CHAPTER 5

RESULTS AND DISCUSSION

5.1 Fuel Properties of Biomass

Results from proximate, ultimate and structural analyses of the biomass samples are listed in Tables 5.1 and 5.2. To compare with other biomass feedstocks, proximate, ultimate and structural analyses of biomass obtained from the literature are shown in Figures 5.1, 5.2 and 5.3, respectively.

Moisture content of the air dried mimosa and bamboo was 1.6 and 5.7%. The ash contents of samples were 3.75 and 5.6%. The volatile were 71.1 and 74.7 %. This value is in similar magnitude to agricultural wastes around (60-90%) as shown in Figure 5.1. Mimosa is slightly lower than woody biomass. Both of them are higher than biomass waste materials, biomass char and coals. The fixed carbons of samples were about 23.6 and 14%. Mimosa is slightly higher than agricultural wastes and woody biomass, but both of them are lower than biomass char and coal. The remainder was ash, which content is comparable to those found in woody biomass materials. This is relatively low when compare with sugarcane bagasse, wheat straw and rice husk in Table 2.2.

From Figure 5.2, mimosa and bamboo were found to contain less carbon and more oxygen content than other woody biomass. H/C molar ratio of bamboo is slightly lower than other biomass material. Biomass has high content of oxygen and hydrogen than biomass char and coal.

An average gross heating value or high heating value of mimosa and bamboo are 17.5 and 17.8 MJ/kg. This value is in similar magnitude to others biomass materials, but lower than biomass char and some coals but higher than other biomass such as biomass waste material, grass and husk as shown in Figures 5.3 and 5.4.

Generally, fixed carbon contents of biomass is lower than biomass char and coals resulting to low gross heating value than char and coals. Biomass contain high content of oxygen while coal contain low content of oxygen but high content of carbon resulting in high gross heating value than biomass.

Biomass offers crucial advantages as a feedstock due to the high volatility of the fuel and the high reactivity of both the fuel and the resulting char. However, it should be noticed that it can compare with solid fossil fuels such as coals. Biomass contains more moisture, less carbon and much more oxygen and has lower heating value than fossil fuels.

Table 5.1 Properties of the air dried Mimosa stalk

Property	Quantity	
	Mimosa	Bamboo
Proximate analysis (% w/w)		
Moisture	1.6	5.7
Volatile	71.1	74.7
Fixed carbon	23.6	14.0
Ash	3.7	5.6
Ultimate analysis (%)		
Carbon	43.9	45.6
Hydrogen	6.0	4.3
Nitrogen	1.4	0.24
Oxygen	48.7	49.7
H/C molar ratio	1.64	1.13
O/C molar ratio	0.83	0.82
Empirical formula	$CH_{1.64}O_{0.83}N_{0.03}$	$CH_{1.14}O_{0.82}N_{0.005}$
Higher heating value (MJ/kg)	17.5	17.8

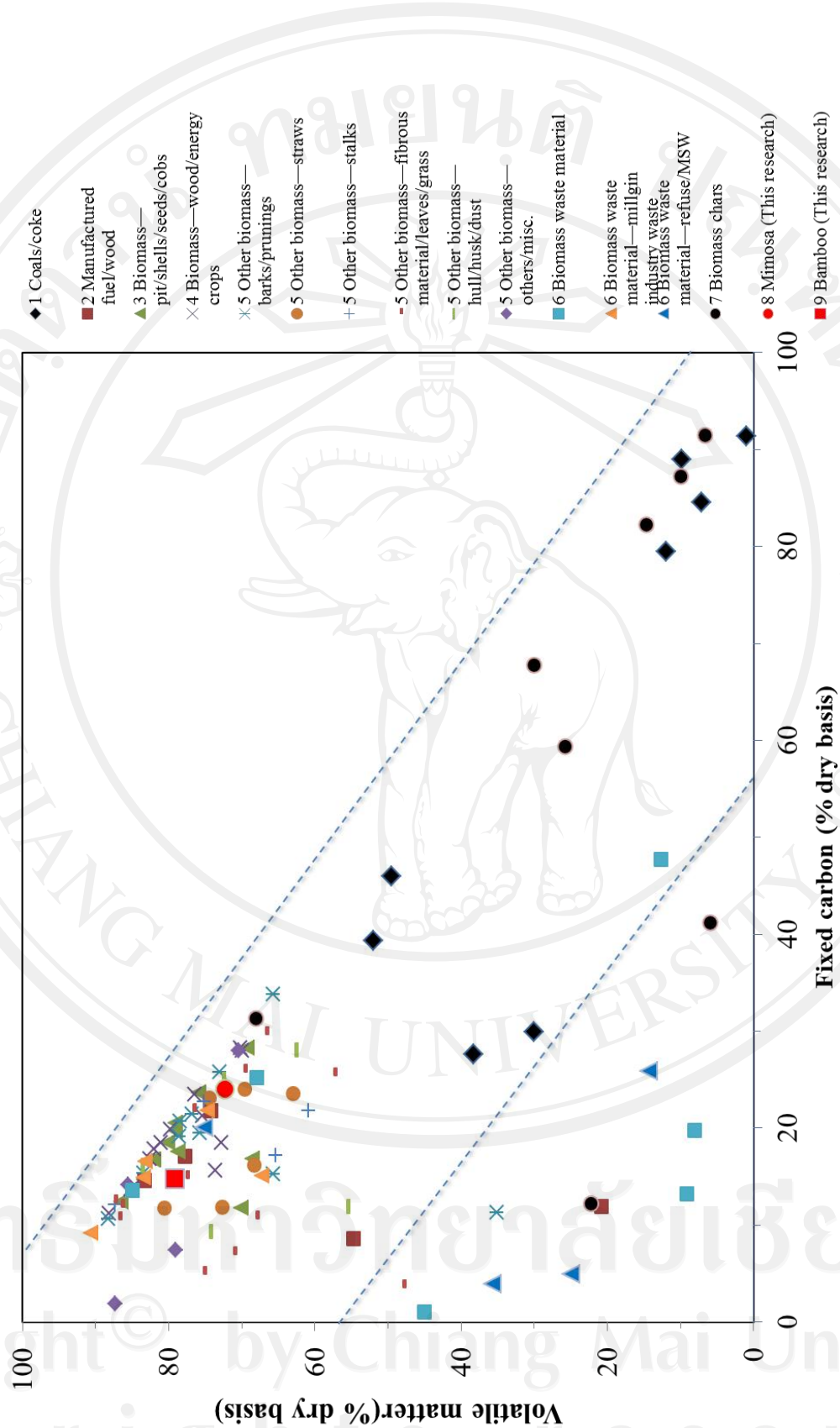

Figure 5.1 Proximate analyses of selected biomass (Parikh et al., 2005)

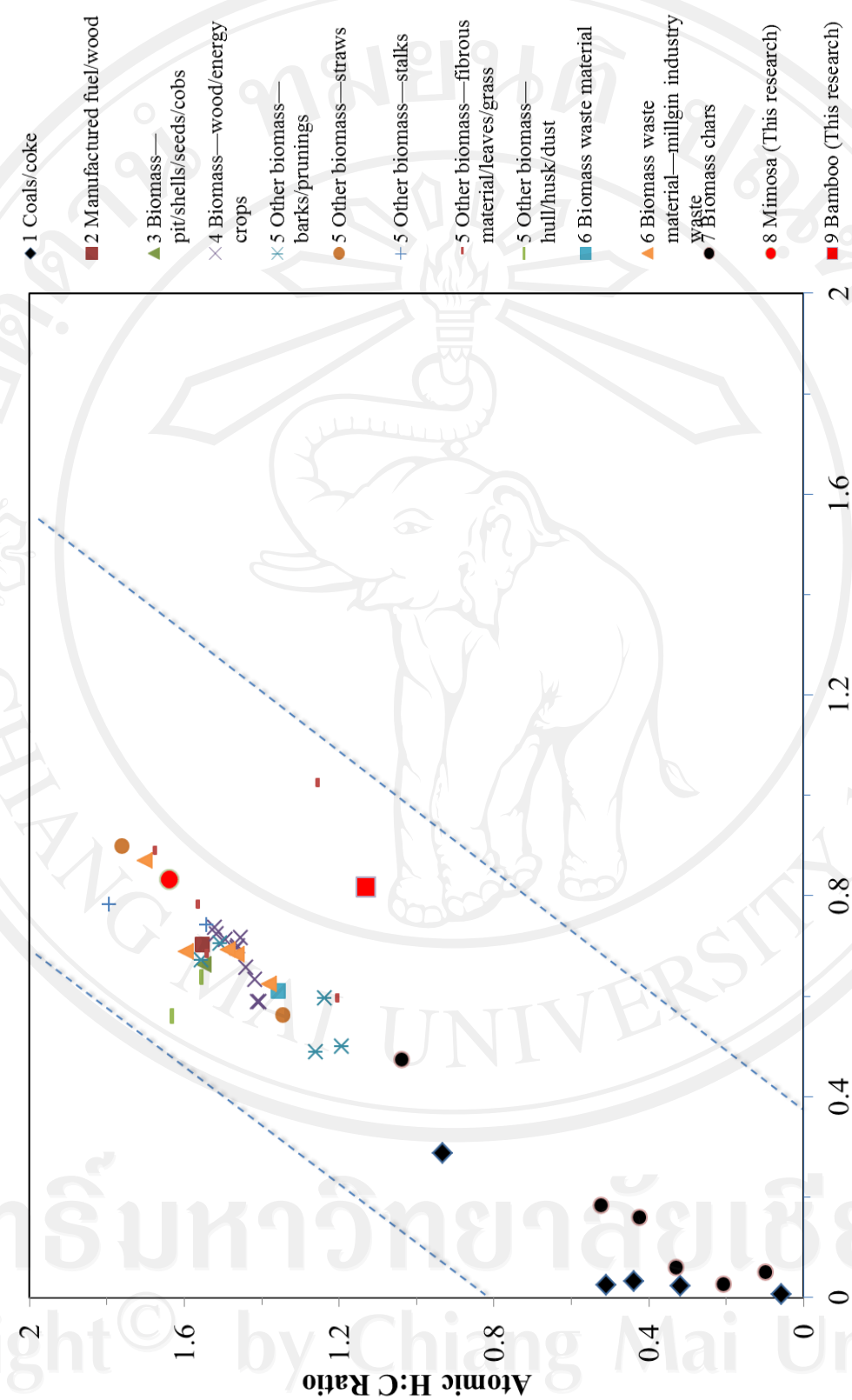

Figure 5.2 Ultimate analyses of selected biomass (Parikh et al., 2005)

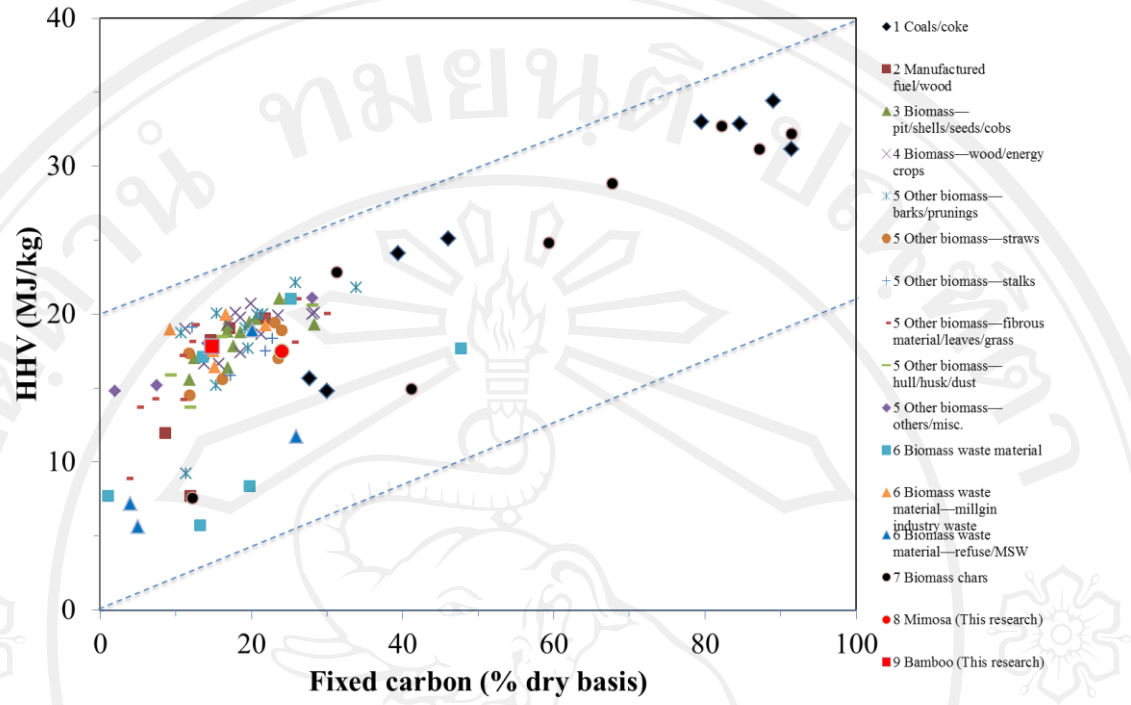

Figure 5.3 Compare fixed carbon with HHV selected biomass (Parikh et al., 2005)

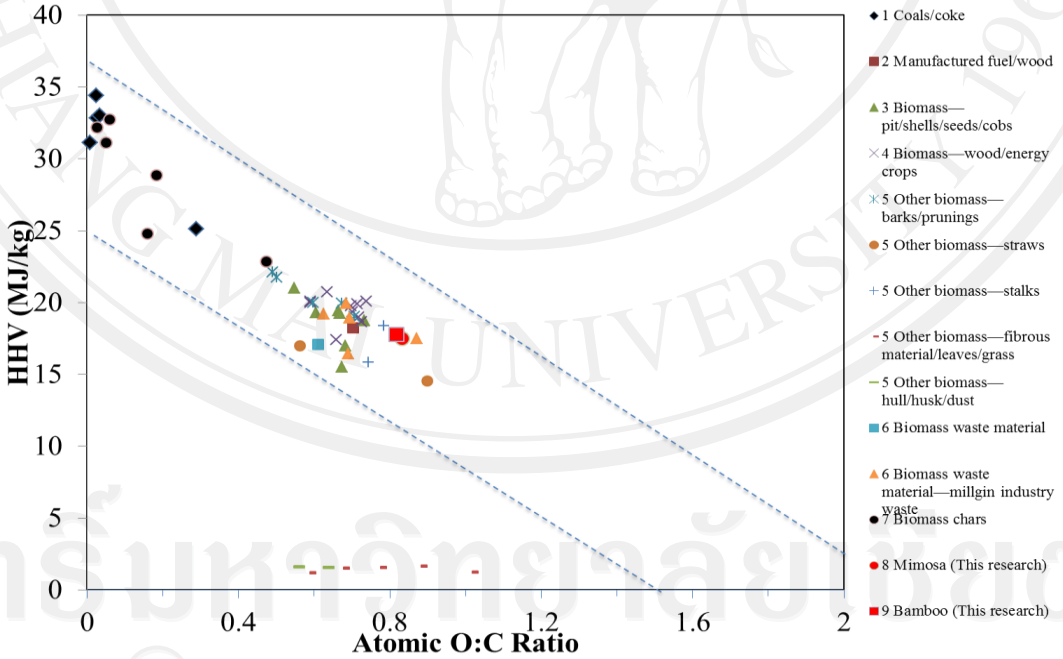

Figure 5.4 Compare O:C ratio with HHV selected biomass (Parikh et al., 2005)

From the analysis results in Table 5.2, it was found that mimosa and bamboo containing high amount of holocellulose (58.2 and 63.1%). From Figure 5.5, to compare mimosa with bamboo, it was found that bamboo has high contents of holocellulose lead to high volatility as shown in Figure 5.6, but low content of lignin resulting in low char content (Raveendran et al., 1996) as shown in Figure 5.7.

Biomass mainly contains holocellulose or hemicellulose and cellulose, and lignin. To compare with other biomass materials, it was found that mimosa and bamboo has slightly low content of holocellulose than woody biomass but volatile content is similar with other biomass. Mimosa has high content of lignin than woody biomass and straw then mimosa has high char content than that.

