

## CHAPTER IV

### Characteristic of biomass and characterization of Ni/dolomite catalyst

#### 4.1 The Properties of biomasses

Biomass resources are abundant in Thailand. There are biological wastes left after industrial processing and are not properly utilized such as coconut and palm shell in southern part of Thailand. It's useful to increase utilization from agricultural residue to transform into energy. In this study, coconut and palm shell were used as feed material with the particle size of 0.75 mm. The proximate analysis and the elemental analysis (CHN/O) of biomass are reported in Table 4.1 and Table 4.2.

Table 4.1 Proximate analysis of biomass

Proximate analysis (wt.%)	Coconut shell	Palm shell
Moisture	5.56	4.06
Fixed carbon	19.68	18.38
Volatile matter	73.86	76.46
Ash	0.9	1.1

Table 4.1 shows that coconut and palm shell have high volatiles matter, 73.86% of coconut shell and 76.46% of palm shell. Normally, biomass contains a great amount of volatiles matter and has high tar content which can be converted to gaseous product (CO, CH<sub>4</sub> and CO<sub>2</sub>) by gasification using catalyst.

Table4.2 Ultimate analysis of biomass

Ultimate analysis wt.%)	Coconut shell	Palm shell
C	46.02	45.78
H	6.04	6.37
N	0.18	2.57
O	47.76	45.28

The elemental analysis (Table 4.2) shows the components of carbon, hydrogen and oxygen which are main components that can be transformed into syn gas production (CO and H<sub>2</sub>).

#### 4.2 Thermal analysis of biomass

The thermogravimetric analysis (TGA) evaluated the change of weight loss of biomasses as a function of temperature as shown in Figure 4.1. The measurement was carried out with a heating rate of 10 °C/min from 50 °C to 900 °C and nitrogen flow rate of 50ml/min.

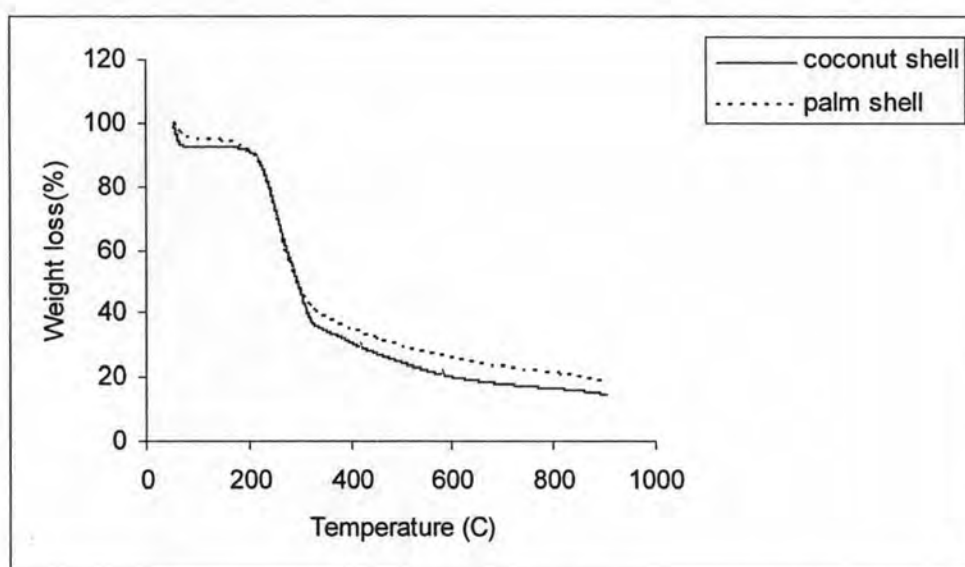


Figure 4.1 Thermal gravimetric analysis (TGA) of coconut and palm shell

Figure 4.1. the thermogravimetric analysis (TGA) shows similar weight loss of coconut and palm shell in Sigmoid curve under nitrogen atmosphere. Firstly, a slight weight loss was observed between 50 to 200 °C which can be attributed to the dehydration. The significant weight loss then follows over 200 to 400 °C which was contributed by formation of gases, tar and char. Finally, at above 400 °C, the weight loss gradually decreased down to approximately 10%. The weight loss due to thermal decomposition of biomass which concerned with pyrolysis process occurs in the temperature range of 180 to 400 °C. The different in weight loss was mainly due to the different structure of the biomasses.

