Development of efficient separation method of extract and solvent in degradative solvent extraction of low-rank coals or biomass wastes

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Abstract:
The authors have recently proposed a novel method that not only dewaters but upgrades low-grade carbonaceous resources such as biomass, peat, lignite, and sub-bituminous coals. The method comprises a treatment of the raw materials in non-polar solvent, such as 1-methylnaphthalene, at temperatures below 350°C, and subsequent separation of the upgraded samples into extract, residue, and gaseous product consisting of CO_2 and a negligible amount of hydrocarbon gases at the treatment temperature. The extract is further separated into solvent-soluble fraction, Soluble, and solvent-insoluble fraction, Deposit, at room temperature. The method can produce a large amount of Soluble which consists of ashless, carbon-rich, low-molecular-weight compounds. From the viewpoint of practical application of the proposed method, it is desired to reduce the energy required to separate the Soluble from solvent. In this study a treatment using the solvent saturated with the Soluble has successfully been proposed in order to omit the energy-consuming distillation process of the solvent by enabling solid-liquid separation of the Soluble and solvent.

Keywords: *Degradative solvent extraction; dewatering; upgrading; low-rank coals; biomass wastes; separation of extract and solvent*

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1. Introduction

It is beyond question that coal is a valuable resource expected as not only fuels but also chemical feedstocks in this century. On the other hand, the minable reserves of high grade coal, bituminous coal, have been depleting very rapidly due to rapid increase of worldwide coal consumption. This inevitably requests to utilize low-rank coal, brown coal/lignite and sub-bituminous coal, instead of high grade coal, because the minable reserve of the low-rank coal is as large as that of high grade coal. Peat and biomass waste are also low-grade but valuable carbonaceous resources that must be utilized effectively.

However, the low grade carbonaceous resources contain a large amount of water (~60%) in general, resulting in low calorific value. This means that dewatering/drying is essential when these resources are transported and stored to be utilized. Dewatered low grade carbonaceous resources unfortunately tend to have high spontaneous combustion tendency as compared to non-dewatered resources. The high spontaneous combustion tendency is mainly caused by the high content of oxygen-containing functional groups, such as carboxyl, carbonyl and phenol groups. So, it is required to reduce the amount of oxygen functional groups to suppress the spontaneous combustibility. This process is called upgrading. Therefore, both dewatering and upgrading are necessary to utilize these resources more effectively even as just fuels. If we utilize these resources as feedstocks of chemicals and materials, we might have to develop methods that enable us to effectively recover precursors of chemicals and/or materials from the raw low-grade resources in addition to dewatering and upgrading methods.

The authors have been proposing methods to dewater, and fractionate coal by using the sequential thermal solvent extraction (Miura et al., 1998, 2001, 2002, 2004). They have recently showed that the degradative extraction at around 350°C using a non-polar solvent such as 1-methylnaphthalene (1-MN) is effective in recovering several fractions having similar chemical and physical properties from various low-rank coals and biomass wastes (Ashida et al., 2009; Wannapeera et al., 2012; Li et al., 2012). The method comprises a treatment of the raw materials in non-polar solvent, such as 1-methylnaphthalene, at temperatures below 350°C, and subsequent separation of the upgraded samples into extract, residue, and gaseous product consisting of CO_2 and a negligible amount of hydrocarbon gases at the treatment temperature. The extract is further separated into solvent-soluble fraction, Soluble, and solvent-insoluble fraction, Deposit, at room temperature. The method can produce a large amount of Soluble which consists of ashless, carbon-rich, low-molecular-weight compounds. In an experimental scale, the Soluble is separated from solvent by distillation of the solvent as shown in Fig. 1. From the viewpoint of practical application of the proposed method, however, it is desired to reduce the energy required to separate the Soluble from solvent. In this study a treatment using the solvent saturated with the Soluble has been proposed as shown schematically in Fig. 2. The proposed separation method can omit the energy-consuming distillation process of the solvent by enabling solid-liquid separation of the Soluble and solvent. In order to examine the validity of the separation method, the solvent treatment using 1-MN saturated with Soluble was performed to confirm whether or not newly-formed “Soluble” can be recovered as “Deposit”. It was also investigated whether it is possible to utilize 1-MN and Soluble repeatedly.

