CHAPTER 4

EXPERIMENTAL RESULTS



4.1 Raw biomass analyses

4.1.1 Chemical properties analyses

The chemical properties of raw biomass: elemental compositions, calorific values, fuel ratios and proximate analyses were studied in this thesis work. The objectives of the chemical properties analyses are to understand the pyrolysis behavior of each biomass and to identify the difference between raw and upgraded biomass. The elemental compositions of raw biomass were identified by ultimate analyses which give the composition of the biomass in weight percentages of carbon, hydrogen and oxygen as well as nitrogen. The elemental compositions of biomass were used to calculate another important property which is calorific value of biomass. Table 4.1 presents the results of ultimate analyses and the calorific values including the proximate analyses of biomass samples. Carbon and oxygen were found as the major components of all studied biomass. Raw jatropha trunk and napier grass have equally the highest percentages of carbon content which is 46.6 wt%. Jatropha trunk shows quite high heating value (17.9 MJ/kg) due to its high carbon content while the heating value of napier grass is quite low (16.0 MJ/kg) due to its high ash content which is about 15.7 wt%. Eucalyptus trunk has the percentage of carbon content about 46.0 wt% but has the highest value of heating value which from its very low ash content. Cassava rhizome has the lowest percentage of carbon content (41.6 wt%) and its heating value is about 16.1 MJ/kg.

The proximate analyses of biomass were studied from their TGA curves which are shown in Figures 4.1 – 4.4. In the experiment, about 5 mg of biomass sample was heated in nitrogen atmosphere from room temperature to 900°C by 10°C/minute heating rate. From TGA curve, the percentage of volatile matter was estimated from the weight loss at the temperature between 110 - 900°C in nitrogen atmosphere while the percentage of fixed carbon was estimated from the weight loss at the 900°C in air atmosphere and the percentage of ash was estimated from the weight remaining at 900°C in air atmosphere. The proximate analyses results from TGA curves of raw biomass samples are presented in Table 4.1. Volatile matter is the majority content of all biomass samples and eucalyptus trunk has the highest percentage of volatile matter which is 86.2 wt%, while napier grass has the lowest percentage of volatile matter which is 74.3 wt%. Eucalyptus trunk and jatropha trunk have quite high percentages of fixed carbon which are 12.3 and 12.7 wt%,

respectively. Among all samples, napier grass has the highest percentage of ash content which is 15.7 wt%, while eucalyptus trunk has very low percentage of ash content which is 1.5 wt%.

One of the most important fuel components is the volatile matter. This component has a very large impact on the ignitability and burnout characteristics of solid fuels. Volatile matter is driven out of the fuel when the fuel is heated and it ignites readily, thus supporting ignition of the fuel. Fixed carbon is the other component in solid fuels that burn. Fixed carbon is more difficult to ignite and burns more slowly than volatile matter but releases more energy [36]. The ratio between fixed carbon and volatile matter which is called a fuel ratio has been used as an index of combustion performance. This ratio can be calculated from the information of proximate analyses. It is well-known that fuel with a higher fuel ratio is more difficult to burn but releases the higher energy than a fuel with a lower ratio. From the studied samples, jatropha trunk which has the highest percentage of carbon content also has the highest value of fuel ratio which is about 0.15. On the other hand, cassava rhizome which has lowest percentage of carbon content also has the lowest value of fuel ratio which is about 0.11.

Figure 4.5 compares the TGA curves of all studied samples. Pyrolysis behavior of each biomass from TGA curve does not look much different, especially in dry ash free basis. From TGA curves, jatropha trunk was decomposed at the lowest temperature, while the others were decomposed at the same temperature range which is higher than the initial decomposition temperature of jatropha trunk. The decomposition behavior of each biomass sample is significant according to their physical composition, chemical composition and chemical bond as well.

Table 4.1 Chemical properties analyses of raw biomass samples

	Raw sample					
	Cassava rhizome	Eucalyptus trunk	Jatropha trunk	Napier grass		
Ultimate analyses (wt%, d.a.f.)						
С	41.6	46.0	46.6	46.6		
Н	5.6	6.1	6.0	6.5		
N	2.2	0.3	0.6	1.3		
0	50.6	47.6	46.8	45.6		
HHV (MJ/kg, d.b.)	16.1	18.0	17.9	16.0		
Proximate analyses (wt%, d.b.)						
Volatile matter	85.1	86.2	83.8	74.3		
Fixed carbon	9.2	12.3	12.7	10.0		
Ash	5.7	1.5	3.5	15.7		
Fuel ratio (-)	0.11	0.14	0.15	0.13		

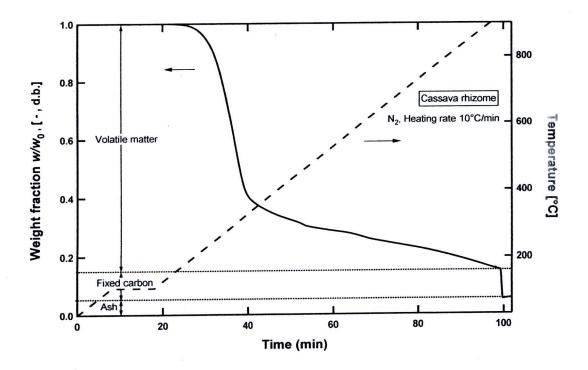


Figure 4.1 TGA curve of raw cassava rhizome

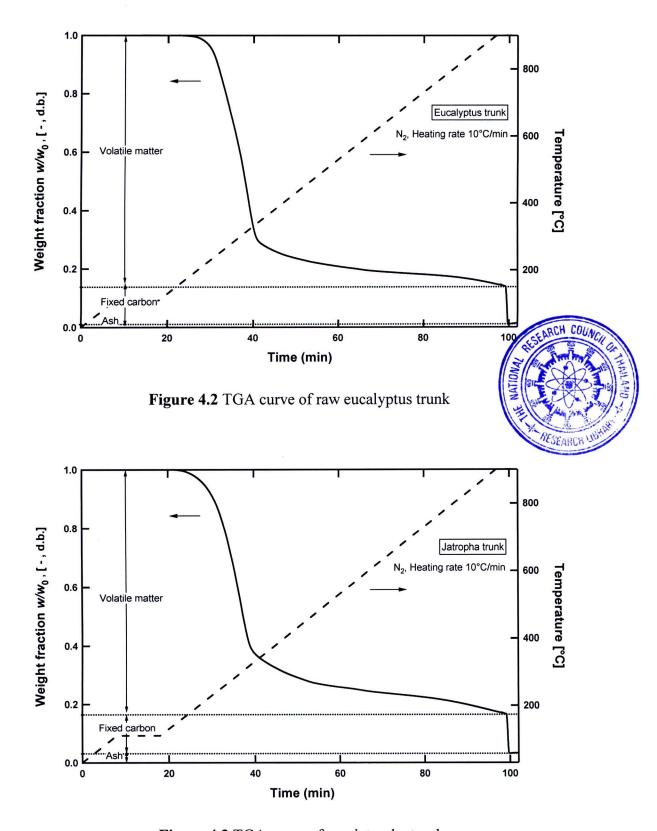


Figure 4.3 TGA curve of raw jatropha trunk

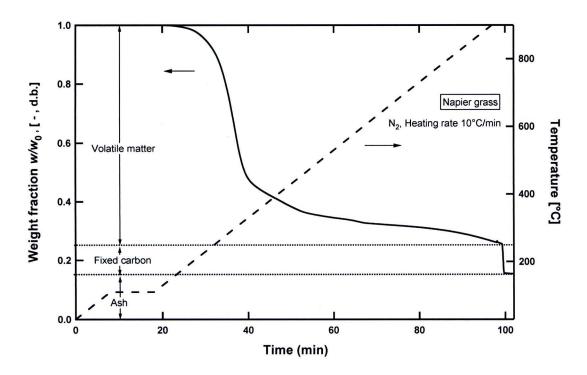


Figure 4.4 TGA curve of raw napier grass

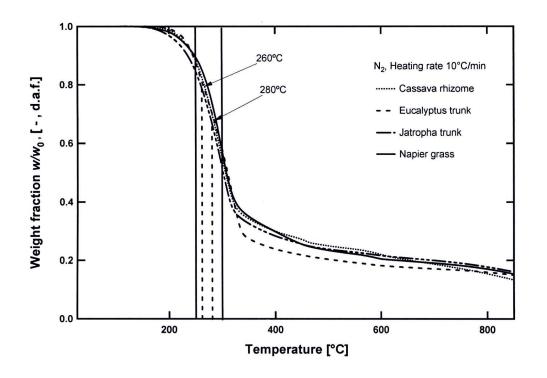


Figure 4.5 TGA curves of raw cassava rhizome, eucalyptus trunk, jatropha trunk, and napier grass

4.1.2 Chemical composition analyses

The chemical composition of lignocellulosic biomass is highly variable because of its genetic and environmental influences. The chemical compositions of raw biomass samples are presented in Table 4.2. Napier grass has the highest percentage of extractive (13.3 wt%), while eucalyptus trunk has the lowest percentage of extractive which is only 1.1 wt%. The percentages of hemicellulose of raw samples are between 33.9 – 42.1 wt%. Napier grass and jatropha trunk have high hemicellulose contents which are 42.1 and 38.3 wt%. The early decomposition of napier grass and jatropha trunk from the compared TGA curves in figure 4.5 may be because of their high hemicellulose contents which was decomposed in lower temperature than cellulose and lignin. The percentages of cellulose of raw samples are in between 29.1 – 37.1 wt%. Among all samples, eucalyptus trunk has the highest percentage of cellulose which is 37.1 wt%, cassava rhizome and eucalyptus trunk have the highest percentage of lignin content (25.9 wt%), whereas napier grass has the lowest lignin content (15.4 wt%). The percentages of lignin of raw samples are between 15.4 – 25.9 wt%.

