CHAPTER 3

LITERATURE REVIEW

3.1 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a study on kinetics of mass change under thermal process of various feedstocks. This method is used for determining the reaction rates that calculated from dehydration, and volatilization of feedstocks and subsequent reactions in pyrolysis, gasification and combustion that occur under thermal degradation. The reaction kinetics of pyrolysis, gasification and combustion are used to calculate the yield rate of gas product by mathematical modeling.

There are a number of literatures that use TGA to determine the kinetics parameters of biomass structures such as hemicellulose (Yang et al., 2007; Chen and Kuo, 2011; Pasangulapati et al., 2012), cellulose (Yang et al., 2007; Lv et al., 2010; Chen and Kuo, 2011; Gao et al., 2012; Pasangulapati et al., 2012), xylan (Chen and Kuo, 2011), holocellulose (Haykiri-Acma et al., 2010) and lignin (Raveendran et al., 1996; Yang et al., 2007; Lv et al., 2010; Chen and Kuo, 2011; Pasangulapati et al., 2012), as shown in Figures 3.1 and 3.2.

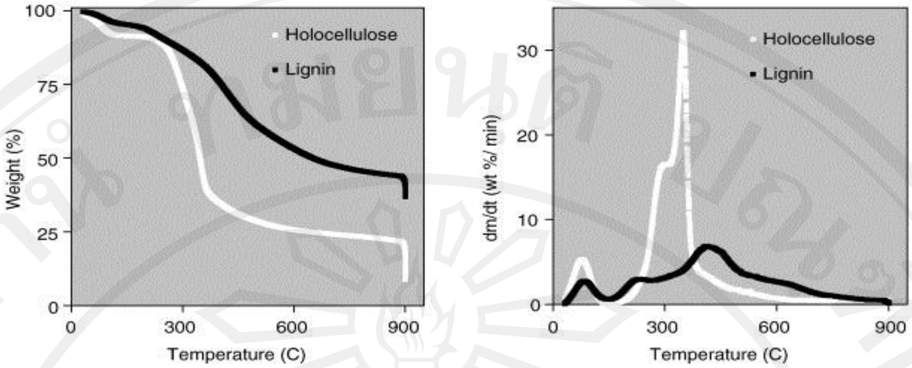

Figure 3.1 TGA and DTG curves for holocellulose and lignin (Haykiri-Acma et al., 2010)

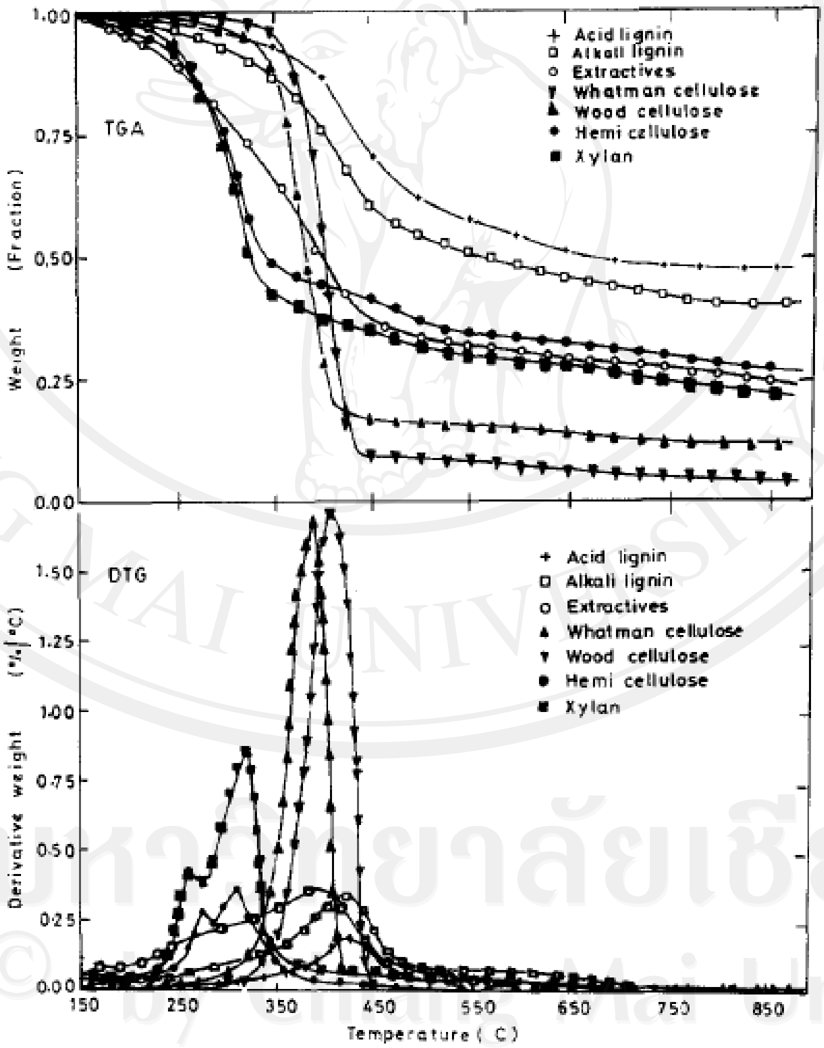

Figure 3.2 TGA and DTG curves for biomass components (Raveendran et al., 1996)

Raveendran et al. (1996) divided pyrolysis into five zones, as shown in Figure 3.2. Zone 1 (<100°C) is mainly moisture evolution, zone 2 (100- 250°C) is for extractives to start decomposing, zone 3 (250-350°C) is predominantly hemicellulose decomposition, zone 4 (350-500°C) is generally cellulose and lignin decomposition and zone 5 (> 500°C) is mainly lignin decomposition, respectively. While Huang et al. (2011) suggested that the biomass are decomposed into four stages as shown in Figure 3.3. Initially, the weight loss of the biomass occurs at temperatures lower than 150 °C. This is the moisture evaporation or drying stage. Subsequent stage is hemicelluloses degradation in the temperature range between 150–250 °C. Some light hydrocarbons are produced in the early pyrolysis process. Third stage is cellulose degradation occuring in the range of 250–350 °C, and lignin decomposition in the temperature ranges of 200–500 °C. Lignin decomposes slowly over a wide temperature range. Between 250-500°C, biomass was mainly pyrolyzed with higher reaction rates than other stages. The last stage is char gasification whose temperature is higher than 500°C. H_2 and CO_2 are produced from auto-gasification at higher temperatures.

Carrier et al. (2011) suggested that the maximum weight loss occurs in the range between 300–350 °C. Above 370 °C, an abrupt change in the slope of the TGA leads to a slower weight loss in the temperature range of 370–400 °C. After 500 °C, more than 70 wt. % of the volatile matter was released.

Various types of biomass have been studied such as agricultural wastes, municipal solid waste (MSW), wood, and weed. Kinetic of agricultural wastes were studied, included rice straw (Worasuwannarak et al., 2007), rice husk (Sharma and Rao, 1999), corn cobs (Worasuwannarak et al., 2007), cotton stalk and sugar cane

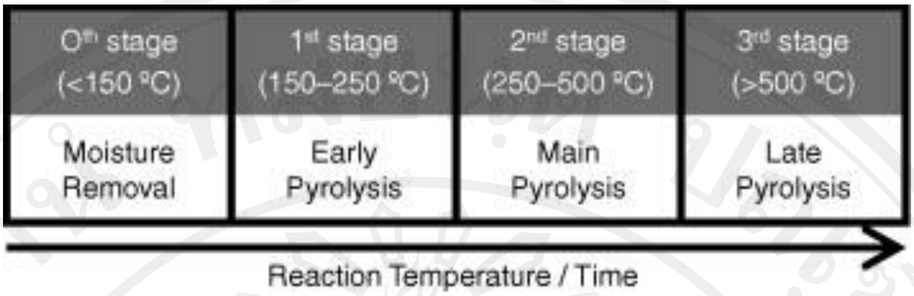

Figure 3.3 Four stages in pyrolysis of biomass (Huang et al., 2011).

bagasse (Munir et al., 2009), pepper (Serrano et al., 2012), sawdust and coffee (González et al., 2010), bamboo leaves (Huang et al., 2011) and hazelnuts (Haykiri-Acma et al., 2010). There are also studied about weed such as mimosa (Wongsiriamnuay and Tippayawong, 2010).