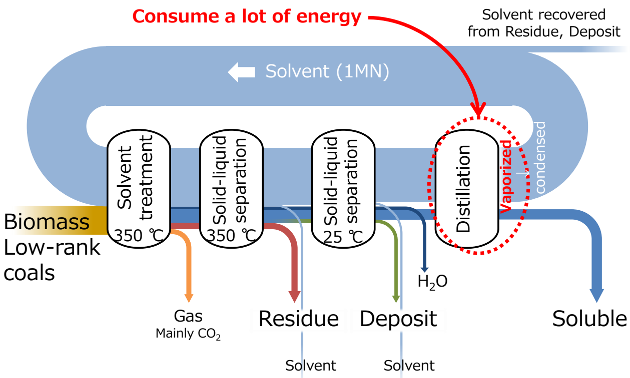

Fig. 1 Flow diagram utilizing distillation for separating solvent and extract.

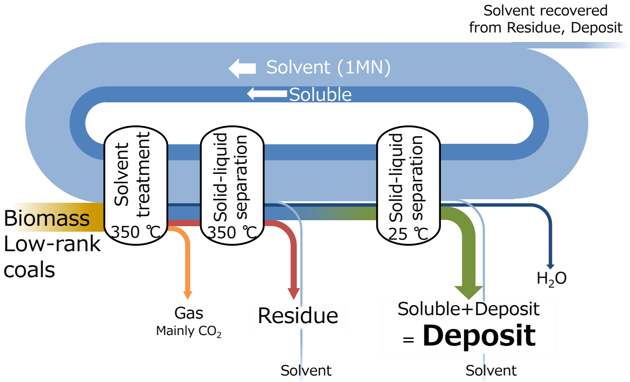

Fig. 2 Flow diagram of the proposed separation method of solvent and extract.

2. Material and methods

A Japanese rice straw was used in this study. The property of the rice straw is given in Table 1. 1-methylnaphthalene (1-MN) was used as non-hydrogen donor solvent.

Table 1 Property of rice straw used

	Elemental Composition [wt%, d.a.f.]				**Ash**	**Moisture**
	C	H	N	O	[wt%, d.b.]	[wt%, d.a.f.]
Rice straw	45.6	5.8	0.7	47.9	11.8	5.3

Since the treatment at around 350°C was found to be effective to upgrade various low rank coals in the previous works (Ashida et al., 2009; Wannapeera et al., 2012; Li et al., 2012), the degradative extraction of the sample was performed using a stainless steel autoclave (350 cm^3, 55 mm I.D.) at 350°C. The autoclave was charged with 25 g-daf of rice straw and 300 cm^3 of either 1-MN saturated with Soluble (prepared from the same rice straw using 1-MN in advance) or 1-MN. A stainless filter (65 mm O.D. and 0.5 µm opening) was equipped at the bottom of the autoclave. After sufficiently purging the autoclave with N_2, the autoclave was heated up to 350°C, where it was kept for 60 min. The extract and the residue (Residue) were separated by opening the valve connected below the filter at the extraction temperature. The extract with the solvent was collected in a stainless steel vessel equipped under the valve which was cooled by water. The solvent containing the extract was filtrated using a PTFE membrane filter (0.5 µm opening) to separate the extract into the extract that precipitates at room temperature (Deposit) and the extract soluble in solvent even at room temperature. The latter fraction was treated by a rotary evaporator at around 140°C under reduced pressure to remove 1-MN and to recover the extract in this fraction as solid. The extract recovered as solid was called "Soluble" and that evaporated with 1-MN was called "Liquid". The yields of Residue, Deposit, and Soluble were determined by weight, and the Liquid yield was estimated by difference.

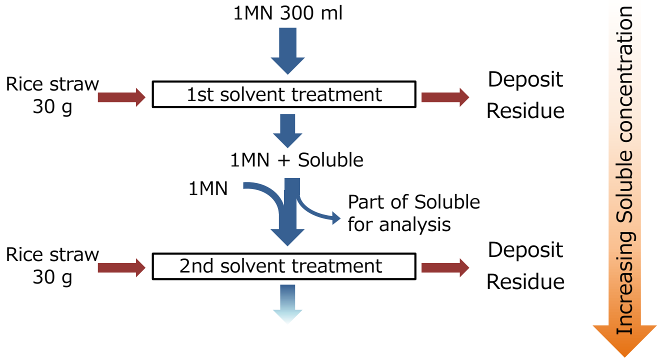

Fig. 3 Scheme of experiments for repeated use of 1-MN and Soluble.