Table 5.2 Lignocellulosic properties and solubility of the air dried Mimosa stalk

Property	Quantity (% w/w)	
	Mimosa	Bamboo
Holocellulose	58.2	63.1
Lignin	33.9	22.1
Extractives, soluble in ethanol and benzene	1.7	-
Solubility in hot water	10.5	9.2
Solubility in cold water	7.4	-
Solubility in 1% NaOH solution	36.2	-
Solubility in ethanol and benzene	5.2	6.0

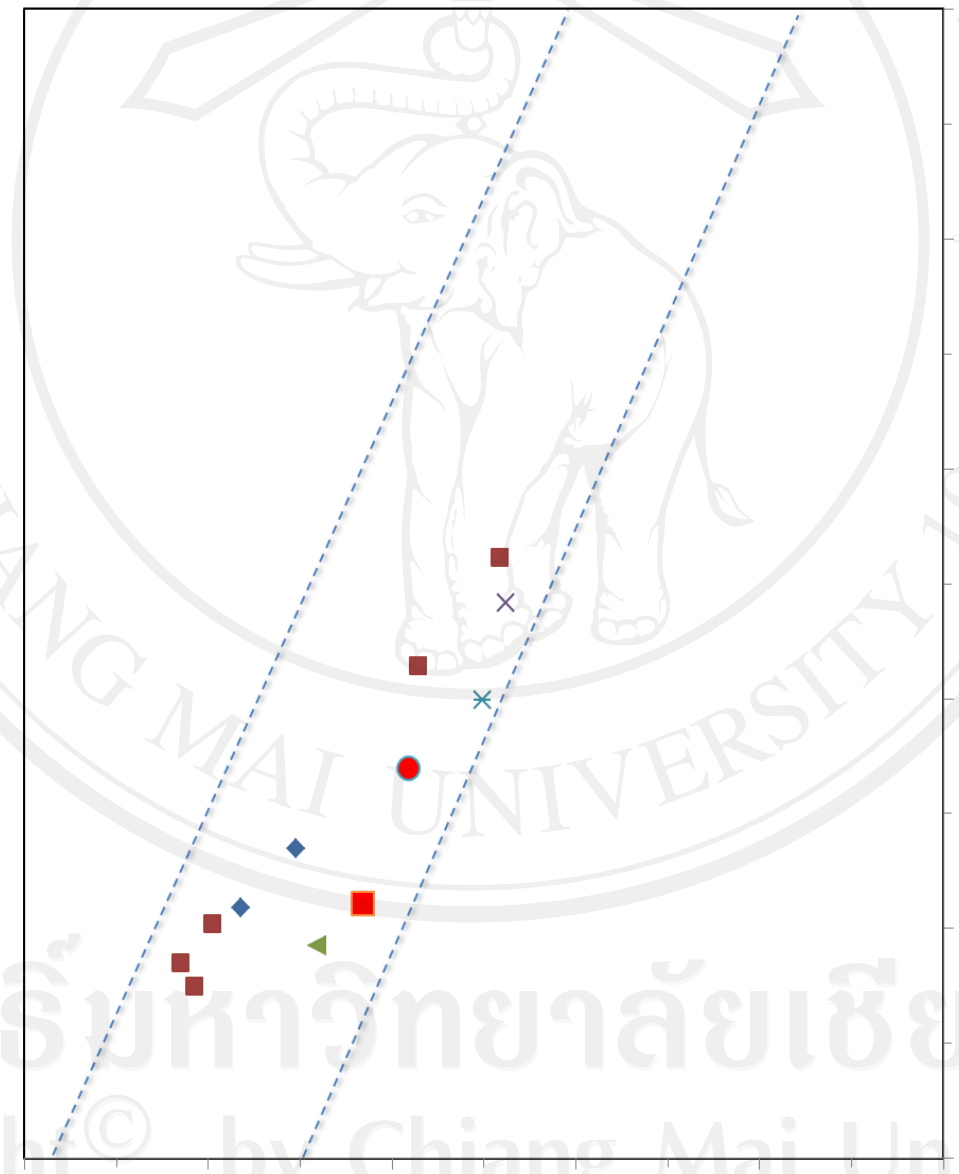

Figure 5.5 Structural analyses of selected biomass

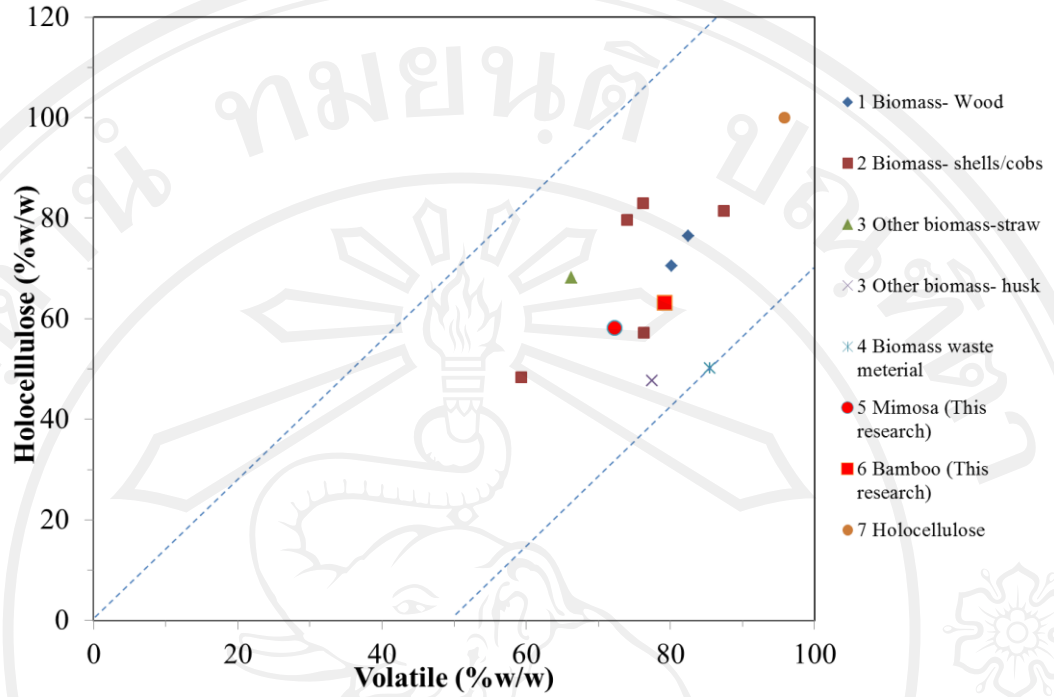

Figure 5.6 Compare volatile with holocellulose of selected biomass

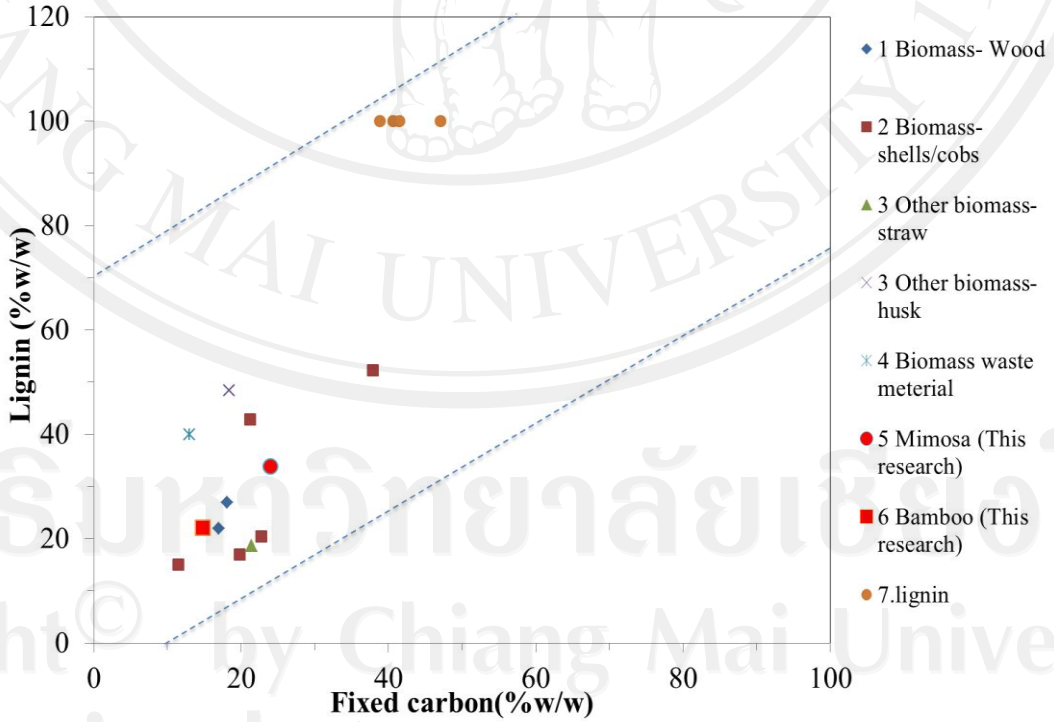

Figure 5.7 Compare fixed carbon with lignin of selected biomass

5.2 Thermogravimetric Analysis

5.2.1 Comparison with Difference Atmospheres

Thermogravimetric analysis was used to determine the thermal degradation of the mimosa. In this study, mimosa was thermally degraded under nitrogen, air and oxygen atmospheres, respectively. From Figures 5.8 and 5.9, it can be seen that there was an initial weight loss of moisture content from 25 to 120^{o}C. After that hemicellulose and lignin decomposed at approximately 200^{o}C and cellulose proceeded around 260^{o}C (Raveendran et al., 1996; Wang et al., 2011). Further thermal decomposition continued gradually up to the environment. Under nitrogen, mimosa proceeded at slower loss rate, the main devolatization proceeded to about 600^{o}C with total weight of 60% (Wongsiriamnuay et al., 2008) and char was left around 20%, towards 1000^{o}C.

Under oxygen and air, when the temperature up to about 200^{o}C, the thermal degradation character was similar to that under N_2 environment but it had higher decomposition rate than nitrogen. However, a major weight loss, due primarily to oxidation, was evidently started at 200 ^{o}C, and completed by about 350 and 550 ^{o}C under oxygen and air environments, respectively. There was essentially no loss observed afterwards. The increased oxygen concentration result in higher decomposition rate and conversion profile shift to lower temperature (Yuzbasi and Selçuk, 2011). The residual char and ash amounted to about 5% (Wongsiriamnuay et al., 2008).

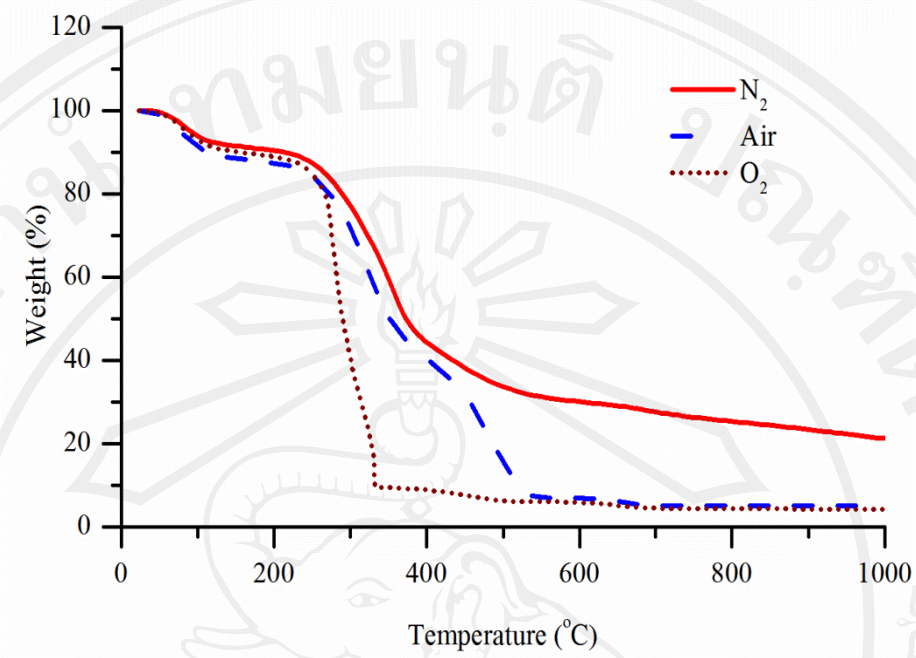

Figure 5.8 TG of Mimosa under N_2, Air and O_2 atmosphere

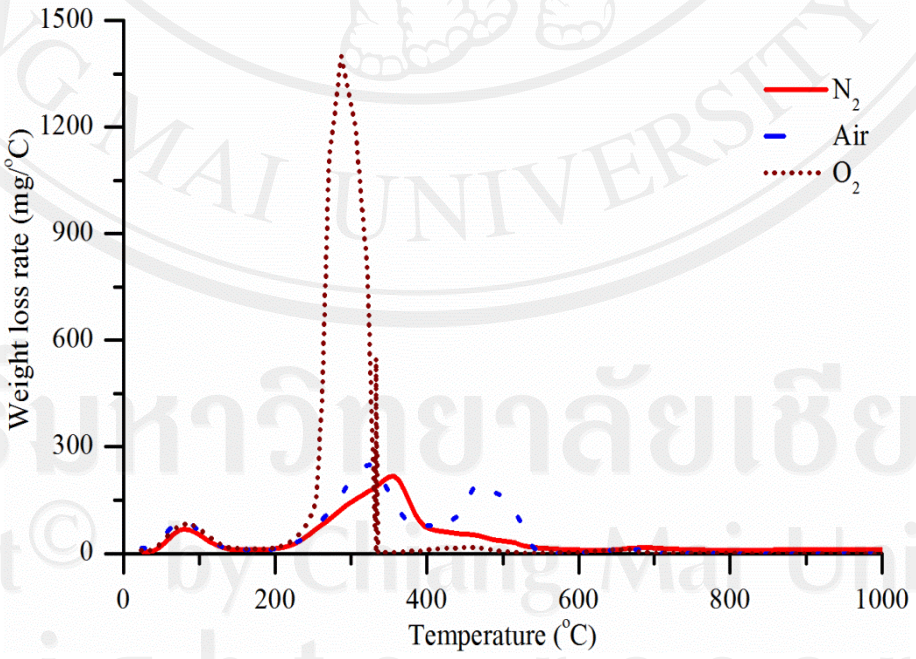

Figure 5.9 DTG of Mimosa under N_2, Air and O_2 atmosphere

5.2.2 Thermal Degradation under N_2 Atmosphere

The TGA/DTG profiles of the mimosa as a function of temperature at heating rate 10, 30 and 50 ^{o}C/min during pyrolysis process are shown in Figures 5.10 and 5.11. The decomposition of mimosa under pyrolysis process can be divided to four stages: moisture evolution (<120 ^{o}C); hemicellulose decomposition (150-310^{o}C); cellulose and lignin degradation (310-400^{o}C) and lignin composition (>400^{o}C). DTG of lignin was the flattest due to slow carbonization, being the main char formation.(Raveendran et al., 1996; Sanchez-Silva et al., 2012)

Effect of heating rate on decomposition rate under nitrogen environment (inert gas) is investigated. It was found that the decomposition rate increased with increasing heating rate. The higher heating rate appeared to produce lower amount of residual char and ash. There was two main decomposition of DTG. First was the main decomposition of hemicellulose and cellulose in the temperature range between 200-400^{o}C. The second was the decomposition of lignin that had a wider DTG peak from 200-550^{o}C.

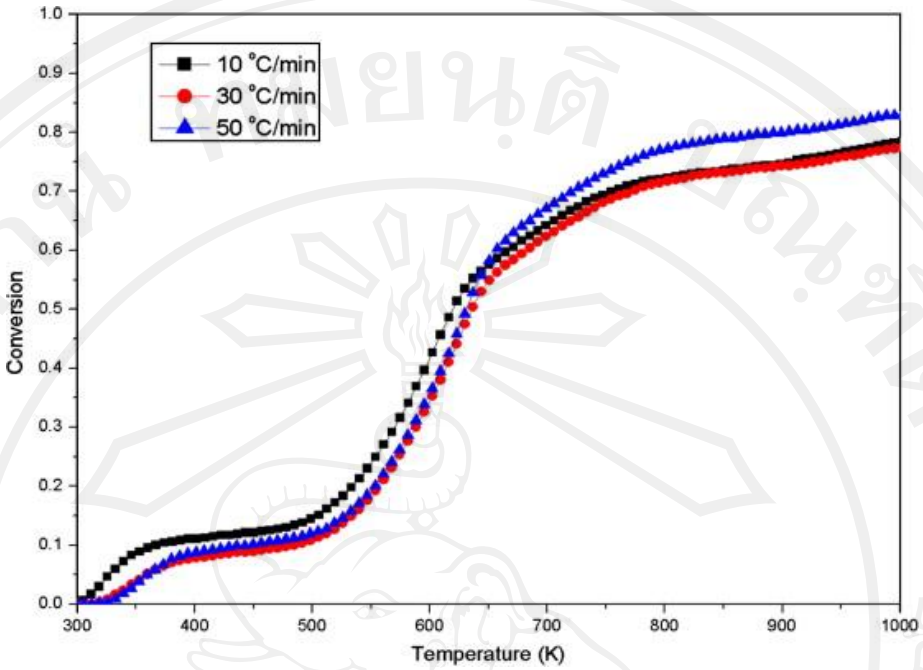

Figure 5.10 Effect of heating rate on TG of Mimosa under nitrogen atmosphere

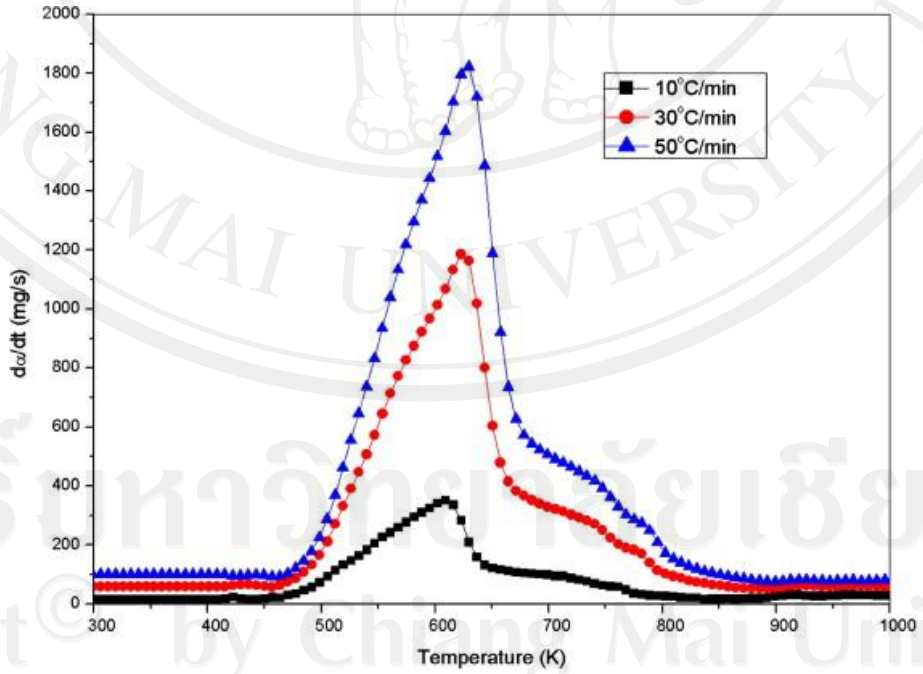

Figure 5.11 Effect of heating rate on DTG of Mimosa under nitrogen atmosphere

Table 5.3 Degradation characteristic of various biomass sources under nitrogen atmosphere

Reference	Biomass	T_{start} (°C)	T_{peak} (°C)	$d\alpha/dt_{peak}$	α_{peak}	$\alpha_{500°C}$	Heating rate (°C/min)
This work	Mimosa	198	336	0.748	0.45	0.29	10
		191	350	2.33	0.42	0.30	30
		197	356	4.11	0.49	0.24	50
Gronli et al. (2002)	Alder	242	349	1.02	0.40	0.17	5
	Beech	248	349	0.91	0.37	0.18	5
	Birch	244	353	0.98	0.32	0.14	5
	Oak	237	338	0.89	0.45	0.23	5
	Douglas fir	243	334	0.87	0.55	0.24	5
	Pine A	238	351	0.91	0.45	0.20	5
	Pine B	209	350	0.81	0.43	0.20	5
	Redwood	235	351	0.83	0.50	0.26	5
	Spruce	249	352	0.77	0.46	0.23	5
	Hard woods	243	347	0.95	0.38	0.18	5
	Soft woods	235	348	0.84	0.47	0.22	5
Kalita and Saikia (2004)	*P. alba*	170	360	–	0.58	–	20
	C. procera	210	290	–	0.85	–	20
	E. neerifolia	180	360	–	0.76	–	20
	N. indicum	140	350	–	0.68	–	20
	M. elengi	170	340	–	0.57	–	20
Gomez et al. (2007)	Thistle	214	334	0.20	–	–	20
	Pine	254	378	0.30	–	–	20
	Beech	259	380	0.35	–	–	20
Yao et al. (2008)	Bagasse	–	299.3	–	0.53	–	2
	Bamboo	–	285.9	–	0.44	–	2
	Cotton stalk	–	293.4	–	0.50	–	2
	Hemp	–	282.3	–	0.38	–	2