Table 4.2 Chemical composition analyses (wt%, d.a.f.) of biomass sample

Cample	Chemical composition analyses (wt%, d.a.f.)								
Sample	Extractive	Hemicellulose	Cellulose	Lignin					
Cassava rhizome	11.1	33.9	29.1	25.9					
Eucalyptus trunk	1.1	35.9	37.1	25.9					
Jatropha trunk	6.7	38.3	31.9	23.1					
Napier grass	13.3	42.1	29.1	15.4					

4.1.3 Study of pyrolysis of raw biomass samples by TG-MS technique

TG-MS technique was used to study the pyrolysis behavior of biomass in more detail than the use of TGA curve. From TG-MS technique, both weight loss curve and the evolving rate of all pyrolysis products were shown. Figures 4.6 – 4.9 show the pyrolysis behavior of eucalyptus trunk, cassava rhizome, jatropha trunk and napier grass from TG-MS technique. The weight fraction of tar can be quantified from the difference between the weight loss curve or TGA curve of biomass sample and the summation of TGA curves of CH₄, CO₂, CO and H₂O. Although, the pyrolysis behavior of raw samples look not much different from each other when compared by TGA curve. However from TG-MS technique, their behaviors look clearly different. H₂O was the majority product gas of all studied sample pyrolysis, while CO and CO₂ were evolved less than H₂O, and CH₄ has very few evolutions. Among all biomass samples, cassava rhizome released the highest amount of H₂O, while napier grass released the highest amount of CO₂ and eucalyptus trunk released the highest amount of CO. From graph, H₂O started to be released at temperature lower than 200°C, while the others are released at temperature higher than 200°C. The early releasing of H₂O was from the early decomposition of hemicellulose in biomass sample.

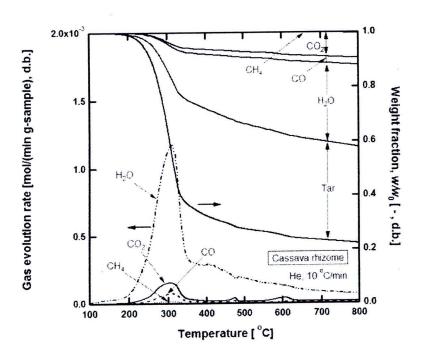


Figure 4.6 TG curves, gas formation rates, and product distribution during the pyrolysis of cassava rhizome

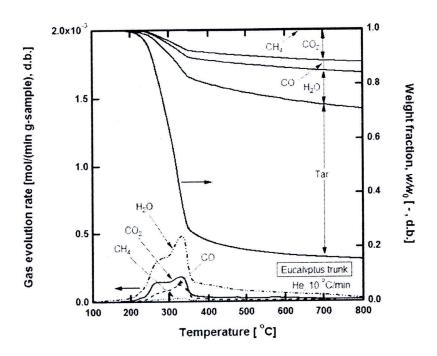


Figure 4.7 TG curves, gas formation rates, and product distribution during the pyrolysis of eucalyptus trunk

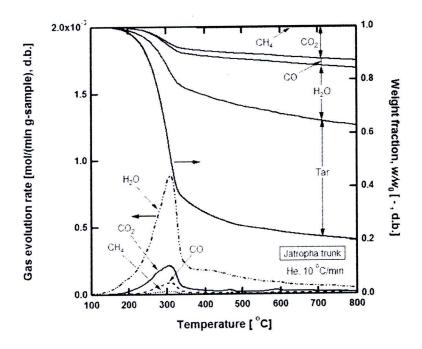


Figure 4.8 TG curves, gas formation rates, and product distribution during the pyrolysis of jatropha trunk

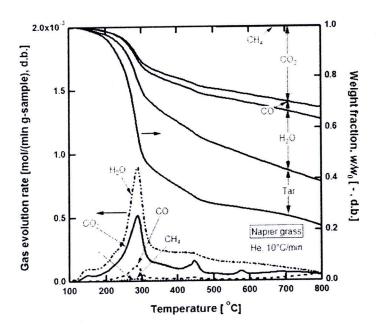


Figure 4.9 TG curves, gas formation rates, and product distribution during the pyrolysis of napier grass.

4.1.4 Study of pyrolysis at different temperatures and holding times by TGA technique

The slow pyrolysis at different final temperatures and holding times were pre-studied by the use of TGA. In this experiment, the raw biomass was heated by 10°C/min in nitrogen atmosphere to 110°C and held at this temperature in order to remove the sample's moisture. Then the dry sample was heated from 110°C to pyrolysis temperatures which are 200, 225 and 250°C and held at these temperatures for more than 1 hour. The results from this experiment were the fraction of remaining weights at different pyrolysis temperatures and holding times.

Figures 4.10 – 4.13 show the TGA curves of low temperature pyrolysis at 200, 225 and 250°C. From the weight decreasing profile, the remaining weights of all biomass were found to decrease with increasing of pyrolysis temperature and holding time. The weights of all biomass were significantly decreased in heating period. From pyrolysis at 200°C, the remaining weights of all studied samples were very high. At 200°C and after 60 min of holding time, the weight remaining of cassava rhizome, eucalyptus trunk, jatropha trunk and napier grass were 93.9, 95.0, 90.8, and 85.6 wt%, respectively. On the other hand, pyrolysis at 250°C with holding step gave quite low remaining solid yields. At 250°C and after 60 min of holding time, the weight remaining of cassava rhizome, eucalyptus trunk, jatropha trunk and napier grass were 62.3, 64.2, 55.6, and 49.8 wt%, respectively.

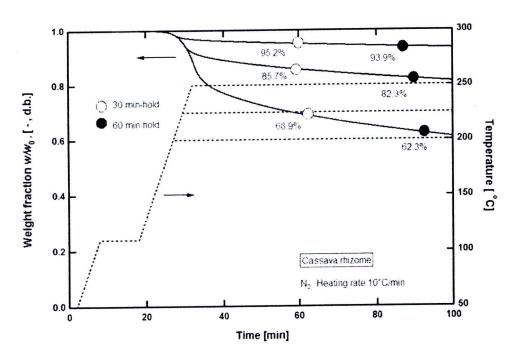


Figure 4.10 Mass loss of cassava rhizome during the pyrolysis at different final temperature

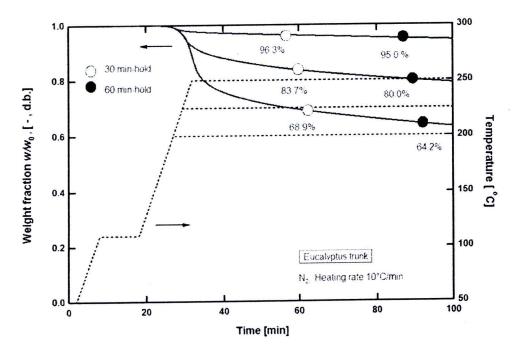


Figure 4.11 Mass loss of eucalyptus trunk during the pyrolysis at different final temperature

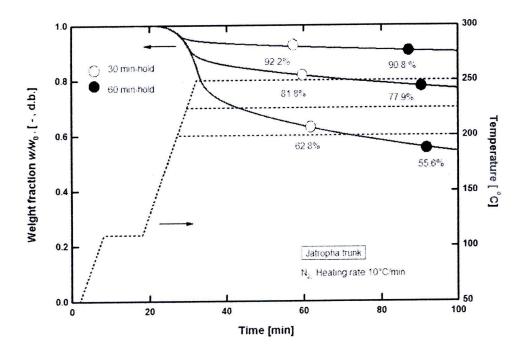


Figure 4.12 Mass loss of jatropha trunk during the pyrolysis at different final temperature

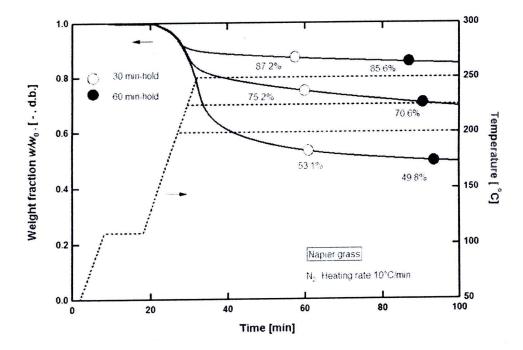


Figure 4.13 Mass loss of napier grass during the pyrolysis at different final temperature

4.2 Analyses of torrefied biomass from fast pyrolysis

4.2.1 Study of pyrolysis behavior of each biomass in fast pyrolysis

Fast pyrolysis was studied by using of drop tube reactor with heating rate more than 200°C/sec in inert atmosphere. The pyrolysis temperatures were 250 °C, 275 °C and 300 °C and the holding times were in the range of 5 - 100 sec. Figures 4.14 – 4.17 show the change in weight of biomass samples through the fast pyrolysis at 250 °C, 275 °C and 300°C in nitrogen atmosphere. At the same reaction time, the treated sample at higher temperature has lower solid yield compared to the treated sample at lower temperature. And for all samples, the differences between solid yields of each reaction time at the same pyrolysis temperature were dominant for short time range and became quite constant at longer reaction times.

