CHAPTER V

Catalytic performance of Ni/dolomite on steam reforming of biomass

In this chapter, the investigations were carried out to determine the efficiency of steam reforming Ni/ dolomite catalyst on gasification of coconut and palm shell. The gasification process was operated in a fluidized bed gasifier. Experiments were carried out to determine what can be the most suitable conditions to produce more gaseous products. The suitable reaction conditions are as follows: biomass feed rate 1.76 g/min, nitrogen gas flow rate 300 ml/min, 10 g of Ni/dolomite catalyst. The purpose of this part is to study the effects of critical parameters on product gas compositions such as calcinations temperature, reaction temperature, steam to carbon ratio (S/C), and oxygen flow rate.

5.1 Effect of Catalyst

The influence of catalytic gasification on product gas compositions by using Ni/dolomite catalyst was investigated at the temperature of 700°C, S/C of 0.24 and biomass feed continuouse rate of 1.76 g/min. . In steam gasification process the presence of Ni/dolomite causes a significant reaction of tar cracking and steam reforming of hydrocarbon to increase more gas products as following reactions;

The experimental results, as shown in Figure 5.1, shows a tendency of gas composition of coconut shell where the H_2 content was increased from 22.68 to 30.31%, CO content was increased from 32.31 to 37.71% (equation 5.1-5.2) and CO_2 content was decreased from 29.90 to 27.22% (equation 5.3), and CH_4 content was decreased from 15.11 to 4.75% (equation 5.4). Where as the content of H_2 in product gas composition of palm shell gasification was increased from 22.42 to 33.94%, as same as the increasing of CO from 32.70 to 34.02%, while CO_2 and CH_4 content were decreased from 28.02 to 25.11%, and 16.85 to 6.91%, respectively

$$C_nH_m + n\,H_2O \xrightarrow{\text{Ni/Dolomite}} n\,CO + \left(n + \frac{m}{2}\right)H_2 \qquad (5.1)\ \text{Steam reforming}$$

$$Tar + H_2O \rightarrow CO + H_2 \qquad (5.2)\ \text{Tar reforming}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (5.3)\ \text{Water-gas shift}$$

$$CH_4 + H_2O \leftrightarrow CO_2 + H_2 \qquad (5.4)\ \text{Methane reforming}$$

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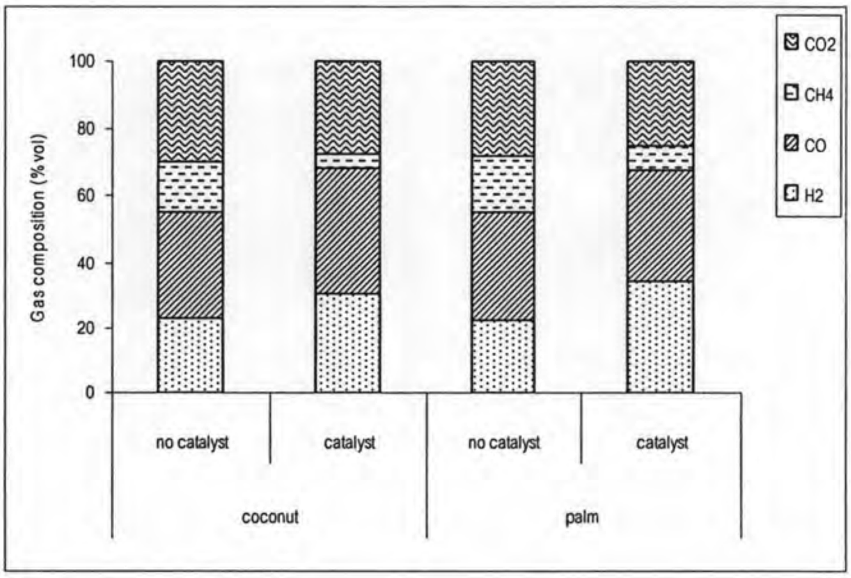