In thermal degradation, mass losses occur. Thermal analysis techniques have been used to determine this, such as, TGA-MS (Widyawati et al., 2011; Singh et al., 2012; Zhang et al., 2012), TGA-FTIR (Singh et al., 2012; Zhang et al., 2012), TGA-DSC (Haykiri-Acma et al., 2010; Zong and Liu, 2012). Advantages of TGA-MS and TGA-FTIR are that they are able to afford real-time and sensitive detection of evolved gases, which is an important and often a difficult task in many thermal applications. TGA-DSC is used to determine the endothermic or exothermic of the process during thermal degradation.

The effects of gas medium in thermal analysis have been studied by various types of gas carriers. Pyrolysis under inert atmosphere such as N_2 and CO_2 has been studied as shown in Figure 3.4 (a) and (b). There are three main weight loss steps between 25-1,000 ^{o}C. First two steps obtained at both atmospheres. First weight loss step occurs between 25-200 ^{o}C, it is moisture release. Second weight loss step within 200-600 ^{o}C is volatile matter release. The last step after 700 ^{o}C, under N2 atmosphere is char degradation. Under CO_2 atmosphere, this step is gasification of CO_2-char gasification reaction. It was found that CO_2 behaves as an inert atmosphere at lower than 700^{o}C (Yuzbasi and Selçuk, 2011).

In N_2 atmosphere within 200-600^{o}C (shown in Figure 3.4 (c)), CO_2 is the major gas released in devolatillization process due to high oxygen content of feedstock. Under N_2, CO_2 atmosphere after 700 ^{o}C, CO intensity increases due to CO_2 –char gasification reaction (Figure 3.4 (d)). CO_2 intensity decreases with water gas shift reaction, resulting in decrease of water (Figure 3.4 (c)). Under CO_2 atmosphere, CO increases with higher rate than in N_2 atmosphere due to higher concentration of $CO_{2.}$ Phenols are releases in the temperature range of 200-700 ^{o}C, due to moisture release and devolatilization during pyrolysis. Under N_2 and CO_2 environments, H_2O, CH_4 and SO_2 yields were not changed (Yuzbasi and Selçuk, 2011).

This was related to pyrolysis as shown in Figure 3.5. Under N_2, there are only pyrolysis process occur while under N_2 and CO_2, pyrolysis and gasification occur in the processes (Li et al., 2009)

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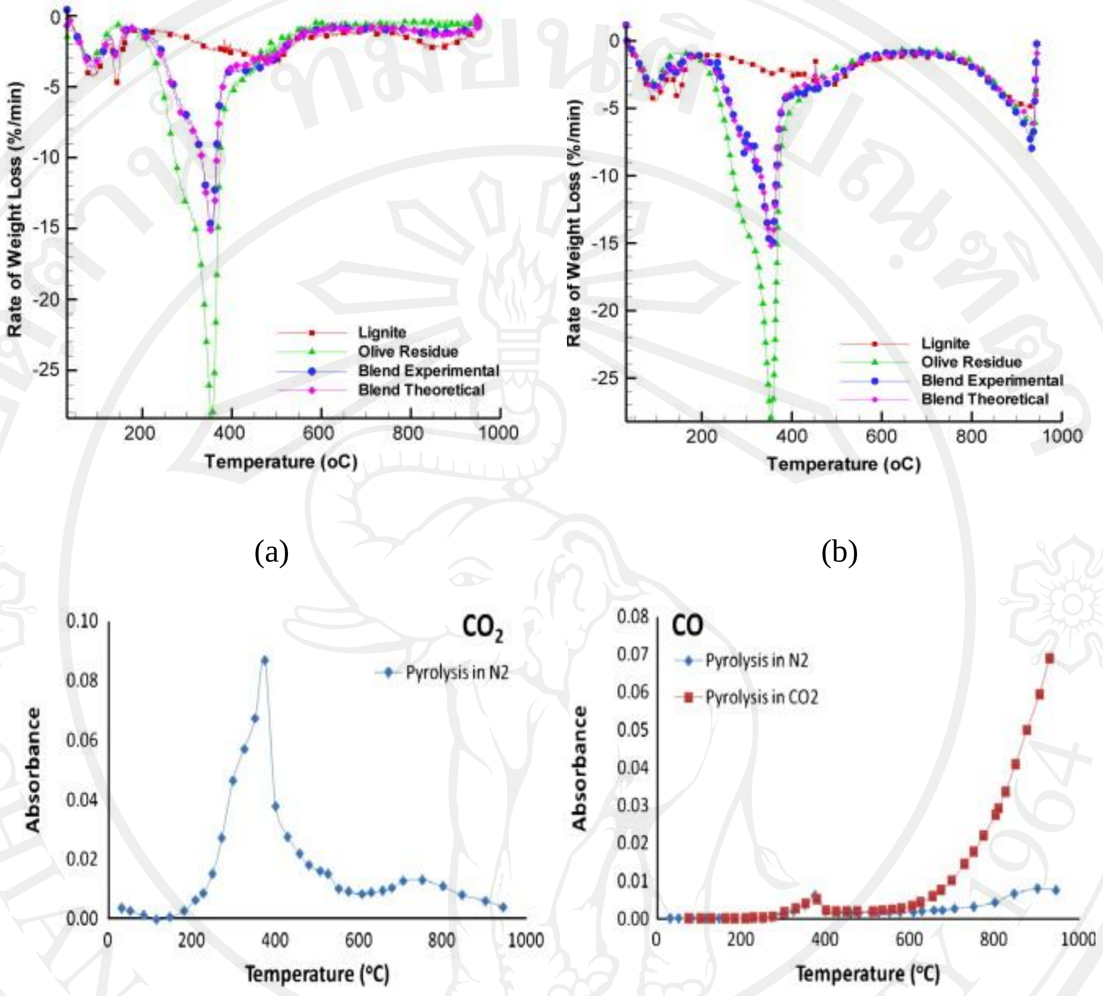
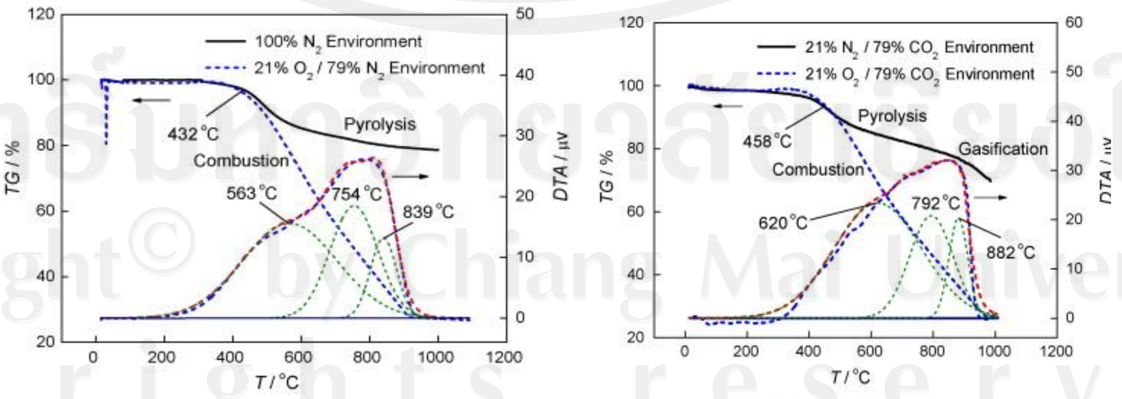


(a) (b)

(c) (d)