Table 5.3 (Continued)

Reference	Biomass	T_{start} (°C)	T_{peak} (°C)	$d\alpha/dt_{peak}$	α_{peak}	$\alpha_{500°C}$	Heating rate (°C/min)
	Jute	–	283.1	–	0.44	–	2
	Kenaf	–	284.1	–	0.42	–	2
	Rice husk	–	297.4	–	0.37	–	2
	Rice straw	–	273.6	–	0.35	–	2
	Maple	–	308.3	–	0.58	–	2
	Pine	–	311.5	–	0.59	–	2
Jeguirim and Trouve (2009)	Giant reed	200	308	0.826	0.58	0.29	5

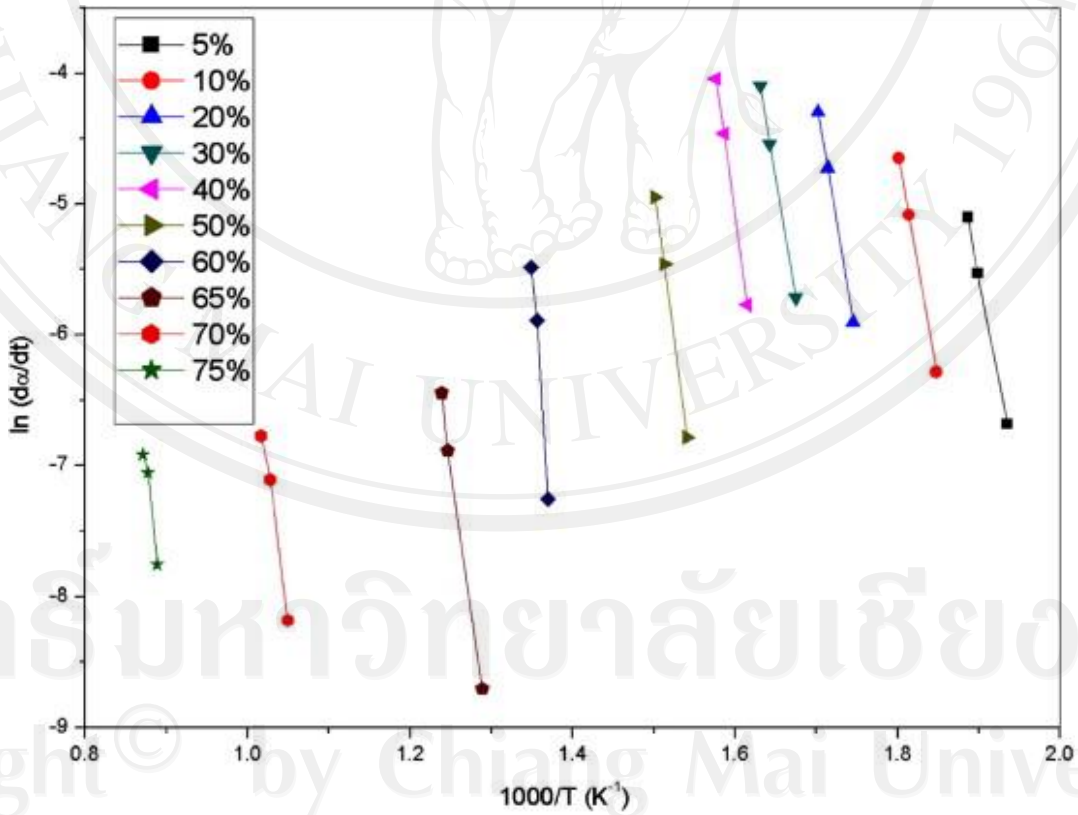

Figure 5.12. Relationships between the rate of conversion with temperature for conversions of 5–75%.

5.2.3 Thermal Degradation under Air Atmosphere

Effect of heating rate on decomposition rate under air environment is shown in Figures 5.13 and 5.14. It was found that the decomposition rate increased with increasing heating rate. The higher heating rate appeared to produce lower amount of residual char and ash. There was two main decomposition of DTG. First was the main decomposition of hemicellulose and cellulose in the temperature range between 200-400^{o}C. The second was the decomposition of lignin that had a wider DTG peak from 200-550^{o}C.

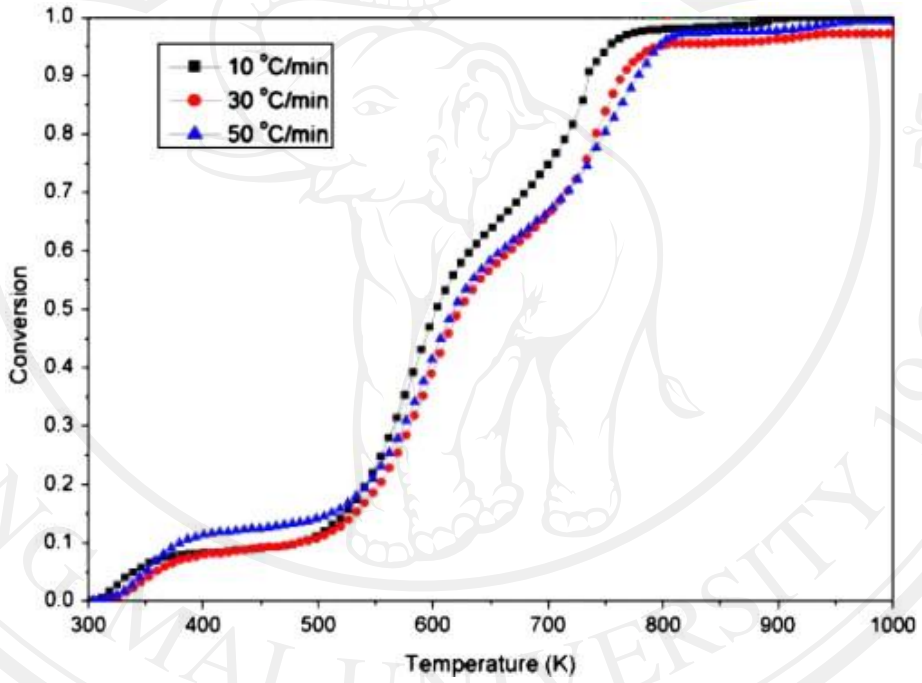

Figure 5.13 Effect of heating rate on TG of Mimosa under air atmosphere

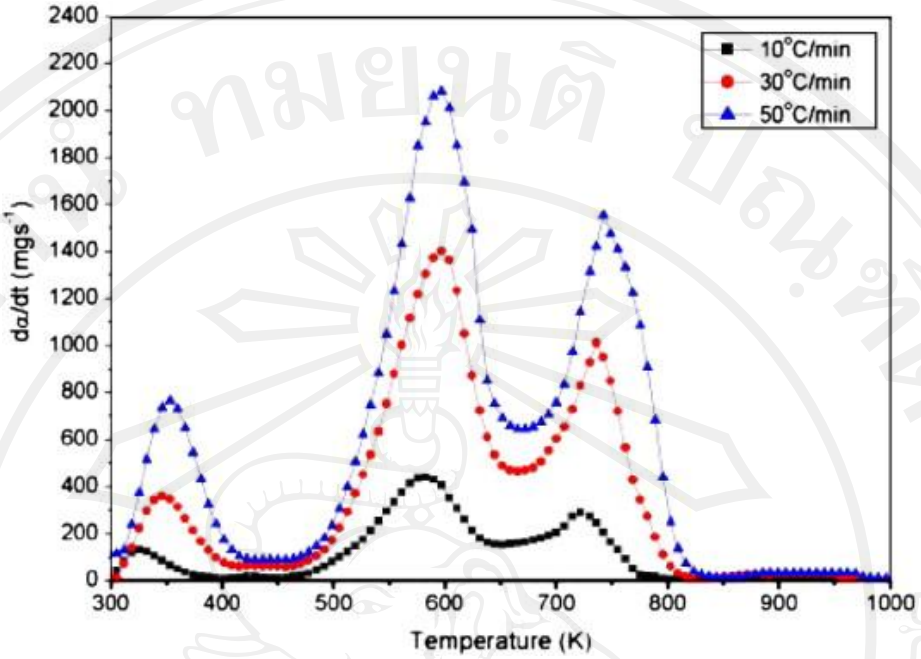

Figure 5.14 Effect of heating rate on DTG of Mimosa under air atmosphere

Table 5.4 Comparison of degradation characteristic of various biomass materials under air atmosphere.

Reference	Biomass	T_1 (°C)	$d\alpha_1/dT$ (%/C)	T_2 (°C)	$d\alpha_2/dT$ (%/C)	Heating rate (°C/min)
This work	Mimosa	310	0.26	448	0.19	10
		326	0.28	469	0.19	30
		326	0.25	469	0.20	50
Jeguirim et al. (2010)	Arundo donax	250	–	337	–	5
	Miscanthus	289	–	401	–	5
Munir et al. (2009)	Cotton stalk	285	0.28	373	0.12	20
	Bagasse	306	0.19	378	0.11	20
	Shea meal	279	0.21	442	0.14	20

Table 5.4 (Continued)

Reference	Biomass	T_1 (°C)	$d\alpha_1/dT$ (%/C)	T_2 (°C)	$d\alpha_2/dT$ (%/C)	Heating rate (°C/min)
Shen et al. (2009)	Pine	329	1.13	443	0.55	10
	Aspens	321	1.23	415	0.79	10
	Birch	323	1.29	428	0.85	10
	Oak	325	1.29	450	0.44	10
Safi et al. (2004)	Pine needles	290	0.71	390	–	15
		310	0.845	370	–	30

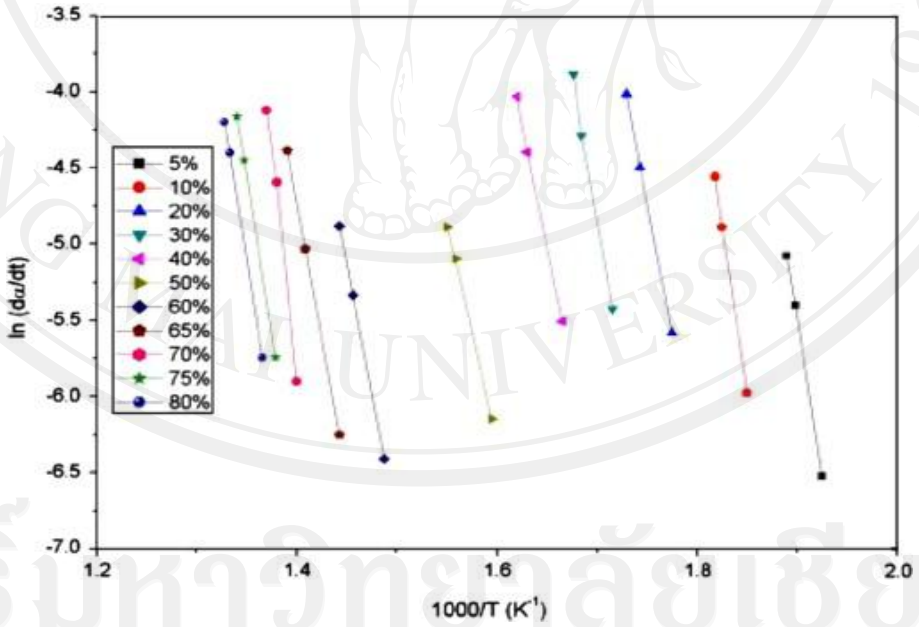

Figure 5.15 Relationships between the rate of conversion with temperature for conversions of 5–80% under air atmosphere

Table 5.5 Comparison of average combustion kinetic parameters between Mimosa and other biomass materials under air atmosphere

Reference	Biomass	Atmosphere	Heating rate (^{o}C/min)	Temperature range (^{o}C)	*E* (kJ/mol)
This work	Mimosa	Air	10, 30, 50	200–500	334
Haykiri-Acma and Yaman (2008)	Rapeseed	Air	20	127–752	21
Kumar et al. (2008)	Corn stover	Air	10	250–560	57
			30	250–560	126
			50	250–560	139
Munir et al. (2009)	Cotton stalk	Air	20	200–500	113
	Bagasse				75
	Shea meal				108
Shen et al. (2009)	Pine	Air	10	200–370	119
	Aspens				114
	Birch				116
	Oak				117
Shen et al. (2009)	Pine	Air	10	370–490	145
	Aspens				205
	Birch				210
	Oak				150
Sun et al. (2010)	Cotton stalk	Air	20	200–360	108
				360–500	125
Otero et al. (2010)	Sewage sludge	Air	5, 10, 25, 50	200–480	129
	Animal manure				133
Safi et al. (2004)	Pine needle	Air	10	192–503	85
			30	181–575	87

5.3 Fixed Bed Gasification

5.3.1 Effect of Temperature on Product Yields

The effect of temperature on product distributions from gasification of bamboo and mimosa are shown in Figure 5.16. It was found that when the reactor temperature was increased from 600 to 900^{o}C, the gas yields increased from 60.4% to 66.2% for bamboo and 50.0% to 56.8% for mimosa, while the tar and char decreased from 13.6% to 11.6% and 26.2% to 22.2% for bamboo, and 24.8% to 21.2% and 25.2% to 22.0% for mimosa, respectively.

Figure 5.17 show the effect of temperature on the gas composition of bamboo and mimosa. It was found that concentrations of H_2 was increased, CO and CH_4 unchanged, whereas CO_2 were decreased at elevated temperatures. At elevated temperature, H_2 increases from 0.42% to 0.82% for bamboo and 0.5% to 1.02% for mimosa. To compare with other literature, H_2 concentrations were less than others.

To improve the gas yields, another experiment had investigated and presented in Figure 5.18. The effect of temperature on the gas composition of high heating rate (100-160^{o}C/min) experiment of mimosa named mimosa* was compared with mimosa and bamboo (heating rate 10^{o}C/min) that had previous presented. At elevated temperature from 600 to 900 ^{o}C, H_2 of mimosa* was higher than bamboo and mimosa with an increase of 4.6% at 600 ^{o}C to 10.8% at 900 ^{o}C. Concentrations of CO, CO_2 and CH_4 were increased from 10.5% to 17.9%, 17.5% to 24.5% and 3.8 to 5.1%, respectively. Similar trends with those reported in (Raveendran et al., 1996; Chen et al., 2003; Wei et al., 2007; Kantarelis and Zabaniotou, 2009; Zhou et al., 2009; Plis and Wilk, 2011).