Figure 5.1 effect of catalytic biomass gasification compared with non catalytic biomass gasification on gas composition product

There are many researches which have proved the effectiveness of nickel based steam reforming and dolomite catalysts to produce high yield of syn gas (Sutton et al. 2001, and Devi et al. 2003). The catalytic biomass gasification increased more gas product and lowered tar content than non catalytic biomass gasification. Ni/Dolomite has excellent activity in tar gasification, the mechanisms of Ni/Dolomite was presented in the reaction (Srinakruang et al. 2005)

$$NiO + H_2 \rightarrow Ni^{\circ} + H_2O \qquad (5.5)$$

$$Ni^{\circ} + C_xH_y \xrightarrow[\text{steam}]{} NiCx + Hy \qquad (5.6)$$

$$NiCx + Hy \rightarrow Ni + CO + H_2 \qquad (5.7)$$

The structure of Ni/Dolomite was usually formed in NiO and was reduced under hydrogen at 700 °C and reduced to nickel Ni^{o} form. During gasification process tar has been derived to react with reduced nickel to form nickel carbide and finally reacted with steam to produce synthesis gas.

5.2 Effect of reaction temperatures

Temperature is a crucial parameter for the overall biomass gasification process. The experimental was performed at various reaction temperatures from 600°C to 800 °C, steam per carbon (S/C) ratio of 0.24 and biomass feed rate of 1.76 g/min. Figure 5.2 and 5.3 present the effect of temperature on gas composition product (H_2, CO, CO_2 and CH_4). The results show that H_2 and CO were increased with increasing temperature and decreased in CO_2 and CH_4 contents. The suitable temperature at 800°C showed the best performance catalytic gasification of coconut and palm shell which gives higher syn gas. As temperature increased, more carbon and steam can be converted and favor the products in endothermic reactions. The effect of temperature is the main role on the gas composition for gasification process. It can be claimed that the hydrocarbon was reformed and more tar was cracked at the higher temperature. This result was similar to those reported by Franco (2003). The mechanism increased the gas yield with temperature, which could be explained by various reasons, such as: (i) higher production of gases in the initial pyrolysis step, whose rate is faster at higher temperatures, (ii) the production of gas through the endothermal char gasification reactions, which are more favorable at elevated temperatures and, (iii) the increase of gas yield resulting from the steam reforming and cracking of heavier hydrocarbons and tars (Franco, 2003). The reaction can be explained as following:

$Tar + H_2O \leftrightarrow CO + H_2$		(5.8)	Tar reforming
pC_nH_x	$\rightarrow qC_mH_y + rH_2$	(5.9)	Thermal cracking:
Tar	$\rightarrow CH_4 + H_2O + C_xH_y + H_2$	(5.10)	Tar cracking
C_nH_x	$\rightarrow nC + x/2H_2$	(5.11)	Carbon formation
$C + CO_2$	$\rightarrow 2CO$	(5.12)	Boudouard
$CH_4 + H_2O \leftrightarrow CO + 3H_2$		(5.13)	Methane reforming