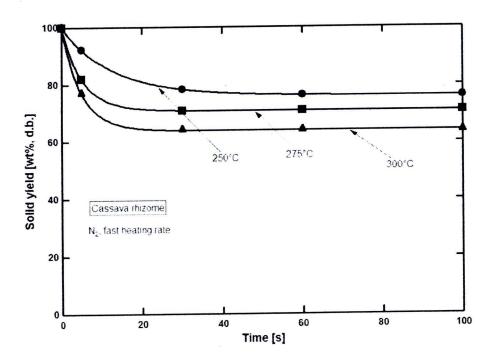


Figure 4.14 Change of weight of cassava rhizome through the fast pyrolysis

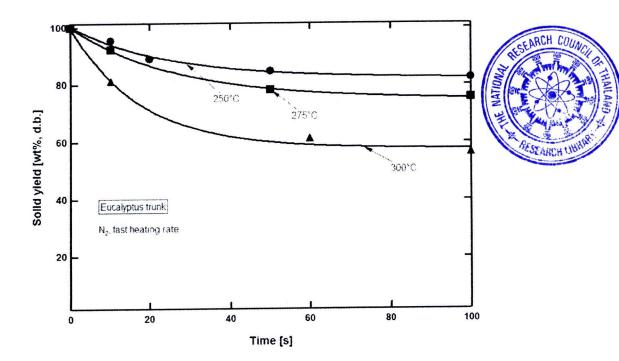


Figure 4.15 Change of weight of eucalyptus trunk through the fast pyrolysis

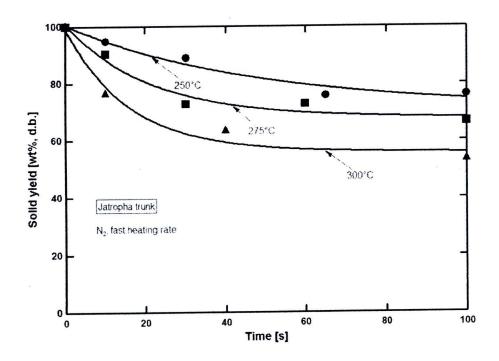


Figure 4.16 Change of weight of jatropha trunk through the fast pyrolysis

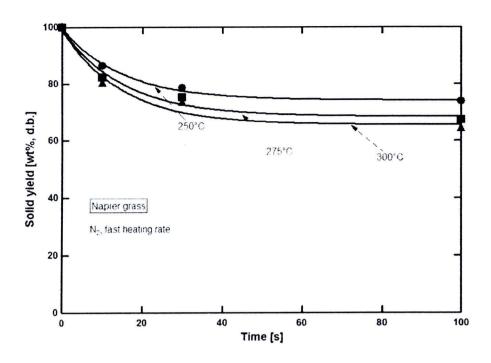


Figure 4.17 Change of weight of napier grass through the fast pyrolysis

4.2.2 Ultimate analyses and calorific values of torrefied biomass from fast pyrolysis

The ultimate analyses and calorific values of torrefied biomass from fast pyrolysis are presented in Tables 4.3 – 4.6. For all pyrolysis temperatures, the percentages of carbon contents were found to be increased when increasing the retention time of pyrolysis. Apart from that, the carbon contents of all torrefied samples were also found to be increased when increasing the pyrolysis temperature. On the other hand, the percentages of hydrogen and oxygen were found to be decreased when the pyrolysis temperature and retention time were increased while the percentages of nitrogen contents of torrefied samples through the fast pyrolysis were quite constant. The torrefied samples have higher heating values due to their higher carbon contents compared to raw sample. Apart from that, the percentages of ash content in torrefied samples were also increased due to the decrease in their mass yields. The fast pyrolysis at 300°C with 100 s retention time give the highest increase in carbon content and heating value among all studied fast pyrolysis conditions. By fast pyrolysis at 300°C for 100 s, the heating value of torrefied cassava rhizome, eucalyptus trunk, jatropha trunk and napier grass were increased to 16.6, 19.0, 19.5 and 16.3 MJ/kg, respectively.

From fast pyrolysis experiment, even the heating values of torrefied samples were increased but the increase was very little compared to the decrease in their torrefied yields.

For example, the heating value of torrefied eucalyptus trunk was increased only from 18.0 to 19.0 MJ/kg while the torrefied yield was decreased by almost 50%wt by fast pyrolysis at 300°C for 100 s. These results indicate that fast pyrolysis may not be suitable for biomass upgrading which requires significant increase in heating value but acceptable decrease in torrefied yield.

Table 4.3 Ultimate analyses (wt%, d.a.f.), solid yields (wt%, d.b.), ash contents (wt%, d.b.) and calorific values (MJ/kg, d.b.) of torrefied cassava rhizome from fast pyrolysis

	U	Iltimate (wt%,		S	Yield	Ash	HHV
Cassava rhizome	C	Н	N	О	(wt%, d.b.)	(wt%, d.b.)	(MJ/kg, d.b.)
Raw	41.6	5.6	2.2	50.6	100.0	5.7	16.1
250°C, 5s	41.7	5.5	2.3	50.5	92.3	6.2	16.1
250°C, 30s	420	5.1	2.4	50.5	78.3	7.3	16.2
250°C, 60s	42.4	5.3	2.2	50.1	76.3	7.5	16.2
250°C, 100s	42.6	5.2	2.2	50.0	76.0	7.5	16.3
275°C, 5s	42.1	5.6	2.2	50.1	82.1	6.9	16.1
275°C, 30s	42.9	5.5	2.3	49.3	70.9	8.0	16.2
275°C, 60s	43.1	5.3	2.2	49.5	70.8	8.0	16.3
275°C, 100s	43.6	5.4	2.3	48.7	70.8	8.5	16.4
300°C, 5s	42.4	5.5	2.2	49.9	77.1	6.9	16.2
300°C, 30s	43.0	5.4	2.2	49.4	64.1	8.0	16.3
300°C, 60s	43.4	5.0	2.3	49.3	63.9	8.0	16.5
300°C, 100s	43.9	4.6	2.3	49.2	63.7	8.5	16.6

Table 4.4 Ultimate analyses (wt%, d.a.f.), solid yields (wt%, d.b.), ash contents (wt%, d.b.) and calorific values (MJ/kg, d.b.) of torrefied eucalyptus trunk from fast pyrolysis

	U	Ultimate (wt%,	analyse d.a.f.)	es	Yield	Ash	нну
Eucalyptus trunk	C	Н	N	О	(wt%, d.b.)	(wt%, d.b.)	(MJ/kg, d.b.)
Raw	46.0	6.1	0.3	47.6	100.0	1.5	18.0
250°C, 10s	46.5	6.0	0.3	47.2	95.4	1.6	18.2
250°C, 20s	46.9	6.0	0.3	46.8	89.1	1.7	18.3
250°C, 50s	47.7	6.2	0.2	45.9	84.6	1.8	18.6
250°C, 100s	48.2	6.0	0.2	45.6	82.4	1.8	18.8
275°C, 10s	46.8	5.9	0.3	47.0	92.4	1.7	18.3
275°C, 50s	47.5	5.9	0.3	46.3	78.3	1.9	18.5
275°C, 100s	48.3	5.8	0.3	45.6	75.4	2.0	18.8
300°C, 10s	47.2	5.6	0.3	46.9	80.9	1.9	18.3
300°C, 30s	48.2	5.4	0.3	46.1	76.6	2.0	18.7
300°C, 60s	49.3	5.3	0.3	45.1	61.1	2.5	18.9
300°C, 100s	49.7	5.2	0.3	44.8	56.1	2.7	19.0

Table 4.5 Ultimate analyses (wt%, d.a.f.), solid yields (wt%, d.b.), ash contents (wt%, d.b.) and calorific values (MJ/kg, d.b.) of torrefied jatropha trunk from fast pyrolysis

	l	Ultimate (wt%,	analyse d.a.f.)	S	Yield	Ash	нну
Jatropha trunk	C	Н	N	0	(wt%, d.b.)	(wt%, d.b.)	(MJ/kg, d.b.)
Raw	46.6	6.0	0.6	46.8	100.0	3.5	17.9
250°C, 10s	46.9	5.8	0.6	46.7	94.8	3.7	18.0
250°C, 30s	47.3	5.7	0.6	46.4	88.9	3.9	18.1
250°C, 65s	47.4	6.0	0.6	46.0	75.7	4.6	18.0
250°C, 100s	49.7	5.8	0.6	43.9	73.6	4.8	18.8
275°C, 10s	47.1	5.5	0.6	46.8	90.4	3.9	18.0
275°C, 30s	50.3	5.7	0.7	43.3	72.8	4.8	19.0
275°C, 60s	50.4	5.1	0.6	43.9	72.7	4.8	18.9
275°C, 100s	51.5	5.9	0.7	41.9	66.5	5.3	19.4
300°C, 10s	48.7	5.8	0.7	44.8	76.5	4.6	18.4
300°C, 40s	50.6	5.6	0.7	43.1	63.4	5.5	18.9
300°C, 100s	52.7	5.7	0.9	40.7	53.1	6.6	19.5

Table 4.6 Ultimate analyses (wt%, d.a.f.), solid yields (wt%, d.b.), ash contents (wt%, d.b.) and calorific values (MJ/kg, d.b.) of torrefied napier grass from fast pyrolysis

	Į	Iltimate (wt%,	100	es	Yield	Ash	HHV
Napier grass	C	Н	N	О	(wt%, d.b.)	(wt%, d.b.)	(MJ/kg, d.b.)
Raw	46.6	6.5	1.3	45.6	100.0	15.7	16.0
250°C, 10s	47.8	6.4	1.2	44.6	86.4	18.2	15.9
250°C, 50s	48.8	6.3	1.3	43.7	78.5	20.0	16.0
250°C, 100s	49.3	6.3	1.3	43.1	73.7	21.3	15.9
275°C, 10s	48.7	6.3	1.2	43.8	82.3	19.1	16.1
275°C, 50s	49.9	6.2	1.3	42.7	75.3	20.8	16.1
275°C, 100s	52.1	5.9	1.3	40.7	67.2	23.4	16.4
300°C, 10s	48.5	6.3	1.2	44.0	80.0	19.6	16.0
300°C, 60s	50.5	6.3	1.3	41.9	73.2	21.4	16.2
300°C, 100s	52.8	6.0	1.3	39.9	63.9	24.6	16.3