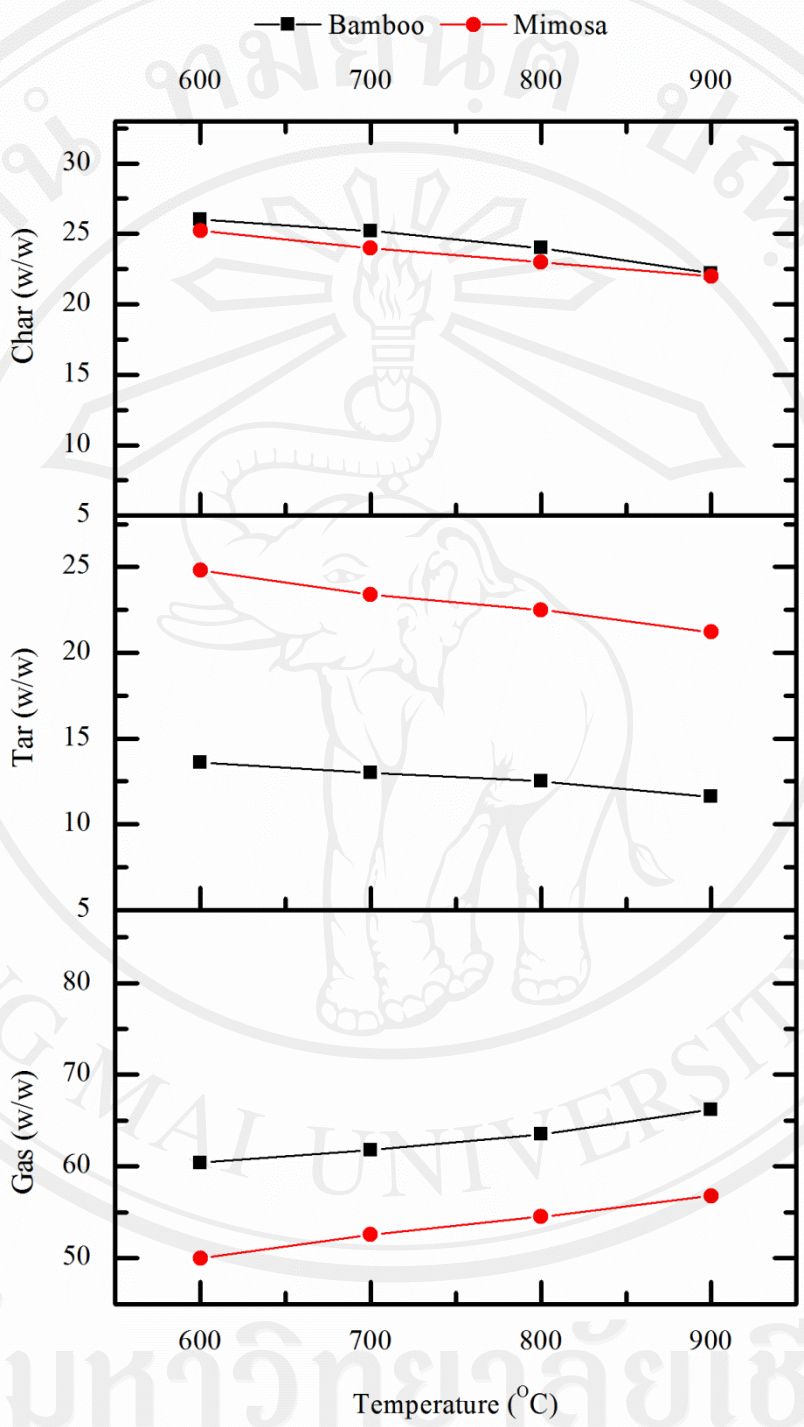

Figure 5.16 Effect of temperature on product yields in a fixed bed reactor

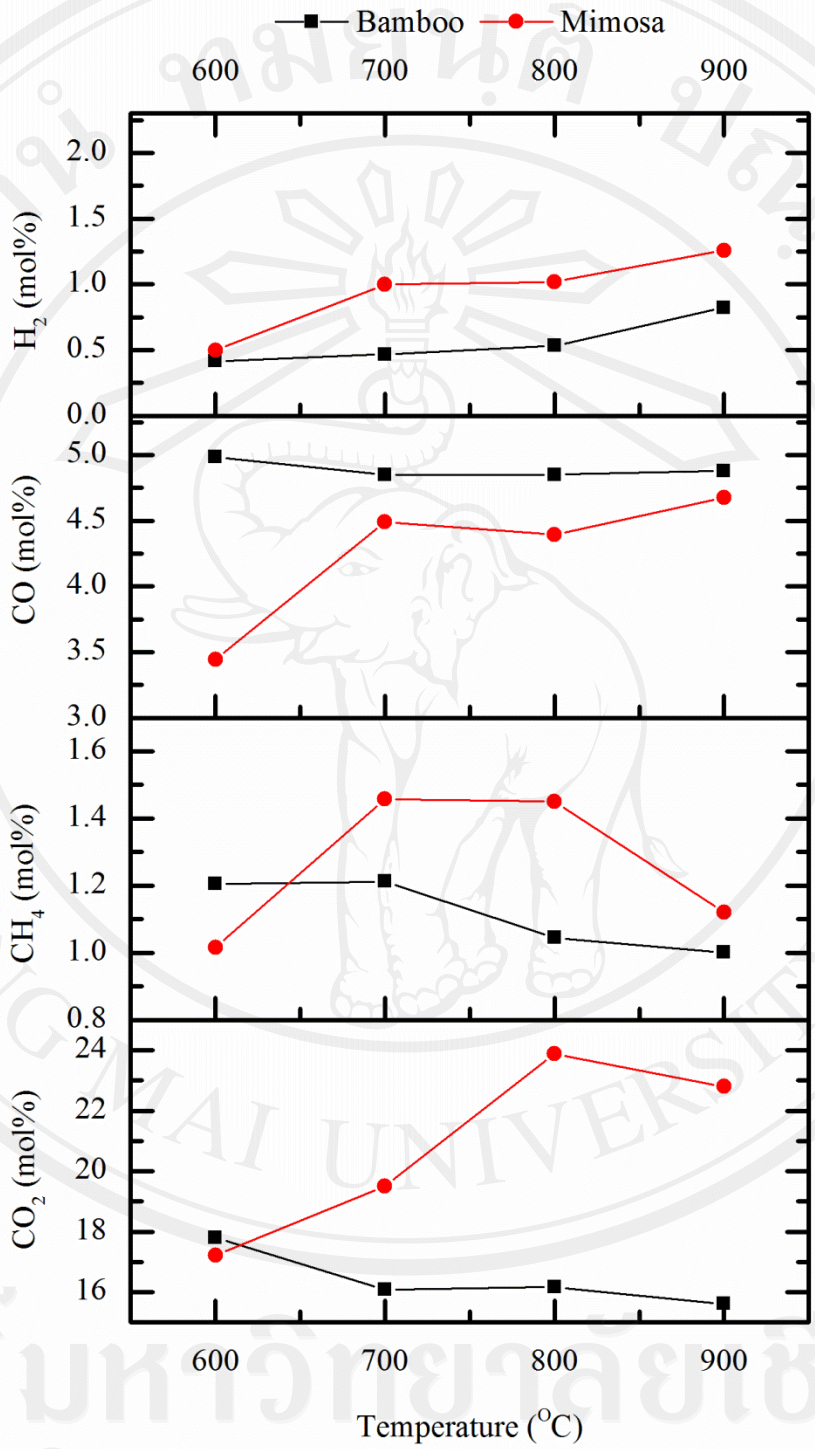

Figure 5.17 Effect of temperature on gas yields in a fixed bed reactor.

It was found that at elevated temperatures, concentrations of CO, CO_2 and CH_4 were increased from 10.5% to 17.9%, 17.5% to 24.5% and 3.8 to 5.1%, respectively. Similar trends with those reported in (Raveendran et al., 1996; Chen et al., 2003; Wei et al., 2007; Kantarelis and Zabaniotou, 2009; Zhou et al., 2009; Plis and Wilk, 2011).

At low temperature, there was high content of CO_2 because CO_2 and CO were the major release gas products from pyrolysis due to high oxygen content in biomass. (Di Nola et al., 2010; Yuzbasi and Selçuk, 2011). More CO lead to more vapors from devolatization convert into non-condensable gases especially CO_2 by conversion of oxygen in tar product into CO_2. Then there is lower content in CO with highest CO_2 yield (Zhang et al., 2011). If the temperature was lower than 700^oC, CO_2 behaves as an inert gas (Duan et al., 2009; Yuzbasi and Selçuk, 2011).

Char combustion with O_2/CO_2 O_2/N_2 have similar reaction rates (Liu, 2009). When the temperature was higher than 700^oC, this leads to significance increase in CO formation due to CO_2-char gasification reaction (Duan et al., 2009; Li et al., 2009; Rathnam et al., 2009; Yuzbasi and Selçuk, 2011). Increasing oxygen concentration results in higher rate of weight loss (Li et al., 2009; Yuzbasi and Selçuk, 2011).

From Figure 5.19, increasing temperature resulted in an increase in the H_2/CO and CO/CO_2 at molar ratios from 0.4 to 0.6 and 0.6 to 0.7 for mimosa*,0.17 to 0.26 and 0.31 to 0.44 for bamboo, 0.14 to 0.27 and 0.18 to 0.23 for mimosa. Increase in temperature appeared to strengthen the endothermic reactions, such as reactions boudouard reaction, steam reforming reaction and water gas reaction and hydrogasification, leading to increased H_2 and CH_4 contents and decreased CO_2 contents. High concentrations of H_2 may come from thermal decomposition of heavy hydrocarbons and tars into lighter hydrocarbons (Ahmed and Gupta, 2009). It was

found to increase due to endothermic reactions with steam reforming reaction and Water gas reaction at low temperatures and exothermic reaction with water–gas shift reaction at high temperatures. The increase in gas yields was also observed from 600 to 900^{o}C. It might be attributed to the fact that reactions boudouard reaction and water gas reaction were favored at high temperature (Wang et al., 2008), and reforming of tar and char were accelerated. From 600 to 900^{o}C, the H_2 content was found to increase greatly. This observation could be a result of exothermic behaviors of reactions hydrogasification and methane steam reforming reaction (Pohořelý et al., 2006; Lapuerta et al., 2008). High CO_2 was produced from decomposition of carboxyl groups and from the exothermic reactions with water–gas shift reaction and carbon oxidation. When temperature was increased, the CO_2 concentration was found to increased. The product gas from wood that has high content in lignin have high yields of CO_2 (Hanaoka et al., 2005), similar to our observation here.

Gas heating value, gas yield and carbon conversion efficiency of air gasification are shown in Figure 5.20. Increasing temperature effect on an increase in gas yield and gas components product such as H_2 and CO which more favorable at high temperature resulting in higher conversion of carbon (Lv et al., 2004; Kumar et al., 2009). Carbon conversion efficiency of mimosa* increased from 55% to 99% which similar to Kumar et al. (2009), gas calorific value increased from 3.2 to 5.2 MJ/Nm^3. Carbon conversion efficiency and LHV of mimosa was increase from 36 to 49% and 0.8 to 1.1 MJ due to due to an increase in H_2 and CO content in product gas while carbon conversion efficiency and LHV of bamboo was not changed.

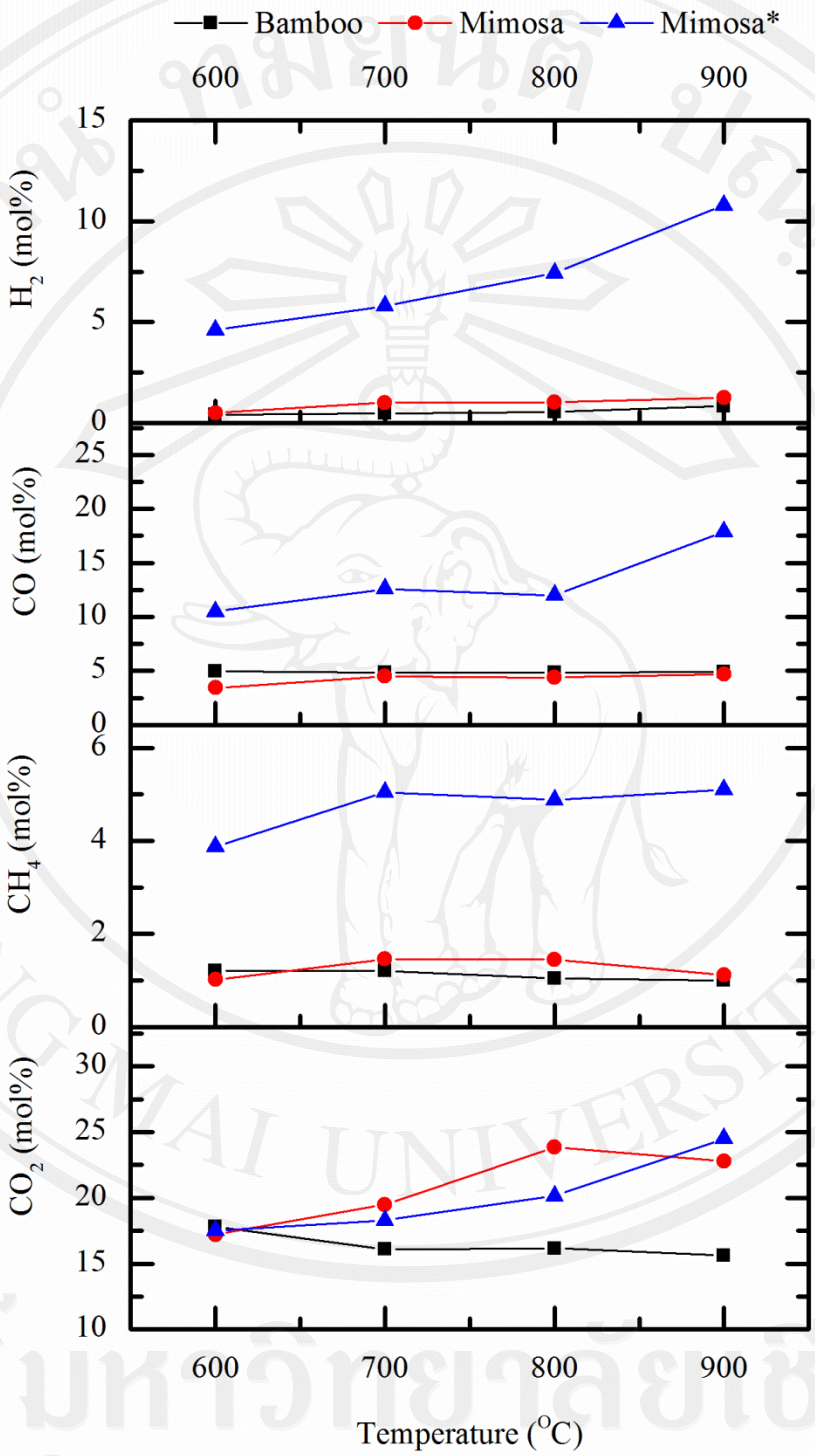

Figure 5.18 Effect of temperature on gas yield in a fixed bed reactor

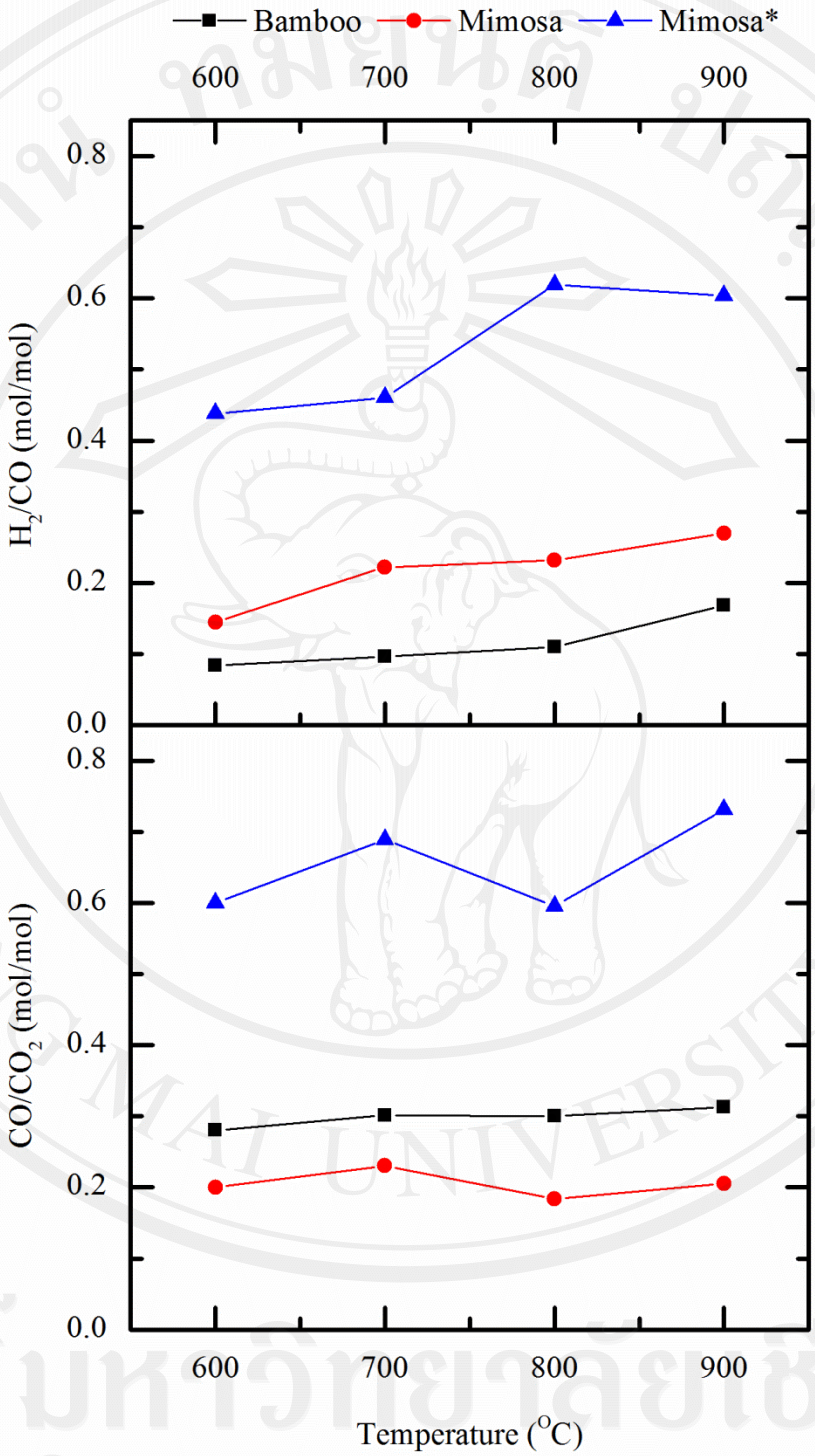

Figure 5.19 Effect of temperature on product gas ratio in a fixed bed reactor

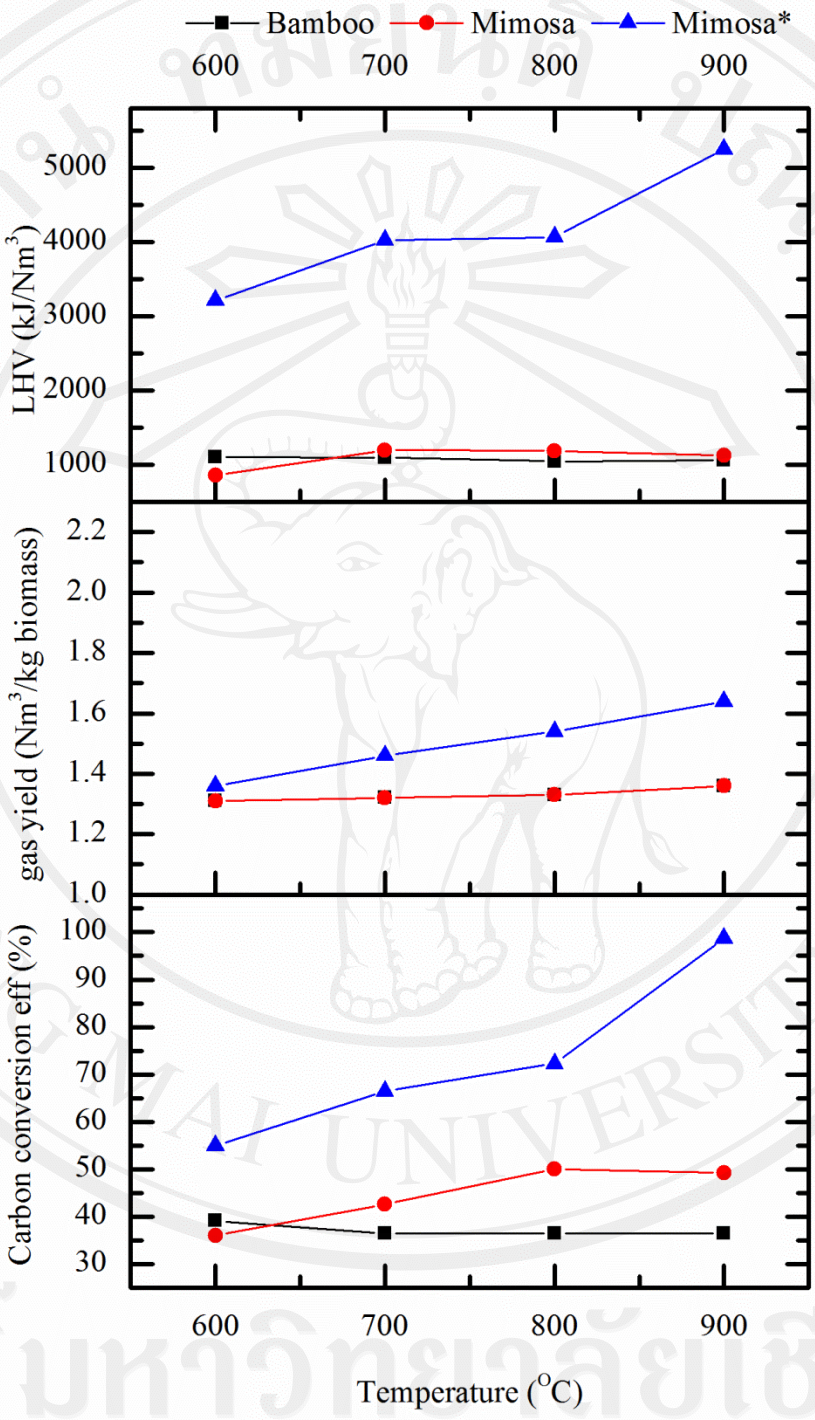

Figure 5.20 Effect of temperature on gas heating value , gas yields and carbon conversion efficiency in a fixed bed reactor.

