ORIGINAL ARTICLE

Upgrading of biomass by carbonization in hot compressed water

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Abstract

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Upgrading of biomass by carbonization in hot compressed water

Songklanakarin J. Sci. Technol., 2006, 28(5) : 1049-1057

Carbonization of biomass (corn cob) in hot compressed water was performed using a small bomb reactor at temperature 300-350ºC and pressure 10-18 MPa for 30 min. Then, the solid product or biochar was subjected to various analyses in order to investigate the effects of the carbonization in hot compressed water on the characteristics of the biochar. It was found that the yield of biochar carbonized in hot compressed water at 350ºC and pressure of 10 MPa for 30 min was 44.7%, whereas the yield of biochar carbonized in nitrogen atmosphere at 350ºC is 36.4%. Based on the information obtained from the elemental analyses of the biochar, it was found that the oxygen functional groups in the corn cob were selectively decomposed during the carbonization in hot compressed water. The pyrolysis and combustion behaviors of the biochar were found to be affected significantly by the carbonization in hot compressed water.

Key words : carbonization, biomass, hot compressed water, hydrothermal, subcritical water

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Received, 16 November 2005 Accepted, 23 March 2006

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การปรับปรุงคุณภาพเชื้อเพลิงชีวมวลโดยกระบวนการคาร์บอนไนเซชันในน้ำร้อนความดันสูง

ว. สงขลานครินทร์ วทท. 2549 28(5) : 1049-1057

กระบวนการคาร์บอนไนเซชันชีวมวล (ซังข้าวโพด) ในน้ำร้อนความดันสูง เตรียมโดยใช้ small bomb reactor และทำการคาร์บอนไนเซชันที่อุณหภูมิ 300-350°Cและความดัน 10-18 MPa เป็นเวลา 30 นาที หลังจากนั้นทำการเก็บส่วนที่เป็นของแข็ง หรือถ่านซังข้าวโพด เพื่อนำไปทำการวิเคราะห์อิทธิพลของกระบวนการคาร์บอนไนเซชันในน้ำร้อนความดันสูงที่มีผลต่อสมบัติทางเคมีของถ่านซังข้าวโพด จากการทดลองพบว่า ผลผลิตของถ่านซังข้าวโพดที่เตรียมจากกระบวนการคาร์บอนไนเซชันในน้ำร้อนความดันสูงที่อุณหภูมิ 350°Cและความดัน 10 MPa เป็นเวลา 30 นาที มีค่า 44.7% ในขณะที่ผลผลิตของถ่านซังข้าวโพดที่เตรียมจากกระบวนการคาร์บอนไนเซชันในบรรยากาศของไนโตรเจนที่ความดันบรรยากาศปกติที่อุณหภูมิ 350°C มีค่า 36.4% และจากข้อมูลการวิเคราะห์ธาตุของถ่านซังข้าวโพด พบว่าหมู่ฟังก์ชันออกซิเจนของซังข้าวโพดจะสลายตัวระหว่างกระบวนการคาร์บอนไนเซชันในน้ำร้อนความดันสูง นอกจากนั้น กระบวนการคาร์บอนไนเซชันในน้ำร้อนความดันสูงมีผลต่อพฤติกรรมการไพโรไลซิสและการเผาไหม้ของถ่านซังข้าวโพดเป็นอย่างมากด้วย

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Renewable energy is of growing importance in satisfying environmental concerns over fossil fuel usage. Biomass including agricultural residues is one of the main renewable energy resources available especially in an agricultural country such as Thailand. Thailand has many kinds of biomass, for example, rice husk, corn cob, coconut shell, palm shell, and sugar cane bagasse. Biomass is considered the renewable energy source with the highest potential to contribute to the energy needs of modern society for both the developed and developing economies world-wide (IEA, 2000).