4.3 Analyses of torrefied biomass from slow pyrolysis

4.3.1 Ultimate analyses and calorific values of torrefied biomass from slow pyrolysis

Slow pyrolysis was studied by the use of a fixed bed reactor at pyrolysis temperatures 260 and 280°C with heating rate about 10°C/min in inert atmosphere. After experiments, the torrefied solids were collected in order to measure the solid weights and do their fuel properties analysis. Table 4.7 presents the ultimate analyses and calorific values of torrefied biomass from slow pyrolysis at 260 and 280°C without holding. For all biomass types, the slow pyrolysis at both temperatures gave the torrefied solid higher carbon contents than raw biomass. Between the two temperatures, slow pyrolysis at 280°C gave the higher increase in percentage of carbon content than slow pyrolysis at 260°C. After pyrolysis, the percentages of hydrogen and oxygen of torrefied samples were found to be decreased, while the percentages of nitrogen were quite constant. In the same way as fast pyrolysis, the ash contents of torrefied samples were increased due to the mass loss during the processes. The calculated heating values of torrefied biomass were also increased. These increases in heating values were brought about by the increasing in carbon content of torrefied biomass. The heating values of torrefied biomass from 280°C pyrolysis were significantly increased in comparison to the decreasing in solid yields. Moreover, the heating values of torrefied samples from slow pyrolysis were also significantly increased in comparison to fast pyrolysis at the same solid yields. By slow pyrolysis at 280°C, the heating value of torrefied eucalyptus trunk was increased from 18.0 up to 20.0 MJ/kg, while the solid yield was decreased by only about 20%wt. Apart from eucalyptus trunk, the heatng values of torrefied cassava rhizome, jatropha trunk and napier grass were also significantly increased by slow pyrolysis at 280°C. From this condition, the heating values of torrefied cassava rhizome, jatropha trunk and napier grass were increased to 19.1, 20.8 and 19.3 MJ/kg, respectively.

Table 4.7 Ultimate analyses (wt%, d.a.f.), solid yields (wt%, d.b.), ash content (wt%, d.b.) and calorific values (MJ/kg, d.b.) of torrefied biomass samples from slow pyrolysis

	U		analyse d.a.f.]	S	Yield	HHV	
Sample	C	Н	N	О	[wt%, d.b.]	[wt%, d.b.]	[MJ/kg, d.b.]
Cassava rhizome							
Raw	41.6	5.6	2.2	50.6	100.0	5.7	16.1
260°C, 0s	45.9	5.3	2.5	46.3	84.0	6.8	17.3
280°C, 0s	52.6	4.9	2.7	39.8	68.3	8.3	19.1
Eucalyptus trunk							
Raw	46.0	6.1	0.3	47.6	100.0	1.5	18.0
260°C, 0s	49.1	5.8	0.3	44.8	88.6	1.7	19.1
280°C, 0s	51.7	5.3	0.3	42.7	83.2	1.8	20.0
Jatropha trunk							
Raw	46.6	6.0	0.6	46.8	100.0	3.5	17.9
260°C, 0s	51.5	6.0	0.8	41.7	83.0	4.2	19.6
280°C, 0s	54.7	5.9	0.8	38.6	74.2	4.7	20.8
Napier grass							
Raw	46.6	6.5	1.3	45.6	100.0	15.7	16.0
260°C, 0s	55.6	6.6	1.5	36.3	78.4	20.0	17.8
280°C, 0s	62.9	6.7	1.6	28.8	69.2	22.7	19.3

4.4 Comparison between fast and slow pyrolysis results

4.4.1 Comparison between torrefied yields and calorific values of torrefied biomass from both types of pyrolysis

Table 4.8 shows the solid yields and the percentage increases in heating value of torrefied biomass from both fast and slow pyrolysis. Considering both solid yield and heating value, slow pyrolysis gave the torrefied products higher heating values and higher torrefied yields in comparison to fast pyrolysis. The heating value of torrefied cassava rhizome from slow pyrolysis at 280°C was increased by about 18.6% at 64.3 wt% solid yield. Meanwhile, the heating value of torrefied cassava rhizome from fast pyrolysis at 300°C was increased by only about 3.0% at 63.7 wt% solid yield. Consistent with cassava rhizome, the increase in heating values of torrefied eucalyptus trunk, jatropha trunk and napier grass from slow pyrolysis is also significantly more than those from fast pyrolysis. From slow pyrolysis at 280°C, the heating values of eucalyptus trunk, jatopha trunk and napier grass were increased about 11.0, 16.1 and 20.7 % at 83.2, 74.2 and 69.2 wt% solid yields, respectively.

Table 4.8 Solid yields (wt%, d.b.), calorific values (MJ/kg, d.b.) and increase in calorific values (%) of torrefied biomass samples from fast and slow pyrolysis

		Yield	HHV		
		(wt%, d.b.)	(MJ/kg, d.b.)	% increase in HHV	
Sample Cassava rhizome					
		100.0	16.1	0.0	
raw					
fast heating rate,	250°C, 100s	76.0	16.3	1.3	
	275°C, 100s	70.8	16.4	1.9	
	300°C, 100s	63.7	16.6	3.1	
slow heating rate,	260°C, 0s	84.0	17.3	7.5	
	280°C, 0s	64.3	19.1	18.6	
Eucalyptus trunk					
raw		100.0	18.0	0.0	
fast heating rate,	250°C, 100s	82.4	18.8	4.3	
	275°C, 100s	75.4	18.8	4.2	
	300°C, 100s	56.1	19.0	5.6	
slow heating rate,	260°C, 0s	88.6	19.1	6.3	
	280°C, 0s	83.2	20.0	11.1	
Jatropha trunk					
raw		100.0	17.9	0.0	
fast heating rate,	250°C, 100s	73.6	18.8	5.0	
	275°C, 100s	66.5	19.4	8.4	
	300°C, 100s	53.1	19.5	8.9	
slow heating rate,	260°C, 0s	83.0	19.6	9.5	
	280°C, 0s	74.2	20.8	16.2	
Napier grass					
raw		100.0	16.0	0.0	
fast heating rate,	250°C, 100s	73.7	15.9	-0.3	
	275°C, 100s	67.2	16.4	2.5	
	300°C, 100s	63.9	16.3	2.1	
slow heating rate,	260°C, 0s	78.4	17.8	11.3	
	280°C, 0s	69.2	19.3	20.7	

4.4.2 Fuel properties of torrefied biomass from both types of pyrolysis

The atomic ratios of H/C and O/C of the raw and torrefied biomass samples were calculated from their ultimate analysis results. The plots between these ratios were used to indicate the change in elemental composition of the torrefied biomass. Figure 4.18 – 4.21 are the diagrams plotted between H/C and O/C of raw, torrefied biomass and Mae moh lignite. From these diagrams, the elementary compositions of torrefied biomass were moved toward Mae moh lignite. The trends of these changes were decreased in both H/C and O/C ratios. It was found that, the elementary compositions of torrefied biomass from slow pyrolysis have more significant change from raw biomass than fast pyrolysis. This result implied that slow pyrolysis gave torrefied biomass more favorable fuel properties than raw and torrefied biomass from fast pyrolysis. Slow pyrolysis at 280°C was found as the optimum condition which gave torrefied biomass fuel properties nearest to coal.

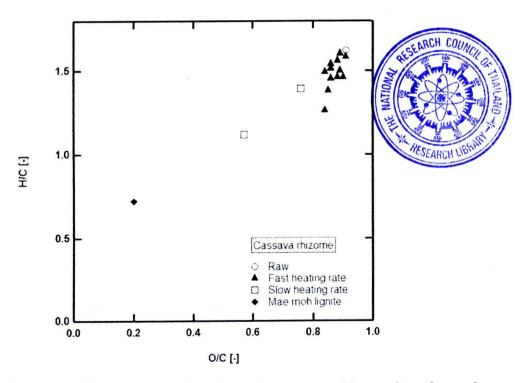


Figure 4.18 H/C versus O/C diagram of raw and torrefied cassava rhizome from fast and slow pyrolysis

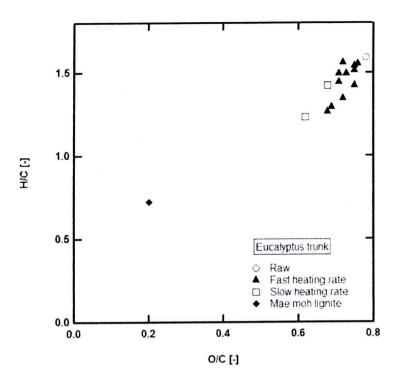


Figure 4.19 H/C versus O/C diagram of raw and torrefied eucalyptus trunk from fast and slow pyrolysis

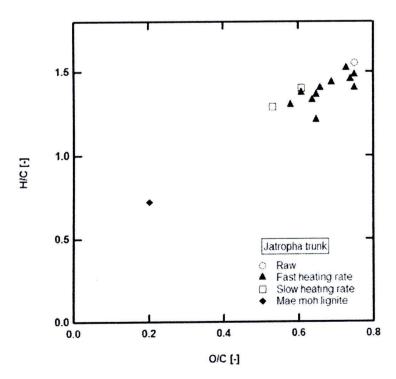


Figure 4.20 H/C versus O/C diagram of raw and torrefied jatropha trunk from fast and slow pyrolysis

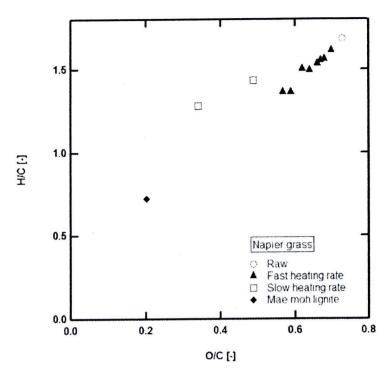


Figure 4.21 H/C versus O/C diagram of raw and torrefied napier grass from fast and slow pyrolysis

Figure 4.22 – 4.25 show the relationships between solid yield and heating value of the torrefied samples from both fast and slow pyrolysis. For both types of pyrolysis, the heating values of torrefied biomass were increased with the decreasing of solid yields. The trend lines of fast heating rate pyrolysis have quite high slopes compared to the trend lines of slow heating rate pyrolysis. It can be concluded from this relationship that to reach the same value of heating value, slow pyrolysis gave the higher torrefied solid yield than fast pyrolysis. Therefore, slow poyrolysis was more suitable than fast pyrolysis in order to increase the heating values of torrefied biomass with not too much decreasing in torrefied yields.