### 4. 3 Characteristic of catalyst

The preparation of 10% Ni/dolomite started by calcination at 500 °C for 2 hours and was done according to the method suggested by Srinakruang et al. (2005). Base on Srinakruang et al. (2005) the percentage of Ni loading varied from 10% to 20%. The result implied that Ni loading at 10% was a suitable concentration. When the amount of Ni loading increased from 10% to 20%, the ratio of NiO changed to increasingly form MgNiO<sub>2</sub>. The formation of NiMgO<sub>2</sub> solid solution was not desirable and was hard to reduce at the temperature below 800 °C (Tomishike et al.1998).

#### 4.3.1 BET surface and elementary composition of catalyst

The chemical composition of bed materials was analyzed by XRF. The BET surface area of calcined dolomite support and 10%Ni/dolomite calcined at 500 °C for 2 hour was measured by N<sub>2</sub> adsorption. The elementary analysis is compiled in Table 4.3.

Table 4.3 Elementary analysis of calcined dolomite and Nickel/dolomite

Composition (%)	Calcined dolomite	Ni/dolomite
CaO	90.38	77.36
MgO	3.25	3.07
Fe <sub>2</sub> O <sub>3</sub>	0.44	0.42
SiO <sub>2</sub>	0.34	0.21
Al <sub>2</sub> O <sub>3</sub>	0.68	0.22
SrO	0.35	0.12
NiO	0.00	14.04
BET surface (m <sup>2</sup> /g)	15.58	14.12

The data indicates that the BET surface area of calcined dolomite was enhanced after calcinations at  $900^{\circ}\text{C}$  for 4 hours, compared with natural dolomite (uncalcined catalyst BET surface area  $2.59\text{ m}^2/\text{g}$ ). Table 4.3 shows that the main composition of dolomite is CaO 77.36 % and MgO 3.07%.

#### 4.3.2 Catalyst characterization

The XRD pattern of calcined Ni/dolomite catalyst is presented in Figure 4.2. The most particular area is situated at  $2\theta$  between  $37.3$  and  $43.2^{\circ}$  characteristic of the cubic NiO phase. It was observed as  $\text{CaCO}_3$  at  $2\theta = 29.4^{\circ}$ , CaO at  $2\theta = 39.5^{\circ}$ , MgO at  $2\theta = 42.9^{\circ}$  and  $\text{NiMgO}_2$  at  $2\theta = 43.1^{\circ}$ .

