Thermal decomposition of upgraded product obtained from rice straw by solvent treatment

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Abstract:
We have developed a new effective method which realizes both dewatering and upgrading of low carbonaceous materials by treating them in a non-polar solvent at temperatures below 350°C. During this treatment, we obtained the solvent-soluble fraction at room temperature, which we call "Soluble". Because Soluble has unique properties, it has a possibility to utilize it as raw materials for carbon materials, such as carbon fiber and binder for coke making. Since the initial step of the preparation of such carbon materials is thermal decomposition, it is essential to understand how the properties of Soluble change when Soluble is pyrolyzed. In this study, the thermal decomposition behavior of Soluble at around 350°C was examined either in an inert gas or in a solvent.

Keywords: *Low carbonaceous materials; Solvent treatment; Solvent-soluble fraction; Thermal decomposition*

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1. Introduction

We have developed a new effective method which realizes both dewatering and upgrading of low carbonaceous materials including biomass, peat, brown coals, and lignites (Li et al. (2012) and Wannapeera et al. (2012)). This method consists of treating low carbonaceous materials in a non-polar solvent, such as 1-methylnaphthalene, at temperatures below 350°C and separating them into extract, residue, and gaseous product consisting of CO_2 and a little amount of hydrocarbon gases at the treatment temperature. Inherent water and water produced were almost completely removed from the raw materials as liquid without phase change and separated from solvent by decantation at room temperature. The extract is further separated into solvent-soluble fraction, Soluble, and solvent-insoluble fraction, Deposit, at room temperature. The three fractions obtained were almost completely dewatered and had the heating values corresponding to subbituminous or bituminous coal.

The unique properties of Soluble such as rather low molecular weight compound with a peak molecular weight at around 300 and melting point of as low as 100°C, are almost completely independent of raw materials. Therefore Soluble has possibility to be utilized as raw materials for value added carbon materials, such as carbon fiber and binder for coke making. Since the initial step of the preparation of such carbon materials is thermal decomposition, it is essential to understand how the property of Soluble changes when it is pyrolyzed. In this study, the thermal decomposition behavior of Soluble at around 350°C was examined either in an inert gas or in a solvent.

2. Material and methods

2.1 Preparation of Soluble

A Japanese rice straw (RS) was used as a raw material in this study. A stainless steel autoclave (55 mm I. D., 350 cm^3 in inner volume) was charged with about 15 g of as-received RS and 200 cm^3 of 1-methylnaphthalene (1-MN). A stainless filter (65 mm O. D., 0.5 μm opening) was equipped at the bottom of the autoclave. After sufficiently purging the autoclave with nitrogen, the sample in the autoclave was heated up to 350°C at which it was kept for 1 h under sufficient agitation. Then the sample was separated into the extract and the residue (Residue) at 350°C by opening the valve

Table 1 The properties of raw rice straw and its Soluble

	Elemental composition[wt% d a f]				Ash	Carbon yield
	C	H	N	O(diff)	[wt% d b]	[wt% d a f]
Rice straw	45.7	5.9	0.9	47.5	19.1	—
RS Soluble	86.6	6.9	0.8	5.7	1.9	56.2

connecting the autoclave and reservoir. The extract recovered at the reservoir was further separated into the solvent-soluble fraction at room temperature (Soluble) and the precipitated fraction at room temperature (Deposit) by filtration. Soluble was recovered as solid by removing the solvent using a rotary evaporator and dried in a vacuum oven at 150°C for 5 h. The properties of RS and RS Soluble were listed in Table1.

2. 2. Thermal decomposition of Soluble

Fig. 1 shows the schematic diagram of experimental apparatus. Thermal decomposition in a N_2 atmosphere and in a solvent (1-MN) was performed by using a batch tubular autoclave made of 3/4 inch of stainless tube (ca. 15 cm^3 in inner volume). For decomposition experiment in N_2 atmosphere, about 5 g of Soluble was charged into the tubular autoclave. For the decomposition experiment in 1-MN, about 8 mL of Soluble-1-MN mixture with either 20 wt% or 36 wt% of Soluble concentration was charged into the autoclave. After sufficiently purging the apparatus with nitrogen, the sample in the tubular autoclave was heated up to either 350 or 400°C at the rate of 10°C/min. The holding time was ranged from 0 to 5 h. After cooled to room temperature, gaseous product was collected in a gas bag and CO, CO_2, and CH_4 gases were quantified by using a micro gas chromatograph (Agilent Technologies, 490 Micro GC). The solid product obtained in 1-MN was separated into solvent-soluble fraction and solvent-insoluble fraction at room temperature by filtration. Thermal decomposition behavior, thermoplastic behavior, and elemental composition of the solid product were measured by using a thermobalance (Shimadzu, TGA-50), a thermomechanical analyzer (Shimadzu, TMA-60), and a CHN corder (J-Science Lab, JM 10) respectively.

