# PRODUCTION OF SOLID FUEL WITH HIGH CALORIFIC VALUE FROM LOW-RANK COAL AND WOODY BIOMASS BY DEGRADATIVE SOLVENT EXTRACTION USING DEEP EUTECTIC SOLVENT

## 深共晶溶媒を用いた分解を伴う溶媒抽出による低品位炭と木質バイオマスからの高発熱量固体燃料の製造

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# Contents

**Chapter 1 Introduction**

**1.1 Importance of low-rank coal and woody biomass utilization**

Coal has been used as fuel for heat and power generation in power plants and other manufacturing industries. Coal consumption is gradually decreased, but still accounted for approximately 27% of the total energy consumption in 2020 as shown in Fig. 1.1 [1,2] because of its abundant reserves and low cost [3].

Coal can be divided into high-rank coal and low-rank coal. High-rank coal is the main raw material for power generation and iron making. This is because high-rank coal has a high heating value, high carbon content, low moisture content, low ash content, and high caking property. However, the amount of available high-rank coal is declining; we will have to resort to utilize low-rank coal and biomass in the future (see Fig. 1.2) [2,4,5].

Low-rank coal, however, has several disadvantages as compared with high-rank coal including a low heating value, low carbon content, high moisture content, and high ash content that contributes to environmental pollution [3, 6,7]. This is a reason why is difficult to use the low-rank coal. It is therefore essential to develop technologies for dewatering and/or upgrading low-rank coal for the effective utilization.

Biomass is also attractive as a fuel source. Biomass contains large amount of water with a correspondingly high oxygen content and low carbon content. The utilization of biomass as fuels has several drawbacks such as low calorific value, high oxygen content, high tendency of spontaneous combustion, inconvenience of storage, and difficulty in application to conventional processes in terms of burning, fermentation, and energy conversion [8,9]. The drawbacks that biomass has typically are similar to those low-rank coal has. Accordingly, the technologies developed for the effective utilization of low-rank coal are believed to be applied with the same effect to the effective utilization of biomass.
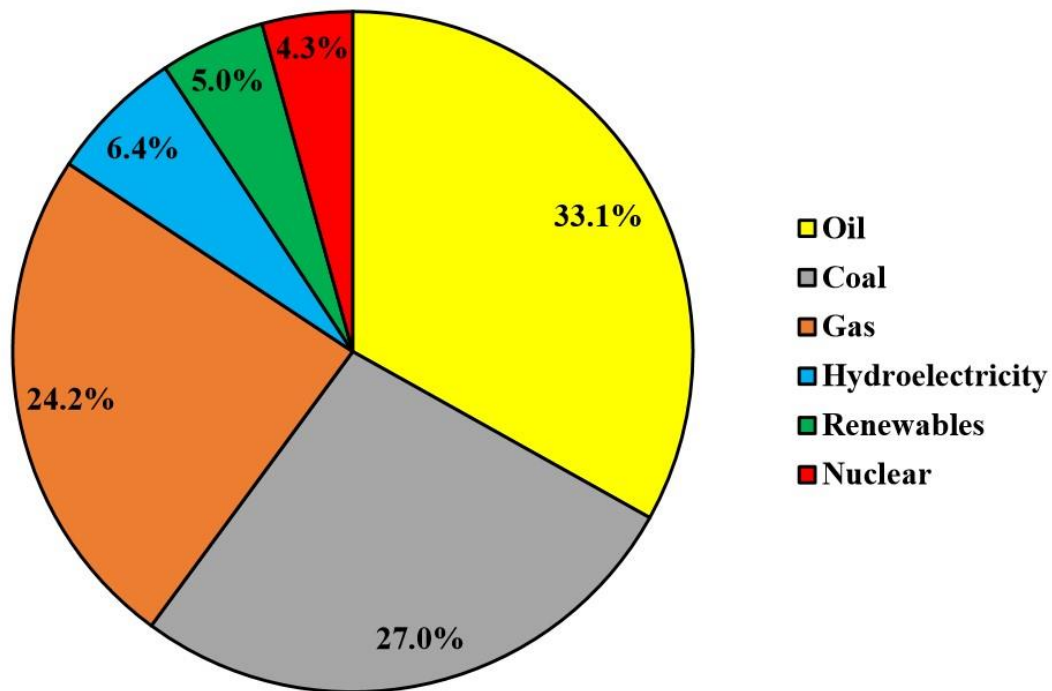
Fig. 1.1 Fuel shares of primary energy [2].
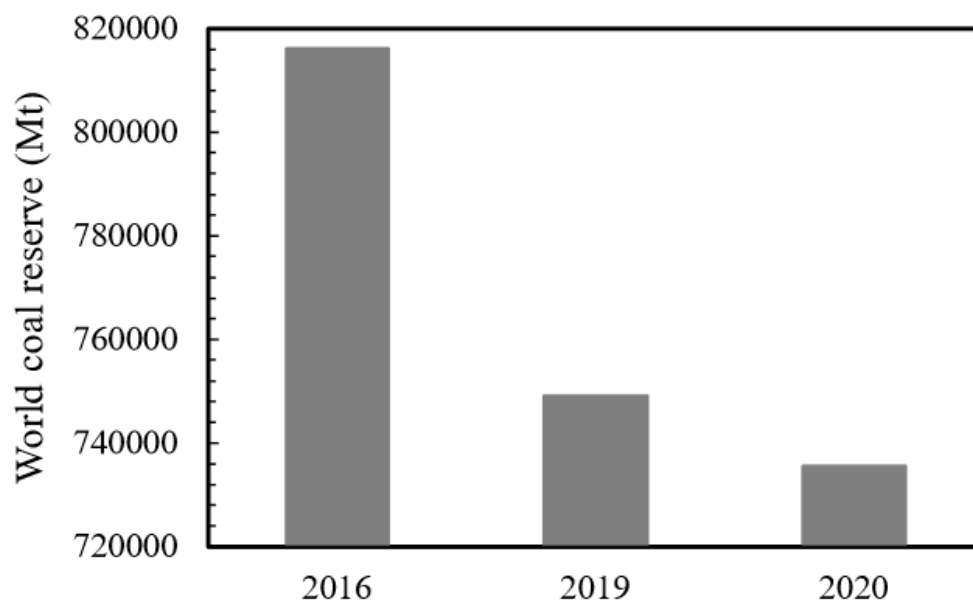


Fig. 1.2 Total proved reserves of high-rank coal at end-2016 [4] end-2019 [2], and at end-2020 [5] in Million tonnes (Mt).

## 1.2 Effective utilization of low-rank coal and biomass

Coal is an important conventional fossil fuel. The common usage of coal is mainly through direct combustion for electricity generation, or as a feedstock to produce coke.

The minable reserve of high-rank coal has been depleting very rapidly due to the rapid

increase of worldwide coal consumption. This inevitably requests us to utilize low-rank coal instead of the high-rank coal, because the reserve of the low-rank coal is abundant. The low-rank coals are currently used just for power generation near coal mines because they have several drawbacks to be overcome for effective utilization. As described above, low-rank coal contains a large amount of water and oxygen functional groups, resulting in low calorific value. When dewatered and/or dried, their propensity to spontaneous heating largely increases, which makes their storage and transportation extremely difficult. It is therefore essential to develop technologies for dewatering and/or upgrading low-rank coal for their effective utilization [10].

Upgrading of low-rank coals in order to reduce the moisture and volatile matter contents is of significant interest in coal research, since this can prevent self-heating and spontaneous combustion during transportation and storage. Various dewatering and upgrading processes have been developed since the 1920s. Among them were the superheated and pressurized steam drying, hot and supercritical water drying and hydrothermal-mechanical compression drying processes [11]. There are many other studies on the upgrading low-rank coal and biomass. Although pyrolysis and liquefaction are methods that require severe conditions of high temperature and high pressure, the product yield is low and the oxygen content in the product is relatively high. The use of acids or alkalis under hydrothermal conditions was considered in order to dissolve minerals and leave a relatively pure organic matrix to produce ultra-clean coal. This method can reduce ash content to <0.5 wt%, but the oxygen content in the sample after demineralization remains high, with decreased calorific value [12,13]. Hence, we have focused on a degradative solvent extraction method. The degradative solvent extraction is very attractive, because this method is operated under mild conditions and can extract low-molecular-weight compounds with low oxygen content as solid fuel even from low-rank coal and biomass.

Fig. 1.3 shows the difference between degradative solvent extraction and conventional heat-treatment [14]. The conventional heat-treatment, which is a method of heating low-rank coal at a low temperature of around 350 °C in inert gas, produces oxygen-containing low-molecular-weight compounds as well as $CO_2$ and $H_2O$ by cleaving some chemical bonds in the low-rank coal. However, since radicals generated by heating are unstable in inert gas atmosphere, polymerization also occurs at the same time. This is because the low-rank coal consists of many low-molecular-weight molecules connecting by hydrogen bonding. As a result, the yield of low-molecular-weight molecules is very low. On the other hand, the degradative solvent extraction is a method of heating low-rank coal at a low temperature of 350 °C in non-polar solvent such as 1-methylnaphthalene (1-MN). In non-polar solvents,

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because the hydrogen bonding is easily cleaved by heating, it is considered to be difficult to combine low-molecular-weight molecules with each other and to increase the molecular weight. In addition, since the oxygen is desorbed as $H_2O$ and $CO_2$, it is considered that the oxygen does not remain in the components soluble in the solvent. Therefore, the yield of low-molecular-weight compounds, which contain a small amount of oxygen, is expected to be high.

Woody biomass has a structure in which cellulose, hemicellulose, and lignin are intricately entangled by intermolecular forces such as hydrogen bonding. Therefore, the method proposed to upgrade low-rank coal can be also applied to woody biomass.
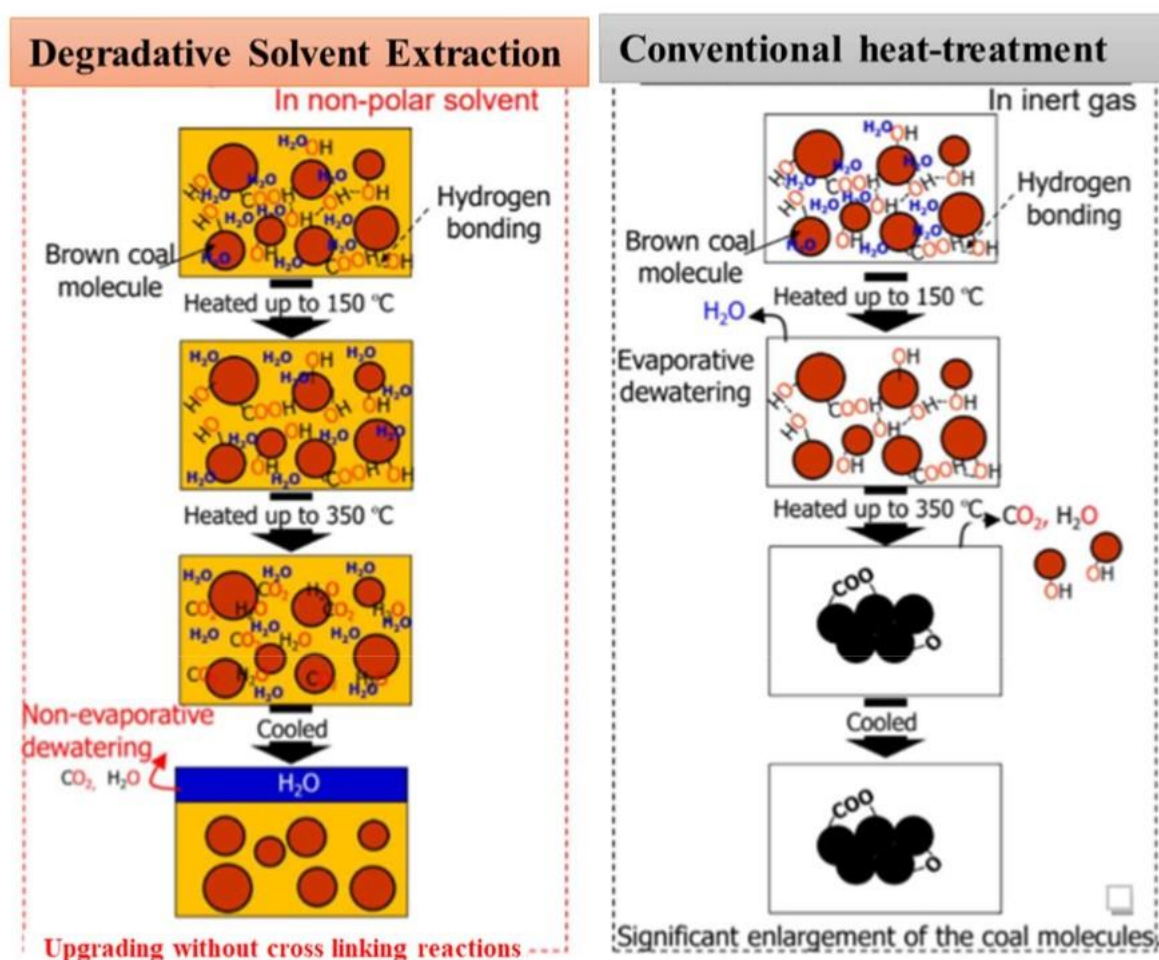


Fig. 1.3 Comparison between degradative solvent extraction process and conventional heat-treatment process [14].