There is a wide range of processes available for converting biomass into more valuable fuels. These include biological processes to make ethanol (Hamelinck *et al*., 2005), and thermal processes to make heat, gaseous fuels, liquid fuels, and solid fuels (Bridgwater, 2003). Biomass offers important advantages as a combustion feedstock due to high volatility of the fuel and high reactivity of both the fuels and the resulting char. Biomass is in part due to the generally higher moisture content and in part due to the high oxygen content. In comparison with fossil fuels, biomass contains much less carbon and more oxygen, and hence has a low heating value. Therefore, biomass is seldom utilized in the energy production schemes (Bridgwater *et al*., 1988). So, it is necessary to upgrade biomass to be a high value fuels by some means.

Several technologies have been developed to convert biomass into a biofuel with a higher heating value, such as gasification (Bridgwater, 1995), fast pyrolysis (Bridgwater *et al*., 2000), and hot compressed water treatment (Goudriaan *et al*., 1990). In the hot compressed water treatment, the biomass is treated with water under subcritical condition (300-350ºC, 10-18 MPa). During this process, the oxygen content of the organic material is reduced from about 40% to between 10% to 15%. Many studies have been performed to investigate the decomposition of biomass in water under subcritical and supercritical conditions (Mok *et al*., 1992; Sasaki *et al*., 1996; Yoshida *et al*., 2001). However, little work has been done to investigate the effects of hot compressed water on the characteristics of the solid product.

In this study the biomass (corn cob) was carbonized in hot compressed water at temperature 300-350ºC and pressure of 10-18 MPa for 30 min. Then, the solid product or biochar was subjected to various analyses in order to investigate the effects of the carbonization in hot compressed water on the characteristics of the biochar. The pyrolysis and combustion behaviors of the biochar were examined in detail through the measurements of changes in weights by using a thermogravimetric analyzer (TGA).

Materials and Methods

1. Sample preparation

The biomass samples used in this study is corn cob. Corn cob sample was ground into less than 1 mm in diameter and dried in vacuo at 70ºC for 24 h before the experiments. The proximate and ultimate analyses of corn cob are shown in Table 1.

2. Carbonization under atmospheric pressure

The carbonization of biomass under atmospheric pressure was conducted in a tube furnace and a horizontal quartz tube reactor (3 cm I.D. and 50 cm in length). About 0.5 g of the corn cob was placed in an alumina boat (20 mm x 100 mm) and then the boat with the sample was inserted into the middle of the reactor. The sample was heated from room temperature to 350ºC at a constant heating rate of 10ºC/min in a nitrogen stream at flow rate of 200 ml/min and it was kept at the desired temperature for 30 min. The carbonized sample was subjected to various analyses.

3. Carbonization in hot compressed water

The carbonization of biomass in hot compressed water was carried out by using a small bomb reactor (1 cm I.D. and 15 cm length). About 1 g of corn cob and 1-7 g of water were added into the reactor, and then the reactor filled with sample and water was immersed into an air fluidized bed of MgO particles (70 µm in diameter). The internal diameter of the fluidized bed was 8 cm and the bed height was 50 cm. The reactor was heated from 30ºC up to 300ºC or 350ºC at which it was kept for 30 min. The pressure inside the reactor was measured by a pressure transducer (Kyowa, PGM-500 KD) connected to the reactor. Figure 1 shows the experimental set up used for the carbonization of biomass in hot compressed water. After the reaction time was reached, the reactor was immersed into the water bath to stop the reaction. The gaseous product was collected by a gas bag and then analyzed by using a gas chromatography with a TCD detector (Shimadzu, GC-14B) for CO, CO_2, and CH_4. The reaction mixtures were separated into the solid and liquid fractions by filtration. The liquid fraction was diluted with water to 100 ml and then analyzed for the total organic carbon by using a TOC analyzer (Shimadzu, TOC-VCSH). The solid fraction was dried at 70ºC for 24 h in vacuo. After drying, the solid was determined for the elemental composition by using a CHNS analyzer (Thermofinnigan, Flash EA 1112 series).