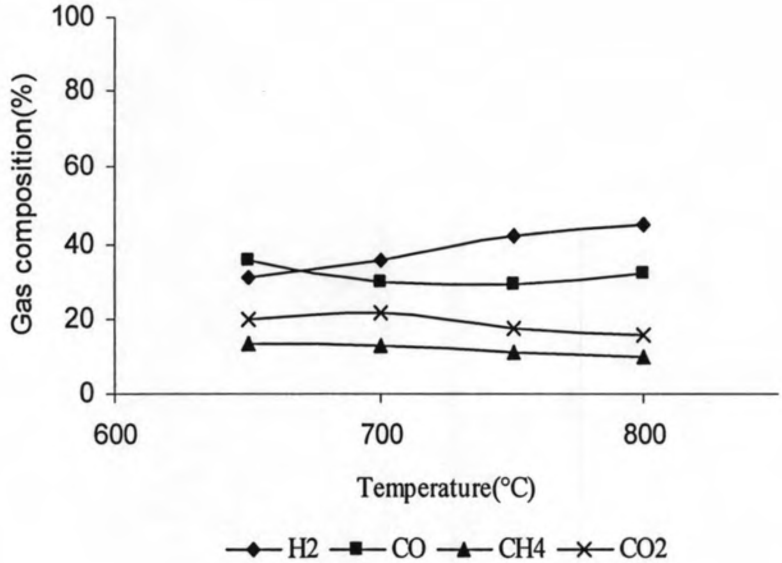


Figure 5.2 Effect of temperature on gas composition of coconut shell, S/C 0.24, biomass feed rate 1.76 g/min.

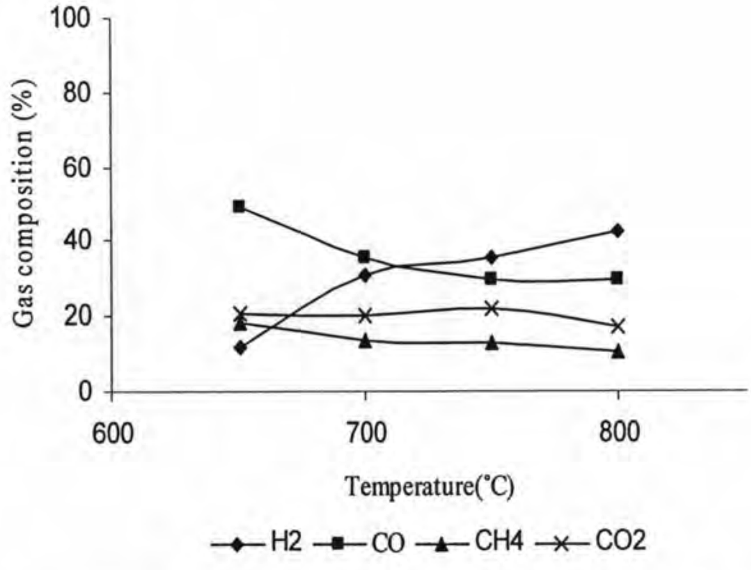


Figure 5.3 Effect of temperature on gas composition of palm shell, S/C 0.24, biomass feed rate 1.76 g/min.

5.3 Effect of steam to carbon ratio on biomass gasification

The influence of steam to carbon ratio (S/C) on the steam gasification for each biomass was also studied. The steam to carbon ratio (S/C) could be varied by changing steam flow rate while keeping the biomass feed rate constant. The steam to carbon(S/C) ratio varied from 0.24, 0.44 and 0.95, respectively. The experiments operated at temperature of 800°C, fluidization flow rate of nitrogen 300 ml/min, and biomass feed rate 1.76 g/min. The result shows the effect of steam flow rate on gas composition as shown in Figures 5.3 and 5.4. It can be seen that an increase of steam to carbon ratio (S/C) from 0.24 to 0.95 results in higher H_2 and CO_2 contents, decrease in CO content, and slightly decrease in CH_4. The suitable (S/C) ratio was 0.95 which was more favor to H_2 formation and higher carbon conversion at around 74%.