The relationships between solid yields and heating values of the torrefied samples from slow pyrolysis were shown in Figure 4.26. From the diagram, the slopes of trend lines of all samples were quite similar which means the relationship between an increase in calorific value and a decrease in solid yields of each studied sample were in the same trend.

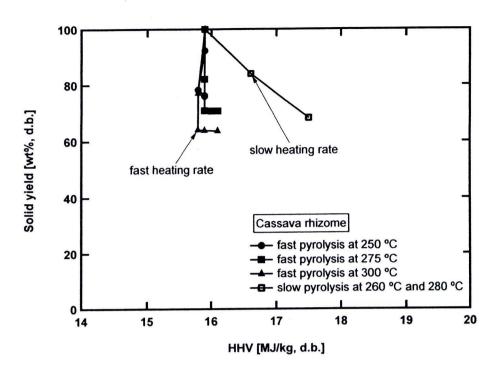


Figure 4.22 Solid yield versus heating value diagram torrefied cassava rhizome from fast and slow pyrolysis

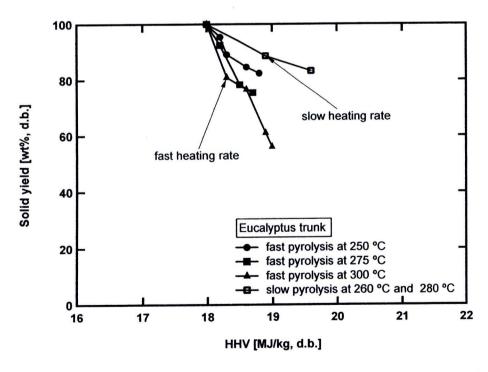


Figure 4.23 Solid yield versus heating value diagram of torrefied eucalyptus trunk from fast and slow pyrolysis

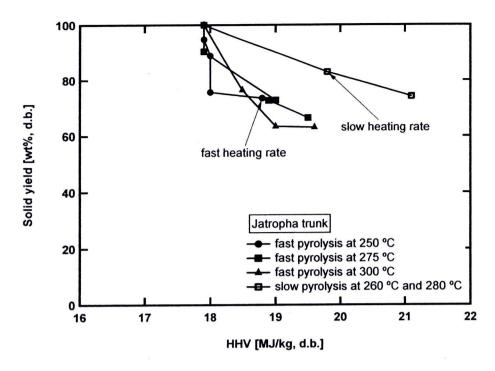


Figure 4.24 Solid yield versus heating value diagram of torrefied jatropha trunk from fast and slow pyrolysis

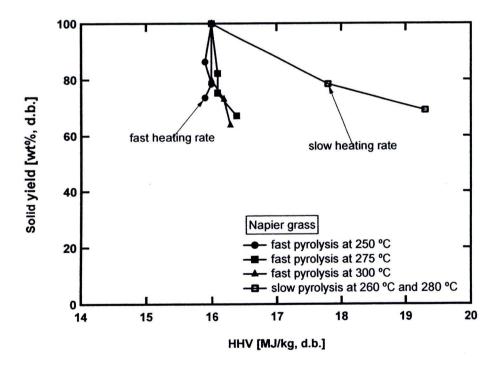


Figure 4.25 Solid yield versus heating value diagram of torrefied napier grass from fast and slow pyrolysis

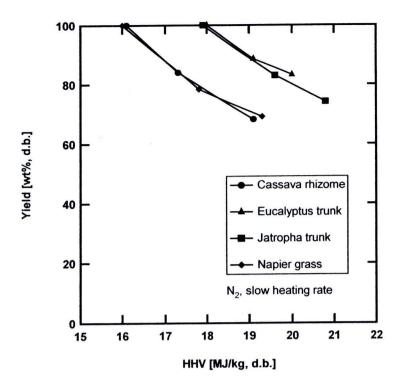


Figure 4.26 Solid yield versus heating value diagram of torrefied biomass samples from slow pyrolysis

The energy density is one of an important indicator for the solid fuel property comparison. The values of energy density were calculated from the mass and energy yields of biomass. Figures 27 - 30 show the bar graphs of energy density of raw and torrefied biomass from both fast and slow pyrolysis. For each biomass, the torrefied samples from fast pyrolysis were found to have lower energy density compared to the torrefied sample from slow pyrolysis. The torrefied cassava rhizome from fast pyrolysis at 300°C has the energy density only 1.03 - while the energy density of torrefied cassava rhizome from slow pyrolysis at 280°C was up to 1.19. Of the two slow pyrolysis conditions, the slow pyrolysis at 280°C gave the torrefied biomass with higher energy density than the slow pyrolysis at 260°C. For example, the energy density of torrefied napier grass from slow pyrolysis at 280°C was about 1.21 while the energy density from slow pyrolysis at 260°C was only about 1.11. Considering the energy density, slow pyrolysis at 280°C was the best condition among all studied conditions which gave the torrefied biomass with the highest energy density.

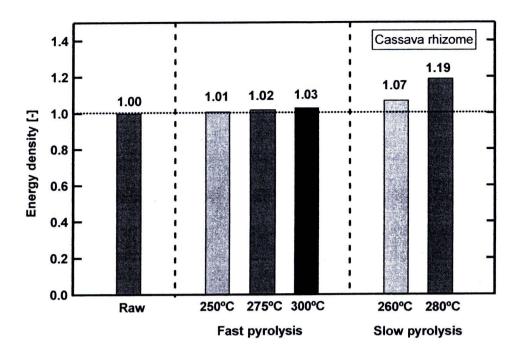


Figure 4.27 Energy density of raw and torrefied cassava rhizome from both fast and slow pyrolysis

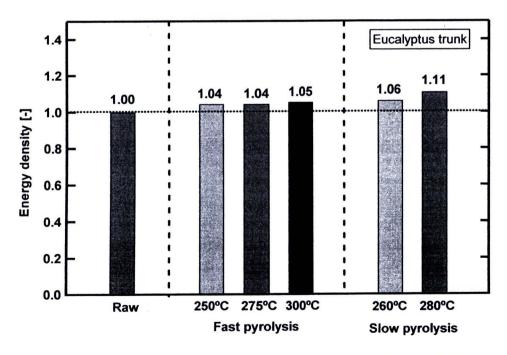


Figure 4.28 Energy density of raw and torrefied eucalyptus trunk from both fast and slow pyrolysis

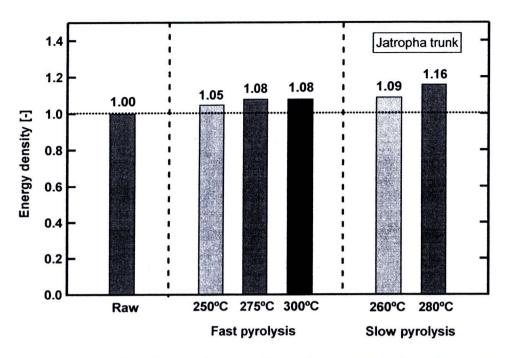


Figure 4.29 Energy density of raw and torrefied jatropha trunk from both fast and slow pyrolysis

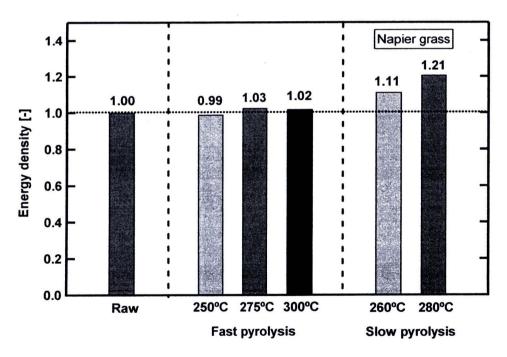


Figure 4.30 Energy density of raw and torrefied napier grass from both fast and slow pyrolysis

4.5 In-depth study of slow pyrolysis processes

4.5.1 Mass and energy yields of torrefied biomass from slow pyrolysis

Mass and energy yields are the other indicators used to study the performance of upgrading technique. The energy yield of each torrefied biomass was calculated from its heating value and mass yield. The mass and energy yields of torrefied biomass are shown in Figure 4.31 – 4.34. The mass yields of torrefied biomass were found to decrease when increasing the pyrolysis temperature. The trend of energy yields of torrefied biomass were consistent with mass yields which were decreased when increasing the pyrolysis temperature. The energy yields of all torrefied biomass were higher than mass yields which mean the energy loss during pyrolysis was less than the mass loss. From slow pyrolysis at 260°C and 280°C, torrefied eucalyptus trunks have the highest mass and energy yields among all studied samples.