4. Pyrolysis behaviors of the biochar

The weight change of the biochar during the pyrolysis was measured by using a sensitive thermogravimetric analyzer (Perkin Elmer, Pyris1 TGA). Fine particles of less than 74 µm and small samples of around 5 mg were used to ensure uniform heating of the samples. The sample was heated from room temperature to 900ºC at a constant heating rate of 10ºC/min in a nitrogen stream and flow rate of 50 ml/min.

5. Combustion behaviors of the biochar

The weight change of the biochar during the

Table 1. Proximate and ultimate analyses of biomass samples

Sample	Proximate analyses [wt%,dry basis]			Ultimate analyses [wt%, daf]			
	VM	FC	Ash	C	H	N	O (diff)
Corncob	75.3	16.1	8.6	48.2	6.5	0.7	44.6

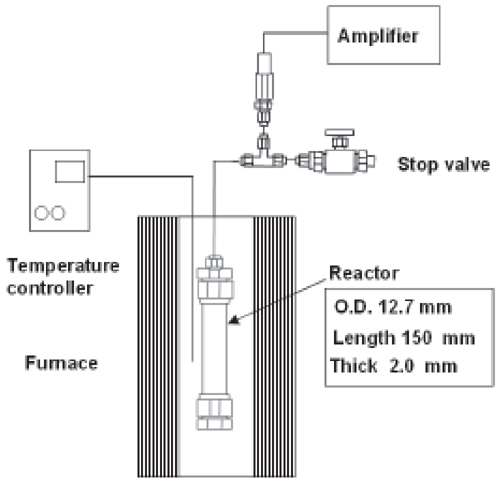

Figure 1. Apparatus used for carbonization in hot compressed water.

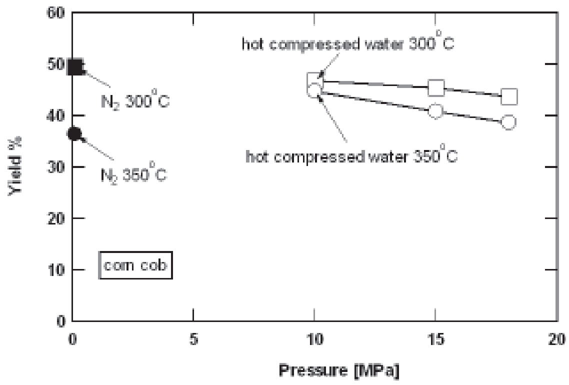

Figure 2. Yields of biochar carbonized in hot compressed water and in nitrogen atmosphere.

combustion was measured by using a sensitive thermogravimetric analyzer (Perkin Elmer, Pyris1 TGA). Fine particles of less than 74 µm and small samples of around 5 mg were used to ensure uniform heating of the samples. The sample was heated from room temperature to 600ºC at a constant heating rate of 10ºC/min in an air stream and flow rate of 50 ml/min.

Results and Discussion

1. Effect of reaction temperature and pressure on the conversion of the biomass

The biochar carbonized in hot compressed water were abbreviated by attaching the final temperature and pressure after H_2O, for example H_2O-300-10 means the biochar was carbonized in hot compressed water at temperature of 300ºC and pressure of 10 MPa. On the other hand, the biochar samples carbonized in the nitrogen atmosphere were abbreviated by attaching the final temperature and pressure after N_2, for example N_2-300-0.1 means the biochar sample was carbonized in the nitrogen atmosphere at temperature of 300ºC.

Figure 2 shows the yield of biochar carbonized in hot compressed water at 300-350ºC and pressure of 10-18 MPa. The yields of biochar carbonized in hot compressed water at 300ºC decreased from 46.8% to 43.7% when increasing pressure from 10 MPa to 18 MPa. The yields of biochar carbonized in hot compressed water at 350ºC decreased from 44.7% to 38.6% when increasing pressure from 10 MPa to 18 MPa. On the other hand, the yields of biochar carbonized in the nitrogen atmosphere at 300ºC and 350ºC were 49.8% and 36.4%, respectively. These results clearly indicated that pressure significantly affected the yield of biochar and the yield decreased with increasing pressure. These results also suggested that we could increase the yield of biochar by carbonization in hot compressed water at 350ºC.