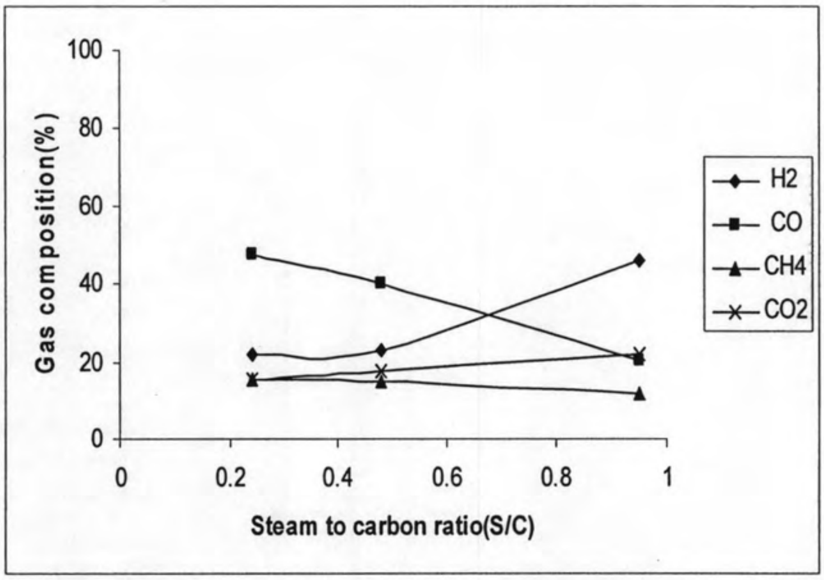


Figure 5.4 effect of steam to carbon ratio on gas composition of coconut shell, biomass feed rate 1.76 g/min, at temperature of 800°C, flow rate of nitrogen 300 ml/min.

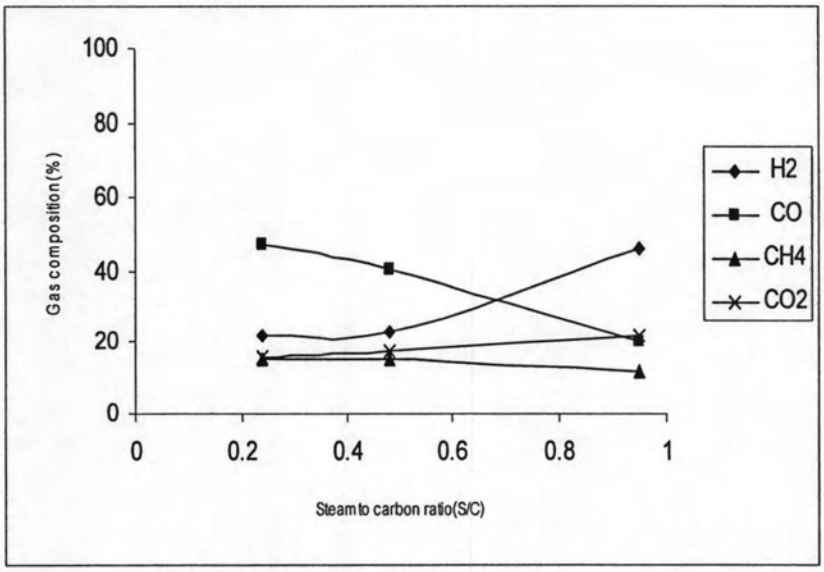


Figure 5.5 effect of steam to carbon ratio on gas composition of palm shell, biomass feed rate 1.76 g/min, at temperature of 800°C, flow rate of nitrogen 300 ml/min.

The results are also similar with Franco et al. (2003). The experimental results can be explained that water gas and water-gas shift reaction including steam reforming are the main role to produce more of the synthesis gas and hydrogen. The reaction can be explained as following:

$$C + H_2O \rightarrow CO + H_2 \quad (5.14) \text{ Primary water gas}$$

$$C + 2H_2O \rightarrow CO_2 + 2H_2 \quad (5.15) \text{ Secondary water gas}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (5.16) \text{ Water-gas shift}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (5.17) \text{ Steam reforming}$$