From Figure 5.21, mimosa was compared with mimosa and bamboo. It was found that when the reactor temperature was increased from 600 to 900^{o}C, the gas yields increased from 59.5% to 81.1%, while the tar and char decreased from 20.5% to 11.9% and 20.0% to 7.0%, respectively. To compare mimosa* with mimosa and bamboo, it was found that the char yield of mimosa* is lower less than other, while gas yield was higher than mimosa at 900^{o}C about 25% and bamboo 15%. Tar content of mimosa* also decreased and compared with bamboo less than 12 %. Tar content decreased with increasing of temperature following the Equation (5.1)

Thermal cracking $$pC_nH_x \rightarrow qC_mH_y + rH_2 \quad (5.1)$$

This is similar to that reported in Chen et al. (2003) and Wang et al. (2008). At higher temperatures, higher gas production may be attributed to the pyrolysis step (Raveendran et al., 1996) with the volatilization process of endothermic of hemicellulose, cellulose and lignin. The full decomposition of cellulose might be attributed to the quick devolatization reactions, leading to very few solid residues left. Charring process was highly exothermal with cellulose (Yang et al., 2007).

Ball et al. (2004) pointed out that with the much higher solid residues generated from hemicellulose and lignin pyrolysis, the exothermal peaks observed in hemicellulose and lignin pyrolysis could be attributed to the charring, while reduction of the char yields occurred with increasing temperature was due to higher degree of carbonization reaction with air (González et al., 2008). Yang et al. (2007) suggested that at higher temperature, charring process of hemicellulose and lignin were endothermic process.

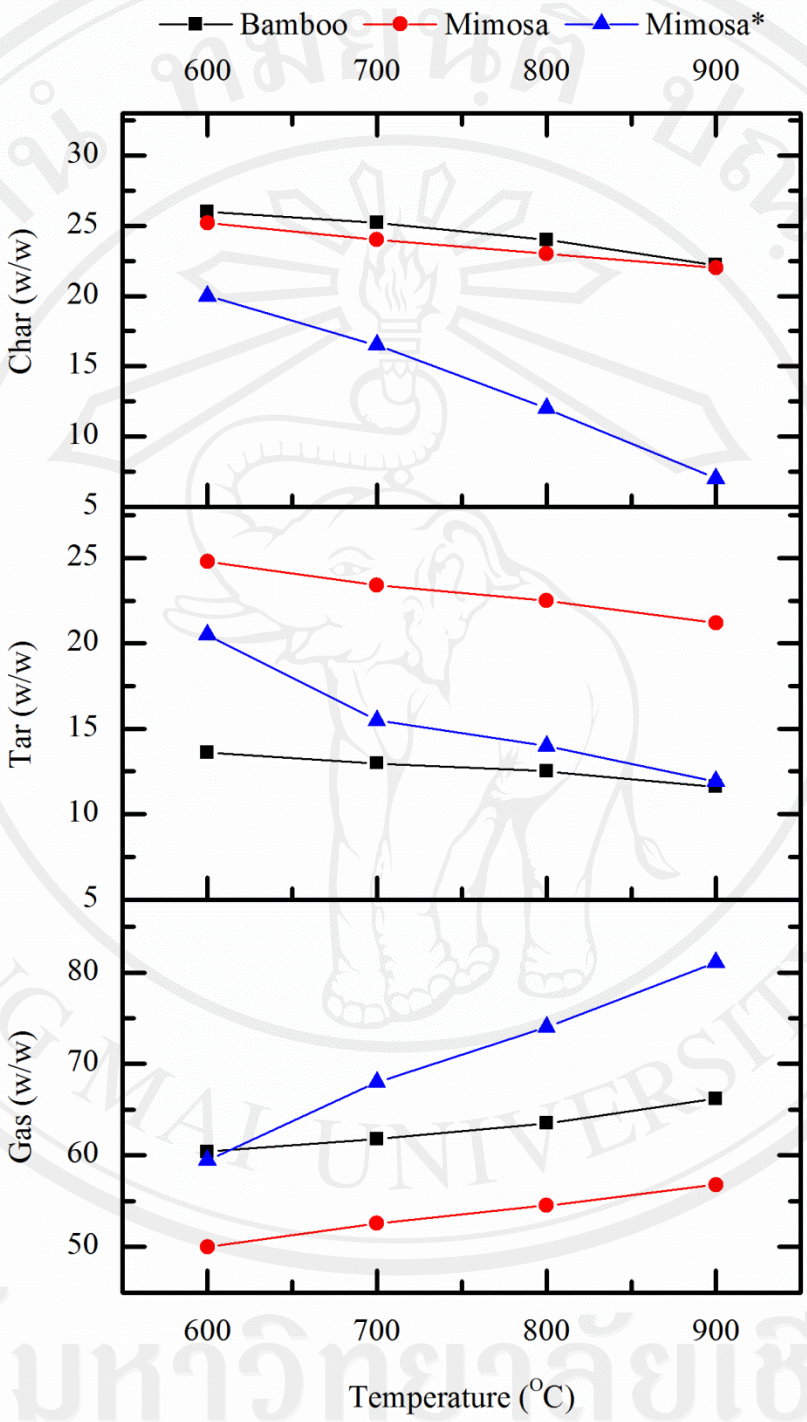

Figure 5.21 Effect of temperature on product yields in a fixed bed reactor

The collection time at 800^{o}C on gas yield is shown in Figure 5.22. It was found that H_2 and CO increased from 7% and 18% to 14% and 29% after 20 min, and subsequently decreased to 5% and 10% at 110 min. Meanwhile, CO_2 was found to increase with time from 5% to 33%. Changes in H_2 and CO were similar to those reported by. Encinar et al. (1998). The first 10 min, biomass temperature increased from room temperature to 790°C as shown in Figure 5.23, this was devolatilization process. High volatile matter content biomass material will have long devolatilization time which can delay the subsequent char gasification and carbonization processes (Ahmed and Gupta, 2009).

An increase in residence time of the volatile phase resulted in increasing gas yield. There were many highly competitive reactions in these processes. Formation of H_2 and CO appeared to be more rapid than other gases during hemicellulose, cellulose and lignin decomposition and gasification. Within reaction time of 60 min, the yields of CO and CO_2 were parity, but after that, CO_2 was found to be more competitive (Ahmed and Gupta, 2009). High concentration of CO_2 seemed to suppress CO yield, in line with those reported by Mitsuoka et al. (Mitsuoka et al., 2011). The high content of CO_2 in the product gas was generated during char gasification, and it was the higher content than CO in gas composition.

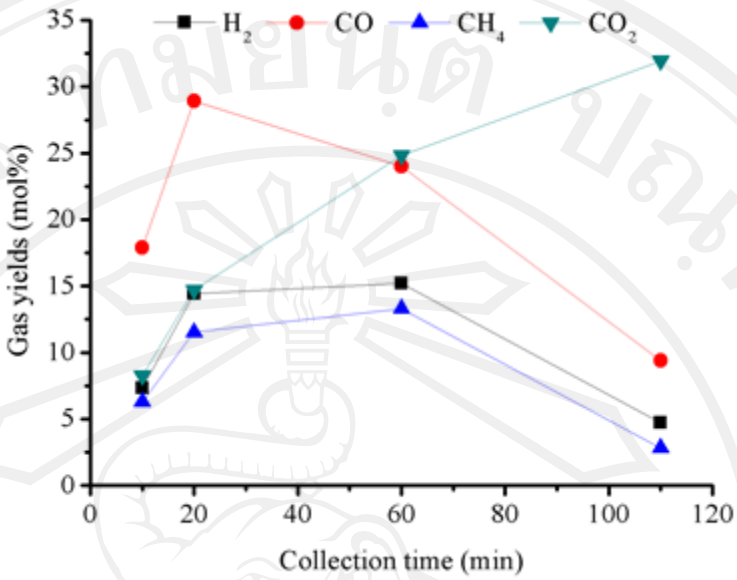

Figure 5.22 Effect of collection time on product gas composition at 800°C in a fixed bed reactor

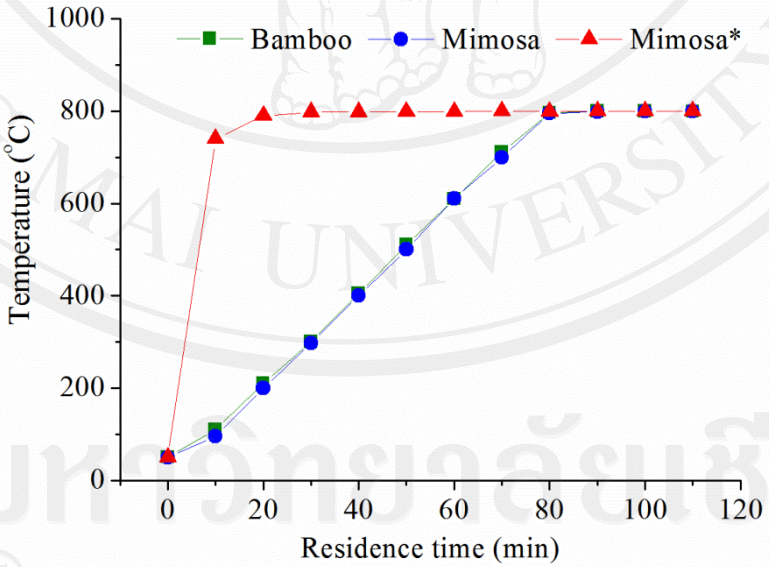

Figure 5.23 Temperature profile of biomass in fixed bed during gasification process in a fixed bed reactor

5.3.2 Effect of Catalyst on Product Yields

In this work, dolomite was used as in-bed catalytic additives by mixing dolomite with biomass in air gasification. The effect of catalyst on product yields and gas composition was studied for the temperature at 900^{o}C as shown in Figure 5.24. This shows the gas, tar and char yields between the non-catalytic (catalyst : biomass 0) and catalytic (catalyst : biomass between 0.5 to 1 for bamboo and mimosa, and 0.5 to 2 for mimosa*) processes.

Increased of catalyst to biomass ratio (CBR) resulted to decrease of char yield about 2% for all biomass. Char content of bamboo and mimosa decreased around 1% and 4% while mimosa* unchanged between CBR of 0% to 1%.Gas yield increase almost 4% and highest around 84.8% for mimosa*, mimosa and bamboo increased around 6% and 3% and highest around 63.4% and 69% at CBR of 1.

It can be seen that the gas yields were higher when catalyst was used, while tar and char yields were lower than the uncatalyzed process. Tar content decrease around 4%, 2%, 1.6%, while gas yield increased around 2%, 6% and 3% for mimosa*, mimosa and bamboo, respectively

This observation was in line with Hanaoka et al. (2005) and (Olivares et al., 1997). Catalyst was found to have positive effect on tar elimination causing improve in the gas composition (Narváez et al., 1996; Gil et al., 1999) due to secondary reaction of primary tar was catalyzed by CaO (Chen et al., 2012; Han et al., 2010). CaO in dolomite absorbed CO_2 in product gas and improved the water gas and water gas shift reactions. CO_2 was also reaction with tar (Olivares et al., 1997) as following the Equation (5.2). The reaction of tar and dry CO_2 resulted in a decreased of tar and

CO_2, while yields of H_2 and CO increased at CBR from 0 to 1 as shown in Figures 5.24 and 5.25.

Dry reforming $$C_nH_x + nCO_2 \rightarrow \left(\frac{x}{2}\right) H_2 + 2nCO \quad (5.2)$$

The evolution of the concentrations of the gas produced (%mol) as a function of catalyst to biomass ratio at 900°C was shown in Figure 5.25. It can be seen that the presence of dolomite clearly encouraged the production of H_2.

At the catalyst to biomass ratio equal to 1, H_2 content was amounted to 13.3, 3.2 and 2 mol% and CO was about 23, 8.3 and 7.7 mol% for mimosa*, mimosa and bamboo, respectively. The quantity of CO_2 was found to be higher than that obtained from the uncatalyzed case (Asadullah et al., 2002; Hanaoka et al., 2005).

As far as the product gas ratio was concerned (Figure 5.26), H_2/CO was found to increase with increasing catalyst to biomass ratio at CBR from 0 to 1 while CBR from 1 to 2, H_2/CO was found to increase although H_2 and CO appeared to decrease. H_2/CO and CO/CO_2 reached maximum at the catalyst to biomass ratio of 2 and 1, respectively. The catalyst used appeared to cause higher CO_2 content in the product gas after CBR higher than 1 (Dennis and Hayhurst, 1987; González et al., 2008).

Figures 5.27 show gas calorific value, carbon conversion efficiency and gas yield of air gasification of mimosa with catalyst at different ratio. Increasing of CBR effected on an increase of gas yield and LHV with maximum at CBR of 1 due to increase of gas components product such as H_2 and CO. CBR was higher than 1, LHV decrease due to decrease of H_2 and CO content, and increased of CO_2 content. While carbon conversion decreased with presence of catalyst, and unchanged with CBR increased although content of CO_2 increased and CO decreased.

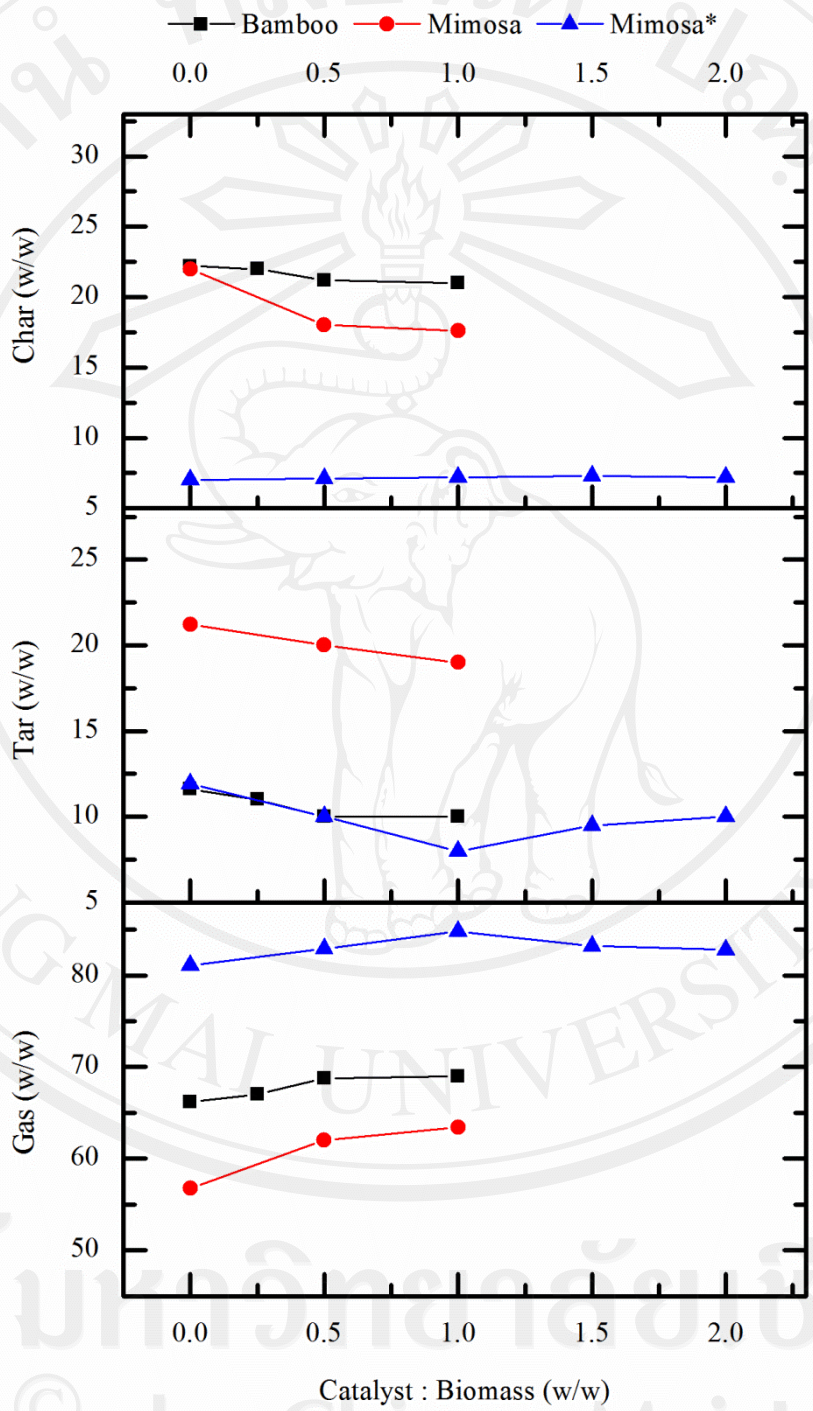

Figure 5.24 Effect of catalyst to biomass ratio on product yields in a fixed bed reactor