Table 2 lists the proximate analyses and the yields of biochar carbonized in hot compressed water and in nitrogen atmosphere. The volatile matter of biochar carbonized in hot compressed water increased with increasing pressure while the volatile matter of biochar carbonized in nitrogen atmosphere decreased with increasing temperature. The ash contents of biochar carbonized in hot compressed water at some conditions were null comparing with the ash content of the raw corn cob of 8.6%. This result showed that the mineral matter in corn cob could be dissolved in water at high pressure.

The proportion of products (solid, liquid, and gas) from corn cob carbonized in hot compressed water can be described as carbon distribution. Figure 3 shows the carbon distribution of biochar carbonized in hot compressed water. The carbon in solid products of biochar carbonized in hot compressed water at 300ºC decreased from 78.5% to 67.1% when increasing the pressure from 10 MPa to 18 MPa. On the other hand, the carbon in liquid products at 300ºC increased from 16.7% to 22.7% when increasing the pressure from 10 MPa to 18 MPa. The carbon in solid products of biochar carbonized in hot compressed water at pressure of 18 MPa increased from 67.1% to 69.6% when increasing the temperature from 300ºC to 350ºC. This result indicates that the conversion of corn cob in hot compressed water is accelerated by increase in pressure. However, small amount of gas, in which CO_2 is the major gas component, was formed at all experimental conditions employed in this study. The carbon balances of all the experiments were more than 85%. The loss of the carbon balances was probably due to the sticky residue deposited on the wall of reactor not being recovered.

2. Elemental analyses of the biochar carbonized in hot compressed water

Next, the elemental compositions and calorific values of the biochar carbonized in hot compressed water as well as the biochar carbonized in the nitrogen atmosphere were examined. Table 3 lists the ultimate analyses and the calorific values of the biochar carbonized in hotcompressed water and in nitrogen atmosphere. The calorific value is calculated from the ultimate analyses by using the SEYLER's formula (D.W. van Krevelen, 1993) as follows:

$$CV\ (cal/g) = 123.9C + 388.1H + 0.25O^{2} - 4269$$

Table 2. The proximate analyses and the yields of biochar carbonized in hot compressed water and in nitrogen atmosphere.

Sample	Proximate analyses [wt%, dry basis]			Yield [wt% dry basis]
	Volatile matter	Fixed carbon	Ash	
N_2-300-0.1	59.3	40.7	0.0	49.8
N_2-350-0.1	34.6	63.2	2.2	36.4
H_2O-300-10	51.7	48.3	0.0	46.8
H_2O-300-15	53.4	46.6	0.0	45.4
H_2O-300-18	53.5	46.6	0.0	43.7
H_2O-350-10	28.7	69.3	1.9	44.7
H_2O-350-15	39.9	60.0	0.0	40.8
H_2O-350-18	48.4	51.6	0.0	38.6

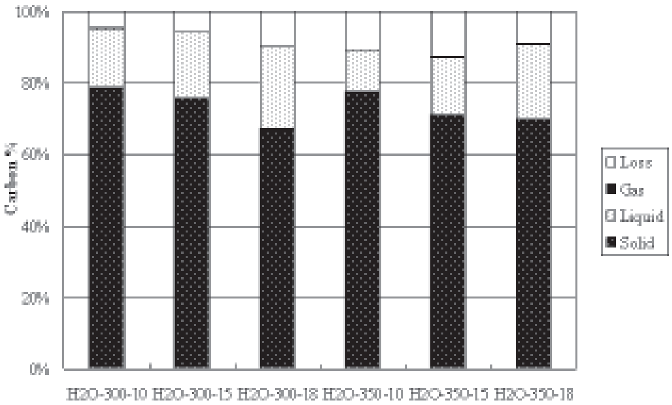

Figure 3. Effects of the reaction temperature and pressure of carbonization in hot compressed water on the carbon distribution.