### 1.3 Degradative solvent extraction of low-rank coal and biomass

In degradative solvent extraction, low-rank coal and biomass with a low carbon content are added to non-polar solvents in an autoclave as shown in Fig. 1.4 [9] and pyrolyzed at high

temperatures and pressures. This method can separate coal or biomass into three types of solids: insoluble components (Residue), high-molecular-weight extract (Deposit), and low-molecular-weight extract (Soluble), which is dissolved in the solvent at room temperature. Also, small amounts of gases and liquid products are generated [15]. It has been reported that Soluble contains a considerable amount of carbon [15-19]. Li et al. [16-18] performed a degradative solvent extraction of lignite (C: 63–76 wt%, O: 16–30 wt%) in a nitrogen atmosphere at 350 °C for 60 min using 1-MN as a solvent. This method produces Soluble that has a carbon content of >80 wt% and is almost ash-free, however, its yield is as low as 20-30 wt% and the oxygen content is as high as approximately 10 wt%. Other studies reported that the degradative solvent extraction had disadvantage of low Soluble yield from low-rank coal and biomass at 350 °C using 1-MN as solvent, for example: the yield of Soluble from Pendopo (PD) (low-rank coal) was 23.2 wt% [10] and the yield of Soluble from rice straw (RS) (biomass) was 20.7 wt% [20]. Soluble component can be used as solid fuel for heat and power generation in power plants and other manufacturing industries. Therefore, it is necessary to extract as much amount of Soluble as possible.
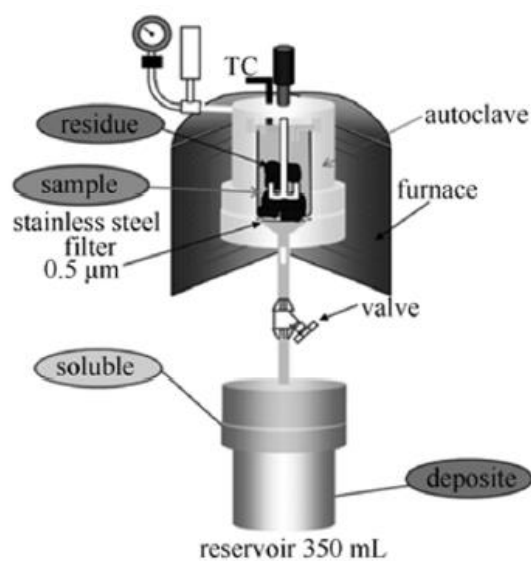


Fig. 1.4 Schematic diagram of degradative solvent extraction equipment (autoclave) [9].

### 1.4 Deep Eutectic Solvent

The inherently high oxygen content lowers the energy density of the low-rank coal and biomass so that deoxygenation is often required when fuels are the target products. The use of deep eutectic solvents (DESs) has attracted significant attention to enhance the Soluble yield and achieve further deoxygenation, because DESs have the role of cleaving the ether moiety in

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low-rank coal and promoting the separation of the oxygen-containing compounds. DESs are liquid eutectic mixtures produced by the simple mixing of two components, hydrogen-bond acceptors (HBAs) and hydrogen-bond donors (HBDs), and heating at low temperature. The freezing or melting points of DESs are significantly lower than those of the individual components. In addition, DESs have advantages such as environmentally acceptable solvents, low cost, low toxicity, biocompatibility, biodegradability, minimum volatility, non-flammability, and suitability for many industrial applications [21-25]. Alhassan et al. [26] prepared a DES by mixing choline chloride (ChCl) as an HBA and iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) as an HBD at a molar ratio of 1:2 and upgraded the biomass (de-oiled *Jatropha curcas* cake) by hydrothermal liquefaction under an initial pressure of 4.5 MPa at 250 °C for 40 min. It is reported that $FeCl_3$ in DES functioned as a Lewis acid and promoted extract aromatization by cleaving the ether bond. Recently, the extraction of phenolic compounds into DES has been performed to separate them from the tar produced by thermal decomposition [27–29]. Jiao et al. [27] reported that phenol was extracted into DES (ChCl: trifluoroacetic acid = molar ratio 1:2) at 30 °C for 60 min, reaching an extraction efficiency of 90 wt%. In addition, oxygen-containing compounds, such as phenol, are separated from aromatic compounds by intermolecular interactions, particularly by forming hydrogen bonds with DES [28]. Previous studies have shown that the physicochemical properties of DESs have a significant influence on the extraction efficiency and higher yields of biomass by decarboxylation reaction [30,31].

In this way, DESs have been applied in different research fields such as electrochemistry, catalytic reactions, materials preparation, molecular purification, chromatographic separation, etc., as well as in the production of environmentally friendly liquid fuels [32,33]. However, there have been no researches using DES for the degradative solvent extraction. Herein, we have performed the degradative solvent extraction of low-rank coal and biomass with DES that is prepared using ChCl and $FeCl_3 \cdot 6H_2O$.

### 1.5 Purpose of doctoral thesis

The objective of this doctoral thesis is to investigate the Soluble yield and the oxygen content in Soluble and to clarify the role of DES on the extraction of Soluble when the degradative solvent extraction of Indonesian Adaro sub-bituminous coal and cedar powder under various conditions are carried out.

This thesis is composed of 5 chapters.

In the chapter 2, the degradative solvent extraction method of Indonesian Adaro sub-

bituminous coal (AC) (150-250 μm) was performed at 200-350 °C for 90 min in 1-MN to obtain a substance dissolved in the solvent at room temperature (Soluble). And, the effect of DESs addition amount and the reaction temperature on the Soluble yield and the oxygen content in Soluble was investigated. The collected gas products were qualitatively and quantitatively analyzed by gas chromatography (GC). The structure of Soluble and Residue was analyzed by infrared spectroscopy (IR), thermogravimetry (TG) and elemental analyses.

In the chapter 3, production of solid fuel with high calorific value from cedar powder (425 – 600 μm) as the feed biomass by degradative solvent extraction at 300-350 °C for 90 min in 1-MN using deep eutectic solvent (DES) was investigated.

In the chapter 4, the effect of DES addition and reaction temperature on degradative solvent extraction of low-rank coal and woody biomass was discussed by comparing with the results of lignin and cellulose. And the role of DES on the degradative solvent extraction of low-rank coal and woody biomass was supposed from these results.

In the chapter 5, the conclusions obtained in this study are summarized. Finally, the necessity of the upgrading of low-rank coal and woody biomass by degradative solvent extraction in Mozambique is described.

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**Chapter 2 Degradative solvent extraction of low-rank coal with deep eutectic solvent and effect of reaction conditions on products**

**2.1 Introduction**

The amount of available low-rank coal such as sub-bituminous coal and lignite are abundant as shown in Fig. 2.1. However, low-rank coal has a low heating value, low carbon content, high moisture content, and high ash content. In the future, it will be necessary to actively use the low-rank coal [1-3].
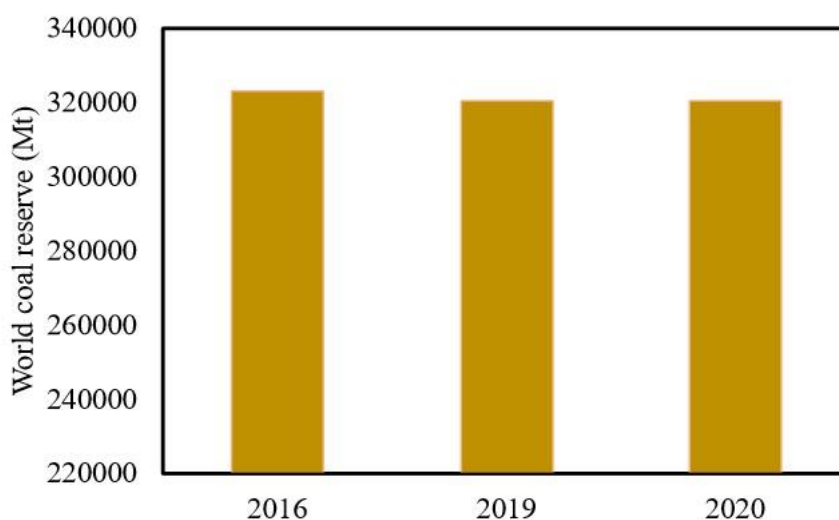


**Fig. 2.1** Total proved reserves of low-rank coal at end-2016 [1], end-2019 [2], and at end-2020 [3] in Million tonnes (Mt).

The typical structure of sub-bituminous coal and lignite (brown coal) is shown in Fig. 2.2 [4,5]. There are a lot of oxygen-containing groups such as phenolic OH, carboxyl, and ether groups in low-rank coal. In order to produce the Soluble component with low oxygen content, the bond involving oxygen must be successfully cleaved. In the previous study, the degradative solvent extraction of low-rank coal such as Loy Yang (LY) and Pendopo (PD) was performed under 0.5 MPa of helium atmosphere at 350 °C for 60 min. Table 2.1 shows the ultimate and proximate analysis of LY and PD as well as Soluble yields [6]. The Soluble obtained from LY and PD has a higher carbon content and a very lower ash content than the original coal.
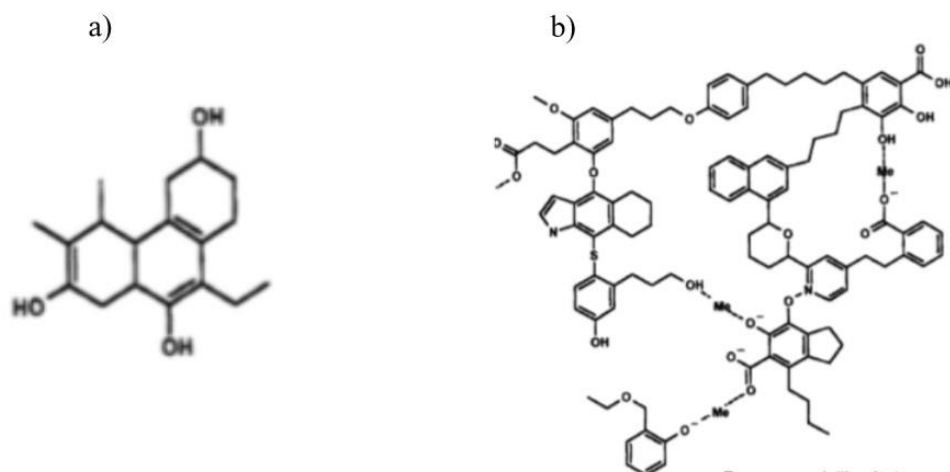
**Fig. 2.2** Typical structure of a) sub-bituminous coal [4] and b) lignite [5].

**Table 2.1** Ultimate and proximate analysis of Loy Yang (LY), Pendopo (PD) and Soluble [6].

| Temperature | Yield | Ultimate analysis wt% (d.a.f) | | | | Proximate analysis wt% (d.b) | | |
|---|---|---|---|---|---|---|---|---|
| (°C) | (wt% d.a.f) | C | H | N | O diff. | V.M. | F.C. | Ash |
| LY | | 66.6 | 4.5 | 0.5 | 28.4 | 50.0 | 47.8 | 2.2 |
| Soluble | 20.0 | 82.2 | 7.7 | 0.5 | 9.6 | 76.3 | 23.7 | 0.1 |
| PD | | 67.5 | 5.1 | 0.8 | 26.6 | 49.4 | 38.0 | 12.6 |
| Soluble | 23.2 | 83.8 | 7.6 | 0.7 | 7.9 | 76.3 | 23.4 | 0.3 |

Previous study on the structure and properties of Soluble obtained from low-rank coal demonstrated that physical and chemical properties of Soluble was almost the same independent of low-rank coal. The elemental composition and heating value of Soluble were very similar to those of bituminous coal [6,7]. From TG, the weight loss of the Soluble was observed to be slightly larger than that of raw low-rank coal, indicating that the Soluble was composed of low-molecular-weight compounds compared with the raw low-rank coal [9]. FT-IR revealed that the absorption peaks referred to oxygen-containing groups in Soluble were smaller than those in raw low-rank coals. Also, the Soluble was relatively richer in aliphatic carbons while the Deposit contained more aromatic structures [7]. The Soluble was composed of low-molecular-weight compounds having a molecular peak at ca. 300 and the volatile compounds in Soluble identified by GC-MS were single and double aromatic ring compound derivatives as well as long-chain aliphatic compounds [8].

From these results, Soluble is a good fuel. However, the yield of Soluble obtained by the degradative solvent extraction of low-rank coal is very low around 20 wt%.

Since the long-chain aliphatic or aromatic compounds are easily extracted by 1-MN, so the

compounds with such a structure must be formed from Residue during degradative solvent extraction to increase Soluble yield. Table 2.2 shows the ultimate and proximate analysis of LY and PD as well as Residue yields [6]. The Residue from LY and PD has a lot of carbon, and the Residue yields are as high as 54-64 wt%. Therefore, it is important to convert as much Residue as possible to Soluble. For this reason, as already described in Chapter 1, the oxygen-containing bonds in low-rank coal must be broken.

**Table 2.2** Ultimate and proximate analysis of Loy Yang (LY), Pendopo (PD) and Residue [6].

| Temperature | Yield | Ultimate analysis wt% (d.a.f) | | | | Proximate analysis wt% (d.b) | | |
|---|---|---|---|---|---|---|---|---|
| (°C) | (wt% d.a.f) | C | H | N | O diff. | V.M. | F.C. | Ash |
| LY | | 66.6 | 4.5 | 0.5 | 28.4 | 50.0 | 47.8 | 2.2 |
| Residue | 63.9 | 77.1 | 4.2 | 0.8 | 18.0 | 35.1 | 59.6 | 5.3 |
| PD | | 67.5 | 5.1 | 0.8 | 26.6 | 49.4 | 38.0 | 12.6 |
| Residue | 54.3 | 76.5 | 4.5 | 1.2 | 17.7 | 40.1 | 42.4 | 17.4 |

The purpose of this chapter is to investigate the effect of DES on the yield and composition of Soluble and Residue obtained from the degradative solvent extraction of low-rank coal performed under various conditions such as the addition amount of DES and the reaction temperature.

