

# Thermoanalytical Characterization of Apple-based Woodceramics Using TG-DTA/MS

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Thermal change of an ecological carbon/carbon hybrid material, wood ceramics (WC) prepared from apple pomace, was studied by mainly using TG-DTA combined with evolved gas analysis technique using mass spectrometry (TG-DTA/MS). Thermal change occurs roughly in four stages; dehydration and release of gaseous carbon dioxide (CO<sub>2</sub>) occur in temperatures lower than ca. 483 K; CO<sub>2</sub> and fragments of phenol resin are mainly found up to 943 K; at higher temperatures, gaseous CO is discharged, showing progressive carbonation. Carbonized materials and woodceramics sintered at 1073 K shows maximum evolution of adsorbed gases, and show dehydration immediately followed by CO<sub>2</sub> evolution at temperatures lower than 483 K; but woodceramics is thermally more stable than carbonized materials and the gas evolution peak temperatures are higher for products sintered at higher temperatures.

Key words: woodceramics, TG-DTA/MS, EGA, apple pomace, ecomaterial, carbon dioxide, gas adsorption, hybrid material

## 1. INTRODUCTION

Woodceramics are so-called hybrid materials in the sense that plant-originated amorphous carbon is reinforced by glassy carbon generated from resin. They are porous carbon/carbon hybrid materials newly developed by carbonizing wood or woody materials impregnated with thermosetting resin, such as phenol resin, in a vacuum furnace [1]. Furthermore, woodceramics are environmental-friendly or so-called ecomaterials, because they may take part as a member of a closed material recycle system because wood-based wastes can be employed, or their by-products, such as the decomposition products, can be recycled [2].

In the apple products industry in Aomori Prefecture, Japan, about 4250 t/year of apple pomace, which corresponds to about 20 % of the raw material, is being wasted (average taken for year 1997 to 2001). From ecological point of view, accordingly, studies on extracting wood vinegar, or on recycling of them as active carbon, friction materials, heater sheets, and woodceramics, have been made [3] on apple pomace.

No thermal analysis data is reported to present on woodceramics based on apple pomace. Concerning thermoanalytical studies of woodceramics, Kano et al [4] provided thermogravimetry (TG) and differential thermal analysis (DTA) data on woodceramics based on Hiba. Arii and Momota [5] reported the simultaneous measurement of mass spectrometry (MS) with TG-DTA on the same material. TG-DTA/MS is particularly effective for examining gas-evolving processes. However, the woodceramics subjected to thermal analysis are obtained by carbonizing systems using cellulosic materials, whereas apple pomace contain considerable amount of sugars as shown in Table 1[3].

Thus, it is interesting to perform thermoanalytical studies on this material, and we report the results obtained mainly by TG-DTA/MS on woodceramics based on apple pomace (referred to simply hereinafter as "apple

woodceramics").

## 2. EXPERIMENTAL

### 2.1 Samples

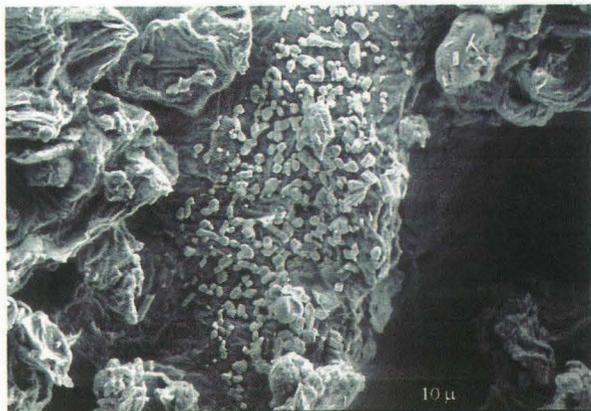
As shown in Table 1, apple pomace differs from the raw materials used in conventional woodceramics in that it contains considerable amount of sugars. Woodceramic samples differing in sintering temperature were prepared by impregnating apple pomace with phenol resin, and, after degassing, by carbonizing the resulting products each at 1073 K and 1473 K. Carbonized apple pomace obtained at the same temperatures were also used as comparative samples. The samples were 250 μm or less in granularity. The samples are

Table 1 Chemical Composition of Apple pomace[3].