Table 3. The elemental analyses and the calorific values of biochar carbonized in hot compressed water and in nitrogen atmosphere.

Sample	Ultimate analyses [wt%, daf.]				Calorific value [cal/g]
	C	H	N	O (diff)	
raw	48.2	6.5	0.7	44.6	4,722.9
N_2-300-0.1	66.0	5.4	0.5	28.1	6,201.5
N_2-350-0.1	76.9	4.4	0.6	18.1	7,048.5
H_2O-300-10	75.7	5.5	0.6	18.1	7,326.7
H_2O-300-15	75.7	5.7	0.5	18.0	7,403.4
H_2O-300-18	69.6	5.7	0.4	24.2	6,713.0
H_2O-350-10	80.2	4.8	0.5	14.1	7,580.4
H_2O-350-15	79.1	5.4	0.5	15.0	7,683.5
H_2O-350-18	82.7	6.0	0.6	10.7	8,334.8

From Table 3, the carbon content of the biochar carbonized in hot compressed water at 350ºC increased from 80.2% to 82.7% while the oxygen content decreased from 14.1% to 10.7% when increasing pressure from 10 MPa to 18 MPa. On the other hand, the carbon content and the oxygen content of the biochar carbonized in nitrogen atmosphere at 350ºC were 76.9% and 18.1%, respectively. The calorific value of the biochar was significantly increased by the carbonization in hot compressed water. These results suggested that the oxygen functional groups in the corn cob were selectively decomposed during the carbonization in hot compressed water resulting in high calorific value of the biochar. Thus, we can upgrade the biomass into biochar with high calorific value and high yield by carbonization in hot compressed water.

3. Pyrolysis behaviors of the biochar

To examine the pyrolysis behaviors of the biochar, the thermogravimetric curves of the biochar during the pyrolysis were examined. Figure 4 compares the weight loss curves during the pyrolysis between the raw corn cob and the biochars carbonized in hot compressed water and carbonized in the nitrogen atmosphere. The weight decreasing profiles of the biochar carbonized in

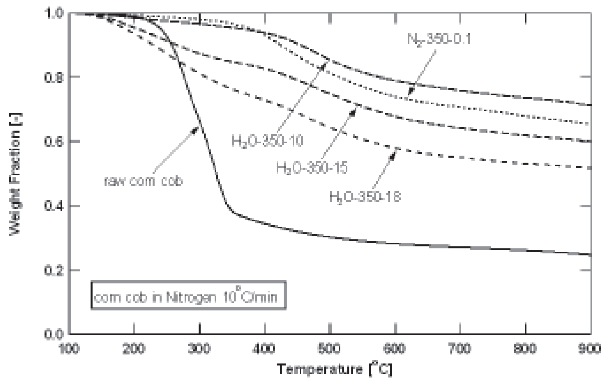

Figure 4. TGA curves for pyrolysis of raw corn cob and biochar carbonized in hot compressed water and carbonized in the nitrogen atmosphere.

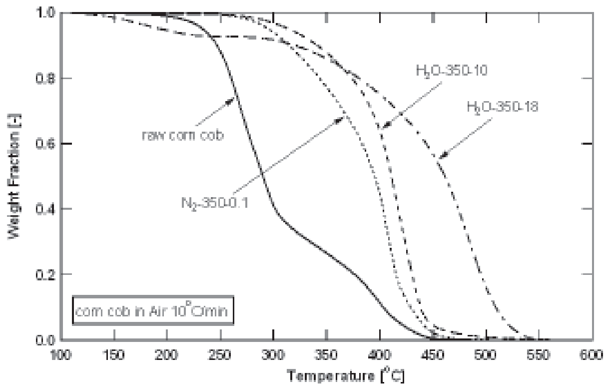

Figure 5. TGA curves for combustion of raw corn cob and biochar carbonized in hot compressed water and carbonized in the nitrogen atmosphere.