## 2.2 Experimental

### 2.2.1 DES preparation

The deep eutectic solvent (DES) is composed of hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD). A total of 10 g of a mixture of choline chloride (ChCl) as HBA and iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) as HBD in a molar ratio of 1:2 was added to a 100 mL beaker. The beaker was placed in a hot water bath at 80 °C, and the mixture was stirred at 500 rpm under a nitrogen atmosphere for 60 min. Finally, the mixture was cooled to room temperature to obtain DES. The moisture content of the DES was measured using a Karl Fischer moisture meter (KEM. Co., Ltd., MKA- 610). The moisture content in prepared DES was 9–11 wt%. Herein, ChCl and $FeCl_3 \cdot 6H_2O$ used for the preparation of DES, were purchased from Nacalai Tesque Inc. and FUJIFILM Wako Pure Chemical Corporation, respectively.

### 2.2.2 Low-rank coal sample

Indonesian Adaro sub-bituminous coal (AC) was used as the low-rank coal sample. Table

2.3 shows the proximate and ultimate analysis of the AC. The AC was ground using a mortar, classified into 150–250 μm particles, and used for the reaction after drying at 110 ºC for 24 h.

**Table 2.3** Ultimate and proximate analysis of Adaro coal.

| Sample | Ultimate analysis wt% (d.a.f) | | | | HHV [MJ/kg] | Proximate analysis wt% (d.b) | | |
|---|---|---|---|---|---|---|---|---|
| | C | H | N | O diff. | | V.M. | F.C. | Ash |
| Adaro coal | 67.5 | 5.4 | 0.9 | 26.1 | 25.9 | 46.7 | 50.8 | 2.5 |

### 2.2.3 Degradative solvent extraction of Adaro Coal

As a non-polar solvent, 1-methylnaphthalene (1-MN) was purchased from Tokyo Chemical Industry Co., Ltd. Fig. 2.3 shows a schematic of the degradative solvent-extraction apparatus. First, 5 g of AC, 100 mL of 1-MN, and 0.5–2.0 g of DES were added in custom autoclave (Nitto Koatsu, START200 high temperature New Quick). The autoclave was purged with nitrogen gas to remove air and the initial pressure was adjusted to 0.2 MPa. The reaction temperature was raised to 200–350 ºC over 80 min, and the reaction was performed for 90 min with agitation at 300 rpm.
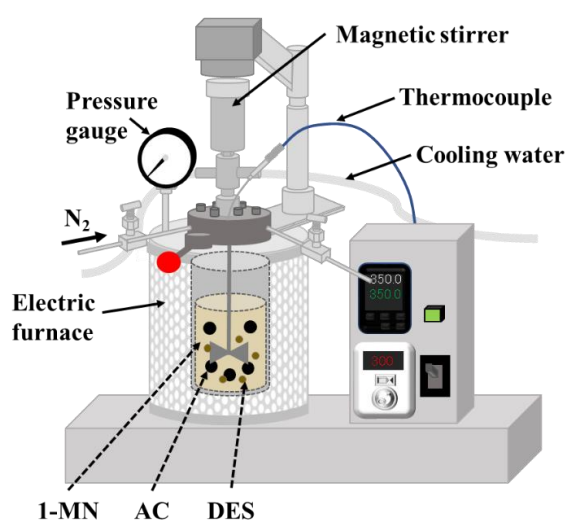


**Fig. 2.3** Schematic diagram of the experimental apparatus for degradative solvent extraction.

### 2.2.4 Method for separating extract

After the reaction, the reactor was cooled to room temperature, the produced gas in autoclave was recovered in the gas bag and measured by gas chromatograph (GC; Shimadzu, GC-2014). Also, the mixture in the autoclave was suction-filtered, washed with 1-MN (30–50 mL), and separated into insoluble substances in 1-MN and the filtrate. The insoluble substance

was collected as Residue after vacuum drying at 150 ℃ for 12 h. Additionally, the 1-MN solvent was separated from the filtrate at 140 ℃ for 60 min, 150 ℃ for 30 min by evaporation, and at 150 ℃ for 24 h by vacuum drying, and the remaining solid was recovered as Soluble. Herein, Deposit was collected as part of the Residue because the mixture in the autoclave was removed after cooling. Fig. 2.4 shows a flowchart of the method for separating the products (Gas, Soluble, and Residue) and 1-MN.
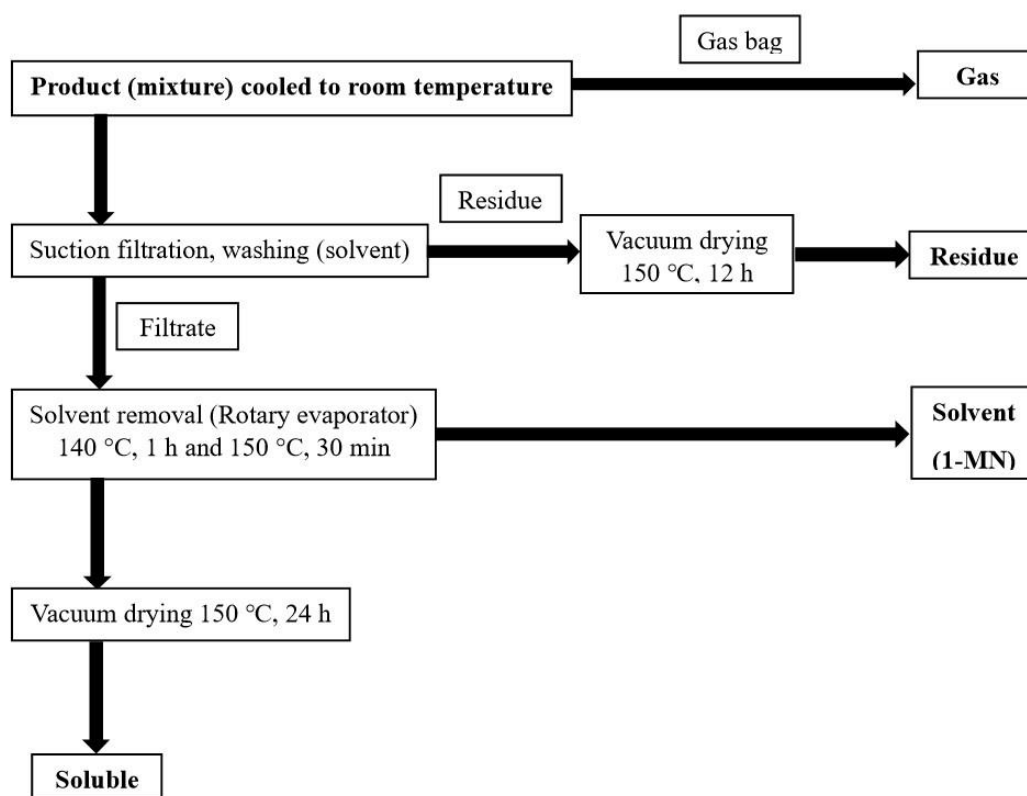


**Fig. 2.4** Scheme of solvent extraction and product separation procedure.

### 2.2.5 Product characterization

The mass fractions of carbon, hydrogen, and nitrogen in Soluble and Residue were measured using CHN analysis (LECO, CHN628). The higher heating value (HHV) of each sample was calculated using Dulong equation (Eq. 2.1) [9,10]:

$$\text{HHV [MJ/kg]} = (338.1m_C + 1441.8m_H - 180.2m_O)/1000 \tag{2.1}$$

where $m_C$, $m_H$, and $m_O$ are the mass fractions of carbon, hydrogen, and oxygen, respectively. The thermal decomposition behavior of AC and its products were analyzed using a thermogravimetric analyzer (TGA; Shimadzu, TG-50). The sample was heated to 900 ℃ at 10

ºC /min under 35 mL/min of nitrogen flow. The chemical structures of product were analyzed using a Fourier transform infrared spectrometer (FTIR; Shimadzu, IRAffinity-1). The sample pellets were prepared by molding a mixture of potassium bromide (99.5 mg) and the sample (0.5 mg) using a hydraulic press. Spectra for each sample were measured in absorption mode at 1800-600 cm$^{-1}$ and 3800-2600 cm$^{-1}$ using 64 scans with a 2 cm$^{-1}$ resolution.

## 2.3 Results and discussion

### 2.3.1 Whereabouts of DES after the degradative solvent extraction

In order to calculate the yield, it is necessary to ensure that the extracts (Soluble and Residue) contain DES. Thus, an iron elution test by the addition of hydrochlor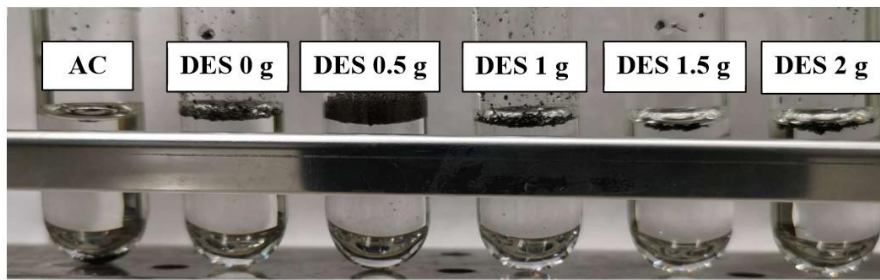ic acid to the extracts was performed to investigate the presence of DES in Soluble and Residue. Fig. 2.5 shows a mixture of 2.5 mL of 6 M hydrochloric acid and 10 mg of Soluble or Residue. The supernatant solution containing Soluble was barely colored, whereas that containing the Residue changed from colorless to yellow. And the yellow color darkened with increasing DES contents. Table 2.4 shows the yield and the ultimate analysis of Residue obtained by the degradative solvent extraction of AC. Furthermore, the ultimate analysis revealed that the nitrogen content of Residue obtained at 200–350 ºC increased with the increasing amounts of DES (Table 2.4). This nitrogen increase was caused by the nitrogen contained in ChCl used for the preparation of DES. These results indicates that most of the added DES remained in Residue.
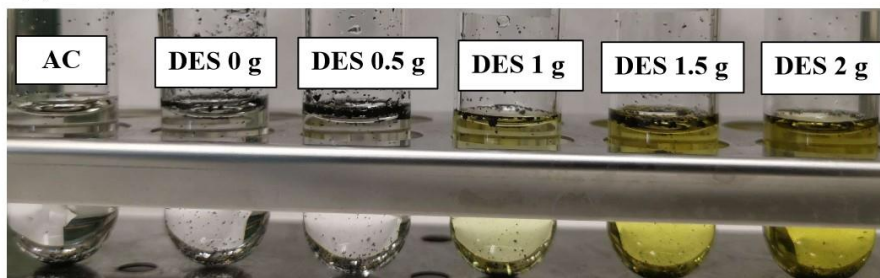
**Fig. 2.5** The images of the hydrochloric acid treatment of AC: (a) Soluble and (b) Residue obtained at 350 ℃ for 90 min (10 mg of sample was added into 2.5 mL of 6 M hydrochloric acid).

**Table 2.4** Yield and ultimate analysis of Residue obtained by the degradative solvent extraction of AC.

| Temperature (°C) | Time (min) | DES (g) | Yield (wt%) | Ultimate Analysis (wt%, d.b.) | | | |
|---|---|---|---|---|---|---|---|
| | | | | C | H | N | Other (diff.)* |
| 200 | 90 | 0.0 | 98.9 | 70.8 | 4.8 | 0.9 | 23.5 |
| 200 | 90 | 0.5 | 93.4 | 70.1 | 5.0 | 1.0 | 23.9 |
| 200 | 90 | 1.0 | 90.2 | 60.3 | 4.2 | 1.2 | 34.3 |
| 200 | 90 | 1.5 | 91.1 | 61.8 | 4.4 | 1.4 | 32.4 |
| 200 | 90 | 2.0 | 89.1 | 58.6 | 4.1 | 1.4 | 35.9 |
| 300 | 90 | 0.0 | 95.8 | 73.9 | 4.7 | 0.9 | 20.5 |
| 300 | 90 | 0.5 | 87.8 | 71.7 | 4.4 | 1.0 | 22.9 |
| 300 | 90 | 1.0 | 89.4 | 65.9 | 3.9 | 1.2 | 29.0 |
| 300 | 90 | 1.5 | 90.1 | 62.4 | 3.8 | 1.3 | 32.5 |
| 300 | 90 | 2.0 | 89.3 | 58.7 | 3.5 | 1.4 | 36.4 |
| 350 | 90 | 0.0 | 81.8 | 75.6 | 4.3 | 1.0 | 19.1 |
| 350 | 90 | 0.5 | 77.1 | 75.6 | 4.2 | 1.0 | 19.2 |
| 350 | 90 | 1.0 | 80.1 | 66.9 | 3.7 | 1.2 | 28.2 |
| 350 | 90 | 1.5 | 79.4 | 64.0 | 3.5 | 1.4 | 31.1 |
| 350 | 90 | 2.0 | 77.1 | 59.1 | 3.3 | 1.4 | 36.2 |

* "Other (diff)" indicates that it mainly composed of oxygen and ash.

**2.3.2 Effect of different reaction conditions on the product yields**

In the degradative solvent extraction, Soluble, Residue, and gas products such as $H_2$, CO, $CH_4$, and $CO_2$ were obtained. The liquids such as water and oil were not observed, indicating that all liquid products were dissolved in 1-MN. Based on the results in subsection 2.3.1 on the whereabouts of DES after the degradative solvent extraction, the Soluble and Residue yields were calculated by using Eq. (2.2).

$$\text{Yields (wt\%)} = \frac{\text{Recovery amount of Soluble or Residue}}{\text{Amount of AC (5 g)} + \text{Amount of DES}} \times 100 \qquad (2.2)$$

The product yields calculated using Eq. (2.2) are summarized in Tables 2.4 and 2.5 as well as Fig. 2.6. The total product yield at 200 °C was approximately 100 wt%, but at ≥300 °C, it significantly exceeded 100 wt% (Fig. 2.6). It should be noted that the excess of total product yield increased significantly with increasing the amounts of DES. This may be related to the failure to recover some of the 1-MN solvent used during the degradative solvent extraction. Fig. 2.7 shows the amount of unrecovered 1-MN increased with increasing the addition amount of DES. However, the presence of 1-MN was not confirmed from the TG profiles of Residue and Soluble (Fig. 2.8). Furthermore, the aromatic C-H vibration was not observed in the FT-IR spectra of Residue (Fig. 2.9), whereas it was observed in the Soluble (Fig. 2.10). Therefore, it is suggested that the total product yield exceeded 100 wt% because the component derived from 1-MN was incorporated into the Soluble by adding DES at ≥300 °C.