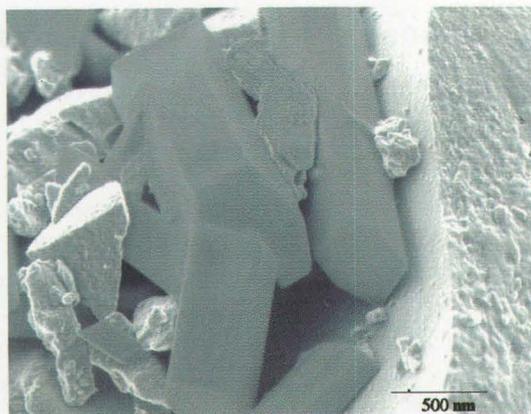
Component (wt%)	Apple pomace	Cedar	Beech
Cellulose	18.0	52.8	56.6
Hemicellulose	13.5	17.3	24.7
Lignin	9.0	31.4	21.3
Fructose	7.1 - 21.5	-	-
Glucose	6.0 - 17.5	-	-
Sucrose	2.0 - 4.3	-	-

Table 2 Samples used.

No	Samples	Sintering temperature
1	Carbonized apple pomace	1073 K (800°C)
2		1473 K (1200°C)
3	Apple woodceramics	1073 K
4		1473 K



**Fig. 1** FE-SEM photograph showing scale-like surface and granules on the surface (magnification: 1560x).



**Fig. 2** FE-SEM photograph showing carbonized crystals of sucrose (magnification: 23,650x).

given in Table 2.

Figures 1 and 2 are the Field-Effect scanning micrographs of the woodceramics sintered at 1073 K. The scaly surface characteristic to apple woodceramics can be observed in Fig. 1, and in Fig. 2 is clearly observed crystalline sucrose developed during sintering.

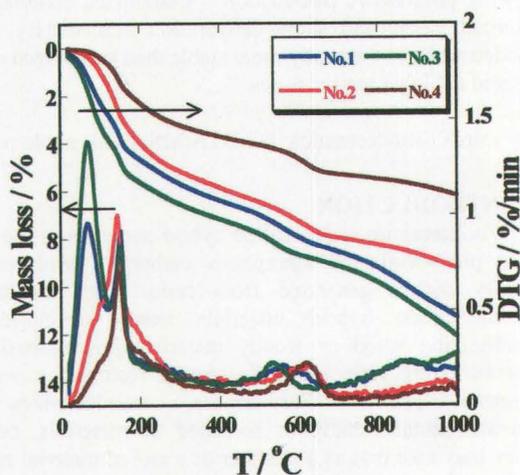
### 2.2 Simultaneous TG-DTA/(GC)-MS

Simultaneous TG-DTA/GC-MS measurements were performed on 15 mg each of samples using a TG-DTA TG8120 (Rigaku Corporation) coupled with QP-5050A (Shimadzu Corporation) in the temperature range of from R.T. to 1273 K at a heating rate of 20 Kmin<sup>-1</sup> under helium gas flow of 300 mlmin<sup>-1</sup>, while holding GC(Gas chromatograph)-oven temperature and GC-Injection temperature both at 533 K, and holding MS-Detection temperature at 573 K.