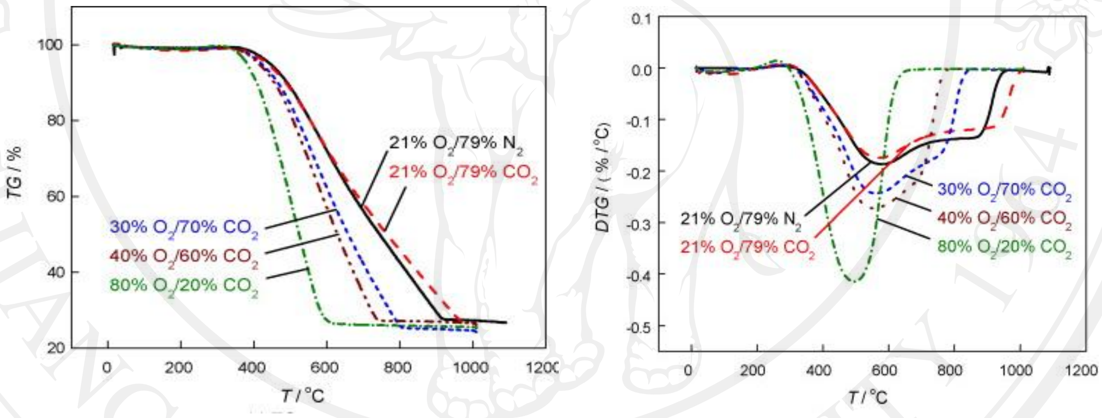
Figure 3.4 Pyrolysis profiles of fuel blend (a) N_2 and (b) CO_2 and formation profiles of evolved gases during pyrolysis (c) CO_2 (d) CO (Yuzbasi and Selçuk, 2011)



N_2 Environment CO_2 Environment

Figure 3.5 TG and DTA of pulverized coal combustion in different environment (Li et al., 2009)

Oxygen and its effect on weight loss were also studied. An increase in oxygen concentration was found to result in higher weight loss rate (Li et al., 2009; Yuzbasi and Selçuk, 2011), as shown in Figure 3.6. CO and CO_2 profiles shift to lower temperatures showing earlier release of gas products in Figure 3.7 (Yuzbasi and Selçuk, 2011).



TG curves DTG curves

Figure 3.6 TG and DTA of pulverized coal combustion in different oxygen concentration (Li et al., 2009)

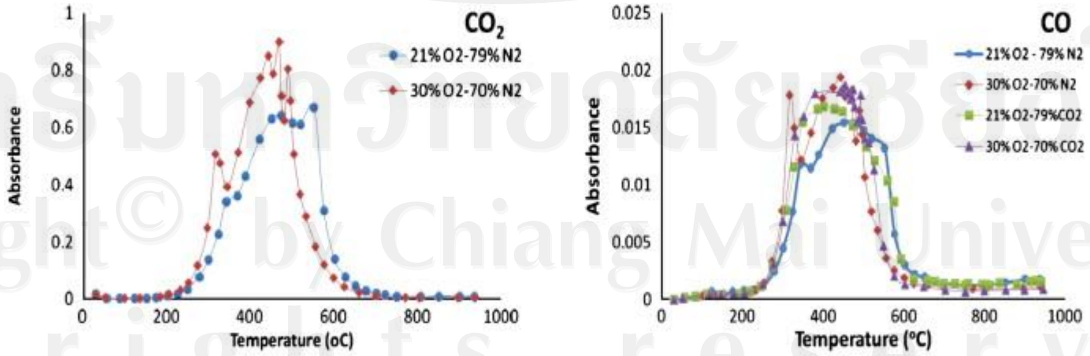


Figure 3.7 Formation profiles of evolved gasses during combustion (Yuzbasi and Selçuk, 2011).

Kinetic parameters of various biomass types were studied. Activation energy distribution curves for lignin decomposition are shown in Figure 3.8. E_a values was observed to be slightly higher in the softwood lignin than in hard wood. E_a is varied with temperature in a process with higher rate of started volatilization and ended char decomposition.

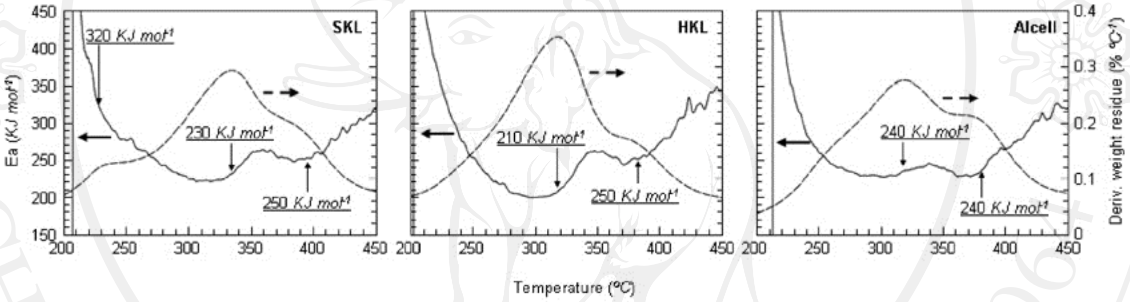


Figure 3.8 Temperature modulated TGA analysis of lignin preparations measured with a constant heating rate (Kubo and Kadla, 2008).

3.2 Effect of Feedstock Characteristics on Product Yields

Design and operation of a gasifier requires understanding of the effect of various types of biomass and operation parameter on the performance of the system. The following section describes the effect of biomass composition, biomass size, and moisture on the gasification products.

3.2.1 Biomass Size

Lv et al. (2003) suggested that size of biomass particle will have the effect on the produced gas composition and gas yield. Smaller particles will produce more gas due to a uniform of temperature through particle, and reaction can take place throughout the particle.

For small particle sizes, the pyrolysis process was mainly controlled by reaction kinetics. As the particle size increases, the product gas inside the particle was more difficult to diffuse outward and the process was mainly controlled by gas diffusion. For gasification process, when reaction controls the process then the rate of reaction will be maximum and increase exponentially with temperature.

Size less than 0.2 cm is reaction controlled. For sizes 0.2-6 cm, both heat transfer and reaction control, while size at above 6 cm heat transfer is controlling rate. To have uniform rate of gasification and uniform yielding composition of producer gas, size should be smaller than 2.5 cm. Goyal et al. (2008) suggested that for fluidization, biomass size should be between 105-250 µm due to require rapid heating. The bigger size needs more energy consumption to make them smaller (Kirubakaran et al., 2008). Decreasing particle size from 0.9 to 0.2 mm. resulted to increase of hydrogen yield from 35 to 55 gH_2/kg biomass.

3.2.2 Biomass Moisture

Fuel with moisture content above about 30% makes ignition difficult and reduces the CV of the product. High moisture content reduces the temperature in the oxidation zone, resulting in the incomplete cracking of hydrocarbons released from the pyrolysis zone. Increased levels of moisture and the presence of CO produce H_2 by the water gas shift reaction and in turn the increased H_2 content of the gas produces more CH_4 by direct hydrogenation. The gain in H_2 and CH_4 of the product gas does not compensate for the loss of energy due to the reduced CO content of the gas. Calculations based on a 2.7 MW gas engine generator using a dryer with a retention time of one hour indicates that sufficient waste heat is available from the engine oil and water cooling systems and the exhaust to dry 7.7 t/h of SRC willow feedstock at 35% moisture down to 15% (McKendry, 2002). H_2O is the main product formed for all the samples (Worasuwannarak et al., 2007).

3.2.3 Lignocellulose Content

The major components of biomass are cellulose, hemicellulose and lignin. Hemicellulose and cellulose decompose between 220 to 360 °C while lignin 200 to 500 °C. Temperature for the maximum weight losses is near maximum decomposed temperature of hemicellulose and cellulose. Biomass with higher cellulose content, the pyrolysis rate became faster, while the biomass with higher lignin content gave slower pyrolysis rate. The overall reaction rate decreases with an increase in lignin content and this controls the reaction rate during combustion. The reaction for the biomass proceeded in two stages. The first stage was rapid mass decrease, caused by cellulose decomposition. At the second stage, lignin decomposed during pyrolysis. The cellulose and lignin content in biomass were among the important parameters to evaluate the pyrolysis characteristics. The combustion characteristics for the biomass depends on the char morphology produced. (Gani and Naruse, 2007)

Carbon and oxygen are the main elements in biomass. During pyrolysis, the product gases have much higher amount of the oxygenated gases such as CO, CO_2, and H_2O than hydrocarbon and hydrogen. CO and CO_2 are the dominant gas products while H_2 and CH_4 are the minor products. Oxygen or bio-oxygen in biomass is available for converting carbon to CO by itself. The conversion of solid combustible matter in the biomass by itself is called auto-gasification (Kirubakaran et al., 2008)

Decreasing weight profiles and gas formation rates were significantly different among the samples although their elemental compositions were almost the same. The differences in the gas formation rates were found to be due to their differences in the composition of hemicellulose, cellulose, and lignin. A higher content of hemicellulose in the biomass such as rice straw resulted in a larger amount of water production. During the pyrolysis, there were significant interactions between cellulose and lignin to form water, ester group and the cross linking reaction contributed to a decrease in tar yield but an increase in char yields. Corncob, which had 50% cellulose and 15% lignin, had the same decomposing trend as lignin 50% and cellulose 50% in pyrolysis zones.(Worasuwannarak et al., 2007)

These compositions may predict yield of product gas when they had similar amount of %C, %H, %O. Similar trend of decomposition in pyrolysis zones and producer gas between biomass and the lignin, cellulose and xylan were identified (Hanaoka et al., 2005; Worasuwannarak et al., 2007).