The effects of the reaction temperature and amount of DES on the product yields are represented in Tables 2.4 and 2.5 as well as Fig. 2.6. The Soluble/Residue yields at 200, 300, and 350 °C without DES were 5.2/98.9 wt%, 11.4/91.7 wt%, and 20.6/77.9 wt%, respectively. The Soluble yields increased with increasing temperature, while the Residue yields decreased. As observed from the TG profiles, the weight of AC started to decrease at approximately 250 °C, and decreased by 3.7 wt% at 300 °C and 9.9 wt% at 350 ◦C (Fig. 2. 11). However, the weight loss of AC measured by TG was not in agreement with the Soluble yield. When the thermal decomposition of coal using TG was performed in the gas phase, the hydroxyl and carboxyl groups, which were hydrogen-bonded in the coal, decomposed to produce water and $CO_2$, allowing the coal molecule to grow by forming thermally stable covalent bonds with adjacent coal molecules. On the other hand, Hu et al. and Ashida et al. reported that the inherent water adsorbed on coal by the hydrogen bonds suppressed the cross-linking reaction between

coal molecules in 1-MN, producing organic substances with low molecular weights [11,12]. Therefore, it is considered that the degradative solvent extraction of AC in 1-MN also suppressed the aggregation of the coal molecules and increased the Soluble yield containing many low molecular-weight components. Increasing the addition amount of DES resulted in an increase in the Soluble yield and a decrease in the Residue yield. The Soluble yields at 200 °C and 350 °C were 8.6 wt% and 47.9 wt%, respectively, in the presence of 2 g of DES. The Soluble, CO, and $CO_2$ yields at >300 °C increased significantly with increasing amounts of DES.
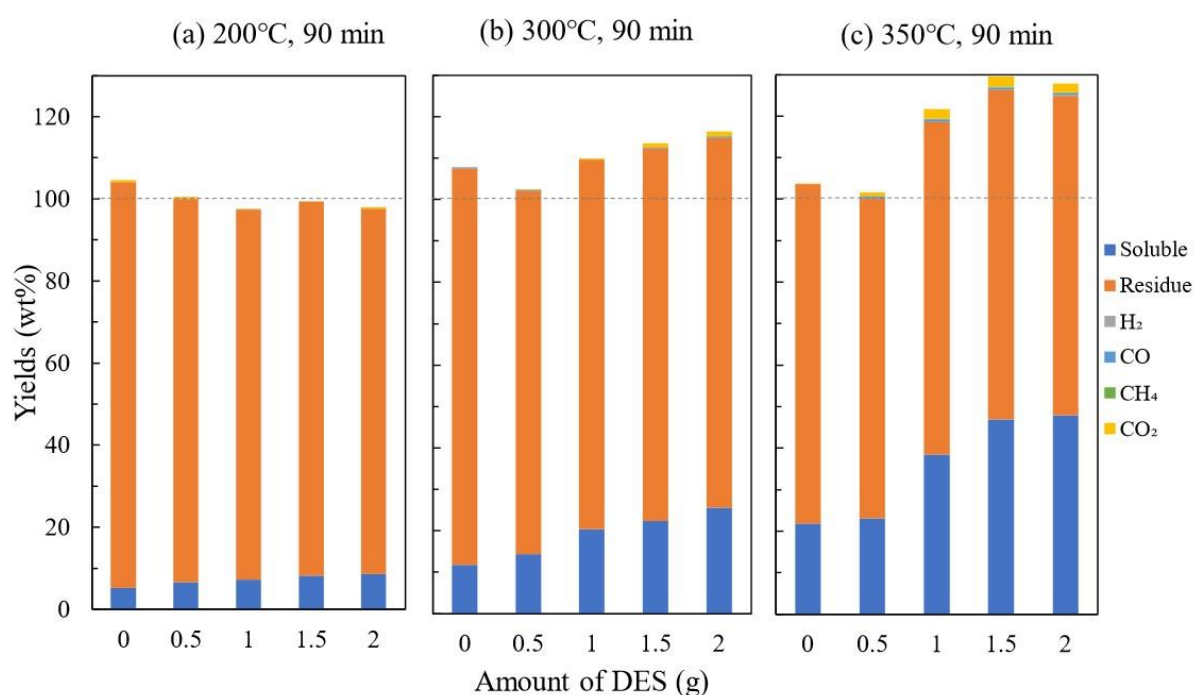


**Fig. 2.6** Product yields of degradative solvent extraction of AC with and without DES at (a) 200 °C, (b) 300 °C, and (c) 350 °C for 90 min.

**Table 2.5** Yield and ultimate analysis of Soluble obtained by the degradative solvent extraction of AC.

| Temperature (°C) | Time (min) | DES (g) | Yield (wt%) | Ultimate Analysis (wt%, d.b.) | | | | HHV (MJ/kg) |
|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | O (diff.)** | |
| 200 | 90 | 0.0 | 5.2 | 80.1 | 10.2 | 0.2 | 9.5 | 40.0 |
| 200 | 90 | 0.5 | 6.6 | 81.9 | 9.7 | 0.2 | 8.2 | 40.2 |
| 200 | 90 | 1.0 | 7.2 | 79.4 | 7.2 | 0.4 | 13.0 | 34.9 |
| 200 | 90 | 1.5 | 8.2 | 78.1 | 8.6 | 0.6 | 12.7 | 36.5 |
| 200 | 90 | 2.0 | 8.6 | 80.0 | 8.5 | 0.5 | 11.0 | 37.3 |
| 300 | 90 | 0.0 | 11.8 | 79.9 | 8.3 | 0.3 | 11.5 | 36.9 |
| 300 | 90 | 0.5 | 14.4 | 82.2 | 8.5 | 0.3 | 9.0 | 38.4 |
| 300 | 90 | 1.0 | 20.3 | 86.0 | 8.0 | 0.2 | 5.8 | 39.5 |
| 300 | 90 | 1.5 | 22.3 | 89.3 | 7.9 | 0.2 | 2.6 | 41.1 |
| 300 | 90 | 2.0 | 25.6 | 88.6 | 7.6 | 0.2 | 3.6 | 40.2 |
| 350 | 90 | 0.0 | 21.8 | 82.9 | 7.7 | 0.4 | 9.0 | 37.5 |
| 350 | 90 | 0.5 | 23.1 | 84.1 | 7.9 | 0.4 | 7.6 | 38.4 |
| 350 | 90 | 1.0 | 38.5 | 88.7 | 7.4 | 0.2 | 3.7 | 40.0 |
| 350 | 90 | 1.5 | 46.9 | 89.9 | 7.3 | 0.2 | 2.7 | 40.4 |
| 350 | 90 | 2.0 | 47.9 | 90.1 | 7.2 | 0.2 | 2.5 | 40.4 |

** "O (diff)" indicates oxygen amount because there is no ash in Soluble.
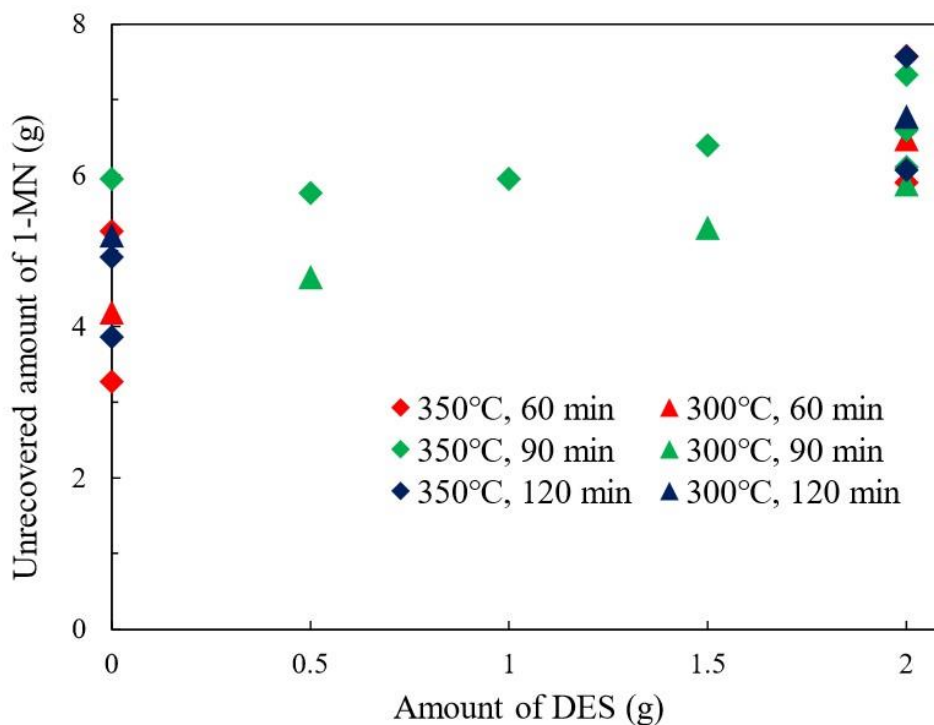


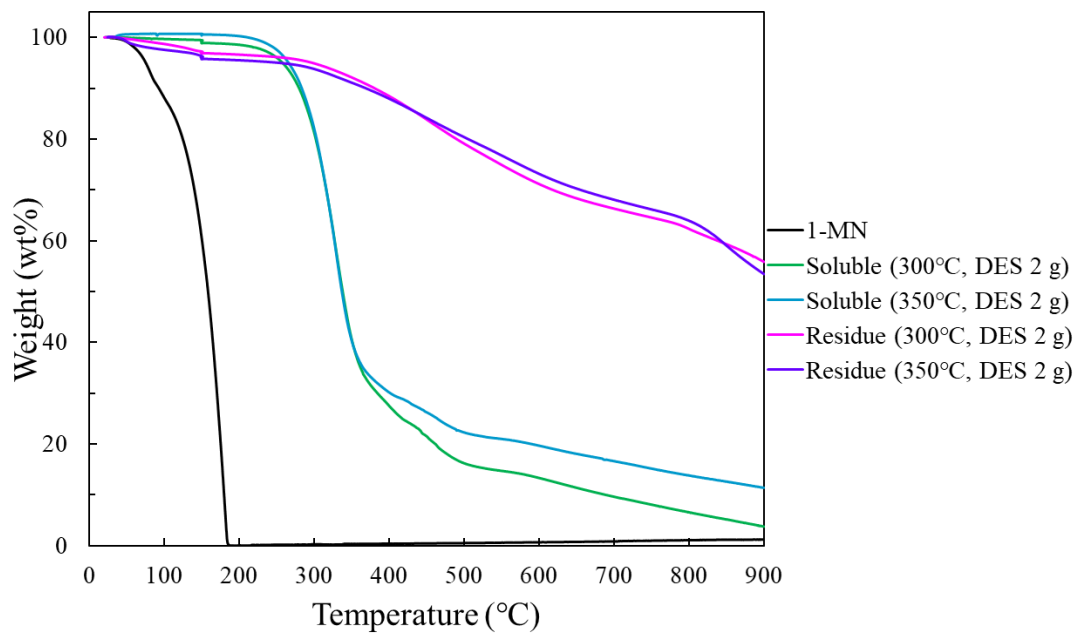**Fig. 2.7** Relationship between addition amount of DES and amount of unrecovered 1-MN.