5.4 Effect of oxygen addition on biomass gasification

In this experiment oxygen used as another gasifying medium to study effect of oxygen on gaseous product. Oxygen flow rate was varied from 10-40 ml/min at gasification temperature of 800°C, flow rate of nitrogen 300 ml/min, biomass feed rate 1.76 g/min. and S/C ratio of 0.95. Figures 5.6 and 5.7 show that CO and CO_2 sharply increased. The partial oxidation occurs at lower oxygen flow rate, which give the higher CO than CO_2. At the highest oxygen flow rate (40ml/min), it can be seen that CO_2 increases because of oxidation reaction. As the oxygen flow rate was increased, H_2 sharply decreased because of hydrogen combustion (equation 5.21). Methane (CH_4) was slightly decreased with increasing oxygen input due to methane partial oxidation. All reaction proposed could be described below:

$$2C + O_2 \rightarrow 2CO \quad (5.18) \text{ Partial oxidation}$$

$$C + O_2 \rightarrow CO_2 \quad (5.19) \text{ Oxidation}$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (5.20) \text{ Reforming}$$

$$2H_2 + O_2 \rightarrow 2H_2O \quad (5.21) \text{ Reforming}$$

$$CH_4 + O_2 \leftrightarrow CO + 2H_2O \quad (5.22) \text{ Methane partial oxidation}$$

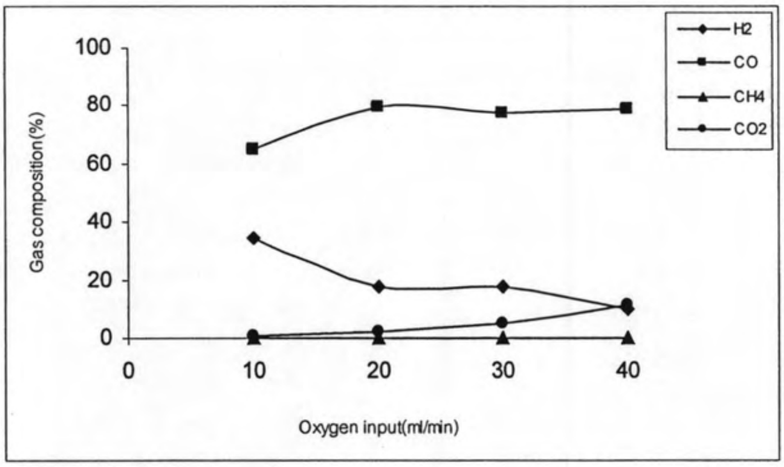


Figure 5.6 Effect of oxygen flow rate addition on gas composition of coconut shell, S/C 0.95, biomass feed rate 1.76 g/min.

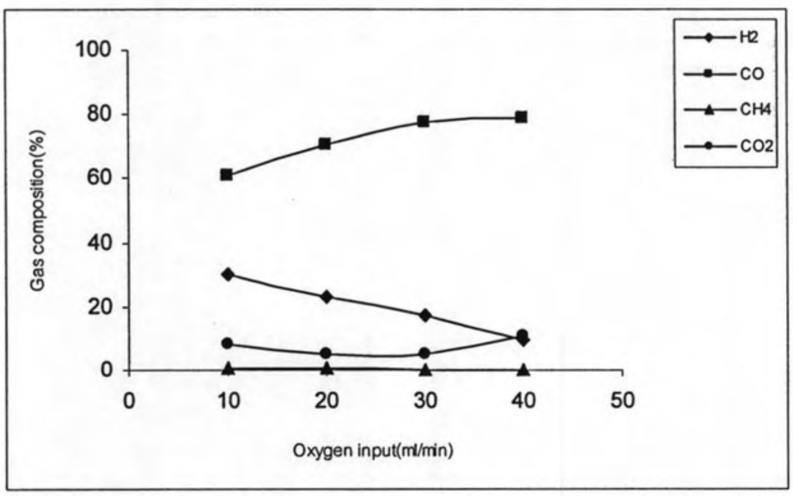


Figure 5.7 Effect of oxygen flow rate addition on gas composition of palm shell, S/C 0.95, biomass feed rate 1.76 g/min.