The product gas compositions from xylan and lignin were similar to those from Japanese red pine bark whose main component was lignin. In contrast, Japanese oak whose main component was cellulose has different gas composition from Japanese red pine bark but similar to cellulose. Cellulose, xylan and Japanese oak has similar amount of %C but less than lignin, while oxygen are similar. Figure 3.9 shows the TG profile in cellulose, xylan, and lignin. From Table 3.1, the results indicate that cellulose was mainly decomposed due to pyrolysis, and that xylan and lignin were decomposed due to pyrolysis and combustion. The gasification conversion in pyrolysis was in order the following: cellulose > xylan > lignin, on a carbon basis. The composition of the gas phase generated in pyrolysis has little effect on that obtained in air-steam gasification.

Raveendran et al. (1996) suggested that cellulose content of the mixture decrease, the char yield increase and the liquid and gas yields decrease. The product yields are direct function of their cellulose or lignin content. The simplified model correlation for prediction the product yields with biomass contents such as cellulose lignin had been presented as shown in Figures 3.10 and 3.11.

Table 3.1 Carbon conversion in gasification between pyrolysis and air-steam (Hanaoka et al., 2005)

Feedstock	conversion (% C basis)	
	Pyrolysis	Air-steam gasification
Cellulose	67.0	97.9
Xylan	35.5	92.2
Lignin	17.2	52.8

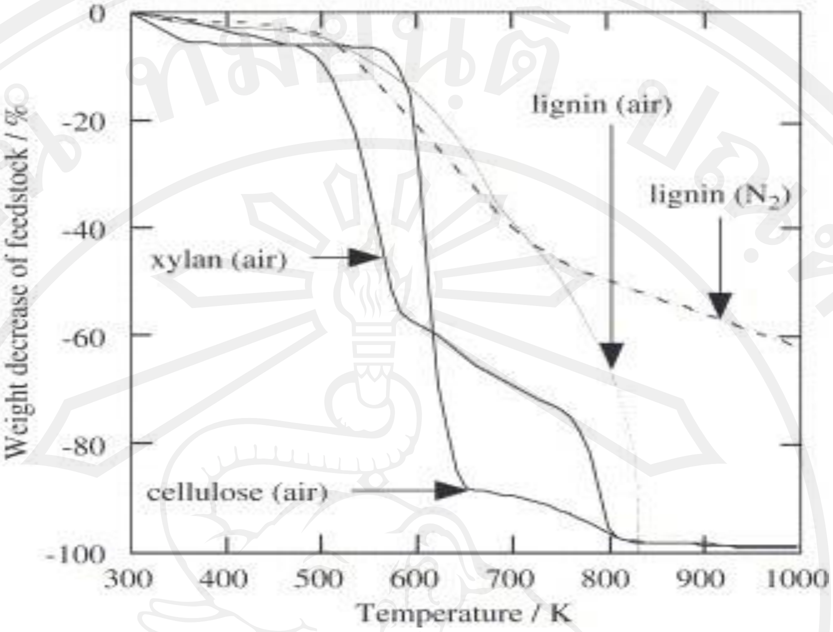


Figure 3.9 TG profiles in each feed stock under air or nitrogen flow (Hanaoka et al., 2005)

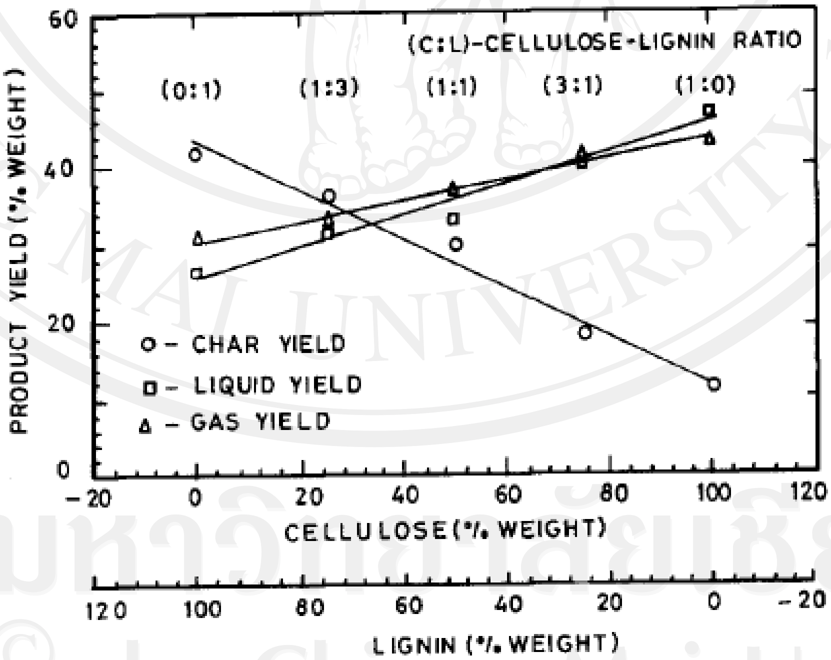


Figure 3.10 Product yields of cellulose –lignin mixtures vs. cellulose and lignin contents (Raveendran et al., 1996).