## 3. RESULTS AND DISCUSSION

### 3.1 Mass loss of as-received Samples in inert (He) atmosphere

Figure 3 shows the TG-DTG (differential TG) curves of the samples, and the mass losses are summarized in Table 3. DTA temperatures read from the curves are also given in Table 3. Considering evolution of adsorbed materials, larger mass losses to ca. 483 K are obtained for



**Fig. 3** TG-DTG curves of the samples in He.

carbonized materials and for woodceramics sintered at 1073 K. It is well known that carbonized materials adsorb moisture and gaseous carbon, and from this point of

**Table 3** TG-DTA results.

Sample No.	1	2	3	4
	Carbonized Apple		Apple woodceramics	
	1073 K	1473 K	1073 K	1473 K
DTA En1 (°C)	68.9	-	69.7	-
DTA En2 (°C)	151.1	140.8	152.1	145.2
TG Mass change (%)				
~120 °C	-2.64	-5.27	-4.95	-3.21
120~210°C	-2.06		-1.84	
210~670°C	-3.66	-2.74	-3.17	-2.19
670~970°C	-2.61	-1.03	-2.65	-0.6

view, it is presumed that carbonized materials are superior adsorbents. However, considering the change in higher temperatures ( $>943$  K), products sintered at 1473 K show better stability. Furthermore, it can be observed that the samples sintered at a lower temperature of 1073 K shows two sharp distinct mass losses at temperatures lower than 473 K; first peak is observed in DTG below 373 K, and the second peak occurs successively below 473 K. However, for the samples sintered at 1473 K, single sharp peak at ca. 443 K is observed. Furthermore, the second sharp mass change is observed in the temperature range of 773 to 943 K. The samples sintered at 1073 K yield the peak at ca. 823 K, whereas the samples sintered at 1273 K yield the peak at temperatures about 100 deg higher than those sintered at lower temperatures; i.e., at ca. 913 K. These results suggest that the adsorption sites or pore sizes differ depending on the sintering temperature.

### 3.2 TG-DTA/MS of as-received Samples in inert (He gas) atmosphere

Figures 4a and 4b are the MS curves for carbonized apple pomace (No.1) and apple-based woodceramics (No.3) sintered at 1073 K, and Figs. 5a and 5b are the MS curves for carbonized apple pomace (No.2) and apple-based woodceramics (No.4) sintered at 1473 K. From these figures, it can be seen that gas evolution occurs roughly in three stages. In the figures, TIC represents the total ion current. In Table 4 are given the possible gas species evolved in the corresponding temperature range. The symbols *ff*, *f*, and *m* given in parenthesis each represent the qualitative expression of the evolved amount.

In the first stage, which may consist of two steps of dehydration ( $m/z$  18) and evolution of gaseous carbon dioxide ( $\text{CO}_2$ ), ( $m/z$  44), occurs up to ca. 483 K. The second stage corresponds from that temperature to ca. 873 K. In the third stage, at temperatures higher than ca. 873 K, carbon monoxide (CO) ( $m/z$  28) is discharged showing progressive carbonization.

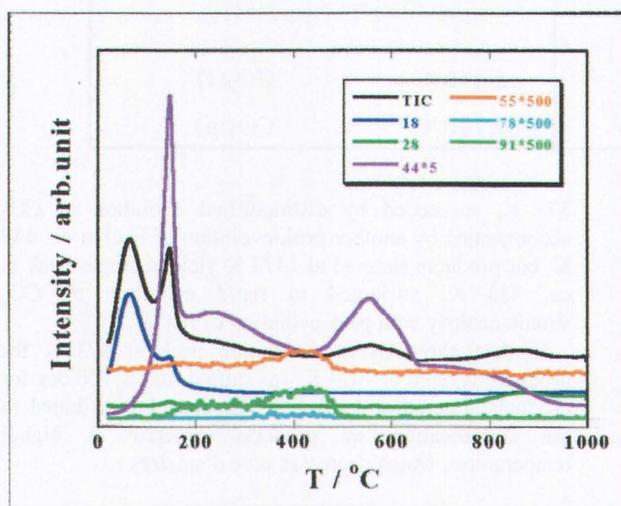


Fig.4a MS curves of apple pomace carbonized at 1073 K (No.1).The numerals indicate m/z.