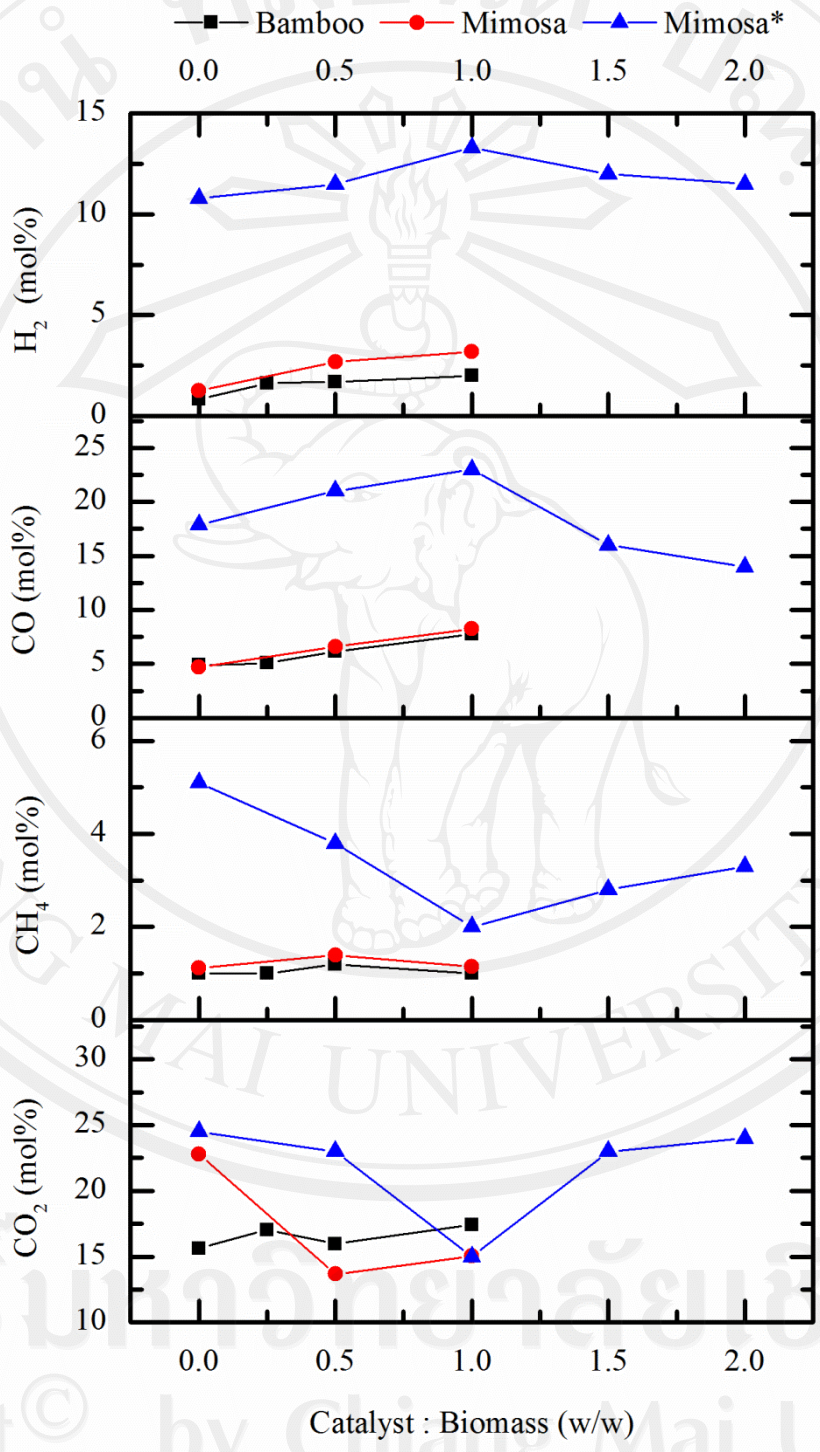

Figure 5.25 Effect of catalyst to biomass ratio on gas yields in a fixed bed reactor

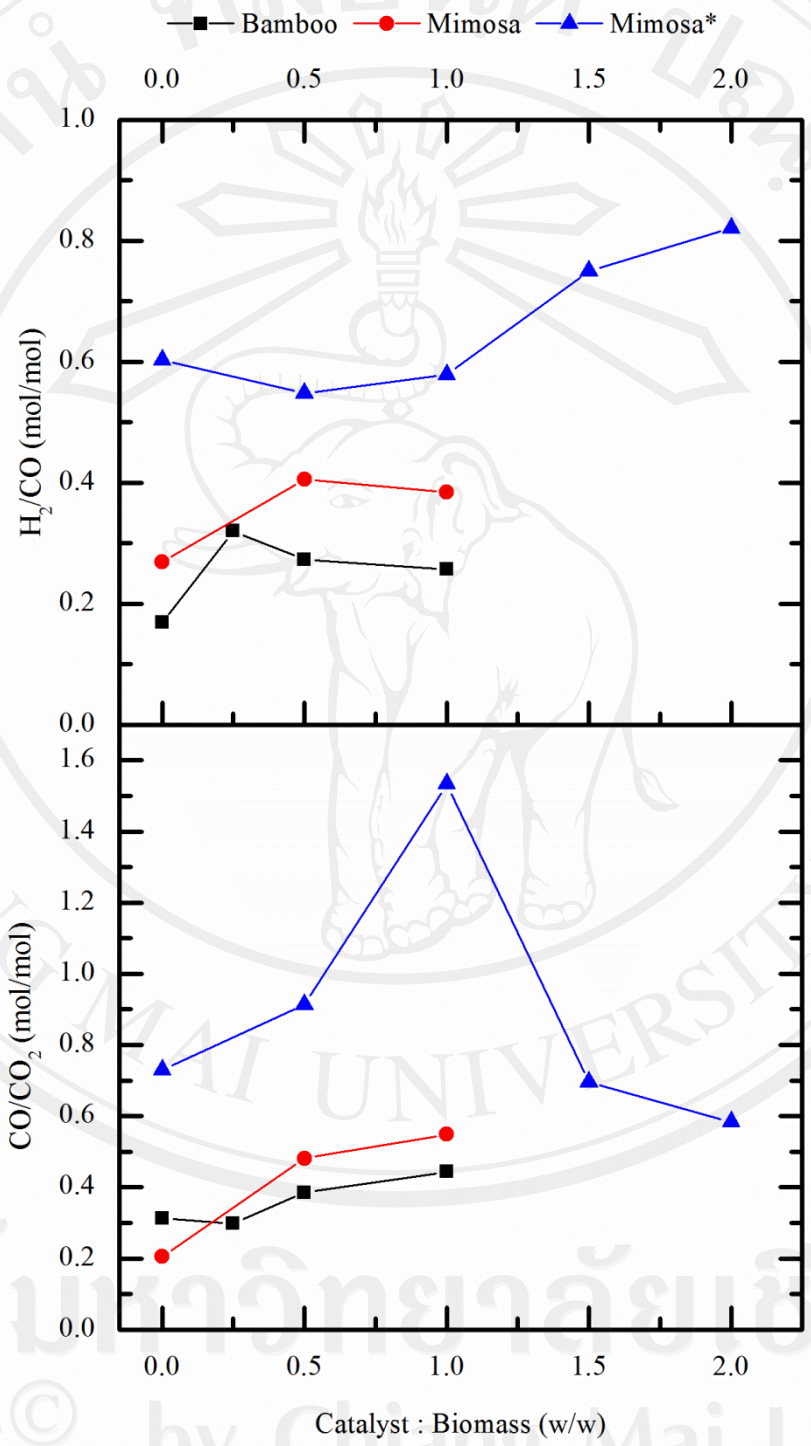

Figure 5.26 Effect of catalyst to biomass ratio on gas ratio in a fixed bed reactor

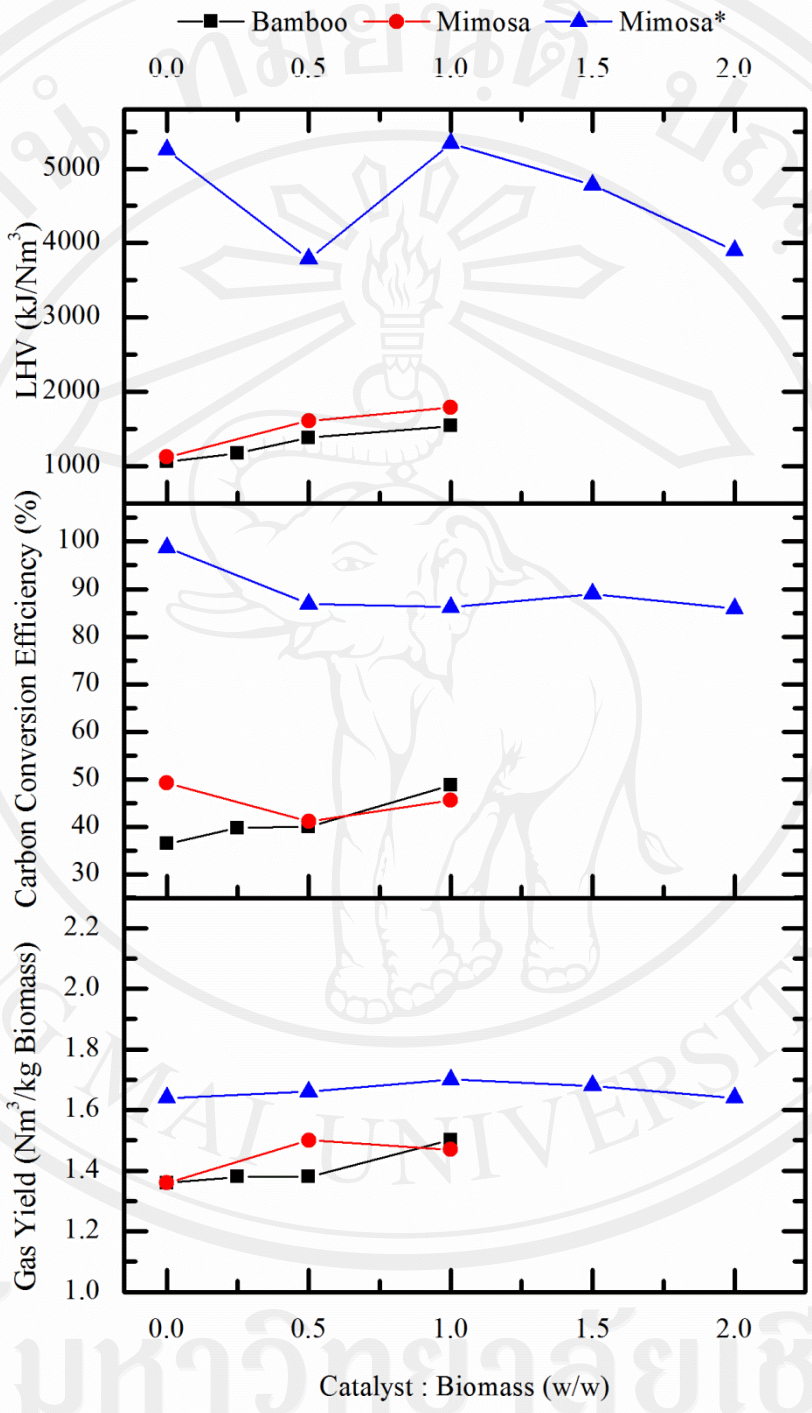

Figure 5.27 Effect of catalyst to biomass ratio on gas heating value, gas yields and carbon conversion efficiency in a fixed bed reactor

5.4 Fluidized Bed Gasification

5.4.1 Effect of Temperature on Gas Yields

The effect of temperature on product distributions from gasification of bamboo and mimosa are shown in Figure 5.28. It was found that when the temperature was increased from 400 to 700^{o}C, the tar yields increased from 31.8% to 42.7% for bamboo and 31.8% to 42.7% for mimosa, while the gas and char decreased from 53.7% to 46.1% and 14.5% to 11.2% for bamboo, and 54.7% to 45.5% and 13.5% to 11.8.0% for mimosa, respectively.

The effect of the temperature on product gas composition in fluidized bed reactor is shown in Figure 5.29. It was found that the content of H_2 and CO in the product gas decreased with increasing temperature, while the content of CO_2 increased. The content of CH_4 was found to slightly decrease. At low temperature, the content of hydrogen in gas product can be obtained from devolatillization of hemicelluloses, cellulose, and lignin, including secondary decomposition of their pyrolyzed products (Zhang et al., 2010). At higher temperatures, the content of hydrogen was decreased due to high reactivity of the char with air. The reaction may occur complete oxidation and partial oxidation (Skoulou et al., 2008). Total combustion may occur to release more CO_2. Combustion reactions hardly produce H_2 (Zhang et al., 2010)

Figure 5.30 shows the effect of temperature on H2/CO and CO/CO_2 ratio. With increasing of temperature resulted in increased of H2/CO and CO/CO_2 ratio, and reached maximum at 500^{o}C with 0.46 and 600^{o}C with 0.28 for mimosa and bamboo, respectively. After that both of them decreased with increasing temperature. CO/CO_2 decreased with elevated of temperature due to an increase of CO_2 content and a decreased of CO content.