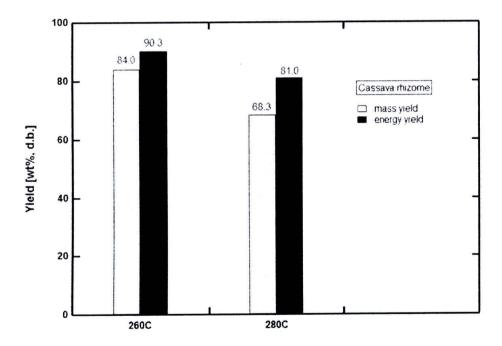


Figure 4.31 Mass and energy yields of treated cassava rhizome from slow pyrolysis at 260°C and 280°C

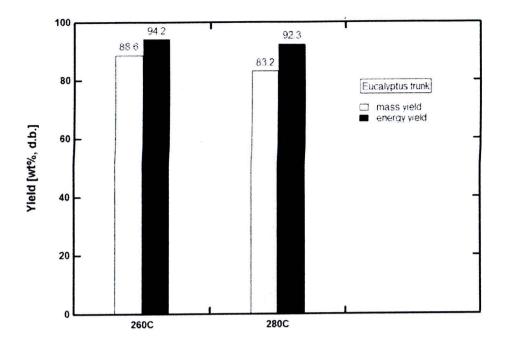


Figure 4.32 Mass and energy yields of treated eucalyptus trunk from slow pyrolysis at 260°C and 280°C

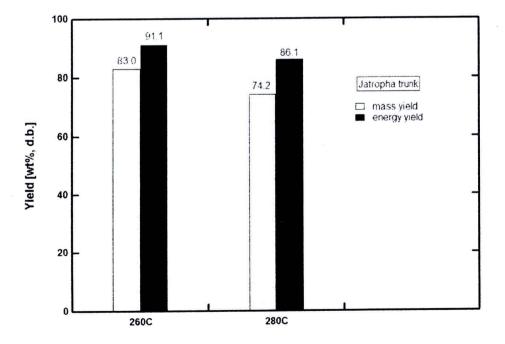


Figure 4.33 Mass and energy yields of treated jatropha trunk from slow pyrolysis at 260°C and 280°C

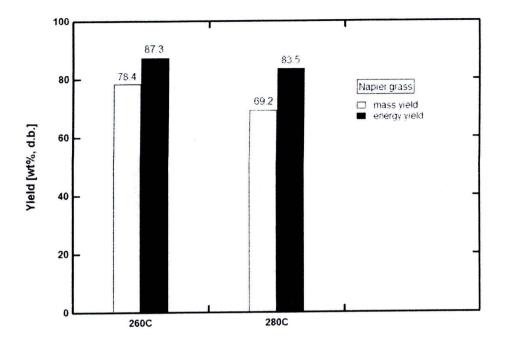


Figure 4.34 Mass and energy yields of treated napier grass from slow pyrolysis at 260°C and 280°C

4.5.2 Pyrolysis behaviors of torrefied biomass from slow pyrolysis

Figures 4.35 – 4.38 compare the pyrolysis behaviors of raw and torrefied cassava rhizome, eucalyptus trunk, jatropha trunk and napier grass, respectively. During the slow pyrolysis in N₂ atmosphere, torrefied biomass started to be decomposed at higher temperature than raw biomass. This late decomposition was from primary decomposition in upgrading process. The proximate analyses of each torrefied biomass can also be studied from its TGA curve. Table 4.9 shows the proximate analyses results and fuel ratios of torrefied biomass from both temperatures. It was found that the torrefied samples have less amount of volatile matter in comparison to raw biomass sample. On the other hand, the fixed carbon of torrefied samples was found to be increased by slow pyrolysis especially from 280°C. From slow pyrolysis at 280°C, the percentages of volatile matter of cassava rhizome, eucalyptus trunk, jatropha trunk, and napier grass were decreased to 73.1, 79.4, 79.5 and 11.5 wt%, respectively. On the other hand, their percentages of fixed carbon were increased to 18.6, 18.8, 15.8 and 14.9 wt%. The decrease in volatile matter and the increase in fixed carbon contents led to the increase in fuel ratios of torrefied biomass. From slow pyrolysis at 280°C,

the fuel ratios of cassava rhizome, eucalyptus trunk, jatropha trunk, and napier grass were increased from 0.11, 0.14, 0.15 and 0.13 to 0.25, 0.24, 0.20 and 0.24, respectively.

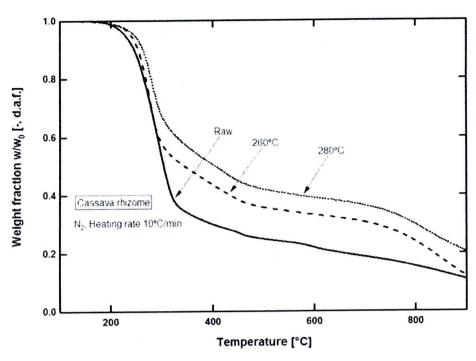


Figure 4.35 Pyrolysis behaviors of raw and torrefied cassava rhizome from slow pyrolysis

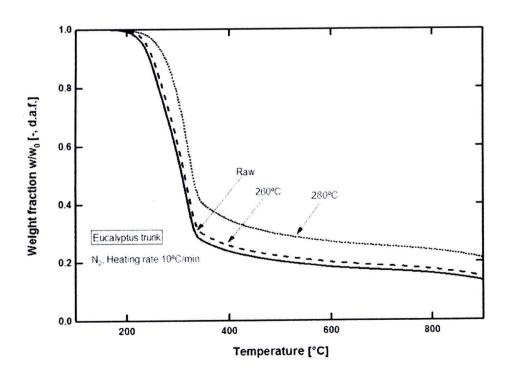


Figure 4.36 Pyrolysis behaviors of raw and torrefied eucalyptus trunk from slow pyrolysis

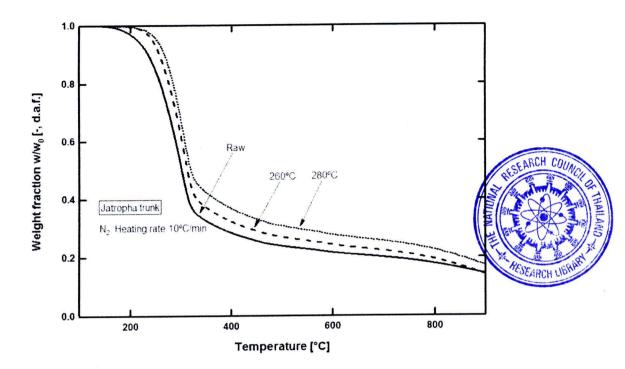


Figure 4.37 Pyrolysis behaviors of raw and torrefied jatropha trunk from slow pyrolysis

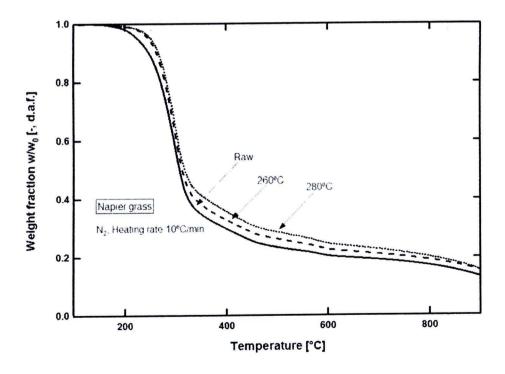


Figure 4.38 Pyrolysis behaviors of raw and torrefied napier grass from slow pyrolysis

Table 4.9 Proximate analyses (wt%, d.b.), and fuel ratio (-) of raw and torrefied biomass from slow pyrolysis at 260 and 280°C

Sla	Proxima	te analyses [wt%, d	.b.]	Fuel ratio [-]
Sample	Volatile matter	Fixed carbon	Ash	
Cassava rhizome				
Raw	85.1	9.2	5.7	0.11
260°C, 0s	79.9	13.3	6.8	0.17
280°C, 0s	73.1	18.6	8.3	0.25
Eucalyptus trunk				
Raw	86.2	12.3	1.5	0.14
260°C, 0s	85.9	12.4	1.7	0.14
280°C, 0s	79.4	18.8	1.8	0.24
Jatropha trunk				
Raw	83.8	12.7	3.5	0.15
260°C, 0s	83.0	12.8	4.2	0.15
280°C, 0s	79.5	15.8	4.7	0.20
Napier grass				
Raw	74.3	10.0	15.7	0.13
260°C, 0s	68.4	11.7	20.0	0.17
280°C, 0s	62.4	14.9	22.7	0.24

4.5.3 Product distributions through the slow pyrolysis

Figures 4.39 and 4.40 show the yields of products: torrefied solid, CO, H₂O, CO₂ and tar for the slow pyrolysis of cassava rhizome, eucalyptus trunk, jatropha trunk and napier grass at 260°C and 280°C, respectively. For slow pyrolysis at 260°C, napier grass produced the largest amount of CO₂ (6.3 wt%) and tar (10.1 wt%) but least amount of torrefied solid (78.4 wt%) among all samples. Cassava rhizome produced the largest amount of H₂O (4.3 wt%), while eucalyptus trunk produced the largest amount of torrefied solid(88.6 wt%). CO produced at this pyrolysis temperature from all samples was very low, napier grass also produced the largest amount of CO which is only 0.6 wt%. The percentage of products apart

from torrefied solid were increased when pyrolysed at 280°C. For slow pyrolysis at 280°C, cassava rhizome produced the largest amount of H₂O (9.4 wt%) and tar (18.4 wt%), whereas napier grass still produced the largest amount of CO₂ (10.1 wt%). Cassava rhizome has the lowest percentage of torrefied solid (68.3 wt%), while eucalyptus trunk still has the highest percentage of torrefied solid (83.2 wt%). The percentages of CO of torrefied products at 280°C were increased a little from that of 260°C. By increasing 20°C of pyrolysis temperature, the product distributions through the slow pyrolysis were clearly different. The increasing in pyrolysis temperature leads to the increasing in both condensable and noncondensable gaseous products, but decreasing in torrefied solid yield. All studied biomass samples have the different devolatilization behaviors, even though their elemental compositions are almost the same. The difference in devolatilization behavior of each biomass was from their differences in the physical and chemical structures and bonds.