hot compressed water were significantly different from the biochar carbonized in the nitrogen atmosphere. Among these biochars, the weight of biochar carbonized in hot compressed water started to decrease before that of the biochar carbonized in the nitrogen atmosphere. The weight of the biochar carbonized in hot compressed water started to decrease at around 150ºC and the char yields at 900ºC for the H_2O-350-10, H_2O-350-15, and H_2O-350-18 were 71.4%, 60.2%, and 51.8%, respectively. On the other hand, the weight of the biochar carbonized in the nitrogen atmosphere started to decrease at above 200ºC and the char yield at 900ºC was 65.6%. These results showed that the pressure significantly affected the pyrolysis behaviors of the biochar and the char yield at 900ºC of the biochar carbonized in hot compressed water decreased with increasing in pressure. These results clearly indicated that the carbonization of corn cob in hot compressed water is significantly different from the carbonization in the nitrogen atmosphere.

4. Combustion behaviors of the biochar

Next the combustion behaviors of the biochar were examined. Figure 5 compares the weight loss curves during the combustion between the raw corn cob and the biochars carbonized in hot compressed water and carbonized in the nitrogen atmosphere. To examine the combustion behaviors of the biochar in more detail, the weight decreasing profile of each sample was differentiated with time and

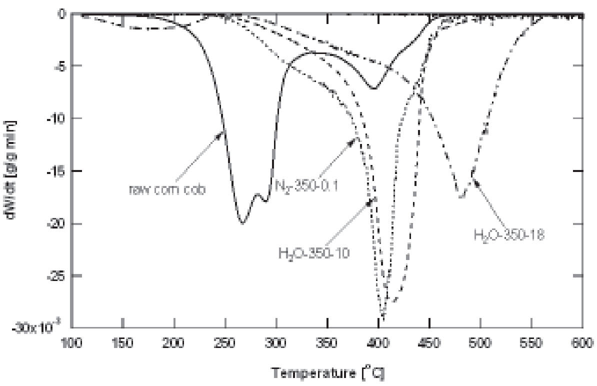

Figure 6. DTG curves for combustion of raw corn cob and biochar carbonized in hot compressed water and carbonized in the nitrogen atmosphere.

the result is shown in Figure 6. The derivative plots showing the rate of weight change as a function of temperature (derivative thermogravimetry, DTG) are useful in attempting to resolve overlapping processes. The DTG curve for raw corn cob showed two sharp peaks at 265ºC and 290ºC and a broad peak at around 400ºC. The DTG curve for N_2-350-0.1 showed a big distinctive peak at around 400ºC. The DTG curve for H_2O-350-10 showed a big sharp peak at around 410ºC. On the other hand, the DTG curve for H_2O-350-18 has two distinctive peaks at 180ºC and 480ºC. Due to high volatile matter content of H_2O-350-18 (48.4%), the first peak of the DTG curve for H_2O-350-18 may probably due to the combustion of the volatile matter evolved at lower temperature. These results clearly indicated that the combustion behaviors of the biochar carbonized in hot compressed water were significantly affected by carbonization in hot compressed water.

Conclusion

In this study the carbonization of biomass in hot compressed water at temperature 300-350ºC and pressure of 10-18 MPa for 30 min was proposed in order to upgrade the biomass into a biochar with a higher heating value. If was found that the yields of the biochar carbonized in hot compressed water at 350ºC were higher than the yield of the biochar carbonized in the nitrogen atmosphere. The yield of the biochar decreased with increasing pressure and temperature during the carbonization in hot compressed water. The effects of carbonization in hot compressed water on the properties of the biochar were examined from several aspects. Based on the information obtained from the elemental analyses of the biochar, it was found that the oxygen functional groups in the corn cob were selectively decomposed during the carbonization in hot compressed water. The heating values calculated from the elemental analyses of the biochar carbonized in hot compressed water were 1.8 times larger than that of the raw corn cob. The pyrolysis and combustion behaviors of the biochar were found to be affected significantly by the carbonization in hot compressed water.

Acknowledgements

The financial support from The Thailand Research Fund (MRG4780123) throughout this study is gratefully acknowledged.

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