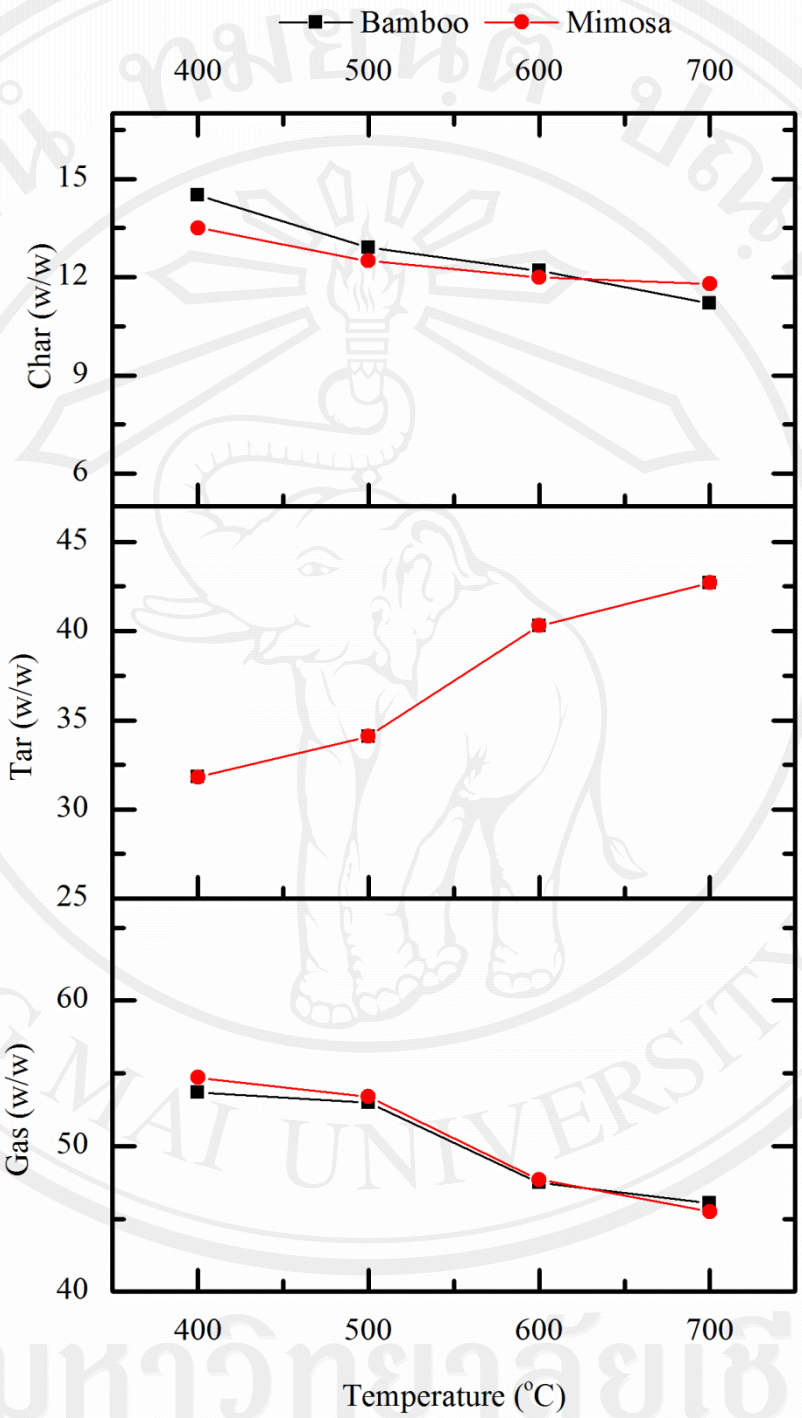

Figure 5.28 Effect of temperature on product yields in a fluidized bed reactor

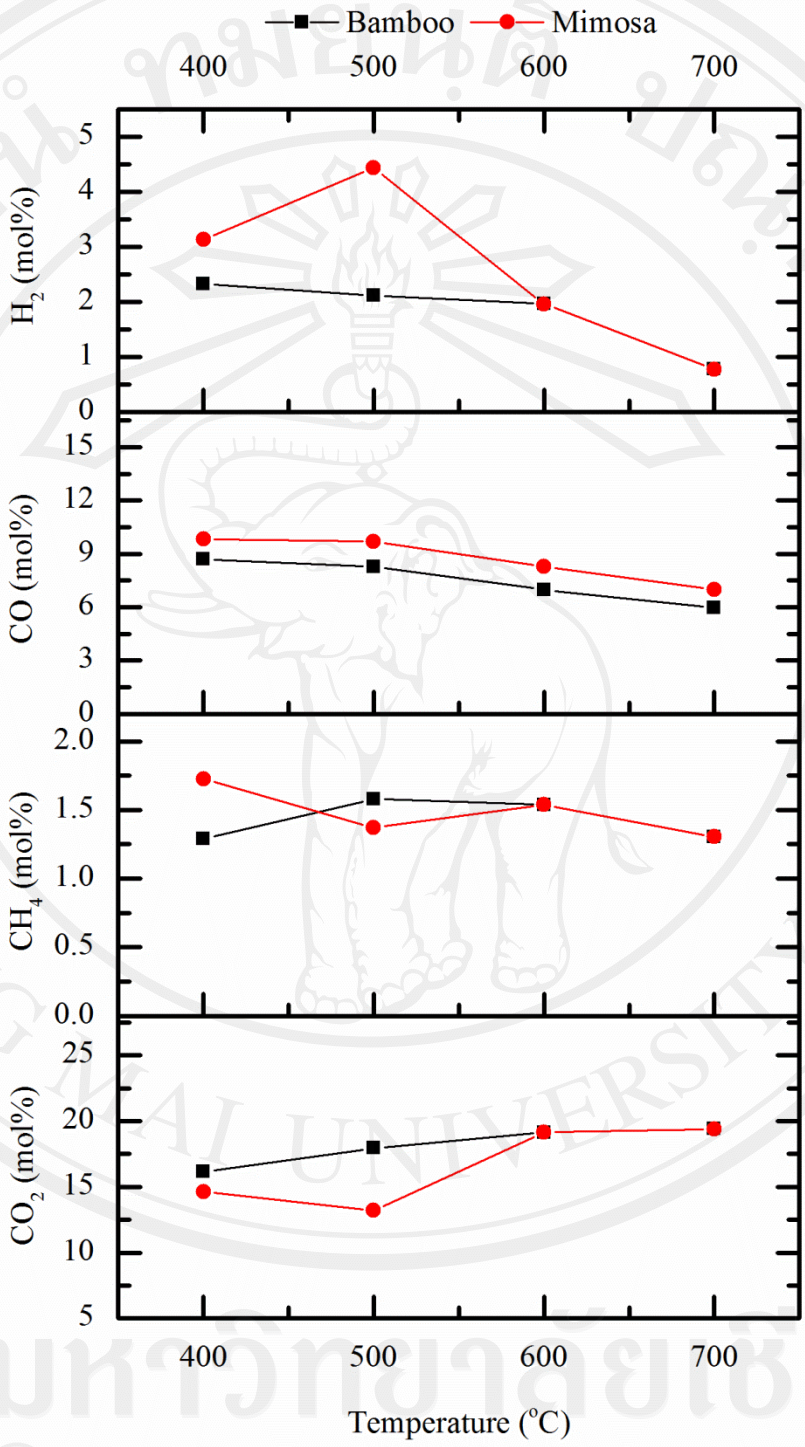

Figure 5.29 Effect of temperature on gas composition in a fluidized bed reactor

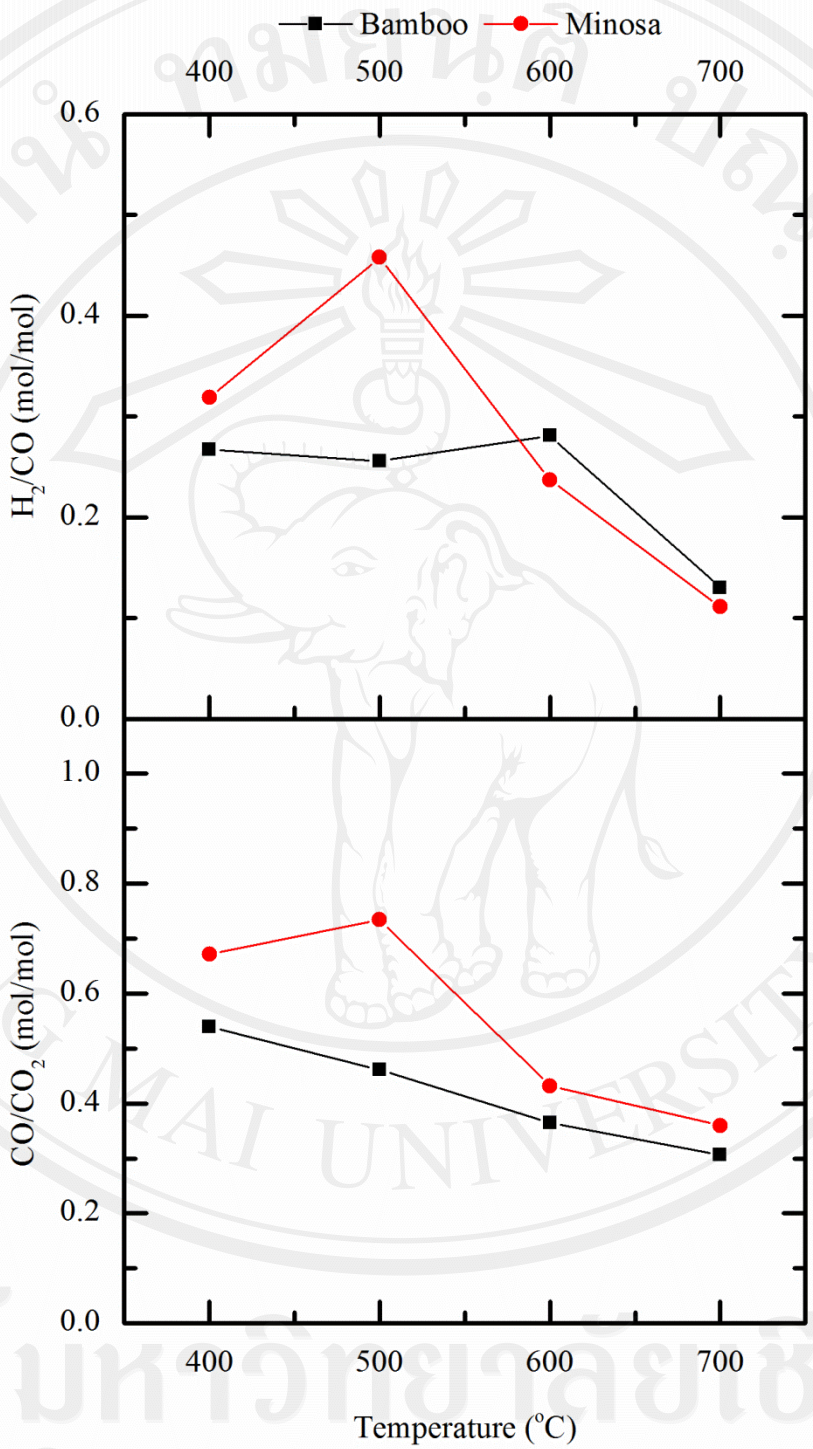

Figure 5.30 Effect of temperature on gas ratio in a fluidized bed reactor

Figure 5.31 shows effect of temperature on the calorific value of gas product, gas yield and carbon conversion efficiency.

Increasing of temperature from 400 to 700^{o}C affected on decreasing of gas calorific value from 2.19 to 1.43 MJ/Nm^3 and 1.81to 1.3 MJ/Nm^3 for mimosa and bamboo, respectively. Due to decrease of H_2, CO and CH_4 content and increase of tar content in the gas product with increasing temperature. Carbon conversion efficiency and gas yield tend to be unchanged.

To compare between fluidized bed gasification and fixed bed gasification, both reactor, mimosa has high content of H2 and CO than bamboo. In fluidized bed, content of H2 and CO of both biomasses had higher value around 2-3 times than in fixed bed. While CO_2 content in fluidized bed was slightly higher than in fixed bed. LHV values of fluidized bed were also higher than in fixed bed.

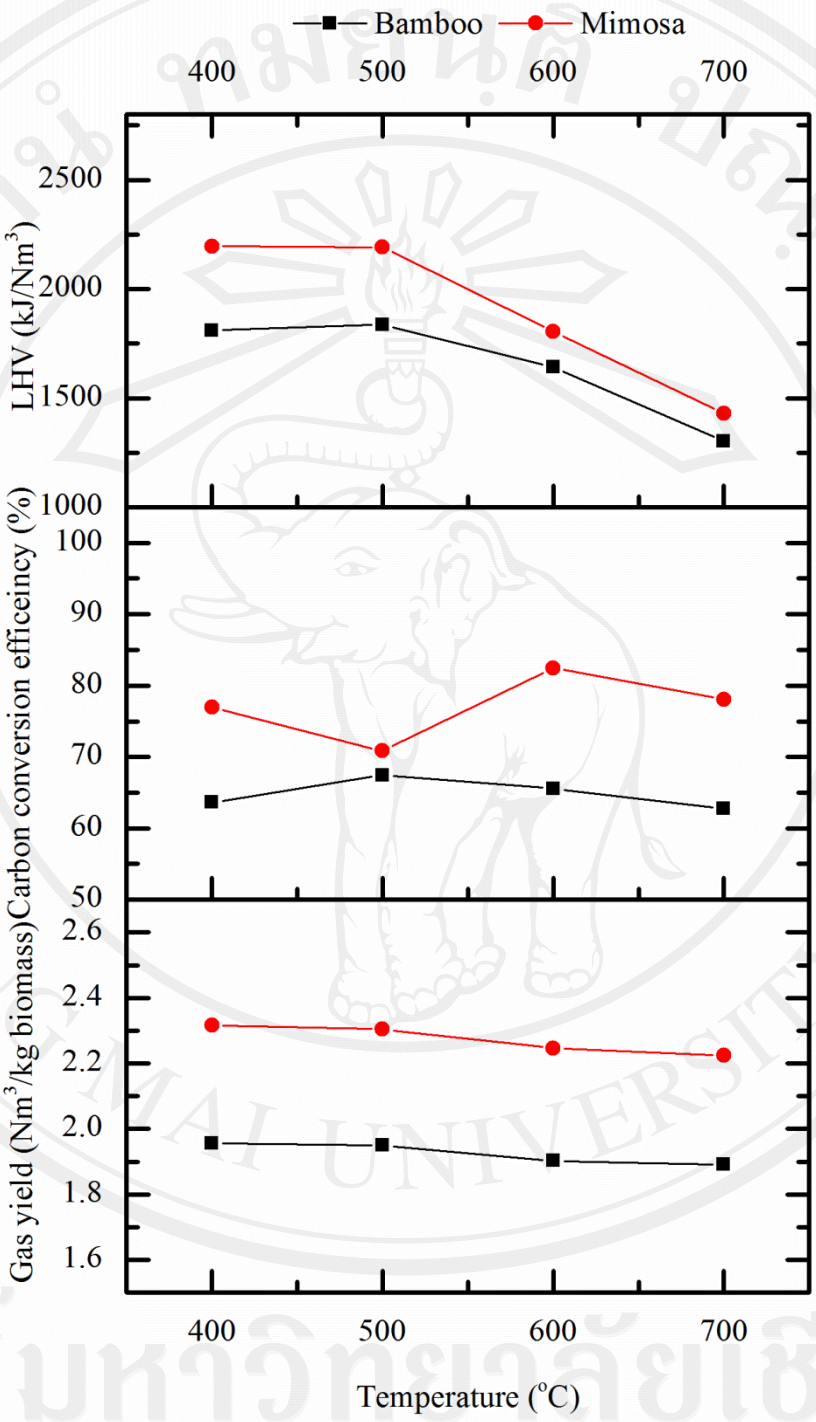

Figure 5.31 Effect of temperature on gas heating value , gas yields and carbon conversion efficiency in a fluidized bed reactor

5.4.2 Effect of Catalyst on Product Yields

In this work, dolomite was used as in-bed catalytic additives by mixing dolomite with sand in fluidized reactor. The effect of presence catalyst (catalyst : biomass 1) on product yields and gas composition was studied for the temperature at 700^{o}C as shown in Figure 5.32. Increased of catalyst to biomass ratio (CBR) from 0 to 1 resulted to decrease of char yield around 2.3% and 1.6% while gas yield increase around 17.5 and 16.8% for mimosa and bamboo. Tar content decrease around 15.2% for all biomass.

The effect of catalyst on gas compositions in fluidized bed are shown in Figure 5.33. It was found that the presence of dolomite with CBR 1, H_2 and CO content increased while CO_2 content decreased due to it was adsorbed by CaO, decomposed with carbon by Boudouard reaction (Han et al., 2012), tar cracking and tar reforming with CO_2 to produce more H_2 (Rapagna et al., 1998; Simell et al., 1999) and CO, CO_2 also reacts with excess carbon in the solid particles, to produce more CO (Caballero et al., 1997). CH_4 is slightly decreased.

With the presence of dolomite result in increased of H_2/CO and CO/CO_2 ratio. Figure 5.34 shows the maximum of H_2/CO ratio with 0.5 and 0.28 for mimosa and bamboo, respectively (Tomishige et al., 2004). The H_2/CO ratio of fluidized bed was higher than fixed bed but CO/CO_2 was lower than fixed bed. Due to H_2 and CO in fluidized bed has higher content than in fixed bed while CO_2 was similar. This ratio may be useful for gasoline and Fischer Tropsch synthesis which H_2/CO ratio should be during 0.5 to 2.0, and methanol should be about 2.0. However, in a commercial gasifier the H_2/CO ratio of the product gas is typically less than 1.0.

Figure 5.35 show the calorific value of gas product. Increasing of CBR ratio affected on increasing of the heating value of the product gas. Due to increase of H_2, CO and CH_4 content in the gas product with increasing temperature. LHV of mimosa was higher than bamboo both in fixed bed and fluidized bed. But LHV in fluidized bed was higher than in fixed bed.

Figures 5.35 show gas calorific value, carbon conversion efficiency and gas yield of air gasification of mimosa and bamboo with catalyst at CBR of 0 and 1. Increasing of CBR affected on an increase of LHV from 1.4 to 2.2 MJ/Nm^3 and 1.3 to 1.9 MJ/Nm^3 for mimosa and bamboo, respectively. Calorific value of gas product increased with temperature due to an increase of gas components product such as H_2 and CO.

Gas yield of mimosa and bamboo also increased from 2.2 to 2.4 Nm^3/kg and 1.8 to 2.0 Nm^3/kg due to a decrease of tar and char yield. Carbon conversion efficiency of bamboo also increased from 62.8 to 68.8% due to CO_2 content decrease with increase of CO. But carbon conversion efficiency of mimosa decreased from 78 to 70% due to an decrease of CO_2 with increase of H_2 and CO.

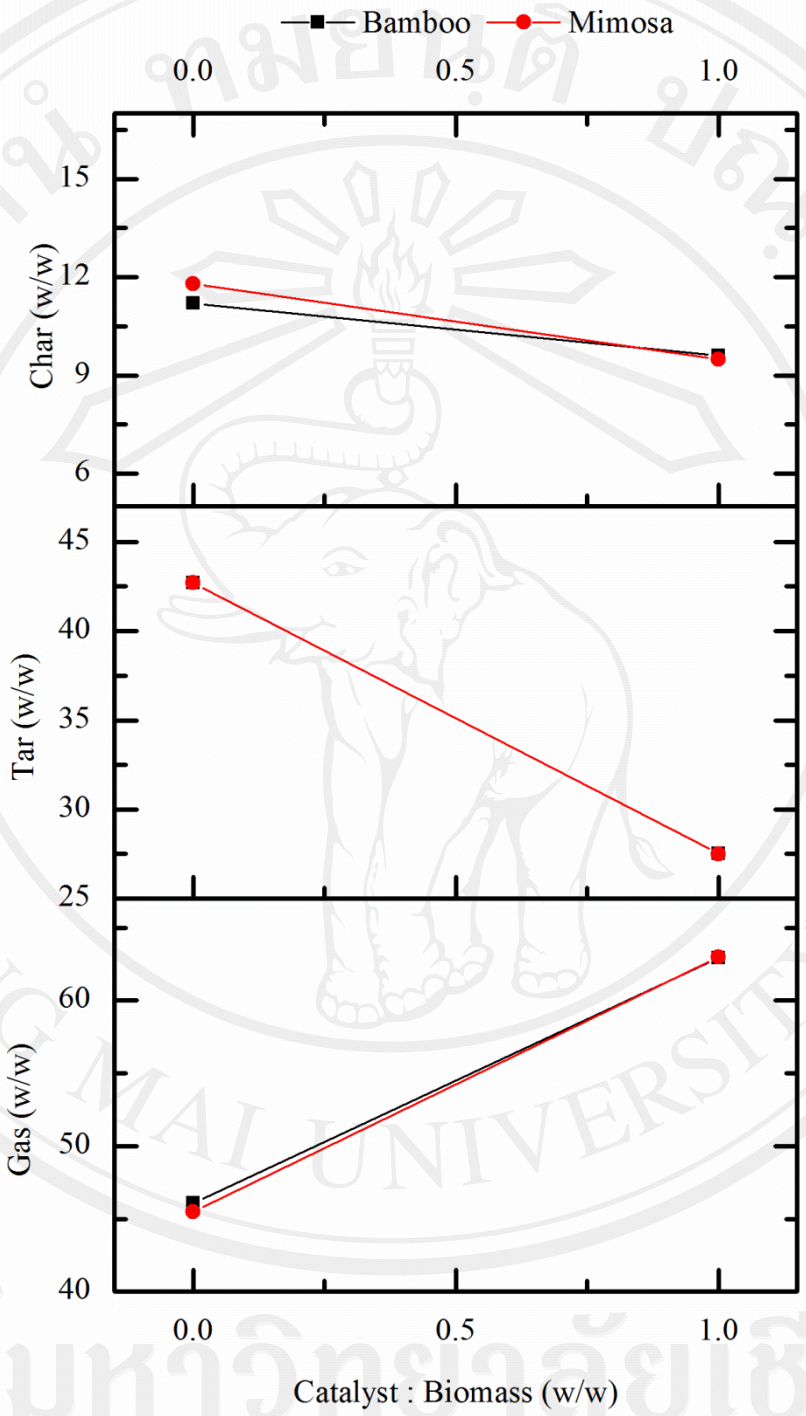

Figure 5.32 Effect of catalyst to biomass ratio on product yields a fluidized bed reactor product yields in a fluidized bed reactor

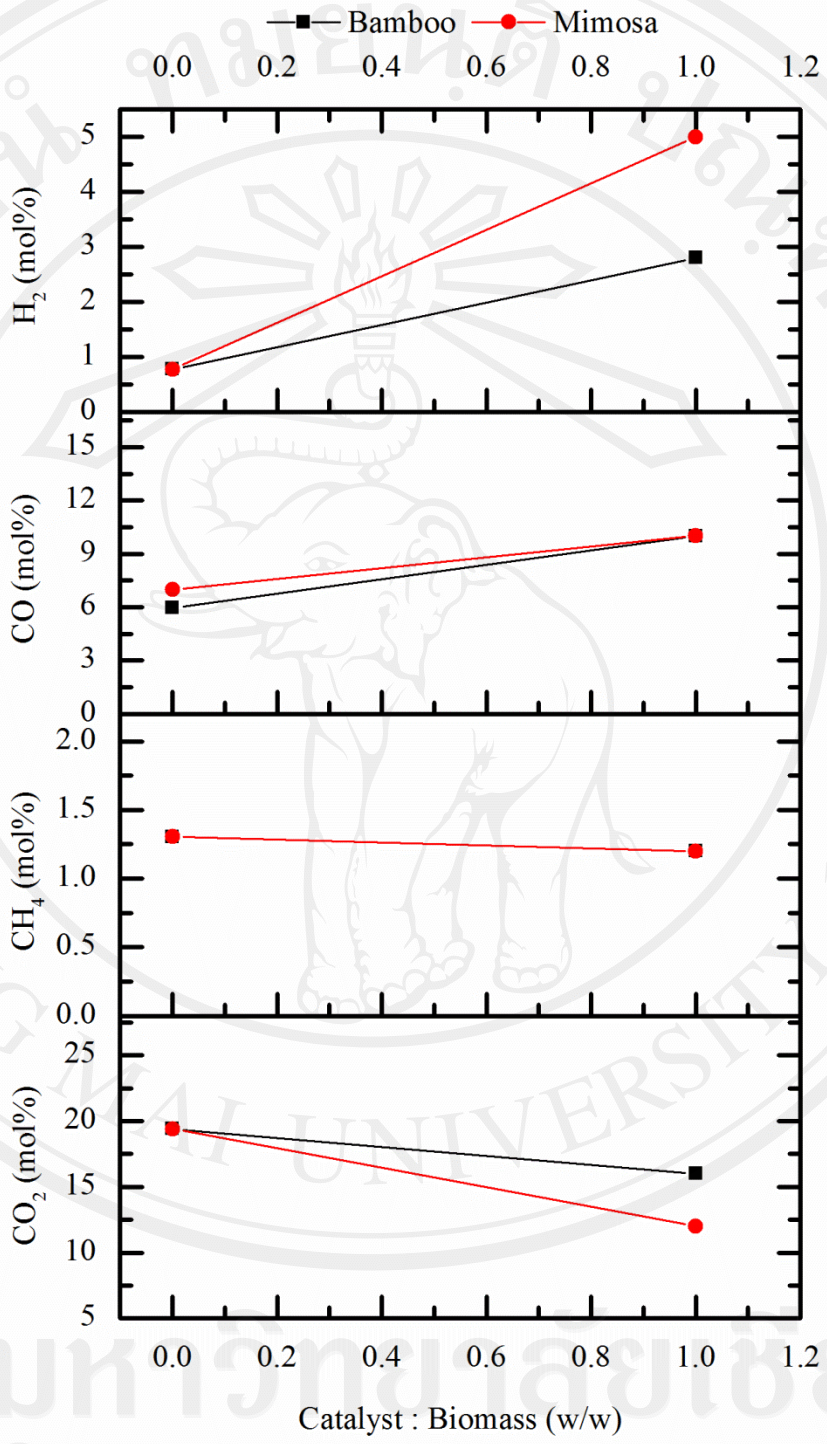

Figure 5.33 Effect of catalyst to biomass ratio on gas composition in a fluidized bed reactor

