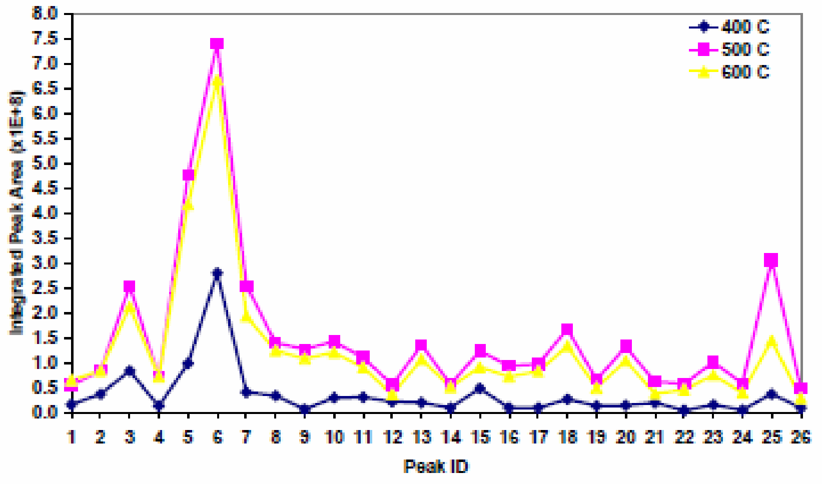


Fig. 2 Product yields from pyrolysis of cassava rhizome at three different temperatures

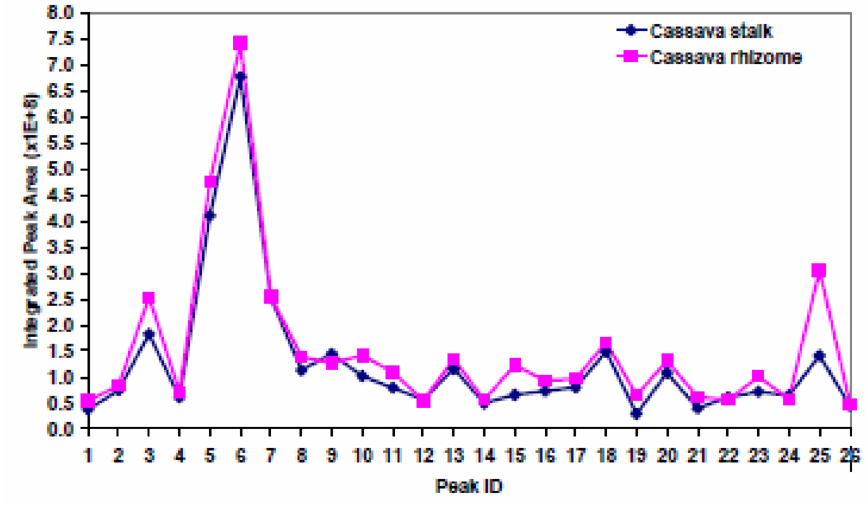


Fig.3 Comparison of pyrolysis products from cassava stalk and rhizome at pyrolysis temperature of 500 °C

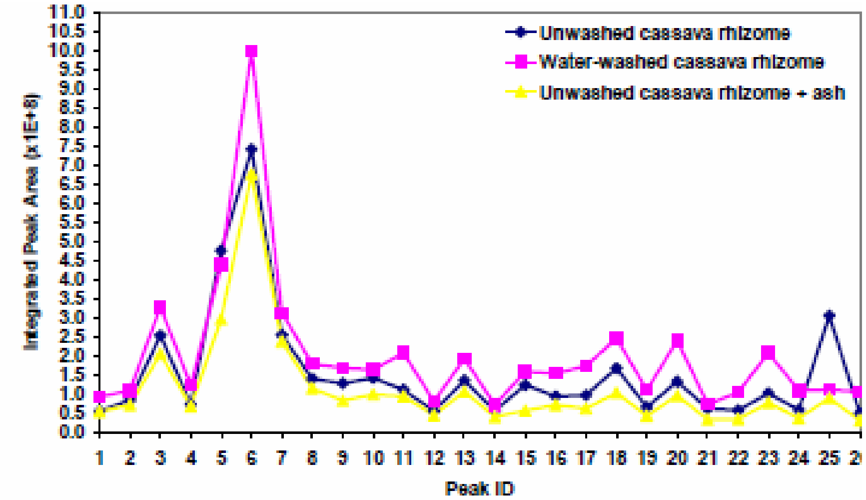


Fig.4 Effect of alkali metals on pyrolysis products of cassava rhizome pyrolysed at 500 °C

Conclusion

Fast pyrolysis technique is proposed in this study as an option for the efficient utilization of agricultural residues from cassava plantation. According to the thermochemical characterization, the biomass feedstocks contain high volatile matter, very low nitrogen and sulphur contents and medium heating values. This indicates that a sustainable and environmentally benign fuel can be produced from pyrolysis technology. The reaction temperature suggested for the highest liquid yield is around 500 °C. In addition, the demineralization of biomass prior to pyrolysis processing is found to be beneficial to the production of pyrolysis liquid.

Acknowledgments

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