**Fig. 2.8** TG profiles of 1-MN, Soluble and Residue obtained by the degradative solvent extraction of AC with 2 g of DES at 300 or 350 ℃.
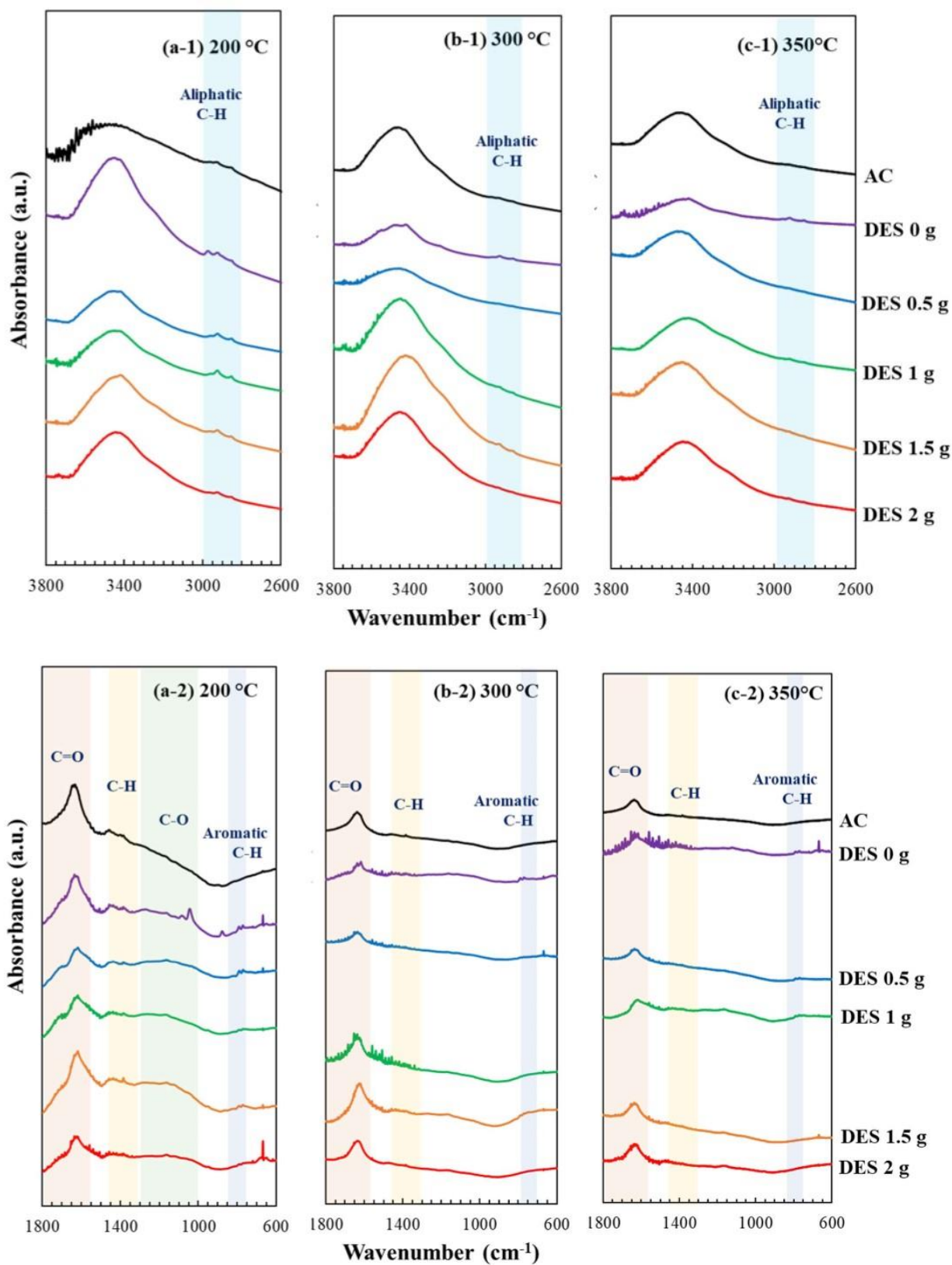
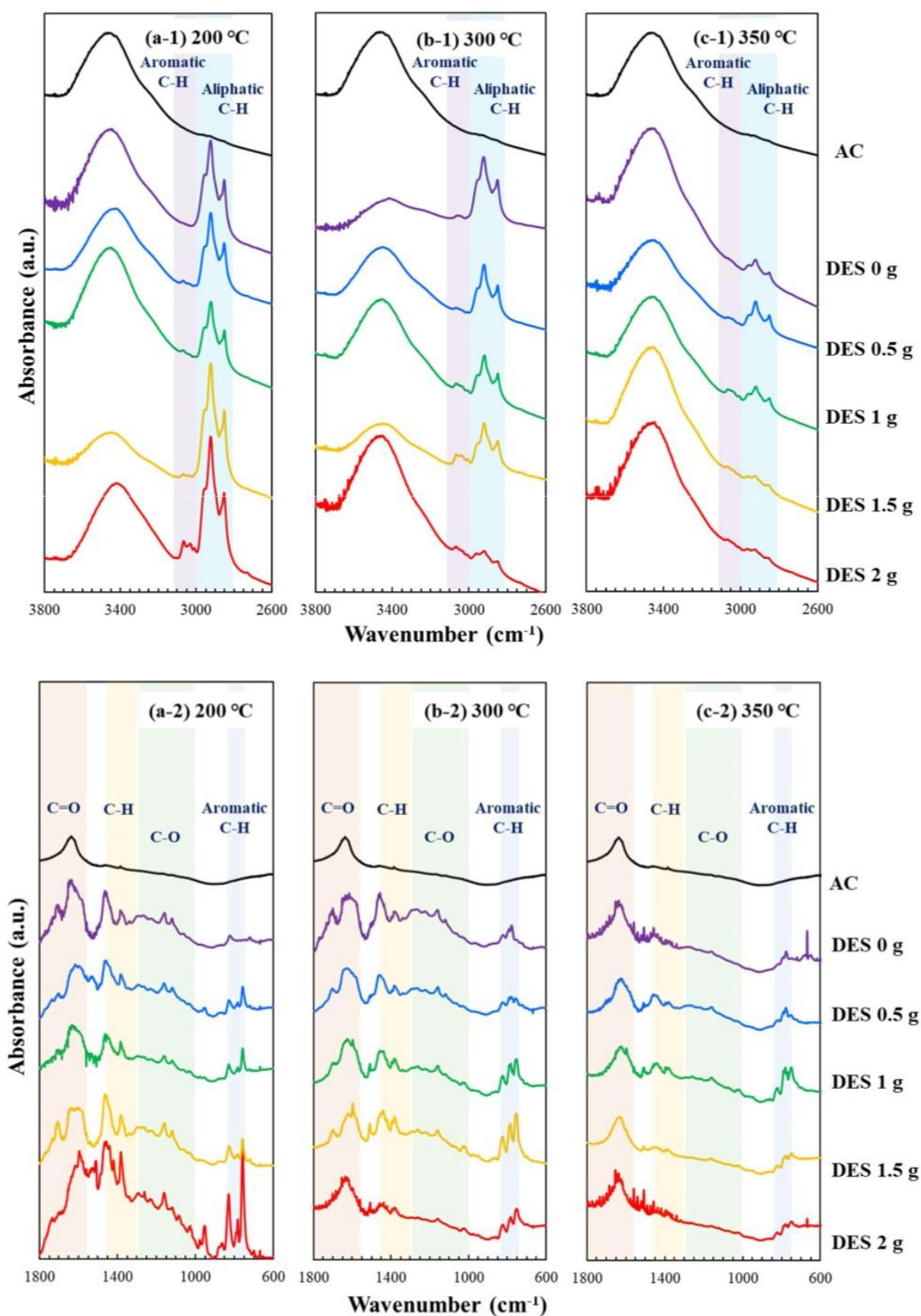**Fig. 2.9** FT-IR spectra of Residue obtained at (a) 200 ℃, (b) 300 ℃, and (c) 350 ℃ for 90 min.

**Fig. 2.10** FT-IR spectra of Soluble obtained at (a) 200 ℃, (b) 300 ℃, and (c) 350 ℃ for 90 min.

**Fig. 2. 11** TG and DTG profiles of AC.

### 2.3.3 Elemental composition of the Soluble

The elemental compositions of Soluble obtained at different reaction temperatures and DES contents were investigated. Fig. 2.12 shows the plot of the carbon and oxygen contents as a function of the Soluble yield at 200-350 °C for 90 min. The carbon and oxygen contents of AC were 67.5 wt% and 26.1 wt%, respectively. On the other hand, with increasing Soluble yield, the carbon content increased from 78 wt% to 90 wt%, and the oxygen content decreased. Soluble with 1–2 g DES at 300–350 °C showed higher soluble yield, higher carbon content, and lower oxygen content compared to Solubles of Hefeng (HF) and Naomaohu (NMH) as sub-bituminous coal (at 350°C and 0.2 MPa for 60 min in 1-MN) [7], and Soluble of Mae Moh coal and Loy Yang coal as lignite (at 350°C and 3–5 MPa for 60 min in 1-MN) [13]. It is interesting that the change of carbon and oxygen contents against the Soluble yields shows the similar tendency in all reaction conditions and in all coals. From this figure, it can be seen that in order to obtain a fuel containing a large amount of carbon, it is necessary to increase the Soluble yield.

**Fig. 2. 12** Relation between carbon/ oxygen contents in Soluble and Soluble yields. This figure also shows the results in the previous paper; Soluble from raw Hefeng (HF-R-SL) and raw Naomaohu (NMH-R-SL) as sub-bituminous coal (at 3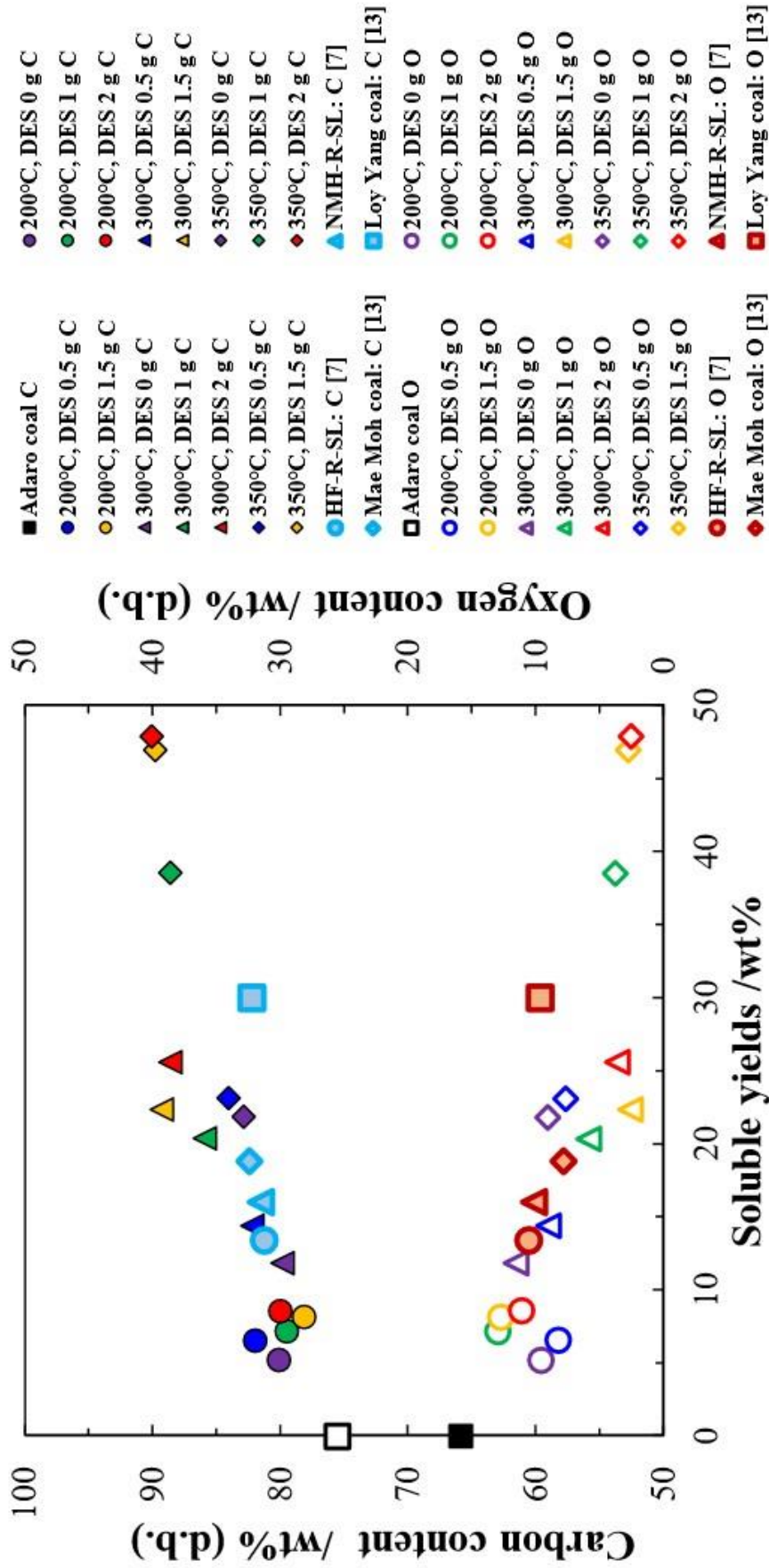50 °C and 0.2 MPa for 60 min in 1-MN) [7], and Mae Moh coal and Loy Yang coal as lignite (at 350 °C and 3–5 MPa for 60 min in 1-MN) [13].