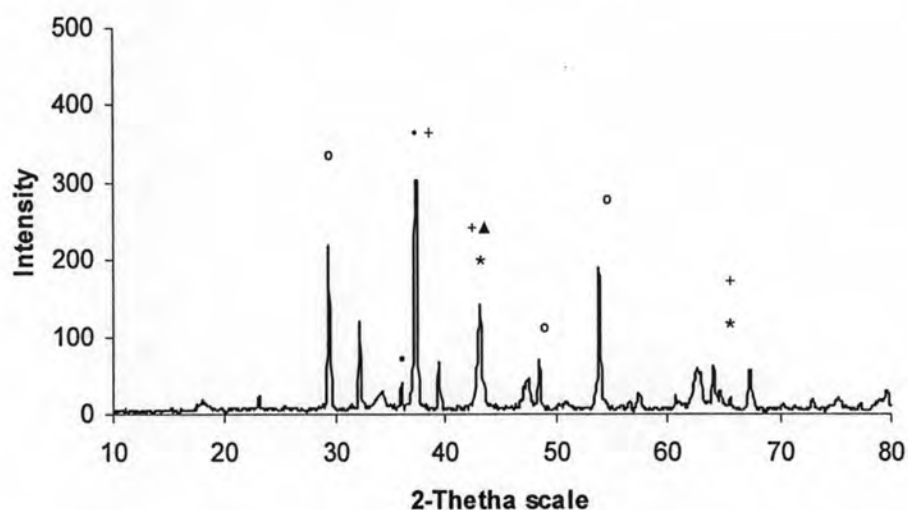


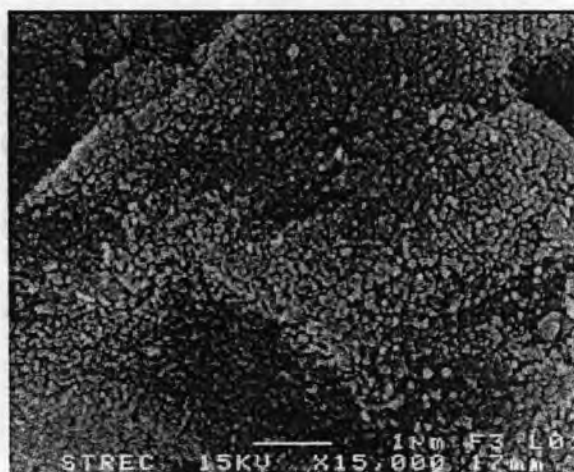
Figure 4.2 X-ray diffraction pattern of Ni/dolomite catalyst

( + NiO, \*  $\text{NiMgO}_2$ , ▲ MgO, ■ CaO, o  $\text{CaCO}_3$  )

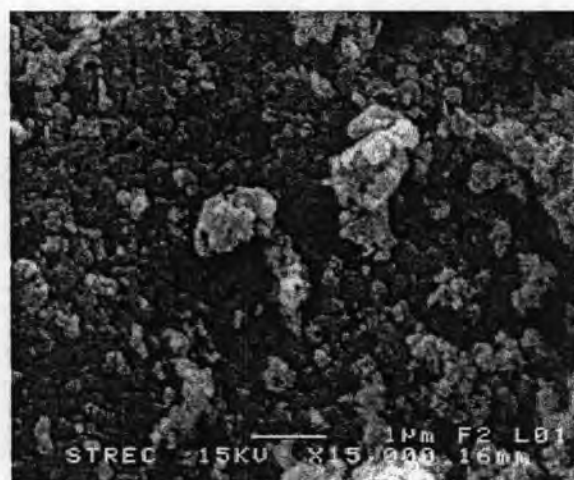
According to the XRD pattern of 10%Ni/dolomite calcined at  $500^{\circ}\text{C}$  for 2 hours, the peak of MgO,  $\text{NiMgO}_2$  and NiO are very close to each other because of their similar structures. NiO and MgO are completely miscible and form solid solution of  $\text{NiMgO}_2$  (Ruckenstein et al. 1999 and Srinakreung et al. 2005). The diffraction peak at  $2\theta = 42.9, 43.1$  and  $43.2^{\circ}$  can be ascribed to MgO,  $\text{MgNiO}_2$  and NiO, respectively.

### 4.3.3 The morphology of the Nickel/dolomite catalyst

The morphology of the catalysts was observed by using scanning electron microscopy (SEM) and the transmission electron microscope (TEM). The result from SEM of Ni/dolomite catalyst is illustrated in Figure 4.3 (A). It shows high porosity of the calcined dolomite support. However, after a loading of Ni 10% and calcined at 500°C, there were significant appearance of the spherical grains of NiO and Ni was deposited onto the surface of dolomite support as shown in Figure 4.3 (B).



(A)



(B)

Figure 4.3 SEM image of (A) Dolomite support and (B) Ni/dolomite catalyst

From the TEM image of Ni/dolomite after being reduced in hydrogen at 700 °C for 2 hours, Figure 4.4 shows that NiO was reduced into nickel ( $\text{Ni}^0$ ) form. Small black particles can be referred to as  $\text{Ni}^0$  particles, which typically have a cubic form and have an average diameter of < 50 nm. It can be observed on the plane of cubic dolomite support.