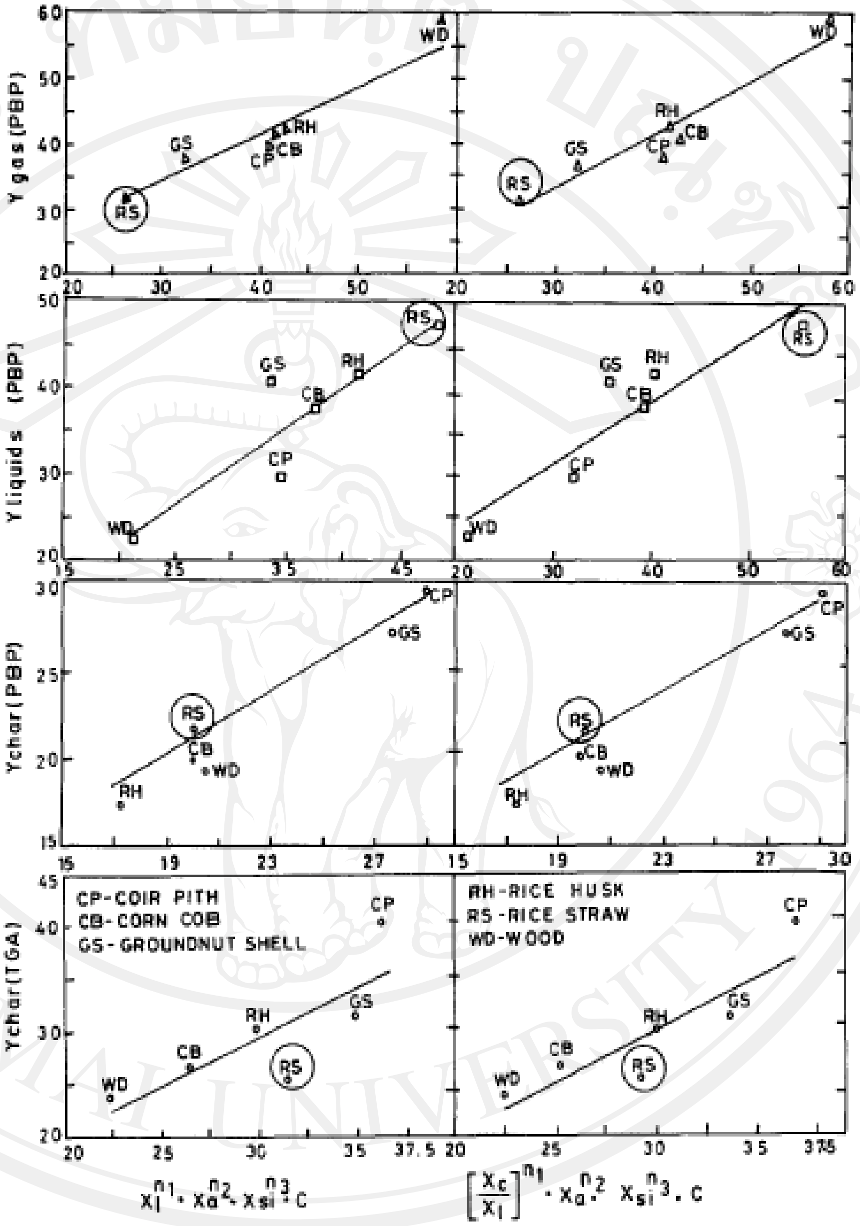


Figure 3.11 Product yields as a function of cellulose, lignin, ash and silica contents (Raveendran et al., 1996).

3.3 Effect of Processes Parameters on Product Yields

Design and operation of a gasifier requires understanding of the effect of various operation parameters on the performance of the system. The following section describes the effect of the gasifier operating conditions on yields and composition of the gasification products.

3.3.1 Gasification Temperature

Many scientists have discussed the effects of the operating conditions on the performance of biomass gasification such as gasification temperature, pressure, equivalent ratio and steam to biomass ratio (SBR).

Gasification temperature is temperature inside the reactor. Temperature is the most influential variable that affecting the product quantity, composition and, properties, carbon conversion, calorific value, cold gas efficiency, including tar and char contents (Emami Taba et al., 2012). The weight reduction at the lower temperature was caused by pyrolysis, and that at the higher temperature was caused by combustion (Hanaoka et al., 2005).

There are three ranges of temperature that had been reported. First is the low temperature gasification between 400-600^{o}C (Xiao et al., 2010). Second is the general gasification temperature of 700-1,000^{o}C. The last one is the high temperature gasification which is above 1,000 ^{o}C (Qin et al., 2012).

From Figure 3.12, at 400 °C, component with lignin 40% was decomposed in pyrolysis around 60% of mass fraction. Around 90% of mass fractions were oxidized. Cellulose was decomposed around 90% while lignin was 30% of mass fraction. It can conclude that different biomass compositions and different types of biomass decomposed at different temperatures. With increasing lignin content in biomass resulted in delay to decompose at high temperature. According to these, biomass containing different amount of lignin, cellulose and hemicellulose, they need appropriate conditions in gasification process (Gani and Naruse, 2007). Biomass which has high content of cellulose and small amount of lignin could be decomposed and combusted at temperatures around 400 °C.

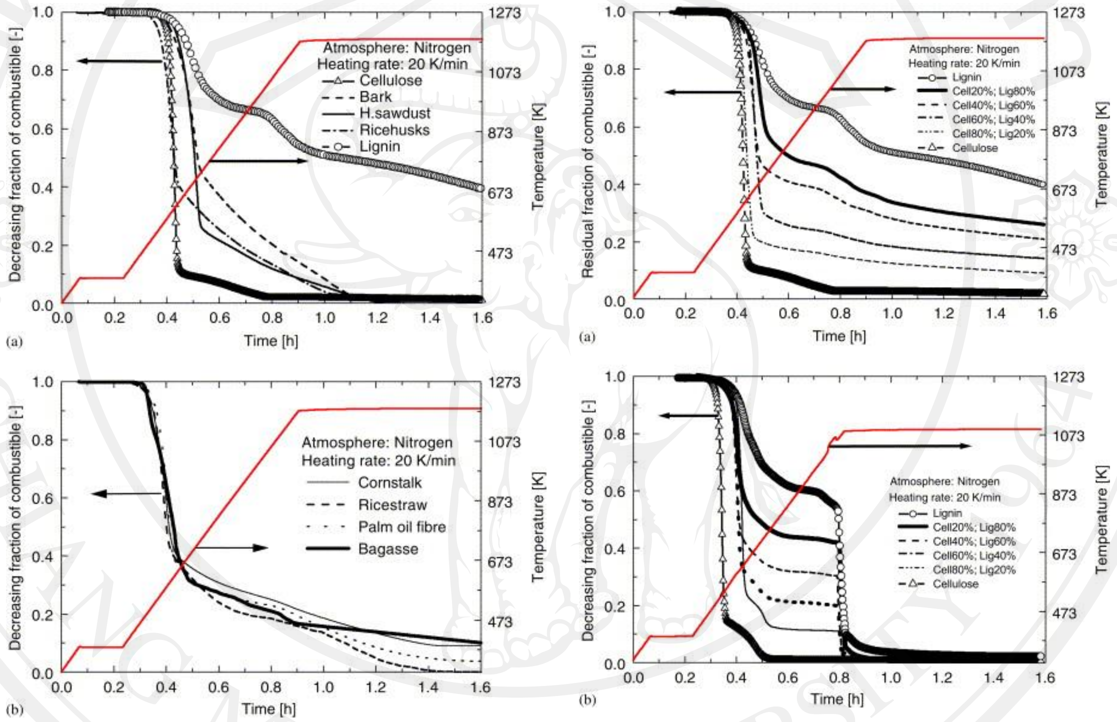


Figure 3.12 Residual fraction of combustibles of several types of biomass, cellulose, lignin and their mixtures. (Gani and Naruse, 2007)

Gasification involve partial combustion at temperature above 500 °C in which carbon reduces carbon dioxide to carbon monoxide (Kirubakaran et al., 2008). The reactor temperature stabilizes at temperatures up to 650 °C, enabled successful gasification of Kentucky bluegrass straw without slagging of the residual char. Carbon conversion was reported to be close to 45% (Boateng et al., 2007).

Weight losses of biomass were mainly from xylan and cellulose, due to the early decomposition of abundant hemicellulose in biomass to form H_2O during pyrolysis process. Weight started to decrease at 150 - 200 °C which is pyrolysis temperature due to biomass decomposed (Gani and Naruse, 2007; Worasuwannarak et al., 2007). More than 80% of cellulose and 50% of xylan, decreased at around 250 - 350 °C, and decreased gradually when temperature increased further from 400-600 °C (Hanaoka et al., 2005; Worasuwannarak et al., 2007). For different biomass types, more than 60% of cellulose and 80% of xylan was decomposed at around 450 -650 °C. With the mixing of lignin and cellulose, ester groups formed at around 250 °C and decomposed at above 350 °C (Hanaoka et al., 2005).

Lv et al. (2004) concluded that higher temperature contributes to more hydrogen production but gas heating value decreased with increasing temperature. Increased gasified temperature contributes to higher gas yield and carbon conversion. Gas yields of H_2, CO, CO_2 increased around 3-5% with increasing temperature from 540-640 °C (Xiao et al., 2010).

Effect of increasing temperature (600-900 °C) resulted in increasing gas yields and the content of H_2 and CO_2 , while the yields of tar, char and the content of CO and CH_4 in the product gas decreased (Midilli et al., 2001; Franco et al., 2003; Lv et al., 2003; Moghtaderi, 2007; Wei et al., 2007)

Boateng et al. (1992) reported that with an increase in gasification temperature from 700 to 800°C, gas yield, HHV, energy efficiency, carbon conversion and H_2 content increased, while CH_4, CO and CO_2 contents decreased. The decrease in CO content may have been due to the comparatively low temperatures (than 850-900 °C) for the Boudouard reaction to predominate. Maschio et al. (1994) observed that higher temperatures (700 to 950°C) linearly increased the gas yield and overall energy content of the gas. Turn et al. (1998) found that with an increase from 750 to 950 °C, H_2 increased from 31 to 45% while CH_4 and CO remained fairly constant, and CO_2 decreased and gas yield increased.