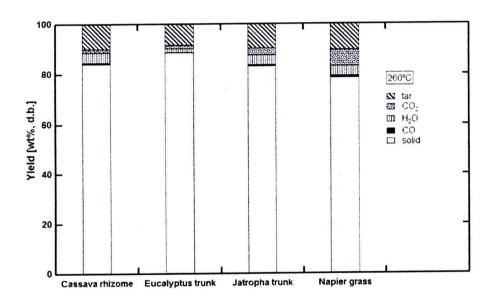


Figure 4.39 Product distributions trough the slow pyrolysis of biomass samples at 260°C

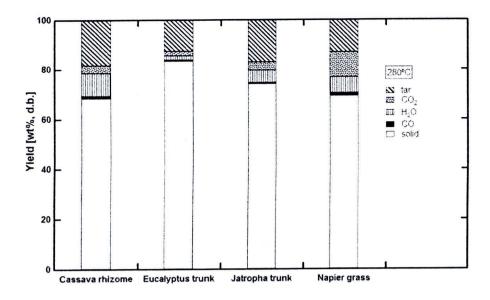


Figure 4.40 Product distributions trough the slow pyrolysis of biomass samples at 280°C

In order to do the mass and energy balances of pyrolysis process, the compositions of condensable volatile matter or tar were analyzed. Tar from pyrolysis process was trapped by quartz wool and then rinsed by liquid solvent which is isopropanol (IPA). The solution of tar in solvent was filtered and injected to GC – MS analyzer to identify the compositions of tar. Figures 4.41 - 4.44 show the intensity of each hydrocarbon species in tar compound from slow pyrolysis of studied biomass at 280°C. There are many light hydrocarbon species released during the pyrolysis process such as acetic acid, acetic anhydride, furfural, and butanal, 3-methyl. Among all species, acetic acid was found as one of the major components of tar formed during slow pyrolysis at low temperature due to its dominant peak area. From this result, acetic acid was used as the representative of condensable volatile or tar for the calculation in mass and energy balances of this study.

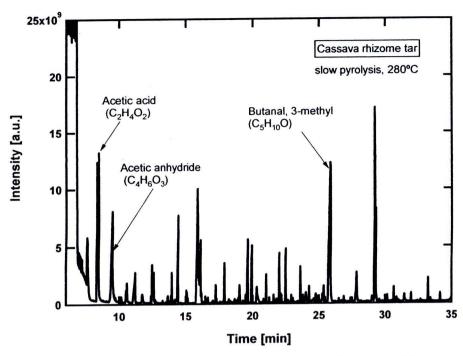


Figure 4.41 Intensity of tar components from slow pyrolysis of cassava rhizome at 280°C

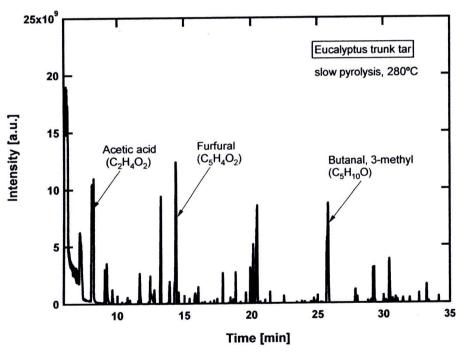


Figure 4.42 Intensity of tar components from slow pyrolysis of eucalyptus trunk at 280°C

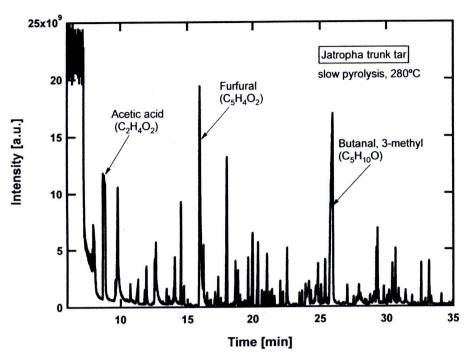


Figure 4.43 Intensity of tar components from slow pyrolysis of jatropha trunk at 280°C

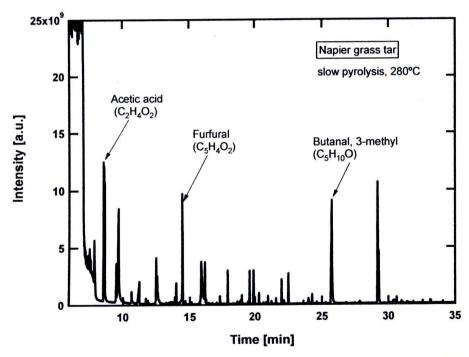


Figure 4.44 Intensity of tar components from slow pyrolysis of napier grass at 280°C

4.5.4 Mass and energy balances of slow pyrolysis processes

The overall pyrolysis processes were studied by the use of mass and energy balances. From these balances, the type of reaction and the differences between energy input from raw biomass and the energy output of pyrolysis products which was called an additional energy input were identified. The heating values used for all calculation were the lower heating values (LHV) normally used in the thermal applications. In addition, the energy balances were calculated under the assumption that there was no heat loss from the pyrolysis system to the environment and the pyrolysis was started from room temperature which is 25°C. The products determined in mass and energy balances are torrefied solid, H₂O, CO₂, CO and others, which were assumed as only acetic acid. The energy input of each process was calculated from the lower heating value of raw biomass. Meanwhile, the energy output from the pyrolysis process was calculated from the summation of the lower heating values and sensible heats of all torrefied products. The differences between the energy input to the process and the energy output from the processes were also calculated and for this study it was called "Additional energy input".

The mass and energy balances of pyrolysis at 260°C and 280°C of studied samples are presented in Tables 4.10 – 4.17 while the diagrams of overall mass and energy balances are shown in Figures 4.45 – 4.48. At higher pyrolysis temperature, the energy outputs of volatile products were higher but the energy outputs of torrefied solids were lower due to the higher mass loss compared to the pyrolysis at lower temperature. For all studied slow pyrolysis processes, the positive values of the additional energy inputs implied that the pyrolysis processes were the endothermic reactions which required some energy to the processes. From calculation, the values of additional energy input were found to increase when increasing the pyrolysis temperature.

Table 4.10 Mass and energy balance of pyrolysis process of cassava rhizome at 260°C

	Torrefaction at 20	60°C		
	Mass [kg]	LHV [kJ]	Sensible heat [kJ]	Output [kJ]
Torrefied product	0.840	13654.1	205.3	13859.4
Volatile				
H_2O	0.043	0.0	18.9	
CO_2	0.013	0.0	2.8	
CO	0.003	30.0	1.0	
Others	0.101	1451.4	25.2	
Total	0.160	1481.4	47.9	1529.3
Energy Input	14969.5			
Energy Output	15388.6			
Add. Energy Input	419.1	N		

Table 4.11 Mass and energy balance of pyrolysis process of cassava rhizome at 280°C

	Torrefaction at 28	80°C		
	Mass [kg]	LHV [kJ]	Sensible heat [kJ]	Output [kJ]
Torrefied product	0.683	12390.7	181.1	12570.9
Volatile				N. C.
H ₂ O	0.094	0.0	44.8	
CO ₂	0.031	0.0	7.3	
CO	0.008	80.0	3.0	
Others	0.184	2644.1	49.7	
Total	0.317	2724.1	104.9	2828.9
Energy Input	14969.5			
Energy Output	15399.8			
Add. Energy Input	430.3			

Table 4.12 Mass and energy balance of pyrolysis process of eucalyptus trunk at 260°C

	Torrefaction at 260°C				
	Mass [kg]	LHV [kJ]	Sensible heat [kJ]	Output [kJ]	
Torrefied product	0.886	15845.4	216.5	16061.9	
Volatile	-				
H ₂ O	0.014	0.0	6.2		
CO ₂	0.014	0.0	3.0		
CO	0.000	0.0	0.0		
Others	0.086	1235.8	21.4		
Total	0.114	1235.8	30.6	1266.4	
Energy Input	16720.2				
Energy Output	17328.4				
Add. Energy Input	608.2				

Table 4.13 Mass and energy balance of pyrolysis process of eucalyptus trunk at 280° C

	Torrefaction at			
	Mass [kg]	LHV [kJ]	Sensible heat [kJ]	Output [kJ]
Torrefied product	0.832	15717.2	220.6	15937.8
Volatile				
H_2O	0.019	0.0	9.1	
CO_2	0.018	0.0	4.2	
CO	0.004	40.0	1.5	
Others	0.126	1810.6	31.4	
Total	0.167	1850.6	46.2	1896.8
Energy Input	16720.2			
Energy Output	17834.6			
Add. Energy Input	1114.4			

Table 4.14 Mass and energy balance of pyrolysis process of jatropha trunk at 260°C

	Torrefaction a	t 260°C		
	Mass [kg]	LHV [kJ]	Sensible heat [kJ]	Output [kJ]
Torrefied product	0.830	15258.9	202.9	15461.7
Volatile	2			
	0.041	0.0	18.0	
H_2O	0.041	0.0		
CO_2	0.025	0.0	5.4	
CO	0.004	40.0	1.4	
Others	0.100	1437.0	24.9	
Total	0.170	1477.0	49.7	1526.7
Energy Input	16662.9			
Energy Output	16988.5			
Add. Energy Input	325.6			