The H/C and O/C of Soluble and Residue obtained in this study as well as those of raw AC were discussed to infer to the reactions that occur when Soluble is generated from raw AC. Fig. 2. 13 shows the relationship between H/C and O/C atomic ratios calculated from the chemical composition of Soluble and Residue. The H/C and O/C of raw AC were 0.9588 and 0.2906, respectively. In Soluble, H/C and O/C decreased with increasing reaction temperature and the addition amount of DES. The H/C and O/C of the soluble obtained at 350 °C and 2 g of DES were the smallest, 0.9524 and 0.0211, respectively. The amounts of CO and $CO_2$ evolution also increased with increasing reaction temperature and the addition amount of DES as shown in Fig. 2.6, indicating that DES promoted the removal of oxygen from AC via decarboxylation and dehydration reactions. As described above, DESs have the ability to cleave the oxygen-containing bonds and produce a carbon-rich extract. Furthermore, the atomic ratios of Soluble obtained in this study were compared with those of other fuels [7, 13-17]. The O/C of Soluble, which was produced by degradative solvent extraction under severer conditions such as high temperature and large addition amount of DES, was similar to that of bituminous coal. In particular, the O/C of Soluble obtained with 1.5-2 g of DES at 300 °C and 1-2 g of DES at 350 °C decreased to a value similar to that of anthracite, hyper-coal and Soluble obtained in previous reports.
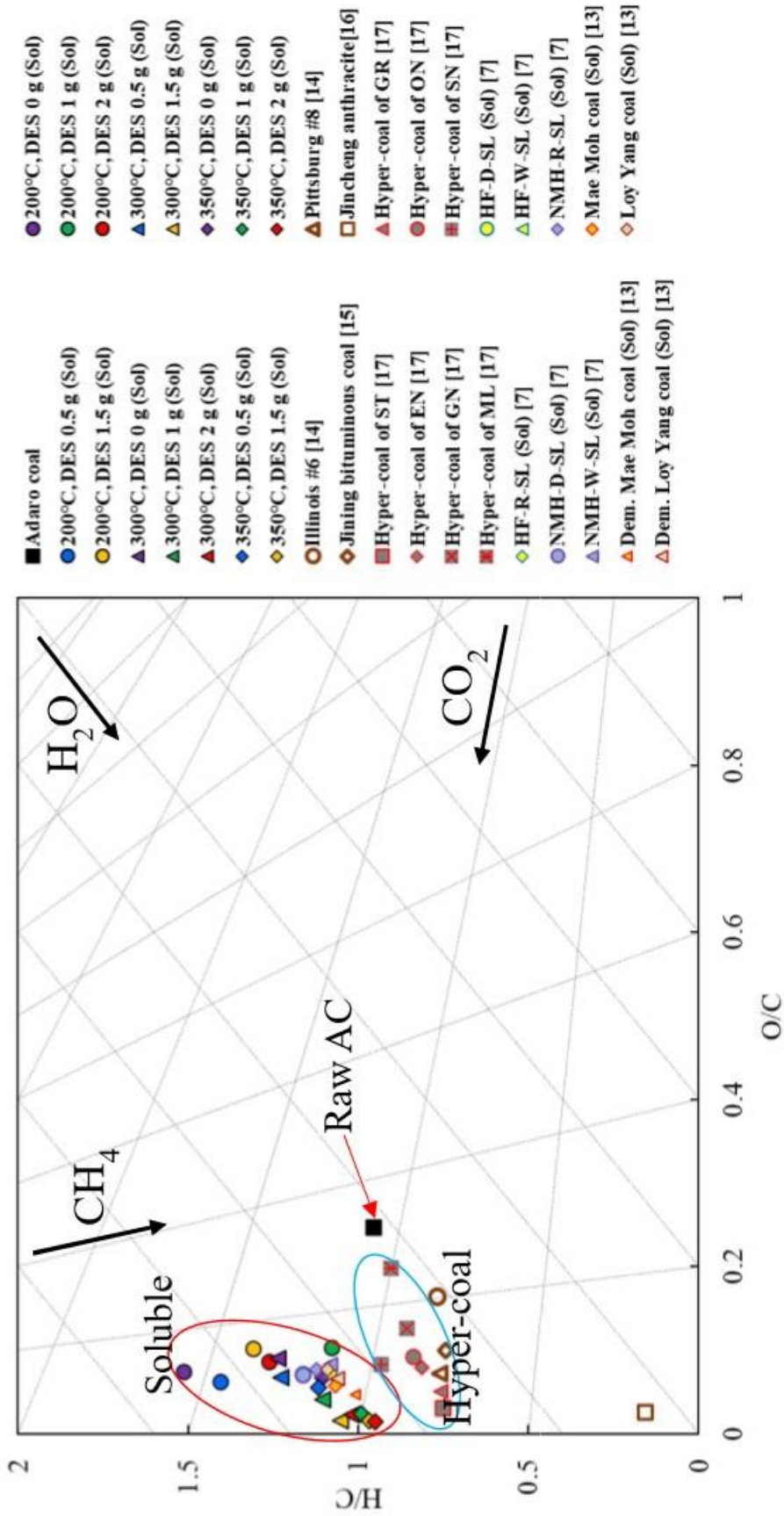
**Fig. 2.13** Relationship between H/C and O/C atomic ratios for AC, Soluble, Residue, various coals, and Hyper-coal. This figure also shows the results in the previous paper; Illinois #6 and Pittsburg #8 as bituminous coal [14], Jining bituminous coal [15] and Jincheng anthracite [16], Hyper coal (at 350 °C and 0.05-0.5 MPa in 1-MN) [17], and Soluble from Hefeng (HF-SL) and Naomaohu (NMH-SL) (R: Raw coal, D: Dried coal, W: Coal containing 30 wt% of moisture) (at 350 °C and 0.2 MPa for 60 min in 1-MN) [7], Soluble from Mae Moh coal and Loy Yang coal (Dem.: demineralization) (at 350 °C and 3-5 MPa for 60 min in 1-MN) [13].

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Fig. 2.14 shows the carbon and oxygen balance in Soluble and Residue at 200-350 °C for 90 min, respectively. The reason why the total carbon content exceeds 100 mol% is probably because 1-MN is included in the extracts, especially in the case of DES addition. As shown in Table 2.4, Other (diff.) in ultimate analysis of Residue contains the oxygen, ash and HBD (hydrogen-bond donor). Therefore, in this study, the oxygen in the Residue was calculated by subtracting ash and HBD from Other (diff). The oxygen present in the Soluble was almost the same independent of experimental conditions, and the oxygen present in the Residue decreased with increasing the reaction temperature and the amount of DES added. It was considered that the carbon-rich components produced by the decomposition of Residue were extracted as Soluble.
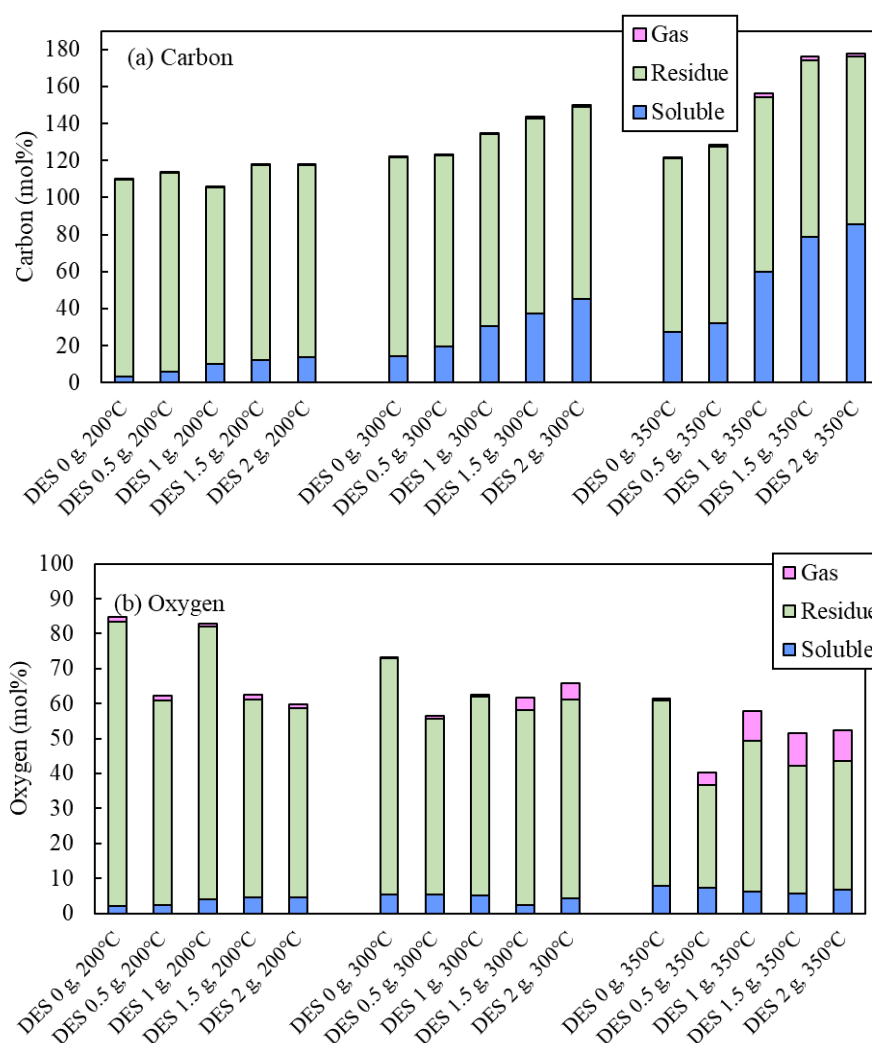


**Fig. 2.14** (a) Carbon and (b) oxygen balance in the degradative solvent extraction of AC.

### 2.3.4 Structural characterization of Soluble and Residue

The TG profiles of Soluble and Residue under various conditions and the results of TG differential (DTG) profiles are shown in Fig. 2.15 (a-c) and Fig. 2.15 (d-f), respectively. The weight of AC began to decrease from approximately 250 °C and remained 50 wt% at 900 °C (Fig. 2.15 (a)). For Soluble obtained without DES at 200-350 °C, the weight loss began at 250 °C, as in AC, and the weight decreased significantly at approximately 400 °C. In addition, the thermal decomposition temperature of the Soluble lowered with increasing reaction temperature. As mentioned above, this was because the low molecular-weight component produced by the thermal decomposition of AC was extracted as Soluble. The weight of Soluble produced with 0.5 g of DES at 200 °C decreased significantly at approximately 400 °C, while a two-step weight loss was observed with 1-2 g of DES. At 300 and 350 °C, the thermal decomposition temperature of Soluble obtained with 1-2 g of DES was lower than that without DES, and a significant weight loss occurred at 350 °C. This suggested that the increased reaction temperature and DES addition promoted the production of low molecular-weight Soluble. The TG profiles of Residue are almost the same as AC (Fig. 2.15 (d–f)). This may be because the structure of Residue does not differ much from that of the raw AC, although Residue contains a large amount of oxygen.
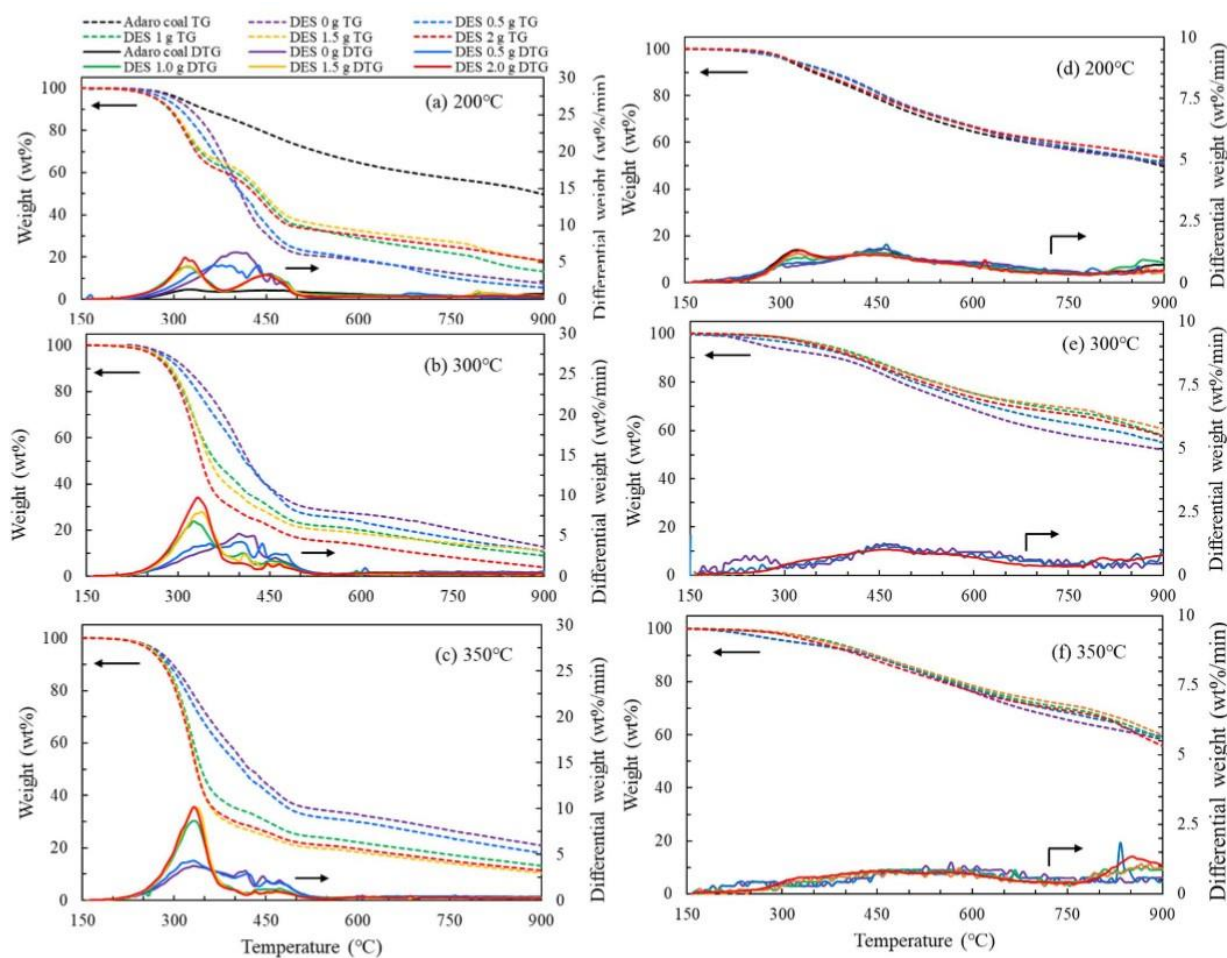
**Fig. 2.15** TG and DTG profiles of the Soluble obtained at (a) 200 °C, (b) 300 °C and (c) 350 °C, and Residue at (d) 200 °C, (e) 300 °C and (f) 350 °C for 90 min.

Figs. 2.9 and 2.10 shows the FTIR spectra of Soluble and Residue produced under various conditions, respectively. In AC spectrum, the peaks at 3600-3400 $cm^{-1}$ and 1630 $cm^{-1}$ were attributed to O-H and C=O stretching vibrations, respectively. Additionally, the bands observed at 2930-2850 $cm^{-1}$ and 1450-1300 $cm^{-1}$ were attributed to aliphatic C-H stretching and bending vibrations, respectively. For Soluble, the peaks attributed to the aromatic and aliphatic C-H stretching vibrations were observed at 3080-3020 $cm^{-1}$ and 2930-2850 $cm^{-1}$ regardless of the reaction temperature. Furthermore, under all reaction conditions, the peaks observed at 1850-1550 $cm^{-1}$, 1450-1300 $cm^{-1}$, 1300-1000 $cm^{-1}$ and 830-750 $cm^{-1}$ were attributed to the C=O stretching, C-H bending, C-O stretching (derived from esters, ethers, and alcohols) and aromatic C-H bending vibrations, respectively [17-23]. In addition, the C=O stretching vibrations derived from the carboxyl group were observed at 1700 $cm^{-1}$ at 200 or 300 °C with 0-1.5 g of DES. With increasing reaction temperatures, the peak intensities attributed to aliphatic C-H stretching, C=O stretching, C-H bending, and C-O stretching

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vibrations decreased. At 350 °C, the C=O stretching vibration derived from the carboxyl group was not observed. When DES was used at 200 °C, no significant change in the spectra was observed regardless of DES addition. By contrast, at 300-350 °C, the peak intensities attributed to aliphatic C-H stretching, C=O stretching, C-H bending, and C-O stretching vibrations decreased with increasing the addition amounts of DES. This trend was similar to that observed for the reaction temperature. The C=O stretching vibration derived from the carboxyl group was not observed at 300 °C with 2.0 g of DES and at 350 °C. Therefore, DES cleaved the carbon-oxygen bond because the absorption intensity of C-O and C=O stretching vibrations decreased with increasing DES contents. Residue must have a large amount of oxygen, but the increase in the absorption bands attributed to the oxygen-containing bonds can not be seen in the FT-IR spectra. Residue is considered to be a substance containing components that are as difficult to decompose as the raw AC.