In order to investigate whether 1-MN and Soluble can be utilized repeatedly, after the above-mentioned upgrading experiment using 1-MN, only Residue and Deposit were collected and solvent containing Soluble was used to upgrade 25 g-daf of fresh rice straw, as shown in Fig. 3. This operation was repeated 7 times.

3. Results and discussion

First, it was confirmed that 1-MN can actually be saturated with Soluble prepared from the same rice straw using 1-MN in advance and the solubility of the Soluble in 1-MN was found to be ~ 13 kg-Soluble/100 kg 1-MN. Fig. 4 compares the product yields obtained using Soluble-saturated 1-MN with those obtained using 1-MN. Deposit yield increased greatly from 3.1%-daf to 20.1%-daf by using Soluble-saturated 1-MN instead of 1-MN while Soluble yield decreased. This result indicates the validity of the proposed separation method.

The upper panel in Fig. 5 shows the yields of the products obtained when upgrading fresh rice straw using 1-MN containing Soluble repeatedly as shown in Fig. 3. The yield of newly-formed Soluble was estimated by the balance of the Soluble through each experiment. The lower panel in Fig. 5 shows Soluble concentrations in 1-MN for each experimental cycle. Soluble concentration increased with the number of cycle and reached 8.9 kg/100 kg-1-MN after 7th cycle. Yield of each product did not vary with the number of cycle, which suggests that upgrading behavior was not affected by repeated use of 1-MN and Soluble.

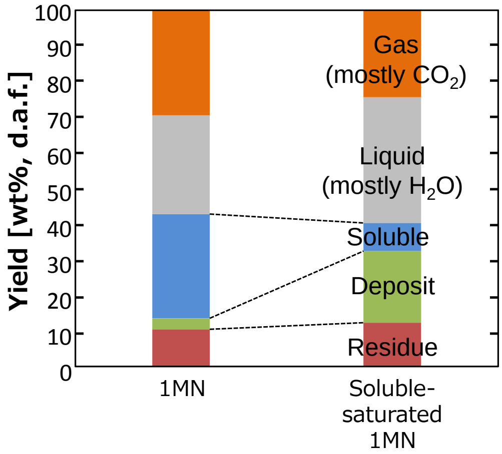

Fig. 4 Comparison of the product yields obtained using Soluble-saturated 1-MN with those obtained using 1-MN.

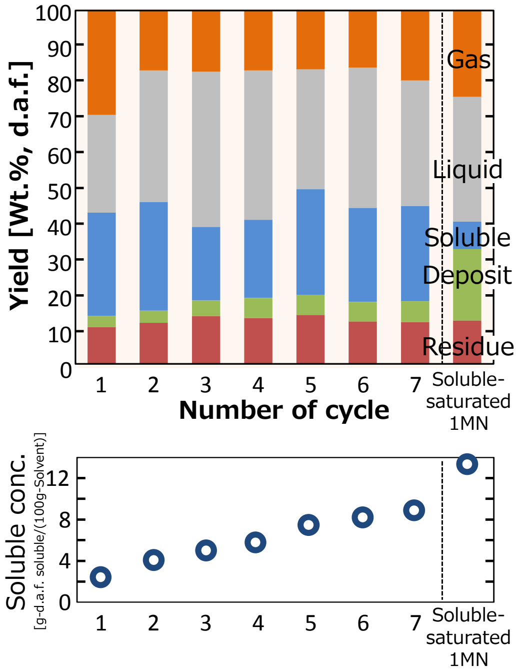

Fig. 5 Yields of the products obtained using 1-MN containing Soluble repeatedly (upper panel) and Soluble concentrations in 1-MN for each experimental cycle (lower panel).

Fig. 6 shows gas chromatogram of the solvent after each cycle of experiment. The main peak seen in Fig. 6 was for 1-MN. Gas chromatogram of 1-MN did not change after repeated use.

Fig. 7 shows the molecular weight distribution of Soluble obtained after each cycle of experiment. The molecular weight distribution of Soluble which has a peak at around 300 in molecular weight did not significantly change with the number of cycle. Fig. 8 compares themomechanical analysis curves of the Solubles obtained after each cycle of experiment. The themomechanical analysis curves were similar to each other. All the Solubles started to melt at less than 100°C. These results show that properties of Soluble did not change after repeated use.