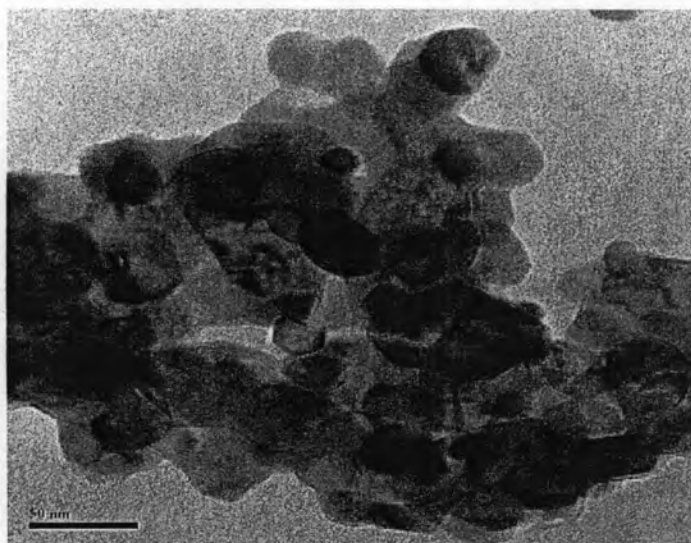


Figure 4.4 TEM image of reduced Ni/dolomite catalyst

#### 4.4 Effect of Calcination temperature

The 10% Ni/dolomite catalyst was calcined at 500, 750 and 950 °C. The calcination temperature has effects significantly on the crystallization of catalyst and formation of solid solution. Data from Table 4.4 indicates that catalyst calcined at 750 °C exhibits the highest BET (14.12 m<sup>2</sup>/g) and metallic surface area (0.79 m<sup>2</sup>/g) than the others calcination temperatures.

XRD diagrams of 10%Ni/dolomite are shown in Figure 4.5, the peaks 2θ at 42.9° are attributed to MgO and the most particular area is situated at 2θ between 37.3° and 43.2° characteristic of the cubic NiO. As reported by Tomishige on steam reforming, the high calcinations temperatures make a strong interaction between Nickel and support, resulting in the formation of NiMgO<sub>2</sub> solid and NiMgO<sub>2</sub> peak 2θ at 43.1°. This suggested that the catalysts prepared by calcined dolomite can easily be formed as NiMgO<sub>2</sub> because Ni<sup>2+</sup> is easily soluble to MgO and the ionic radius of Ni<sup>2+</sup> is close to Mg<sup>2+</sup> (Tomishige et al., 1998).

Table 4.4 Effect of calcination temperature on Ni/dolomite catalyst

Calcination temperature (°C)	Ni form <sup>a</sup>	BET <sup>b</sup> (m <sup>2</sup> /g)	Metallic <sup>c</sup> surface area (m <sup>2</sup> /g)
500	NiO NiMgO <sub>2</sub>	7.08	0.51
750	NiO NiMgO <sub>2</sub>	14.12	0.79
950	NiMgO <sub>2</sub>	10.51	0.16