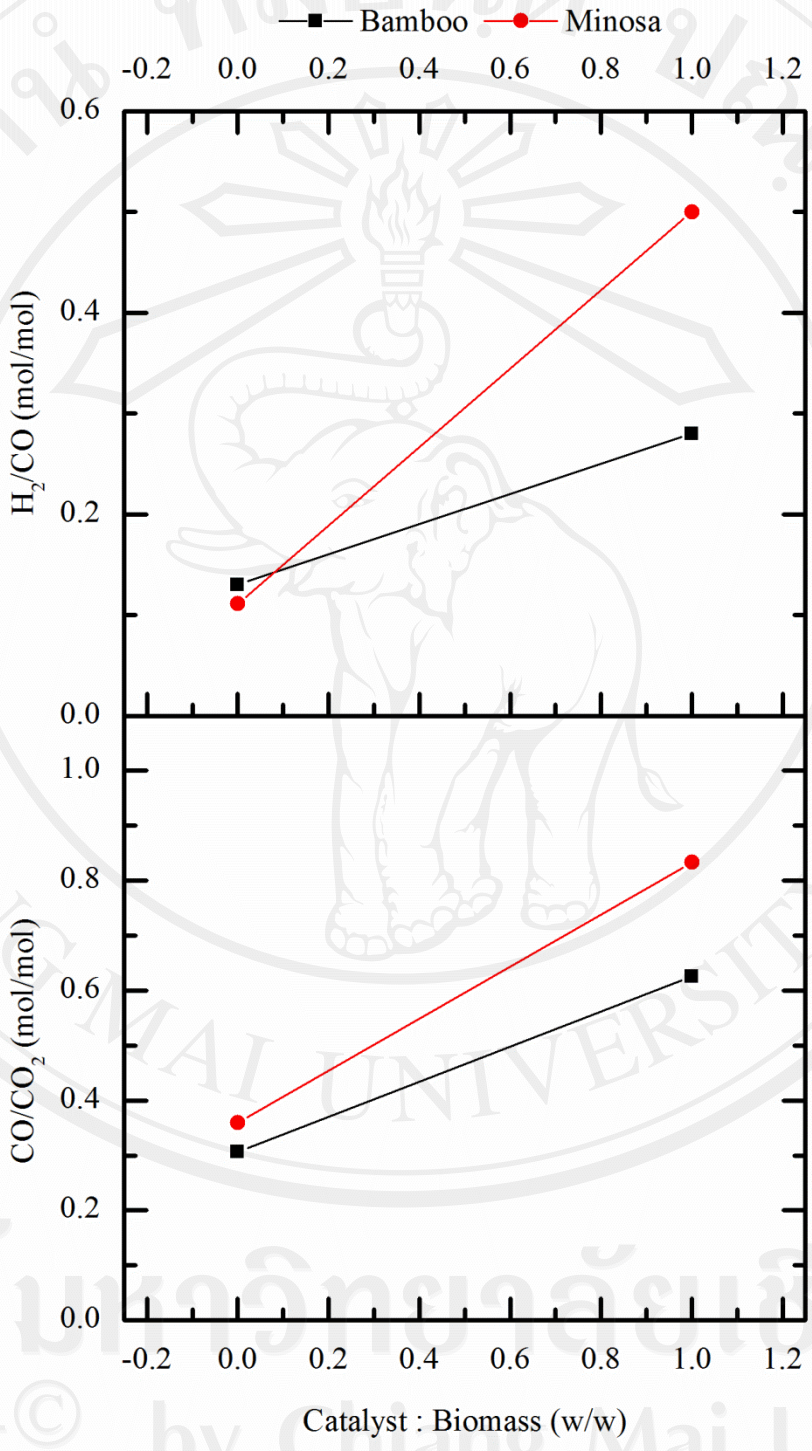

Figure 5.34 Effect of catalyst to biomass ratio on gas ratio in a fluidized bed reactor

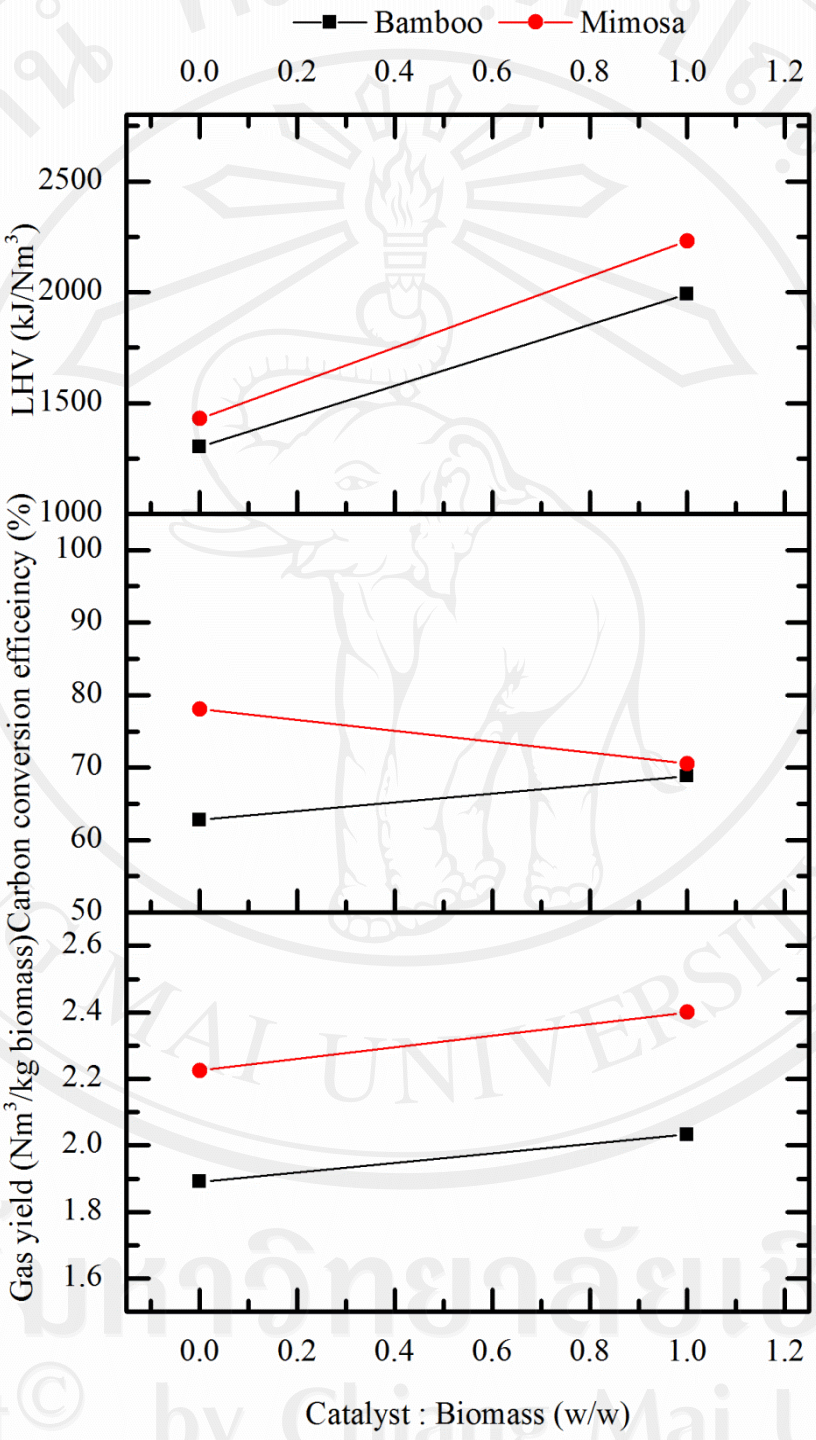

Figure 5.35 Effect of catalyst to biomass ratio on gas heating value , gas yields and carbon conversion efficiency in a fluidized bed reactor

5.5 Gasification Modeling

The comparison between equilibrium modeling and experiment results from air gasification of mimosa and bamboo are shown in Figures 5.34 and 5.35. The model calculated too high H_2 yields than the experiments. The other gas compositions were similar value both for mimosa and bamboo. RSME calculated as shown in Table 5.6

Table 5.6 Compared RMSE between model and adjusted model with experiment

Mimosa				Bamboo			
Model		Adjusted model		Model		Adjusted model	
Fixed bed	Fluidized bed	Fixed bed	Fluidized bed	Fixed bed	Fluidized bed	Fixed bed	Fluidized bed
3.75	4.15	3.08	4.85	2.52	3.14	2.56	2.97

The model was validated with other literature as shown in Table 5.7. It was found that the adjusted model had corrected RMSE. This model was comparable with Guatum (2010) and Sharma (2008b) with RMSE less than 0.33and 1.47. While compared with Sharma (2008a), model calculated too high H_2 yield. Comparison RMSE between model with experimental results and other literature, model can be predicted well with RMSE less than 5 both on experimental results and other literature.

Table 5.7 Compared RMSE between model and adjusted model with other literature

Sharma (2008a)		Sharma (2008b)		Gautum (2010)	
Model	Adjusted model	Model	Adjusted model	Model	Adjusted model
4.07	4.02	1.47	1.24	0.31	0.33

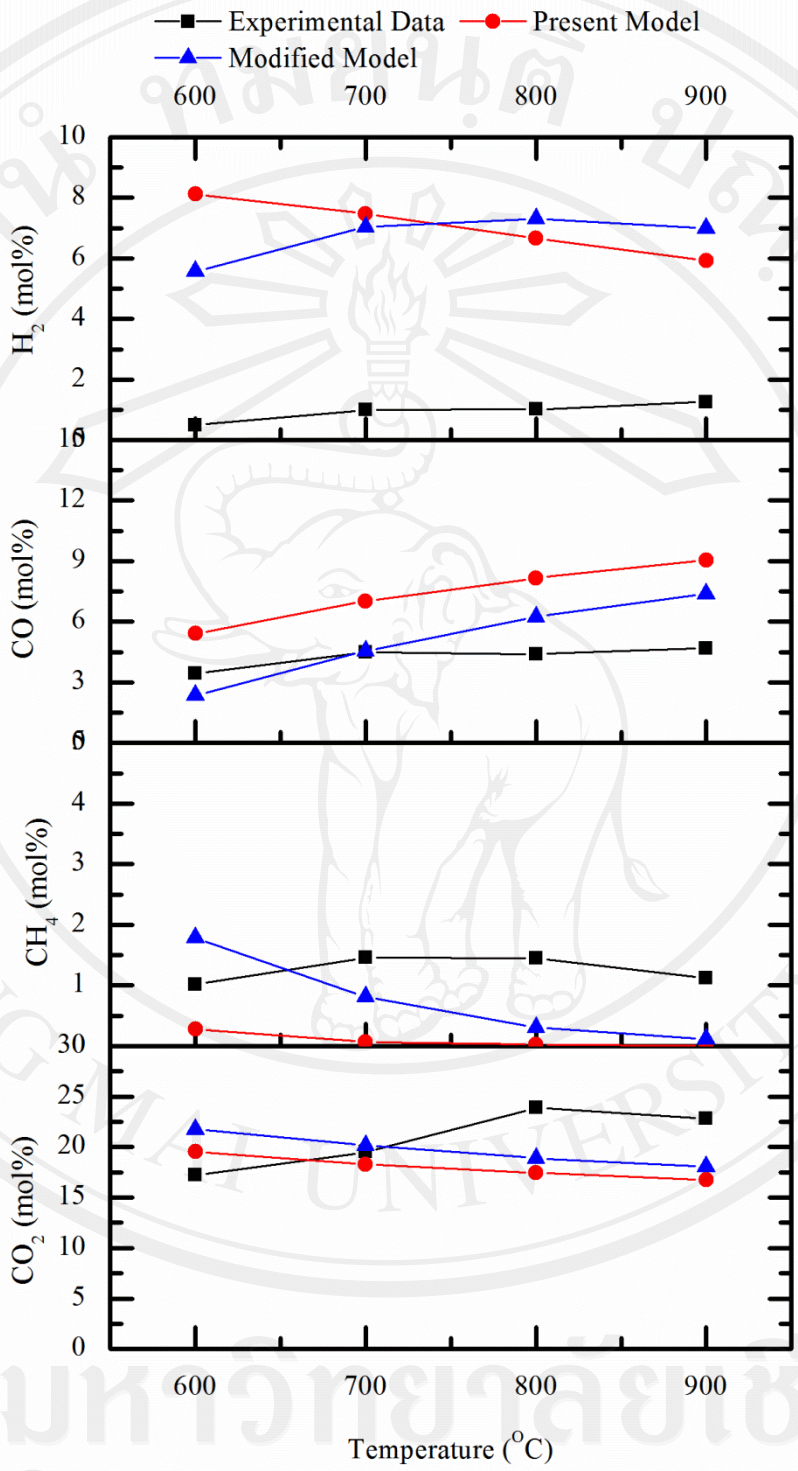

Figure 5.36 Compared experimental result with model of mimosa gasification

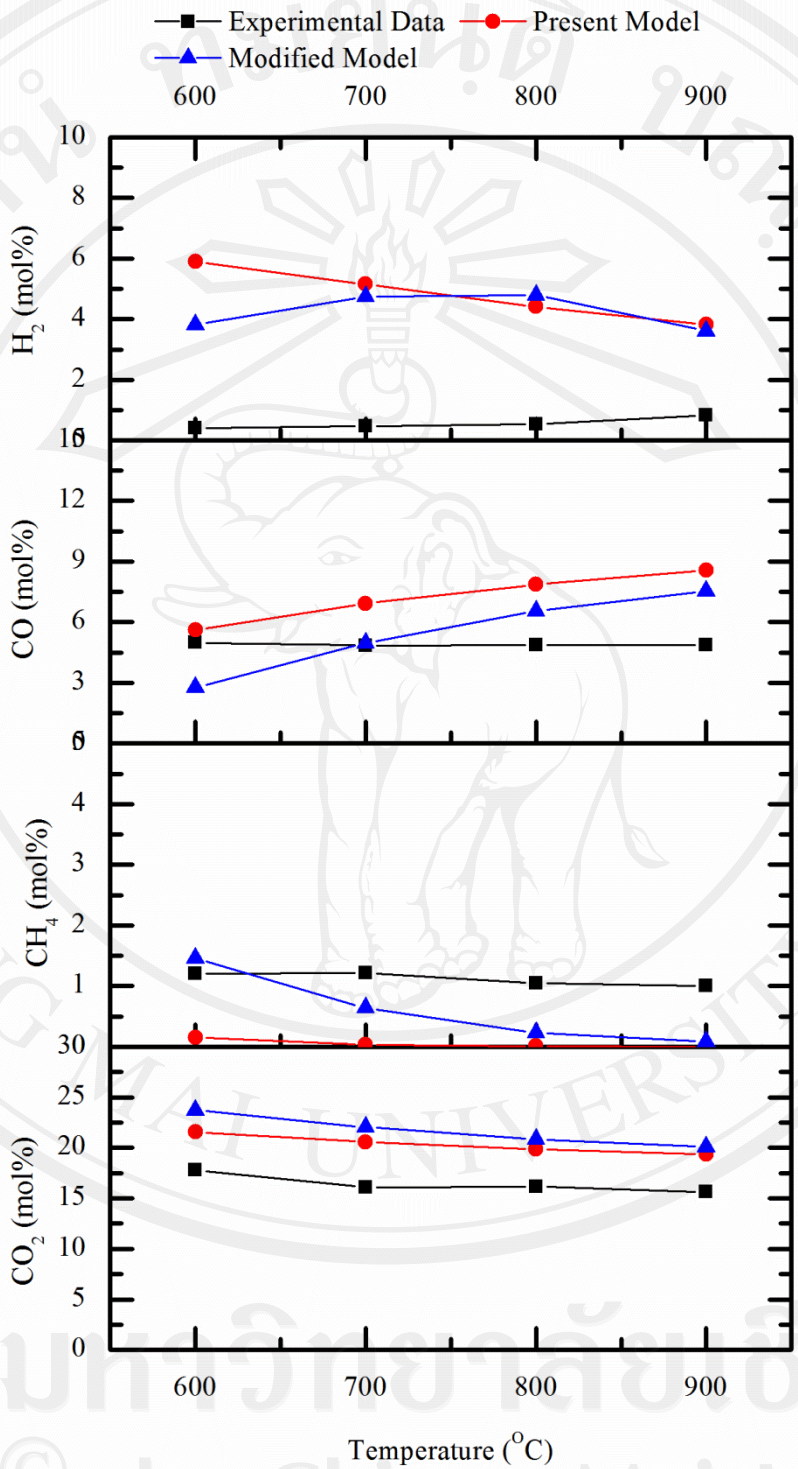

Figure 5.37 Compared experimental result with model of bamboo gasification