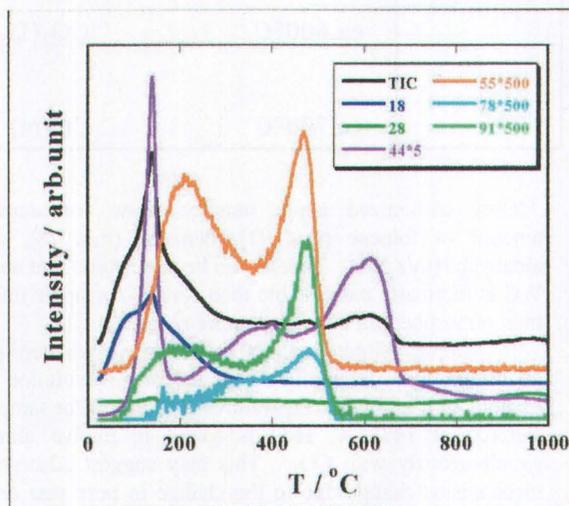


Fig.5a MS curves of apple pomace carbonized at 1473 K (No.2). The numerals indicate m/z.

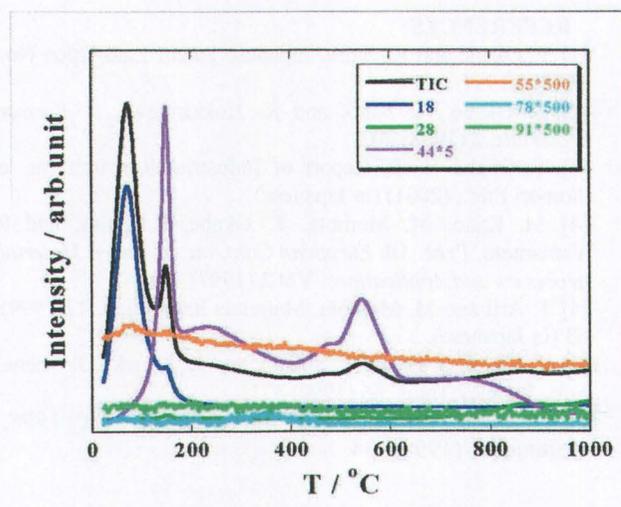


Fig.4b MS curves of apple woodceramics sintered at 1073 K (No.3). The numerals indicate m/z.

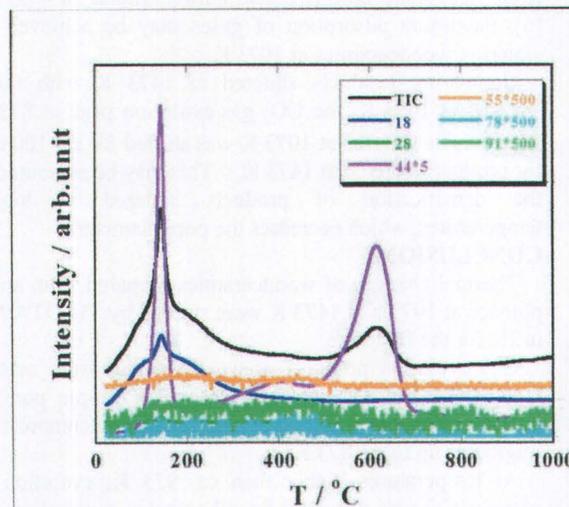


Fig.5b MS curves of apple woodceramics sintered at 1473 K (No.4). The numerals indicate m/z.

**Table 4** Characteristics of thermal change of carbonized apple pomace and apple woodceramics(WC).

Sintering temperature	Species found by MS					
	1073 K		1473 K			
Carbonized Apple	ca.160°C	H <sub>2</sub> O(ff)	ca.210°C	CO <sub>2</sub> (ff)		
	ca.210°C	CO <sub>2</sub> (ff)				
	ca.500-600°C	toluene,benzene,aldehydes			ca.500-600°C	toluene,benzene,aldehydes
	ca.600°C	CO <sub>2</sub> (f)			ca.670°C	CO <sub>2</sub> (f)
	ca.700°C	CO(m)			ca.700°C	CO(m)
Apple WC	ca.160°C	H <sub>2</sub> O(ff)	ca.210°C	CO <sub>2</sub> (ff)		
	ca.210°C	CO <sub>2</sub> (ff)				
	ca.500-600°C	CO <sub>2</sub> (m)			ca.500-600°C	CO <sub>2</sub> (m)
	ca.600°C	CO <sub>2</sub> (f)			ca.670°C	CO <sub>2</sub> (f)
	ca.700°C	CO(m)			ca.700°C	CO(m)