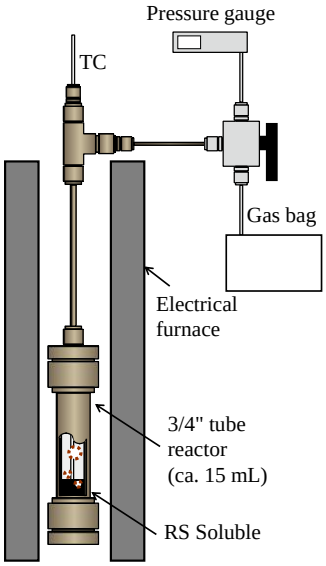

Fig. 1 Schematic diagram of the tubular autoclave

3. Results and Discussion

Table 2 shows the yields of the solid product and gaseous product. “Others” in Table 2 includes water, tar, and gaseous product except for CH_4, CO, and CO_2. CO and CO_2 were formed by the decomposition of oxygen-containing functional groups and CH_4 was judged to be formed by the decomposition of methyl groups in Soluble. The yield of gaseous product obtained by the decomposition experiment

Table 2 The yields of solid product, gaseous products, and others

Treatment condition		Product yield [kg/100 kg of Soluble]						
		Solid	soluble	insoluble	CO	CO_2	CH_4	Others (diff.)
In N_2	350 °C, 0 h	99.3	–	–	0.02	0.10	0.01	0.58
	350 °C, 0.5 h	95.5	–	–	0.13	0.38	0.13	3.85
	350 °C, 1 h	97.3	–	–	0.12	0.34	0.14	2.11
	350 °C, 5 h	94.0	–	–	0.15	0.68	0.17	4.99
	400 °C, 0 h	94.6	–	–	0.21	0.58	0.28	4.34
	400 °C, 0.5 h	91.2	–	–	0.08	0.23	0.13	8.36
	400 °C, 1 h	89.6	–	–	0.12	0.44	0.25	9.54
In 1-MN	350 °C, 1 h , 20 wt%	97.8	86.7	11.1	0.10	0.10	0.07	1.81
	350 °C, 1 h , 36 wt%	94.2	78.6	15.6	0.11	0.14	0.08	5.48

Table 3 Elemental compositions of the solid products

Treatment condition			Elemental composition[wt% d a f] C	H	N	O(diff)
In N_2	RS Soluble		82.3	7.0	1.6	9.1
	350 °C, 0 h		83.4	7.0	1.6	8.0
	350 °C, 0.5 h		84.7	6.8	1.7	6.9
	350 °C, 1 h		85.6	6.6	1.6	6.2
	350 °C, 5 h		–	–	–	–
	400 °C, 0 h		84.4	6.9	1.7	7.1
	400 °C, 0.5 h		86.3	6.4	1.8	5.6
	400 °C, 1 h		86.4	6.3	1.7	5.6
In 1-MN	350 °C, 1 h, 20 wt%	insoluble	85.4	5.5	2.1	7.1
		soluble	84.0	6.8	1.6	7.6
	350 °C, 1 h, 36 wt%	insoluble	–	–	–	–
		soluble	–	–	–	–

in 1-MN was slightly smaller than that obtained by the decomposition experiment in N_2 and decreased with the decrease of Soluble concentration. This is because the intermolecular reaction among Soluble molecules was suppressed when Soluble was dispersed in the solvent. The concentration of the soluble fraction at room temperature was estimated respectively to be 17.9 wt% and 28.2 wt% for the experiments with 20 wt% and 36 wt% of initial Soluble concentrations. The concentrations were much higher than the saturated concentration of Soluble of 11.2 wt% which was obtained by a preliminary experiment. This result suggests that the solubility of Soluble can be increased by treating Soluble in 1-MN at 350°C.

The elemental compositions of the solid products obtained were shown in Table 3. The carbon content of the solid product increased, while the hydrogen and oxygen contents of the solid product decreased with the increase of treatment severity. The hydrogen and oxygen contents of the solvent-insoluble fraction obtained by the thermal decomposition in 1-MN were smaller than those in Soluble and in the solvent-soluble fraction.

Figs. 2 and 3 respectively show the thermal decomposition behavior and the thermoplastic behavior of the solid products obtained by the thermal decomposition of Soluble in N_2. Fig. 2 shows that the weight decrease of the solid product started from 100°C and the amount of volatile matter decreased compared with Soluble, suggesting that the molecular weight distribution of the solid product was wider than that of Soluble. Fig. 3 clearly shows that the melting point of treated Soluble was

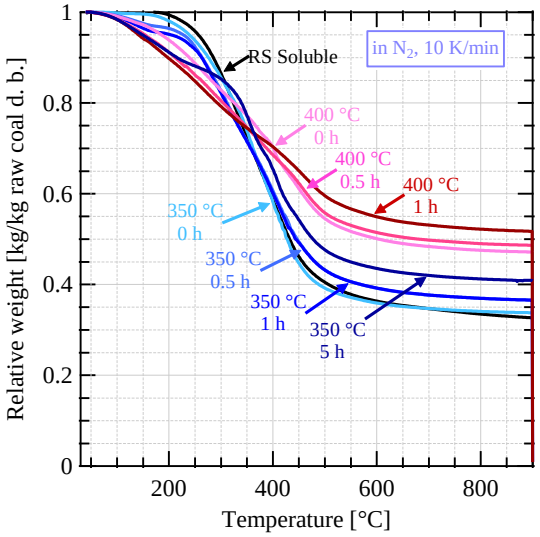

Fig. 2 Thermal decomposition of the solid product obtained by the decomposition experiment in N_2