### 2.3.5 Calorific value of Soluble

The higher heating value (HHV) of raw AC is 25 MJ/kg. The HHV of Soluble is higher than the HHV of raw AC (Table 2.5). The Soluble shows higher carbon contents, lower oxygen contents and higher HHV in comparison with the raw materials. HHV of the Soluble are higher than those of the raw materials [24]. The same tendency was verified in the degradative solvent extraction of AC. However, the HHV value of Soluble at 200 °C was highest without DES and 0.5 g DES, at 300 °C it was highest at 1.5 g DES, and at 350 °C it was highest with 1.5-2 g DES. At 350 °C, the HHV increased with increasing DES amount up to 1.5 g of DES and remained constant even with the use of 2 g of DES.

### 2.4 Conclusion

Degradative solvent extraction of Adaro Subbituminous Coal using DES was performed in 1-MN.

- The Soluble yield increased and the oxygen content decreased with increasing reaction temperature and DES amount;
- As the amount of DES added increased, the low-molecular-weight components and the aromaticity in the Soluble increased;
- The decarboxylation took place by the degradative solvent extraction and the decarboxylation and dehydration took place by the DES addition;
- The HHV of Soluble was higher than raw AC.

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**Chapter 3 Solvent-soluble component obtained from degradative solvent extraction of woody biomass using deep eutectic solvent**

### 3.1 Introduction

The amount of fossil fuels has been reduced by the depletion of resources, and soaring prices and their use creates adverse effects on the environment due to $CO_2$ emissions. The alternative is to use biomass. Among renewable energies with a small impact on the environmental, biomass that can be supplied all over the world is currently attracting attention. Due to the concept of carbon neutral, biomass emits less carbon dioxide, and contains almost no sulfur, nitrogen, resulting in less SOx, NOx, and soot emissions than conventional fossil fuels. However, much of the biomass contains large amount of water with a correspondingly high oxygen content and low carbon content as shown in Table 3.1 [1]. As a result, biomass has drawbacks such as low calorific value, inconvenience of storage because it decays, and difficulty in application to conventional processes in terms of burning, fermentation and energy conversion [2]. Therefore, in the conversion of biomass to fuel, deoxygenation treatment such as degradative solvent extraction is required.

**Table 3.1** Proximate and ultimate analysis, chemical compositions of biomass such as woody, herbaceous, and waste materials; average (standard deviation) [1].

| Feedstock Composition | Woody | Herbaceous | Wastes |
|---|---|---|---|
| *Proximate* | | | |
| Volatiles (%) | 84.0 (2.1) | 79.1 (5,8) | 76.7 (5.5) |
| Ash (%) | 1.3 (0.9) | 5.5 (3.2) | 6.6 (6.7) |
| Fixed Carbon (%) | 14.7 (1,6) | 15.4 (4.0) | 14.8 (5.0) |
| *Ultimate* | | | |
| Hydrogen (%) | 6.0 (0.1) | 5.8 (0.3) | 5.9 (0.4) |
| Carbon (%) | 50.7 (4.71) | 47.4 (1.9) | 46.0 (4.0) |
| Nitrogen (%) | 0.32 (0.01) | 0.75 (0.49) | 1.3 (1.6) |
| Oxygen (%) | 41.9 (1.4) | 41.0 (2.4) | 38.3 (4.2) |
| Sulfur (%) | 0.03 (0.01) | 0.10 (0.32) | 0.15 (0.16) |
| *Structural* | | | |
| Cellulose (%) | 51.2 (8.7) | 32.1 (4.5) | 28.4 (13.2) |
| Hemicellulose (%) | 21.0 (8.7) | 18.6 (3.4) | 16.4 (5.5) |
| Lignin (%) | 26.1 (5.3) | 16.3 (3.3) | 12.5 (2.7) |

In the previous study, the degradative solvent extraction of Rice Straw (RS, 20 g) was performed under 2-3 MPa of nitrogen atmosphere at 200-350 °C for 90 min [3]. As described before, it is considered that aromatic ring compounds are extracted into 1-MN solvent. Because the amount of aromatic components for biomass is quite smaller than that of low-rank coal, so

the yield of Soluble obtained by the degradative solvent extraction of biomass is expected to be low. Table 3.2 shows the ultimate and proximate analysis of RS and Soluble as well as the Soluble yields. In fact, this table shows that the oxygen content of Soluble produced from RS is as high as approximately 10 wt% even at 350 °C. In addition, the Soluble yields were very low, 10-20 wt% at 250-350 °C.

As shown in Fig. 3.1, biomass has a different structure from low-rank coal, that is, the woody biomass used in this chapter as biomass sample consists of cellulose, hemicellulose and lignin. However, since the biomass also has a large amount of carbon-oxygen bonds similar to low-rank coal, the Soluble yield is considered to increase by efficiently cleaving the carbon-oxygen bonds. Addition of DES may be effective as a method for producing a large amount of Soluble with low oxygen content from biomass, as in the case of low-rank coal.

**Table 3.2** Ultimate and proximate analysis of Rice Straw (RS) and Soluble obtained by the degradative solvent extraction of RS at 250, 300 and 350 °C for 90 min [3].

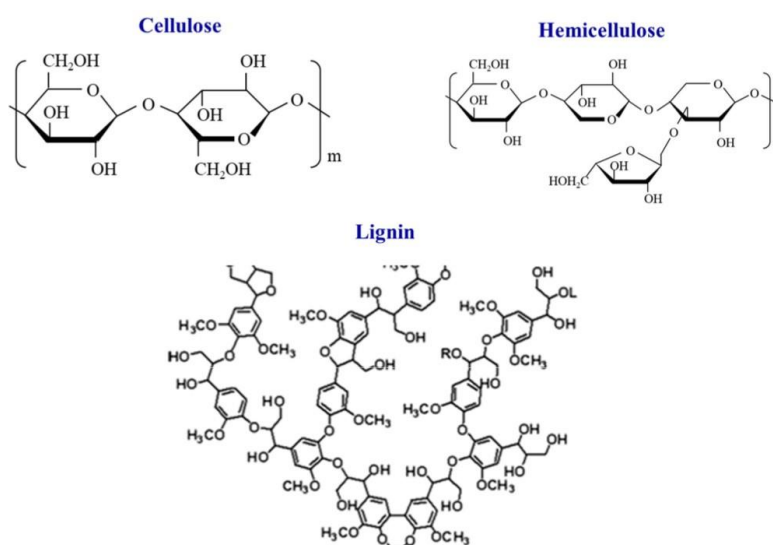| Temperature | Yield | Ultimate analysis wt% (d.a.f) | | | | Proximate analysis wt% (d.b) | | |
|---|---|---|---|---|---|---|---|---|
| (°C) | (wt% d.a.f) | C | H | N | O diff. | V.M. | F.C. | Ash |
| RS | | 49.0 | 5.5 | 0.8 | 44.6 | 75.4 | 14.4 | 10.0 |
| 250 | 11.8 | 75.2 | 7.1 | 1.4 | 16.3 | 80.8 | 18.9 | 0.3 |
| 300 | 14.6 | 77.6 | 6.8 | 1.5 | 14.2 | 81.1 | 18.8 | 0.1 |
| 350 | 19.9 | 82.4 | 6.9 | 1.3 | 9.5 | 78.3 | 21.2 | 0.5 |



**Fig. 3.1** Typical structure of cellulose, hemicellulose and lignin [4].

The purpose of this chapter is to clarify whether the DES is effective in increasing the Soluble yield in the degradative solvent extraction even for woody biomass and to discuss the role of DES on the degradative solvent extraction of woody biomass. The extraction mechanism of the degradative solvent extraction of woody biomass was also discussed.

## 3.2 Experimental

### 3.2.1 DES preparation and sample

As already described in subsection 2.2.1, DES was prepared in the same way as for low-rank coal.

The woody biomass used in this chapter is woody chips (WC) made of cedar and provided from Akita thermal power plant in Tohoku Electric Power Co., Inc. Table 3.3 shows the proximate and ultimate analysis of the WC. The WC was ground using a Wonder Crusher WC-3, classified into 425–600 μm particles, and used for the reaction after drying at 60 ºC for 48 h.

**Table 3.3** Ultimate and proximate analysis of woody chips.

| | Ultimate analysis wt% (d.a.f) | | | | HHV | Proximate analysis wt% (d.b) | | |
|---|---|---|---|---|---|---|---|---|
| Sample | C | H | N | O diff. | [MJ/kg] | V.M. | F.C. | Ash |
| Woody Chips | 49.1 | 6.6 | 0.2 | 44.0 | 18.2 | 79.8 | 19.7 | 0.5 |

### 3.2.2 Degradative solvent extraction of woody biomass, lignin and cellulose

The degradative solvent extraction of WC was performed in the same way as in 2.2.3 and the equipment and methods used were the same as those for low-rank coal. First, 5 g of WC and 100 mL of 1-MN were added in custom autoclave, and then 1.0-2.0 g of DES was also added. After the inside of the equipment was replaced with nitrogen gas three times to remove air, the equipment pressure was set to 0.2 MPa. The reaction temperature was raised to 300-350 ºC over 80 min, and the reaction was performed for 90 min with agitation at 300 rpm. The separation operation of products after the degradative solvent extraction was the same way as already described in subsection 2.3.4. The color of the acid-leaching supernatant solution of Residue produced in the presence of 2 g of DES was yellow as shown in Fig. 3.2, indicating that the DES remains in the Residue. Accordingly, the yields of Soluble and Residue were calculated on the basis of Eq. (3.1) similar to the case of low-rank coal. The characterization of extracts was carried out by FT-IR, TG, and elemental analysis.

$$\text{Yields (wt\%)} = \frac{\text{Recovery amount of Soluble or Residue}}{\text{Amount of WC (5 g)} + \text{Amount of DES}} \times 100 \qquad (3.1)$$
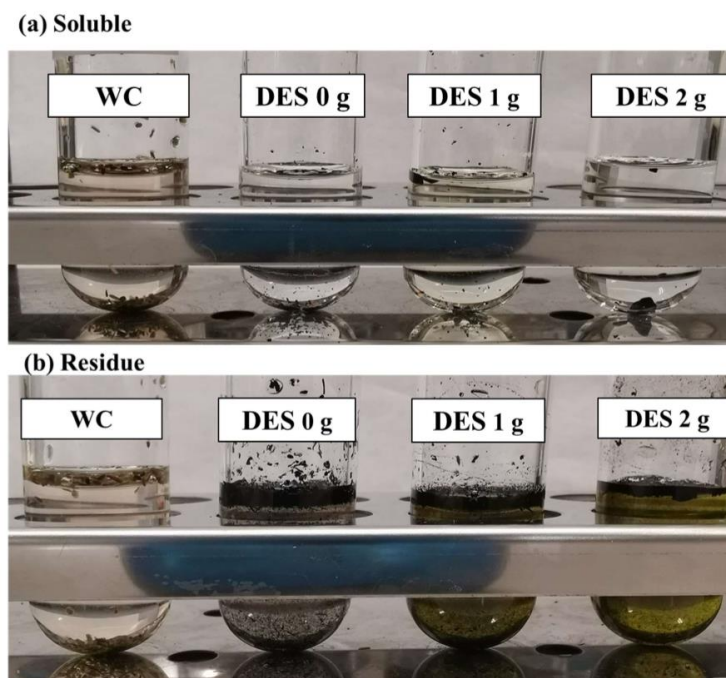


**Fig. 3.2** The images of supernatant solution by the hydrochloric acid treatment of (a) Soluble and (b) Residue when the degradative solvent extraction of WC was performed at 350 ℃ for 90 min. Soluble or Residue (10 mg) was added into 2.5 mL of 6 M hydrochloric acid.