5.5 Effect of Nickel/dolomite on component in tar

In this experiment, we studied the performance of Ni/dolomite, which reported that it has high activity for tar reduction (Sutton, 2001). The experimental was performed at temperature of 800 °C, steam to carbon ratio (S/C) of 0.95, flow rate of nitrogen 300 ml/min, biomass feed rate of 1.76 g/min and without Ni/dolomite as a catalyst (non-catalytic gasification). After experiment, tar was collected from the system by the trap using 2-propanol. Tar derived from gasification of coconut shell was analyzed by GC-MS and the result is shown in Figure 5.8. From the analysis, the main components of coconut tar obtained from non-catalytic gasification are heavy poly-aromatic hydrocarbons such as dibenzofuran, pyrene, 9H-fluorene, indene, 11H-benzofluorene, phenanthrene, methyl anthracene and phenyl napthalene. As the previous research, it has also been reported that the main components of tar were aromatic compounds (Simell et al. 1999).

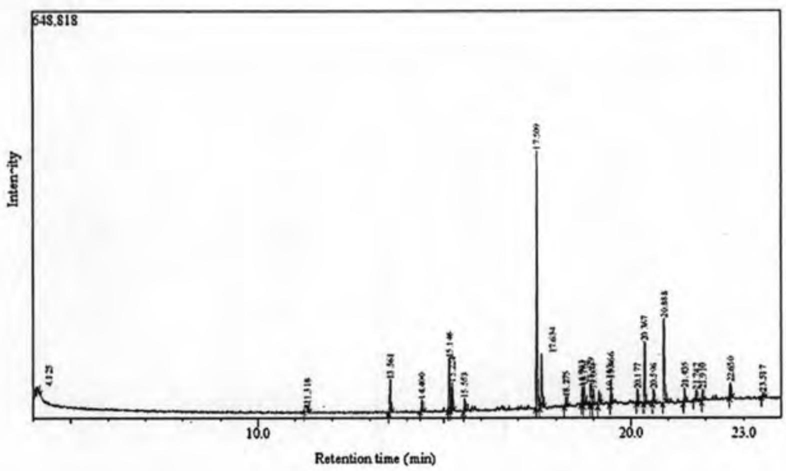


Figure 5.8 GC-MS of tar derived from non-catalytic gasification of coconut shell (Condition; temperature of 800 °C, (S/C) ratio of 0.95, flow rate of nitrogen 300 ml/min, biomass feed rate of 1.76 g/min)

When comparing with the result from experiments with catalytic gasification (Ni/dolomite) and non-catalytic gasification, it was found that in the former case the amount of tar was found to be significantly less. The tar yield of coconut shell was decreased from 19.20 to 3.38% after using Ni/dolomite catalyst. The resulting tar was then analyzed by the GC-MS (Figure 5.9) and was found that the main component is a small concentration of aromatic compounds such as pentanone, diethyl phathalate, anthracene and pyrene reported previously. Furthermore, it was shown that there would be more than 90% tar conversion when Ni catalyst is used at above 700°C. This can be explained by the fact that nickel and dolomite have capability to reduce tar by tar reforming and cracking of heavy hydrocarbon to lower molecular hydrocarbon (Simell et al. 1997).