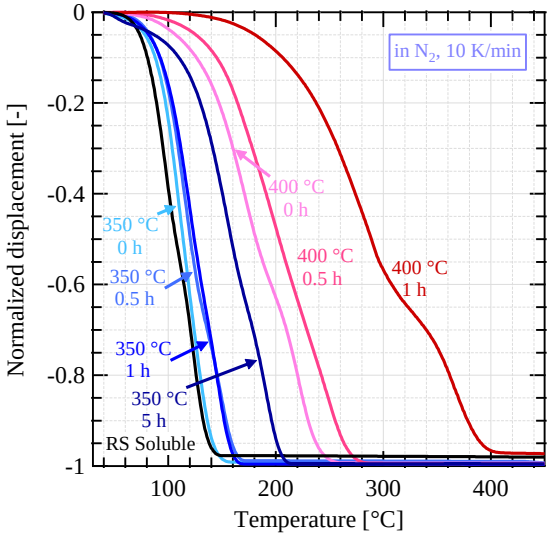

Fig. 3 Thermoplastic behavior of the solid product obtained by the decomposition experiment in N_2

increased with the treatment severity. For using Soluble as a raw material for carbon fiber, it is required to increase the melting point. Then decomposition in N_2 can be the candidate for the pretreatment of Soluble for carbon fiber making.

Figs. 4 and 5 respectively show the thermal decomposition behavior and thermoplastic behavior of the solid products obtained by the thermal decomposition in 1-MN. The thermal behavior of the solvent-soluble fraction was almost completely independent of the initial Soluble concentration. The solvent-soluble fraction started to melt below 40°C, suggesting that the solvent-soluble fraction was richer in small molecular weight compound than Soluble. This may be the reason the solvent-soluble fraction has higher solubility to 1-MN as stated above. On the other hand, the thermal behavior of the solvent-insoluble fraction was significantly different from Soluble. It started to decompose from 200°C at which the displacement in the TMA experiment started. This result indicates that the solvent-insoluble fraction does not show thermoplasticity.

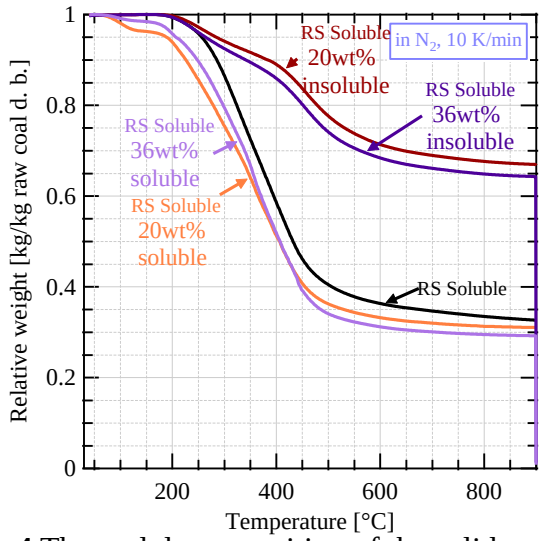

Fig. 4 Thermal decomposition of the solid product obtained by the decomposition experiment in 1-

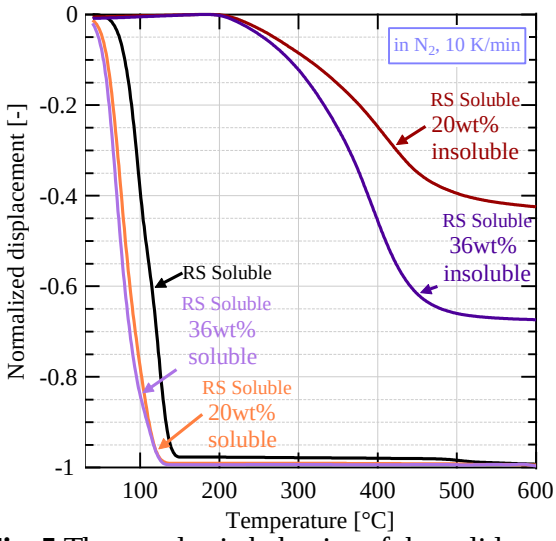

Fig. 5 Thermoplastic behavior of the solid product obtained by the thermal decomposition in 1-MN

4. Conclusion

To examine the possibility of utilizing Soluble as a raw material for noble materials, the thermal decomposition behavior of Soluble at around 350°C was examined either in an inert gas or in a solvent. It was found that the decomposition of oxygen-containing functional groups and polymerization of Soluble accompanied by the decomposition of methyl group occurred even at 350°C. The solid product obtained by the thermal decomposition in N_2 had higher melting point. The solvent-soluble fraction obtained by the thermal decomposition in 1-MN had higher solubility to 1-MN and lower melting point than Soluble. On the other hand, the solvent-insoluble fraction did not show thermoplastic behavior.

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