<sup>a</sup> Analyzed by XRD analysis

<sup>b</sup> Calculated from N<sub>2</sub> adsorption isotherm

<sup>c</sup> Calculated from Hydrogen chemisorption

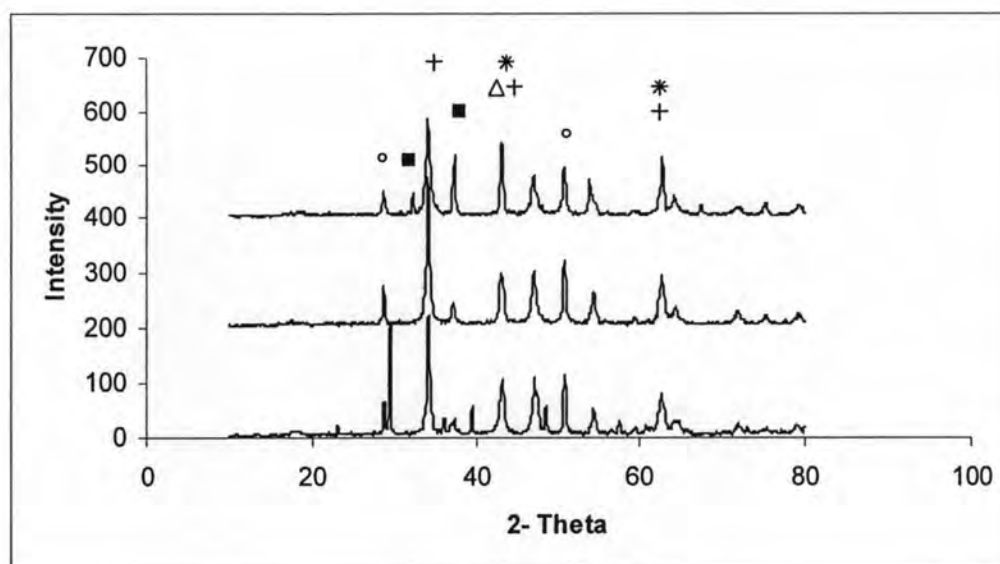


Figure 4.5 X-ray diffraction pattern of 10%Ni/dolomite catalyst (a) calcined 500 °C (b) calcined 750 °C (c) calcined 950 °C ( + NiO, \* NiMgO<sub>2</sub>, ▲MgO, ■ CaO, ° CaCO<sub>3</sub>)

Figure 4.6 shows the total balance at different calcination temperatures varied at calcination temperature of 500, 750 and 950 °C. It can be seen that the catalyst calcined at 750 °C increased higher gas product (71.25%) and lower char (18%) and tar content (10.75%) than the other calcination temperatures. It is because of higher NiO and BET surface area.

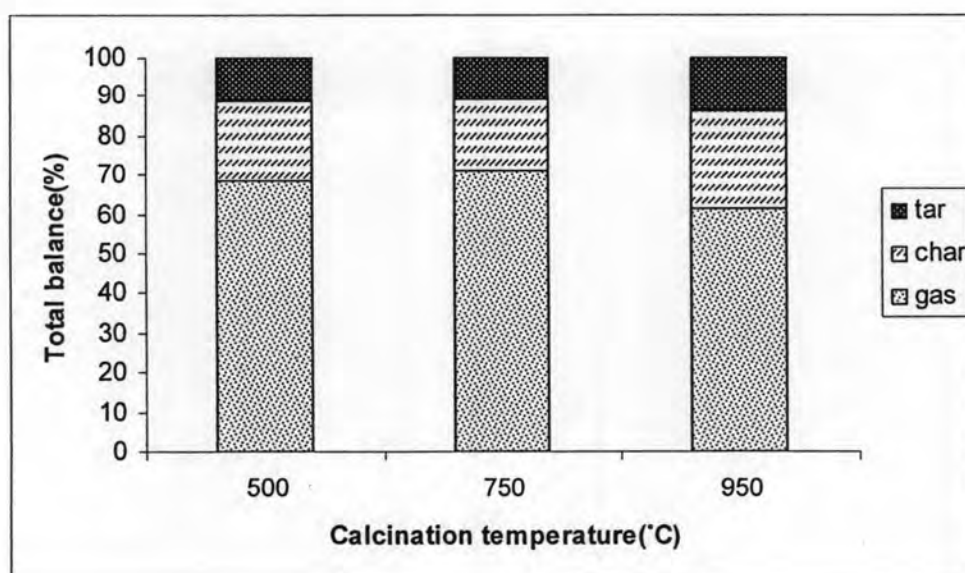


Figure 4.6 Total balance of calcination temperature at 500, 750 and 950 °C



#### 4.5 Conclusions

1. The thermogravimetric analysis (TGA) showed weight loss of coconut and palm shell under nitrogen atmosphere. In the first part, the dehydration of biomass was beginning from 50 to 200 °C. The second part of pyrolysis (between 200 to 400 °C) showed a tremendous loss of weight that was due to the attributes of the gases tar and char formation. The different in weight loss was mainly due to the different structure (cellulose, hemicellulose and lignin) of the biomass.
2. The high calcination temperatures make a strong interaction between Nickel and support, resulting in the formation of NiMgO<sub>2</sub> because Ni<sup>2+</sup> is easily soluble to MgO.
3. Calcination temperature was found to be the significant effect on the structure of Ni/dolomite catalyst. The higher calcinations temperature was the lower BET surface area and metallic surface area. The high calcination resulted in NiMgO<sub>2</sub> formation and less active than NiO structure.
4. The suitable calcination temperature was at 750 °C, increased higher gas product and lower char and tar content than the other calcination temperatures. It is because of higher NiO and BET surface area.