González et al. (2008) observed that from 700 to 900°C in air gasification, contents of H_2 and CO increased, whereas contents of CH_4 and CO_2 decreased. They also observed that the CO/CO_2 ratio linearly increased from 0.85 at 700 °C to 2.7 at 900 °C in two segments. At 700-800 °C, the slope of the regression line was 0.0067, and almost doubled to 0.113 at higher than 800°C, showing the predominance of the Boudouard reaction at higher temperatures.

Kumar et al. (2009) observed that an increase in temperature (furnace set point from 750 to 850 °C) led to increase in energy and carbon conversion efficiencies and H_2. Temperature is the most influential factor for gasification. Increasing temperature resulted in increasing in hydrogen and methane contents, carbon conversion and energy efficiencies. Carbon conversion efficiency increased from 62% at 650 °C to 71% at 750 °C, and 82% at 850 °C. The energy efficiency increased from 10–70% at 650 °C, 22–82% at 750 °C and 28–96% at 850 °C. At high temperature, the energy efficiency reached close to 100% because the heat energy supplied to the gasification systems was not taken into account. This energy efficiency represents the energy of the syngas, compared to energy of consumed biomass and steam.

At temperatures above 700-1000 °C, an increase in temperature results in contents of H_2 and CO increased, and contents of CH_4 and CO_2 decreased. Water gas reaction occurred at two ranges of temperatures, between 500 to 600 °C and above 1000 °C. An endothermic reaction producing hydrogen gas used the heat produced by the exothermic reactions at the oxidation zone, the temperature at oxidation zone, therefore, decreases. On the contrary, when an exothermic reaction producing hydrogen gas occurs, the heat generated increases the temperature at oxidation zone.

High temperature leads to production of H_2 by the endothermic reactions of the steam reforming, water-gas reactions and the Boudouard reactions dominate. Tar contents decreased because of destruction and reforming, leading to an increase in gas yield. (Lv et al, 2007; Lv et al., 2004; Gonzalez et al., 2008; Kumar et al., 2009; Narváez et al., 1996; and Gupta and Cichonski, 2007). At above 1000 °C, hydrogen gas requires the external heat (endothermic reactions) to drive reactions that provided from exothermic reactions. At this temperature, higher content in hydrogen, hydrocarbon achieved (Ponzio et al., 2006; Yang et al., 2006; Hofmann et al., 2008). Tar was decomposed at high temperature above 1000°C (Midilli et al., 2001)

Chang et al. (2011) concluded that air gasification of agriculture wastes in fluidized bed at 1000 °C and ER of 0.2 achieved the maximum yield of hydrogen (29.5%) and CO (23.6%) while CO_2 concentration was 10.9%. Increasing temperature from 700-900 ^{o}C resulted to increase H_2 yields from 15-30 vol%.

3.3.2 Equivalent Ratio

ER is a measure of the amount of external air supplied to the gasifier. ER is obtained by dividing the actual used air to fuel ratio (A/F ratio) by the stoichiometric air to fuel molar ratio. Air is generally supplied as a gasifying and fluidizing medium. Air supplies the oxygen for combustion, air controls the degree of combustion by affect the gasification temperature.

At low values of ER, there are small amounts of solid carbon (C) and CH_4 in the gasifier. While more air is supplied, both of them increase because both of them get oxidized. At high values of ER, H_2 and CO yields decrease but CO_2 increases. This is due to the oxidation of H_2 and CO to H_2O and CO_2. Higher airflow rate results in higher temperature which leads to higher biomass conversion and a higher quality of fuel. An excess air results in decreased energy content of the gas produced because a part of biomass energy is spent during combustion. Higher airflow also shortens the residence time which may decrease the extent of biomass conversion.

Air gasification is an exothermic process and hence using air as a gasifying medium reduces the net energy consumption and improves the overall thermodynamic efficiency. Using air in place of oxygen, though economical, has the negative effect of diluting the product gas, due to the presence of nitrogen. However supplying more air dilutes the product gas by reducing the H_2 yield. The optimum ER would supply enough air for the biomass to be partially oxidized without significant dilution of the product gas.

Increasing ER results in increasing in gas yield (Narváez et al., 1996) while the low heating value (LHV) of fuel gas decreased (Lv et al., 2004). Turn et al. (1998) reported that increasing ER from 0.0 to 0.37, both H_2 and CO yields increased. An increase in ER from 0.07 to 0.25 led to increase in gas yields, carbon conversion and energy efficiencies (Kumar et al., 2009). Increasing ER from 0.16 to 0.26, temperatures increased, in turn an increase in H_2 yield, cold gas efficiency, a higher yield and higher heating value (HHV) of the gas (Wang et al., 2007). Continue increase in ER from 0.20 to 0.45 led to lower heating value (LHV) of the gas and H_2, CO, CH_4 and C_2H_2 and tar contents decreases (Narváez et al., 1996).

Optimum ER was reported by Lv et al. (2004) to be 0.23. Increasing ER from 0.19 to 0.27, the H2 content varied a little but gas yield increased and then decreased.

Kumar et al. (2009) found that increasing ER resulted in decreasing the hydrogen content but increased carbon conversion and energy efficiency. At ER of 0.25, the efficiency achieved maximum of 90% at 850 °C, shown in Figure 3.13. Chang et al. (2011) found that the ER of 0.2 for air gasification of agriculture wastes in fluidized bed led to the maximum yield of the hydrogen and CO. Increasing ER from 0.27-0.34 resulted in decreasing H_2 yields by 2-3 vol%.

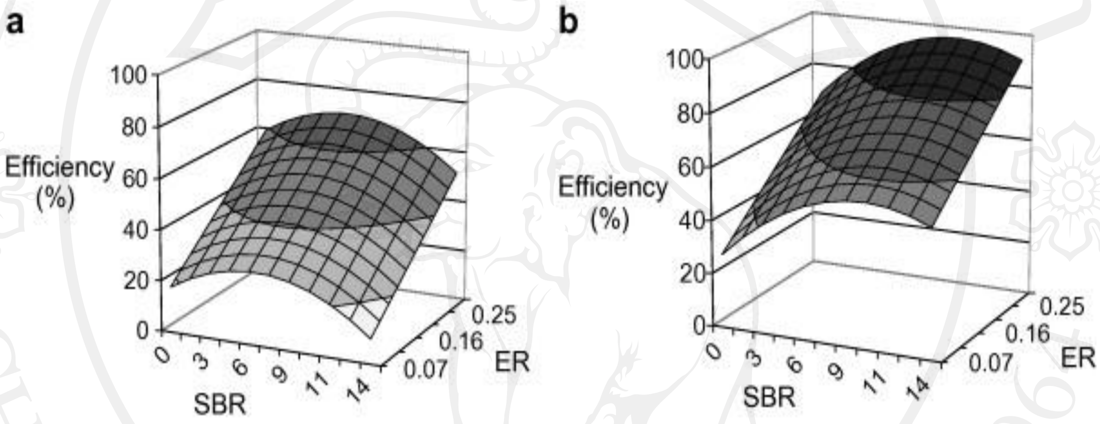


Figure 3.13 Effects of SBR and ER on the energy conversion efficiency at gasification temperatures of (a) 650 °C and (b) 850 °C.

All authors reported increase in gas yields with increasing in ER (from 0.0 to 0.45). The improvement implies that an increased airflow increases conversion rate. However, effects of ER on the contents of H_2, CO, and CH_4 were contradictory. This is logical because the percentage compositions of individual gases depend on both the yield of individual gases and the overall gas yield. If the overall gas yield is more pronounced than the yield of individual gas, then the percentage composition of individual gas decreases, even though the individual gas yield may actually have increased.

Effects of ER on the product gas composition also depend upon other factors such as temperature and SBR. During steam gasification, at high temperature, the H_2 yield is more pronounced than the increase in gas yield which results in an increase in H_2 content. Carbon conversion efficiency increased with increasing ER. At higher ER and high temperature, oxidation of biomass and breakdown of the molecular bonds occur, then higher amount solid carbon converted to gaseous molecules.