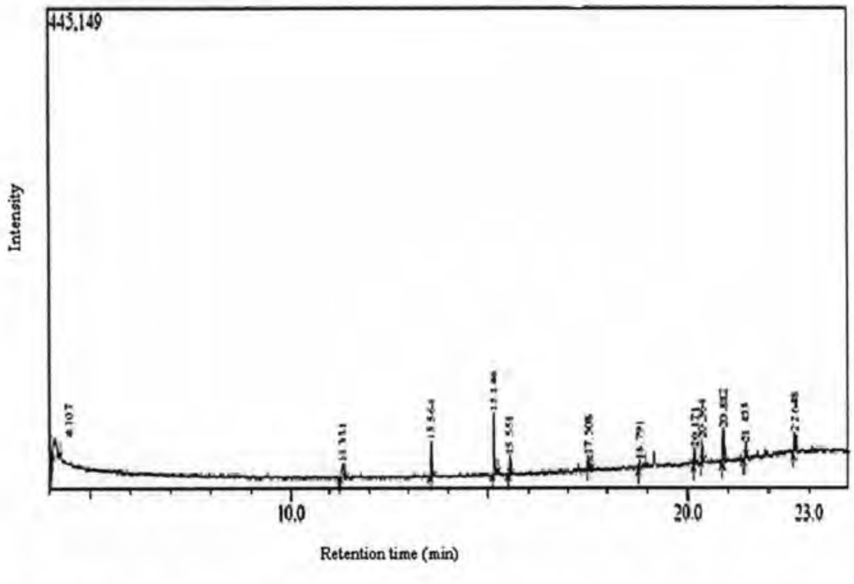


Figure 5.9 GC-MS of tar derived from catalytic gasification of coconut shell (Condition; temperature of 800 °C, (S/C) ratio of 0.95, fluidization flow rate 300 ml/min, biomass feed rate of 1.76 g/min, 10 g of Ni/dolomite catalyst)

Likewise, in the case of tar derived from palm shell, tar was analyzed and the result of GCMS is shown in Figure 5.10. The main components of palm tar obtained from non-catalytic gasification was found to be heavy hydrocarbon such as complex poly-aromatic hydrocarbons such as phenol, diethyl phthalate, phenanthrene, 1H-Indene, 4H-cyclopentaphenanthrene, 2-phenyl naphthalene, fluoranthrene, pyrene, 11H-benzofluorene and benzofluoranthene.

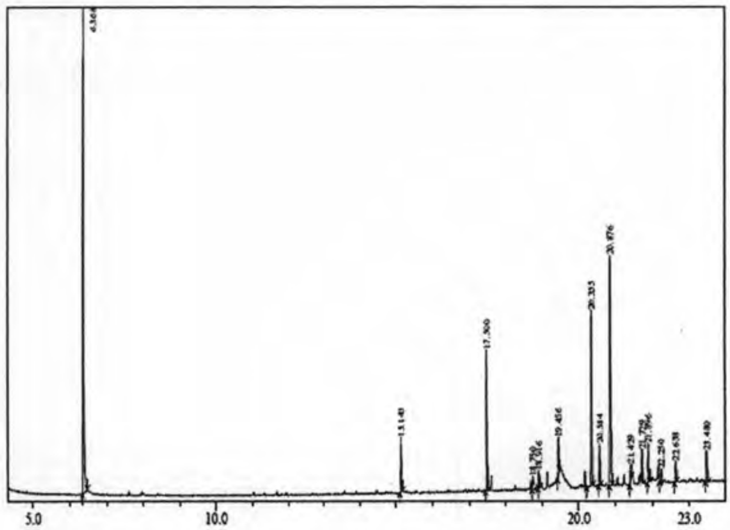


Figure 5.10 GC-MS of tar derived from non-catalytic gasification of palm shell (Condition; temperature of 800 °C, (S/C) ratio of 0.95, fluidization flow rate 300 ml/min, biomass feed rate of 1.76 g/min)

Tar of palm shell derived from catalytic gasification (Ni/dolomite) as shown in Figure 5.11 compared with non-catalytic gasification as shown in Figure 5.10. Ni catalyst used in catalytic gasification was effective for decreasing the tar level. The tar yield of palm shell was decreased from 20.0 to 8.2 % after using catalyst. In Figure.5.11, a small concentration of aromatic compounds such as phenol, dodecanoic acid, diethyl phthalate, tridecyl ester, dibutyl phthalate and pyrene were found.