Thus, the possibility to be able to use 1-MN and Soluble repeatedly was suggested.

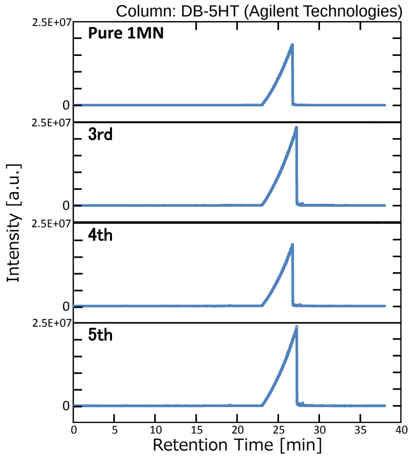

Fig. 6 Gas chromatogram of the solvent after each cycle of experiment.

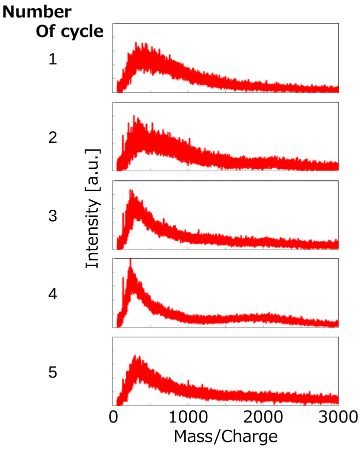

Fig. 7 Molecular weight distribution of Soluble obtained after each cycle of experiment.

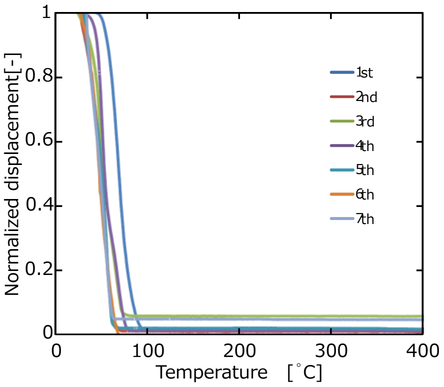

Fig. 8 Comparison of themomechanical analysis curves of the Solubles obtained after each cycle of experiment.

4. Conclusion

We have proposed a new efficient separation method of solvent and extract in our degradative solvent extraction method, in which the newly-formed Soluble can be recovered as solid (Deposit) and solvent can be recovered without distillation by solvent treatment using solvent saturated with the Soluble. It was shown that Deposit yield increased greatly by using 1-MN solvent saturated with Soluble instead of 1-MN. It was also confirmed that properties of 1-MN solvent and Soluble did not change even after repeated use of them. Thus, the validity of the proposed separation method was suggested.

5. Acknowledgement

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References

Ashida, R., Umemoto, S., Hasegawa, Y., Miura, K., Kato, K., Saito, K., and Nomura, S. 2009. Upgrading of low rank coal through mild solvent treatment at temperatures below 350°C. Proceedings of the 26th Annual International Pittsburgh Coal Conference. Paper No. 5–1.

Li, X., Ashida, R., and Miura, K. 2012. Preparation of high-grade carbonaceous materials having similar chemical and physical properties from various low-rank coals by degradative solvent extraction. Energy Fuels 26: 6897–904.

Miura, K., Shimada, M., and Mae, K. 1998. Extraction of coal at 300 to 350°C to produce precursors for chemicals. Proceedings of the 15th Pittsburgh Coal Conference. Paper No. 30–1.

Miura, K., Shimada, M., Mae, K., and Huan, Y.S. 2001. Extraction of coal below 350°C in flowing non-polar solvent. Fuel 80(11): 1573–1582.

Miura, K., Mae, K., Ashida, R., Tamura, T., and Ihara, T. 2002. Dewatering of coal through solvent extraction. Fuel 81(11–12): 1417–1422.

Miura, K., Nakagawa, H., Ashida, R., and Ihara, T. 2004. Production of clean fuels by solvent skimming of coal at around 350°C. Fuel 83(6): 733–738.

Wannapeera, J., Li, X., Worasuwannarak, N., Ashida, R., and Miura, K. 2012. Production of high-grade carbonaceous materials and fuel having similar chemical and physical properties from various types of biomass by degradative solvent extraction. Energy Fuels 26: 4521–31.