3.3.3 Steam to Biomass Ratio

Supplying steam as a gasifying agent increases the partial pressure of H_2O inside the gasification chamber which favors the water gas, water gas shift and methane reforming reactions, leading to increased H_2 production. However, the gasification temperature needs to be high enough (above 750-800°C) for the above reactions to be favorable (Lucas et al., 2004; Kumar et al., 2009) Higher SBR also leads to higher biomass conversion efficiency (Maschio et al., 1994). Reduction in tar was observed at higher SBR, which is attributed to steam reforming of the tar with an increased partial pressure of steam.

Narváez et al. (1996) found that with an increase in H/C ratio (H and C from incoming biomass, moisture and steam) from 1.6 to 2.2, H_2 content increased, LHV increased from 4 to 6 MJ/Nm_3 and tar content decreased from 18 to 2 g/Nm_3, with varying SBR from 0 to 4.04,

Turn et al. (1998) observed that increasing SBR from 1.1 to 4.7 decreased CO, CH_4, C_2H_2 yields, and increased H_2 and gas yields. H_2 increased from 46 to 83 g per kg biomass. At SBR above a threshold, steam had negative effects on the product because excessive steam lowered the gasification temperature which, in turn, lowered the rate of gasification. Increasing temperature of the gasifying agents led to an increase in the heating value of the fuel gas, and reduces the tars, soot and char residues (Lucas et al., 2004). A preheater was recommended before the introduction of gasifying agents (steam and air) to the gasifier to facilitate higher gasification bed temperature.

Xiao et al. (2010) used steam to increase hydrogen yield, via steam reforming and water–gas shift reactions.

Chang et al. (2011) gasified cellulose and bagasse in fluidized bed rand found that varying SB ratio from 0-0.5 resulted increased H_2 yields by 5-6 vol.%.

Kumar et al. (2009) found that SBR was optimal in the intermediate levels for maximal carbon conversion and energy efficiencies. Increasing SBR, the carbon conversion efficiency and the energy efficiency increased and then decreased after reaching a maximum. Optimum values of SBR at the maximum were 2.86 at 650 °C, 4.29 at 750 °C and 7.14 at 850 °C, respectively. The temperature of the steam that supplied below the gasifier bed was between 120 and 150 °C. Increasing SBR resulted in excess steam that decreased the gasifier bed temperature, leading to a decrease in the carbon conversion efficiency and the energy efficiency. Superheating the steam to a temperature comparable to the temperature of the gasifier bed may increase the carbon conversion efficiency of the process.

Lv et al. (2004) observed that with SBR higher than 2.7, the gas composition did not change significantly. With SBR between 0 and 1.35, CO yield decreased, and CH4, CO2 and C2H4 yields increased. With SBR of 1.35 and 2.70, the CO and CH4 yields decreased and CO2 and H2 yields increased which implied higher steam reforming reactions. Steam improved product gas quality when compared with air gasification. An excessive steam would lower gasification temperature and degrade fuel gas quality

Umeki et al. (2010) found that the molar ratio of steam to carbon (*S/C* ratio) and the steam temperature affected the reaction temperature which strongly affects the gasified gas composition. *S*/*C* ratio had a significant effect on the gas composition through the dominant reaction via water–gas shift reaction. The tar concentration in the produced gas from the high temperature steam gasification process was higher than that from the oxygen-blown gasification processes

In the reduction zone, to form hydrogen, steam is injected into this zone while CO_2 is dissipated in this zone, too. CO_2 and H_2O are in competition for reactive surfaces on char. The slower C–CO_2 reaction inhibits the H_2O reaction by decreasing the availability of reactive surface. The presence of CO_2 reduces the rate of the C–H_2O reaction (Roberts and Harris, 2007). The fundamental information obtained in the air-steam gasification of each component would possibly be used to predict the composition of product gas generated in air-steam gasification of woody biomass. The relative rate of gasification in oxygen is approximately 900 times that in steam gasification

When steam was supplied, the HHV of the reformed gas and the cold gas efficiency increased. At SBR of 0.50, both of them reached maximum values at 3.9 MJ/m^3 and 66%, respectively. But, when the SBR was higher than 0.50, both of them decreased. An increased SBR led to the increase of H_2 around 7 vol.%, the decrease of CO around 11 vol.%, the increase of CH_4 and C_2H_4 around 2 and 0.36 vol.%, respectively. Changes of CO and H_2 were mainly due to reaction of char with steam and the water–gas shift reaction. HHV is increased due to increase in CH_4 and C_2H_4. When the steam biomass ratio was higher than 0.50, the decrease in HHV is probably due to the fact that excess steam led to the decrease of the gasifier temperatures (Henriksen et al., 2006), which led to increase in CO_2 concentration in the pyrolysis gas (Wang et al., 2007). It was also reported that H_2 increased until steam biomass ratio was up to 1.35 and after that decreased (Lv et al., 2003).

From Figure 3.14, CH_4 concentrations decreased with an increase in SBR from 0.0 to 0.6 g/g, whereas the CO_2 and H_2 concentrations increase. H_2 concentration of gas produced from legume straw was found to reach the maximum of 40.3 mol% at SBR of 0.6 g/g, while that from pine sawdust is 36.8 mol%. H_2/CO molar ratio increases with the increase in SBR, while CO/CO_2 molar ratio decreases. It can be inferred that the water–gas shift reaction plays an important role in determining the dry gas compositions and H_2 production even in a short gas residence time in the free-fall reactor. The optimal gas yields and compositions were obtained at SBR of 0.6–0.8 g/g in biomass steam gasification process (Wei et al., 2007).

Increasing in steam biomass ratio, the gas yield increases, while the tar and char yield slightly decreases, as shown in Figure 3.15. With an increasing of S/B mass ratio from 0.0 to 0.6 g/g, the tar yield from legume straw decreases from 5.5 to 2.8 wt.% daf, while the char yield decreases from 7.4 to 4.2 wt% db. At the same time, the tar yield from pine sawdust decreases from 3.6 to 1.5 wt% daf, while the char yield decreases from 5.5 to 3.0 wt% db. It can be inferred that steam reforming of tar and gasification reactions of char may simultaneously occur at high heating rate with biomass pyrolysis in the free-fall reactor. The addition of steam favors tar and char reduction, and the increase of the gas yields mainly results from tar steam reforming, cracking and char gasification. At higher SBR from 0.8 to 1.0 g/g, the product yields stayed nearly constant (Wei et al., 2007). At SBR of 0.6–0.7, producer gas was richer in hydrogen and poorer in hydrocarbons and tars. These conditions also favored greater energy, gas yield and carbon conversions (Franco et al., 2003).

Steam gasification showed benefit in increasing the gas and hydrogen yields. However, excessive steam will lower the reaction temperature and cause gas and hydrogen yields to decrease (Lv et al., 2003). There are a number of literature that studied steam gasification using a large range of SBR, 0–2.7 (Franco et al., 2003; Lv et al., 2003; Boateng et al., 2007; Lv et al., 2007a; Lv et al., 2007b; Wei et al., 2007). The effect of this ratio is not clear, where the greater variations of the characteristics parameters of the steam gasification process occur. Besides, most of the results were obtained for a temperature in range of 700-900 °C. When the results were presented as a function of the temperature, they were given only for a fixed SBR or vice versa (Franco et al., 2003).

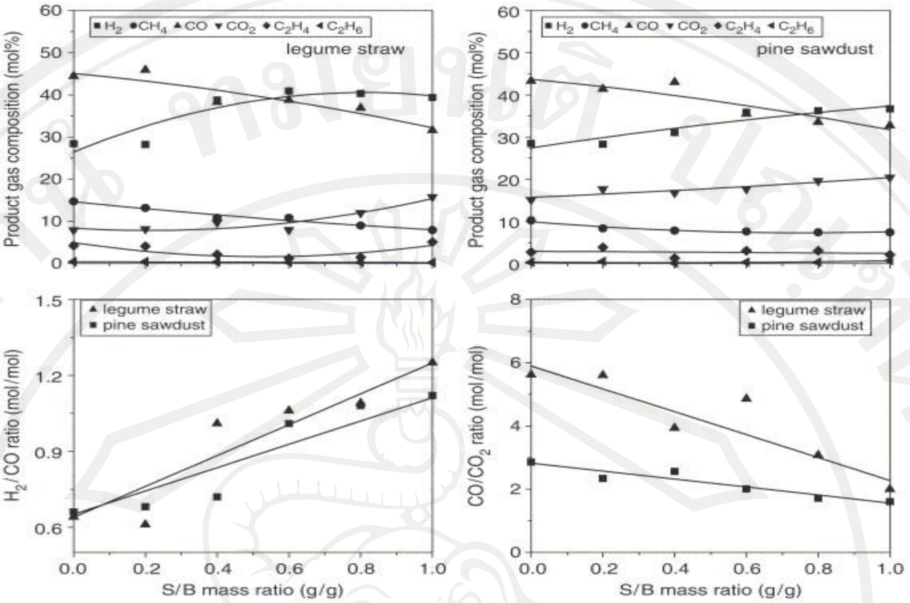


Figure 3.14 Effect of SBR on the product compositions (Wei et al., 2007).