Table 4.15 Mass and energy balance of pyrolysis process of jatropha trunk at 280°C

	Torrefaction a	t 280°C		
	Mass [kg]	LHV [kJ]	Sensible heat [kJ]	Output [kJ]
Torrefied product	0.742	14547.3	196.8	14744.1
Volatile				
H ₂ O	0.051	0.0	24.3	
CO_2	0.033	0.0	7.7	
CO	0.005	50.0	1.9	
Others	0.169	2428.5	45.7	
Total	0.258	2478.5	79.6	2558.2
Energy Input	16662.9			
Energy Output	17302.2			
Add. Energy Input	639.4			

Table 4.16 Mass and energy balance of pyrolysis process of napier grass at 260°C

	Torrefaction	1 at 260°C		
	Mass [kg]	LHV [kJ]	Sensible heat [kJ]	Output [kJ]
Torrefied product	0.784	13068.9	191.6	13260.5
Volatile				
H_2O	0.041	0.0	18.0	
CO_2	0.063	0.0	13.6	
CO	0.006	60.0	2.1	
Others	0.106	1523.2	26.4	
Total	0.216	1583.2	60.1	1643.3
Energy Input	14826.9			
Energy Output	14903.9			
Add. Energy Input	77.0			

Table 4.17 Mass and energy balance of pyrolysis process of napier grass at 280°C

	Torrefaction at			
	Mass [kg]	LHV [kJ]	Sensible heat [kJ]	Output [kJ]
Torrefied product	0.692	12657.3	183.5	12840.8
Volatile				
H_2O	0.064	0.0	30.5	
CO_2	0.101	0.0	23.7	
CO	0.011	110.0	4.2	
Others	0.132	1896.8	32.9	
Total	0.308	2006.8	91.2	2098.1
Energy Input	14826.9			
Energy Output	14938.9			
Add. Energy Input	112.0			



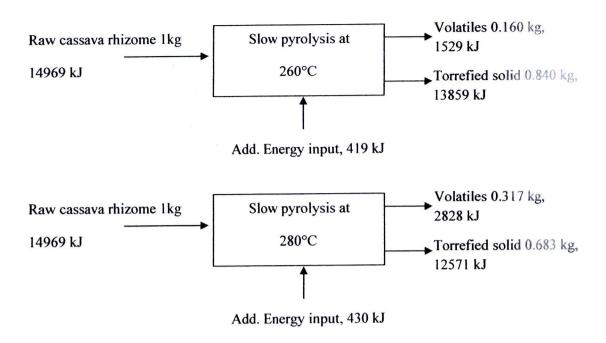


Figure 4.45 Overall mass and energy balances for slow pyrolysis processes at 260°C and 280°C of cassava rhizome

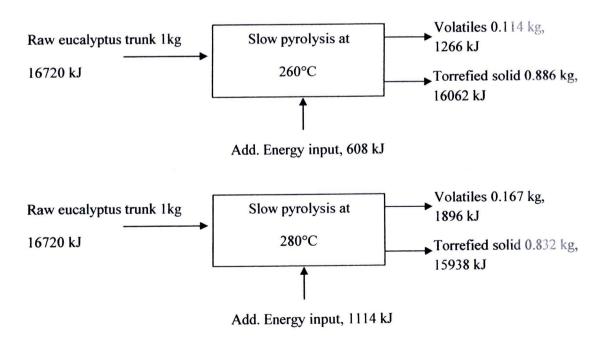


Figure 4.46 Overall mass and energy balances for slow pyrolysis processes at 260°C and 280°C of eucalyptus trunk

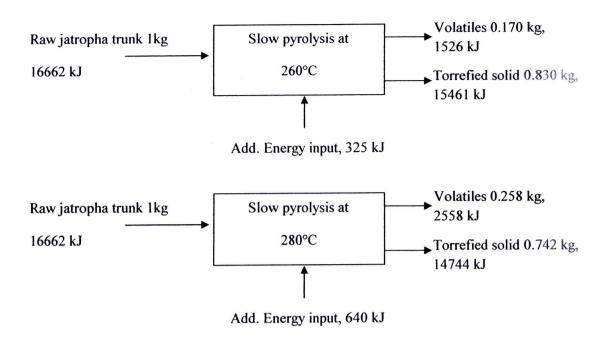


Figure 4.47 Overall mass and energy balances for slow pyrolysis processes at 260°C and 280°C of jatropha trunk

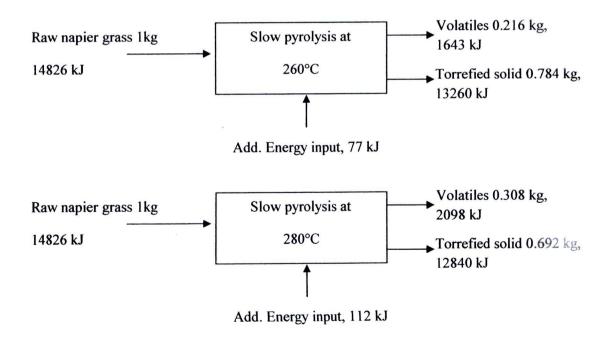


Figure 4.48 Overall mass and energy balances for slow pyrolysis processes at 260°C and 280°C of napier grass

4.5.5 Combustion behaviors of raw and torrefied biomass from slow pyrolysis processes

The biomass pyrolysed at 260°C and 280°C were combusted in air at the heating rate of 10°C/min by using of TGA. Then, the combustion behaviors or burning profiles of raw and torrefied biomass were analyzed by derivative thermogravimetry curves or DTG curves. There are two separated peaks for biomass combustion process. The first peak started at a temperature of about 150°C, corresponding to the volatile combustion period the second peak started at the temperature higher than 300°C corresponding to the char combustion period. Figures 4.49 – 4.52 show the DTG curves of raw and torrefied biomass which were from the combustion by 10°C/min heating rate. It was found that the DTG curves of all torrefied samples were shifted to higher temperature. For example, the first peak of DTG curve was shifted from 215°C for raw cassava rhizome to 230 and 245°C for cassava rhizome torrefied at 260 and 280°C, respectively. This behavior implies that the treated biomass at higher temperature started to be decomposed at higher temperature than the raw biomass due to the preliminary decompositions during their torrefaction processes. Moreover, the first peak or the peak represents volatile combustion of torrefied samples were found to be narrower than that of raw samples. The narrower peak indicates the shorter period of combustion time and narrower range of temperature for volatile combustion [10]. The shape of DTG curves of torrefied eucalyptus and jatropha trunk at 280°C were totally different from the shape of their raw DTG curves. These dominant changes were from the high hemicellulose content in raw eucalyptus and jatropha trunk which was already decomposed during the slow pyrolysis at 280°C. Considering the second peak or char combustion period, torrefied samples from 280°C of all biomass except napier grass showed the higher maximum char combustion rate in comparison to torrefied sample at 260°C and raw sample. The maximum char combustion rates of raw cassava rhizome and eucalyptus trunk at temperature of about 400°C were -0.055 and -0.058 min⁻¹, while the rates of torrefied samples at 280°C were -0.094 and -0.081 min⁻¹, respectively.

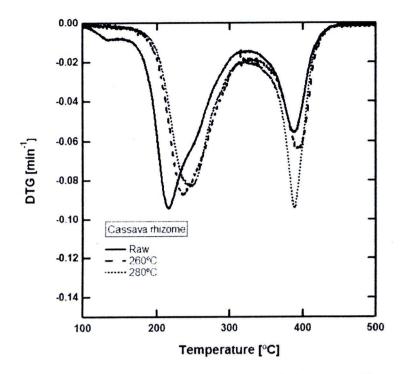


Figure 4.49 DTG curves of raw and torrefied cassava rhizome

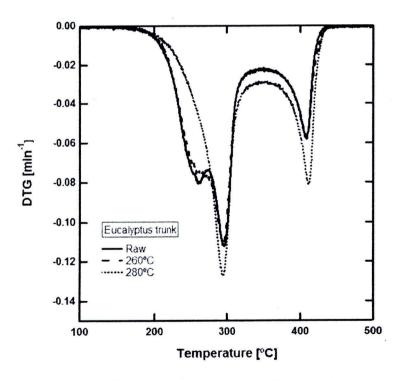


Figure 4.50 DTG curves of raw and torrefied eucalyptus trunk

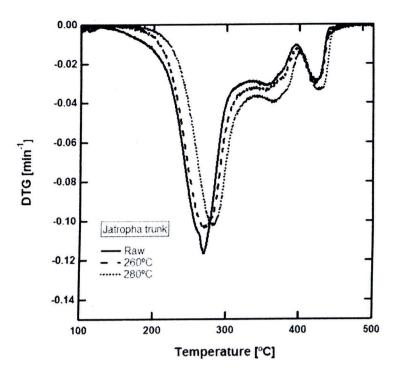


Figure 4.51 DTG curves of raw and torrefied jatropha trunk

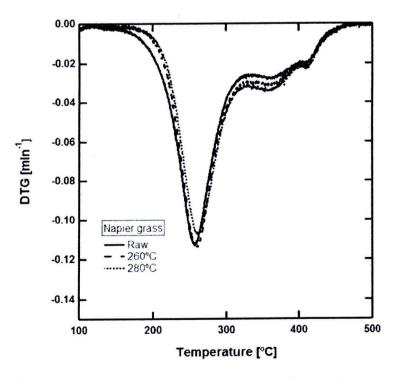


Figure 4.52 DTG curves of raw and torrefied napier grass