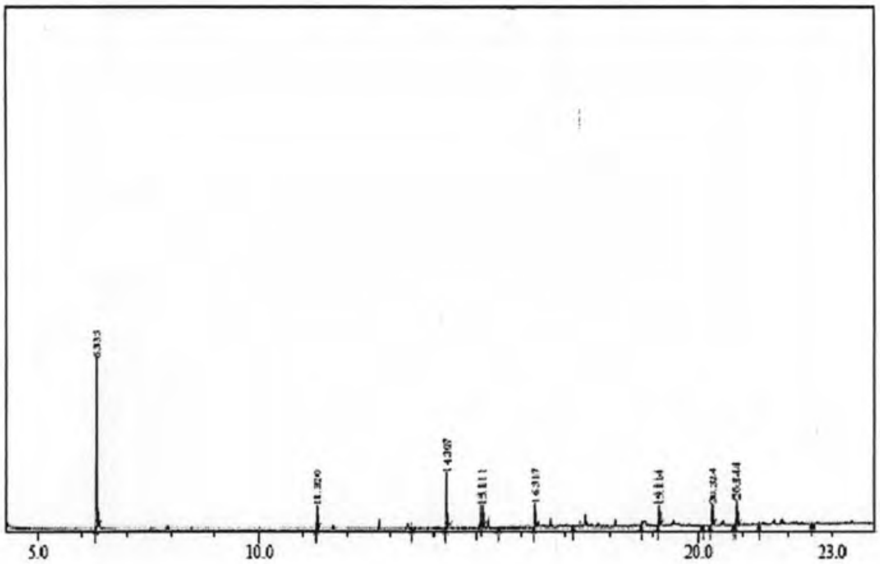
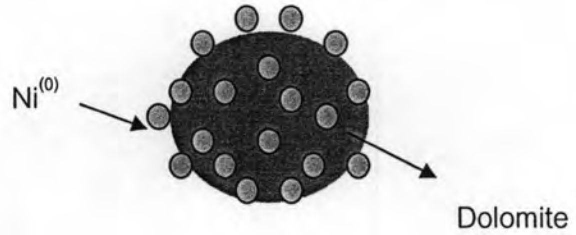


Figure 5.11 GC-MS of tar derived from catalytic gasification of palm shell (Condition; temperature of 800 °C, (S/C) ratio of 0.95, fluidization flow rate 300 ml/min, biomass feed rate of 1.76 g/min, 10 g of Ni/dolomite catalyst)

From the previous work, Srinakruang et al. (2005) had shown the performance of Ni/dolomite catalyst that can eliminate tar formation. NiO was reduced with hydrogen at 700°C to be reduced Nickel (Ni°) form. Tar (C_xH_y) derived from gasification, which reacted with reduced nickel (Ni°) to form nickel carbide (NiC_x) and steam reforming to produce syngas as shown in Figure 5.12.



$$NiC_x + C_xH_y \rightarrow Ni + CO + H_2$$

Figure 5.12 Steam reforming of tar on Ni/dolomite

5.6 Conclusions

1. Base on the above results, it was found that Ni/dolomite catalyst plays a significant role in steam reforming biomass gasification. The effectiveness of Ni/dolomite has influenced the reforming reaction, tar cracking, water-gas shift and methane reforming, which eventually increases the gas product and lowers the tar and char content.

2. The effects of critical parameters such as reaction temperature, steam to carbon ratio influence the gas composition. The suitable condition was at temperature of 800°C and steam to carbon ratio of 0.95 which showed the best catalytic gasification performance on coconut and palm shell, and eventually increases syn gas.

3. The effect of oxygen on gaseous products promoted the partial oxidation at lower oxygen flow rate, which gave higher CO than CO_2. The highest oxygen flow rate was 40 ml/min, which resulted in the increased CO_2 content because of oxidation reaction. H_2 sharply decreased because of hydrogen combustion. Methane slightly decreased with increasing oxygen input due to methane partial oxidation.

4. The performance of Ni/dolomite has proved its activity in tar reduction. The tar content of coconut shell decreased from 19.20 to 3.38% and tar content of palm shell decreased from 20.0 to 8.2 %. Data from GC-MS concluded the fact that nickel and dolomite have high activity to reduce tar by tar cracking of heavy poly aromatic hydrocarbon (PAH) to lower molecular hydrocarbon.