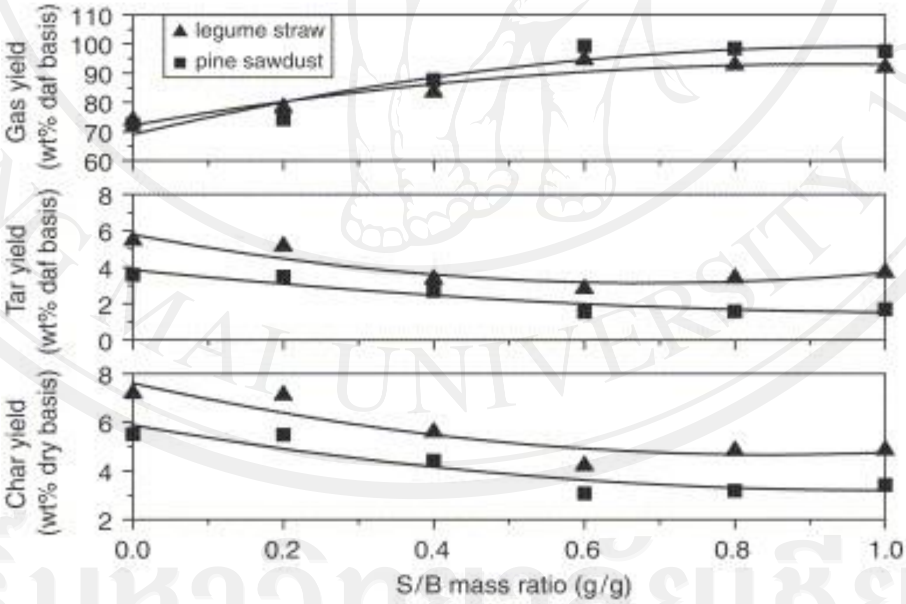


Figure 3.15 Effect of SBR on the product gas yields (Wei et al., 2007).

3.4 Effect of Catalyst on Product Yields

Calcined dolomites (OCa, OMg) are cheap catalyst that have proved their catalytic actvity, effectiveness for tar elimination (Delgado et al., 1996; Caballero et al., 1997; Simell et al., 1997; Sutton et al., 2001; Myren et al., 2002; Corella et al., 2004; Zhang et al., 2004; Wang et al., 2005; Cao et al., 2006; Lv et al., 2007b; Nacken et al., 2007) and producing syngas as hydrogen (Rapagna et al., 1998; Simell et al., 1999; Asadullah et al., 2002; Asadullah et al., 2004; Zhang et al., 2004; Hu et al., 2006; Wei et al., 2006; Wei et al., 2007) and CO yield with presence of CaO as additive (Han et al., 2010). CO_2 was captured by CaO have been reported (Johnsen et al., 2006; Widyawati et al., 2011; Chen et al., 2012). Tar elimination over dolomites is mostly due to steam and dry (CO_2) reforming reactions. There are a great number of literature about the use of dolomites downstream of biomass gasifiers (Caballero et al., 1997).

Dolomite composition is showed in Table 3.2, Catalytic activity of natural occurring catalysts reveals a comparably good performance of tar destruction and the consequential increase of gas production in a short contact time. However, at 800 °C even in presence of dolomite, it was found that a longer residence time could be beneficial to bring to completion of such reacting processes.

Table 3.2 Chemical composition of uncalcined dolomite (wt.%) (Lv et al., 2007b)

Sample	**CaO**	**MgO**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**Loss**	**Total**
Dolomite	31.2	19.5	2.35	0.34	0.24	46.15	99.78

3.5 Thermodynamic Equilibrium Modeling

There are attempts to predict the efficiency of the gasification process and design the reactor with exceptional performance for different operation conditions. Gasification models can be useful to do this.

The gasification models were studied in various types of reactor. In fixed bed reactor (Barman et al., 2012), the models were predicted in each gasification zone such as pyrolysis zones (Jayah et al., 2003; Gao and Li, 2008), gasification or reduction zones (Jayah et al., 2003; Babu and Sheth, 2006; Gao and Li, 2008). The fluidized bed were also studied such as in bubbling fluidized bed (Wang and Kinoshita, 1992; Kaushal et al., 2010), dual fluidized bed (Sadaka et al., 2002a; Nguyen et al., 2012) and circulating fluidized bed (Ngo et al., 2011).

Various methods of model calculation were also studied by considering the processes that occur in the reactor, including heat and mass transfer such as finite difference (Gao and Li, 2008; Kempegowda et al., 2010), two sub-models in pyrolysis and gasification zones (Jayah et al., 2003), char reactivity factor (Babu and Sheth, 2006), steady state model (Kaushal et al., 2010), in drying zone (Kaushal et al., 2011), pyrolysis zone (Kaushal et al., 2011; Nguyen et al., 2012), char-gas reaction or char gasification (Kaushal et al., 2011; Nguyen et al., 2012), gas phase reaction (Nguyen et al., 2012) and quasi-equilibrium three-stage gasification (Ngo et al., 2011). Hydrodynamic phenomena occurring in the reactor are included, dividing the fluidized bed into three zones such as jetting, bubbling and slugging (Sadaka et al., 2002b).

Puig-Arnavat et al. (2010) suggested that the gasification models can be divided into kinetic rate models, thermodynamic equilibrium models, and neural network models. There are some commercial software such as Aspen Plus (Withag et al., 2012) that can simulate various processes of gasification. Further studies are combining these models together for improving the models such as using the Aspen Plus with thermodynamic and kinetic rate models.

Thermodynamic equilibrium models have many advantages such as independent of gasifier design or types, biomass and operation processes. At chemical equilibrium, a reacting system is at its most stable composition, a condition achieved when the entropy of the system is maximum while its Gibbs free energy is minimum.

The models can predict yields and composition of the gas product and performance of gasifiers using only the biomass elements. Good agreement between equilibrium models and experimental data in entrained-flow and downdraft gasifier was shown with operation conditions such as high temperature and long residence time (Puig-Arnavat et al., 2010), dual fluidized bed (Sadaka et al., 2002a) and the spout-fluid bed (Jarungthammachote and Dutta, 2008).

However, Puig-Arnavat et al. (2010) suggested that the equilibrium models did not fit precisely with experimental data from updraft gasifier, dual fluidized bed and stand-alone fluidized bed gasifier. Thermodynamic equilibrium may not be achieved, due to the low operation temperature. Gasification rate is not fast enough, and residence time is not long enough to meet the equilibrium state. The error between the models and the experiments come from the overestimation of H_2 and CO and underestimation of CO_2 and CH_4.

Some modified models have been studied to correct deviations, by using carbon conversion coefficient (Li et al., 2001; Jarungthammachote and Dutta, 2008), and hydrogen conversion coefficient (Li et al., 2004). Jarungthammachote and Dutta

(2007) multiplied the coefficients calculation for correction from the experiments, to equilibrium constant (K) of the water-gas shift reaction and methane reactions. Barman et al. (2012) developed thermodynamic equilibrium model by including tar and correcting CH_4 using similar method to Jarungthammachote and Dutta (2007).

Tar yield from steam gasification of straw was predicted by Corella et al. (1989) using equation (3.1) . Barman et al. (2012) used the tar model (equation 3.2)

$$Tar = 3598e^{-0.0029T} \tag{3.1}$$

$$Tar = CH_{1.003}O_{0.33} \tag{3.2}$$

Where T is an average temperature (K) of the particle. The model approximates tar and C_2 as CH_4.