Only carbonized apple samples show considerable amount of toluene (m/z 91), benzene (m/z 78), and aldehydes (m/z 55). Thus, it can be understood that apple WC is thermally more stable than carbonized apple under inert atmosphere in this temperature range.

In samples sintered at 1073 K only, two-step gas evolution, i.e., dehydration succeeded by evolution of gaseous CO<sub>2</sub> at lower temperatures is found. For samples sintered at 1473 K, H<sub>2</sub>O is found to evolve almost simultaneously with CO<sub>2</sub>. This may suggest adsorption mechanisms change due to the change in pore size or in adsorption mechanism as pointed out in section 3.1 above. Since cellulosic materials yield heterogeneous pore structure and large specific surface area [5] while phenol resin yield sharp pore size distribution around 50 – 60 nm [6], maximum adsorption of gases may be achieved by sintering woodceramics at 1073 K.

Comparing products sintered at 1473 K with those sintered at 1073 K, the CO<sub>2</sub> gas evolution peak at 873 K for products sintered at 1073 K was shifted for ca. 100 deg for products sintered at 1473 K. This may be attributed to the densification of products sintered at higher temperatures, which decreases the pore diameters.

#### CONCLUSIONS

Thermal changes of woodceramics prepared from apple pomace at 1073 and 1473 K were studied by TG-DTA/MS in He for the first time.

Gas evolution products of woodceramics were mainly H<sub>2</sub>O, CO<sub>2</sub>, and CO, whereas carbonized apple pomace evolved benzene, toluene, and other decomposition fragments up to ca. 873 K.

At temperatures higher than ca. 973 K, evolution of gaseous CO was observed for all samples, suggesting the occurrence of progressive carbonization.

Concerning difference in carbonization, products sintered at 1073 K evolved H<sub>2</sub>O at temperatures lower than

373 K, succeeded by distinguished evolution of CO<sub>2</sub> accompanied by another peak evolution of H<sub>2</sub>O at ca. 433 K, but products sintered at 1473 K yielded single peak at ca. 433 K, attributed to rapid evolution of CO<sub>2</sub> simultaneously with peak evolution of H<sub>2</sub>O.

Further, the CO<sub>2</sub> gas evolution peak at 873 K for products sintered at 1073 K was shifted for ca. 100 deg for products sintered at 1473 K. This may be attributed to the densification of products sintered at higher temperatures, which decreases pore diameters.

#### ACKNOWLEDGEMENTS

The authors are grateful to Mr. S. Tachibana of Carl Zeiss, Co. Ltd., for providing us the FE-SEM photographs..

#### REFERENCES

- [1] T. Okabe and K. Saito, Japanese Patent Laid-Open No. 164806/1992
- [2] T. Okabe, K. Saito, and K. Hokkirigawa, *J. Porous Materials*, 2 (1998) 202.
- [3] T. Okabe et al., Report of Industrial Research Ins. of Aomori Pref., (2001) (in Japanese)
- [4] M. Kano, M. Momota, T. Okabe, K. Saito, and R. Yamamoto, *Proc. 5th European Conf. on Advanced Materials, processes and Applications*, Vol.2 (1997) 431.
- [4] T. Ariei and M. Momota, *Materials Integration*, 12(1999) 63 (in Japanese).
- [5] K. Kakei, S. Ozeki, T. Suzuki, and K. Kaneko, *J. Chem. Soc., Faraday Trans. 86* (1990) 371.
- [6] A. Braun, et al., *PSI Scientific Report 1998*, Volume V, (1999), 34.

(Received December 20, 2002; Accepted October 11, 2003)