**3.3 Results and discussion**

**3.3.1 Effect of DES addition on the yields and chemical compositions of Soluble and Residue from biomass**

The product yields are summarized in Tables 3.4 and 3.5 as well as Fig. 3.3 at 300-350 ℃ for 90 min. Without DES, the Soluble yield increased from 23 wt% at 300 °C to 33 wt% at 350 °C, whereas the Residue yield decreased from 29 wt% to 18 wt%. Unlike the case of low-rank coal, total product yields were well below 100 wt%. Fig. 3. 4 shows the product yield distribution for the degradative solvent extraction of RS [5]. From this figure, it can be seen that the Liquid yield is around 40 wt%, which is largely consistent with the shortfall of total product yields in this work. The authors described that the molar ratios of H to O distributed to Liquid are roughly 2, showing that the main component in Liquid is $H_2O$ produced by the degradation reaction [5]. Thus, it is considered that around 40 wt% of the shortfall in Fig. 3.3

is also liquid, mainly water. The addition of DES had an effect of increase in Soluble yields, particularly 350 °C. The maximum Soluble yield reached 44 wt% at 350 ºC with 2 g of DES. However, the tendency of Residue yield is unlike to that of low-rank coal: the higher amount of DES, the higher the Residue yield. The gases produced are mostly $CO_2$ and CO and a small amount of $CH_4$ and $H_2$. The amount of $CO_2$ and CO yields decreased with increasing amounts of DES. On the other hand, the total product yield exceeded 100 wt% in the case of the degradative solvent extraction with 2 g of DES at 350 °C (Fig. 3.3 (b)). This may be because a part of 1-MN is incorporated into the Soluble by the presence of DES.
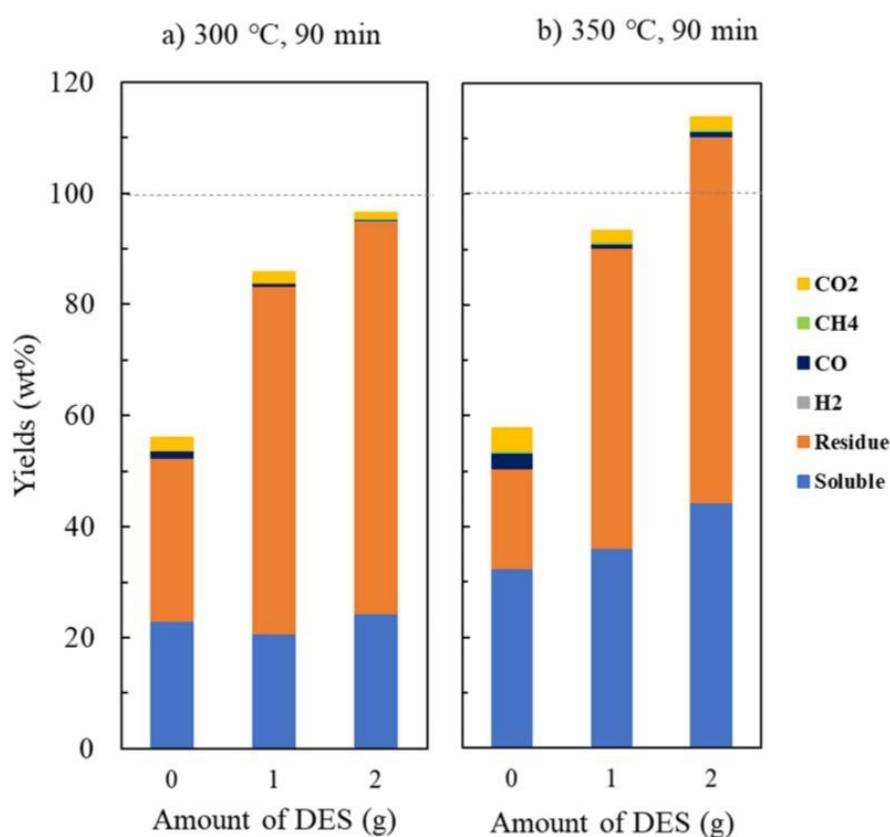


**Fig. 3.3** Product yield distribution of degradative solvent extraction of WC with and without DES at 300 °C (a) and 350 °C (b) for 90 min.
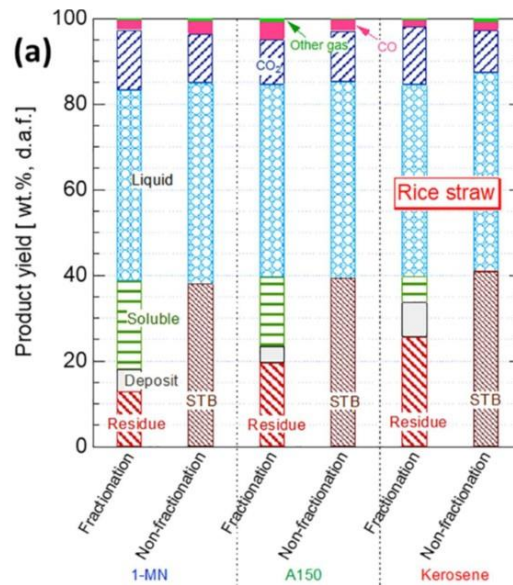
**Fig. 3.4** The product yield distribution for rice straw [5].

**Table 3.4** Yield and ultimate analysis of Soluble obtained by the degradative solvent extraction of WC.

| Temperature (°C) | Time (min) | DES (g) | Yield (wt%) | Ultimate Analysis (wt%, d.b.) | | | | HHV (MJ/kg) |
|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | O (diff.)** | |
| 300 | 90 | 0.0 | 23.0 | 74.4 | 6.1 | 0.2 | 19.4 | 30.4 |
| 300 | 90 | 1.0 | 20.8 | 85.0 | 6.5 | 0.3 | 8.2 | 36.6 |
| 300 | 90 | 2.0 | 24.4 | 88.7 | 6.6 | 0.2 | 4.4 | 38.8 |
| 350 | 90 | 0.0 | 32.6 | 80.7 | 6.5 | 0.1 | 12.7 | 34.3 |
| 350 | 90 | 1.0 | 36.2 | 86.5 | 6.4 | 0.3 | 6.8 | 37.3 |
| 350 | 90 | 2.0 | 44.4 | 89.0 | 6.5 | 0.3 | 4.2 | 38.7 |

** "O (diff)" indicates oxygen amount because there is no ash in Soluble.

**Table 3. 5** Yield and ultimate analysis of Residue obtained by the degradative solvent extraction of WC.

| Temperature (°C) | Time (min) | DES (g) | Yield (wt%) | Ultimate Analysis (wt%, d.b.) | | | |
|---|---|---|---|---|---|---|---|
| | | | | C | H | N | O (diff.)[*] |
| 300 | 90 | 0.0 | 29.4 | 67.7 | 5.9 | 0.4 | 26.0 |
| 300 | 90 | 1.0 | 62.5 | 58.9 | 4.4 | 0.7 | 36.0 |
| 300 | 90 | 2.0 | 70.6 | 52.7 | 4.0 | 0.9 | 42.4 |
| 350 | 90 | 0.0 | 17.8 | 72.9 | 4.8 | 0.4 | 21.9 |
| 350 | 90 | 1.0 | 54.1 | 58.1 | 3.7 | 0.7 | 37.6 |
| 350 | 90 | 2.0 | 65.9 | 50.2 | 3.3 | 0.7 | 45.7 |

* "Other (diff)" indicates that it mainly composed of oxygen and ash.

The elemental compositions of Soluble obtained at different reaction temperatures and DES contents were investigated. Fig. 3.5 shows the plot of the carbon and oxygen contents as a function of the Soluble yield. This figure also shows the results of AC and other studies [6,7]. The carbon and oxygen contents of WC were 49.1wt% and 44.0 wt%, respectively. In the Soluble obtained by the degradative solvent extraction of WC, with increasing Soluble yield, the carbon content increased from 74 wt% to 89 wt%, and the oxygen content decreased from 19 wt% to 4 wt%. Interestingly, the relationship between the Soluble yield and elemental compositions for WC was not significantly different from that for AC. In the case of WC as well, it was clarified that the Soluble yield should be increased in order to produce the Soluble with a high carbon content. Soluble obtained by the degradative solvent extraction of WC with 1-2 g of DES at 350 ℃ had higher carbon content and lower oxygen content compared to the Soluble from HF and NMH sub-bituminous coals treated at 350℃ and 0.2 MPa for 60 min [6], and the Soluble from Mae Moh lignite and Loy Yang brown coal treated at 350℃ and 3–5 MPa for 60 min [7].

● Adaro coal C
■ Woody Chips C
▲ 300°C, DES 1 g WC C
▲ 300°C, DES 0 g WC C
◇ 300°C, DES 2 g WC C
● 350°C, DES 0 g WC C
● 300°C, DES 1 g WC C
▲ 350°C, DES 2 g WC C
◆ 350°C, DES 1 g WC C
● 350°C, DES 2 g WC C
● NMH-R-SL C [6]
● HF-R-SL C [6]
● Loy Yang coal C [7]
● Mae Moh coal C [7]
■ Woody Chips O
● 350°C, DES 2 g AC C
▲ 300°C, DES 0 g WC O
○ Adaro coal O
○ 300°C, DES 2 g WC O
▲ 300°C, DES 1 g WC O
○ 350°C, DES 0 g WC O
▲ 350°C, DES 2 g WC O
◇ 350°C, DES 1 g WC O
○ 350°C, DES 2 g WC O
○ HF-R-SL O [6]
○ NMH-R-SL O [6]
○ Mae Moh coal O [7]
○ Loy Yang coal O [7]
○ 350°C, DES 2 g AC O

Oxygen content /wt% (d.b.)

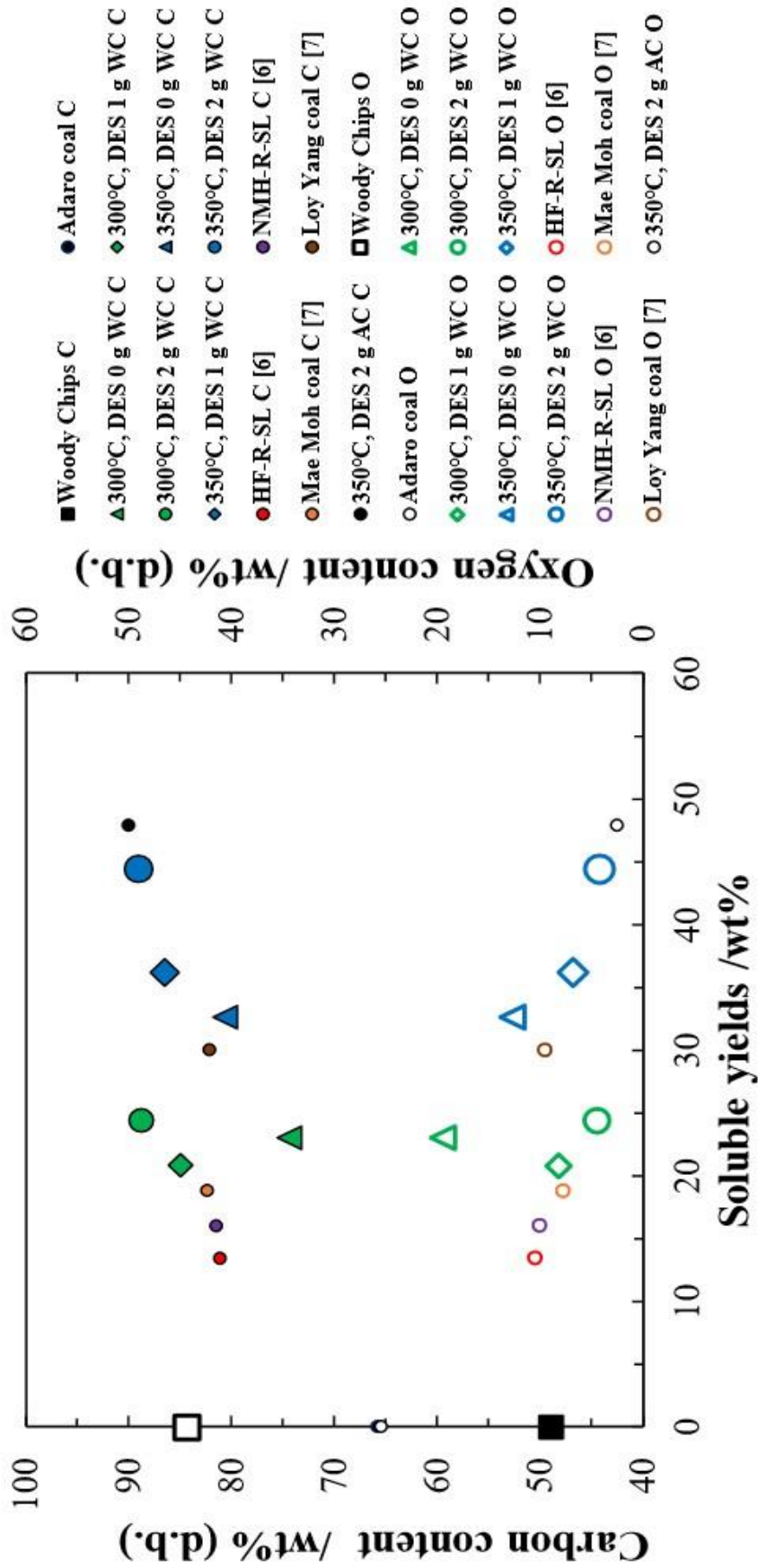Carbon content /wt% (d.b.)

Soluble yields /wt%

**Fig. 3.5** Relation between carbon/ oxygen contents in Soluble and Soluble yields. This figure also shows the results of AC and other studies. Soluble from raw Hefeng (HF-R-SL) and raw Naomaohu (NMH-R-SL) as sub-bituminous coal (at 350°C and 0.2 MPa for 60 min in 1-MN) [6], and Mae Moh lignite and Loy Yang brown coal (at 350°C and 3–5 MPa for 60 min in 1-MN) [7].

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Fig. 3.6 shows the relationship between H/C and O/C atomic ratios calculated from the elemental analysis of Soluble and Residue. In this figure, the H/C and O/C of other samples [6-11] are also shown. The H/C and O/C for WC were 1.61 and 0.68, respectively, both of which were higher than those of AC (Fig. 2.13). In Soluble, H/C and O/C decreased with increasing reaction temperature and DES content; this indicates that a large amount of water produced, which is consistent with the result of product yield distribution (Fig. 3.3). Furthermore, Fig. 3.6 shows that the O/C of Soluble is significantly smaller than that of WC, suggesting that $CO_2$ evolves during the degradative solvent extraction shown in Fig. 3.3. In Residue, O/C increased with increasing DES content; this indicates that the oxygen which is removed as $H_2O$ and $CO_2$ in the absence of DES is incorporated into Residue by the presence of DES. This is considered to be appropriate from the fact that the amount of Liquid (mainly $H_2O$) and CO and $CO_2$ evolution decreased with increasing the addition amount of DES The O/C ratio of Soluble, which was produced by degradative solvent extraction under severer conditions such as high temperature and DES addition conditions, was similar to that of bituminous coal. In particular, the O/C of Soluble obtained with DES decreased to a value similar to that of anthracite. The H/C and O/C of raw WC were higher than H/C and O/C of raw AC. Hence, Soluble obtained at 300-350 °C with DES, was expected to be used as a fuel with high calorific value.
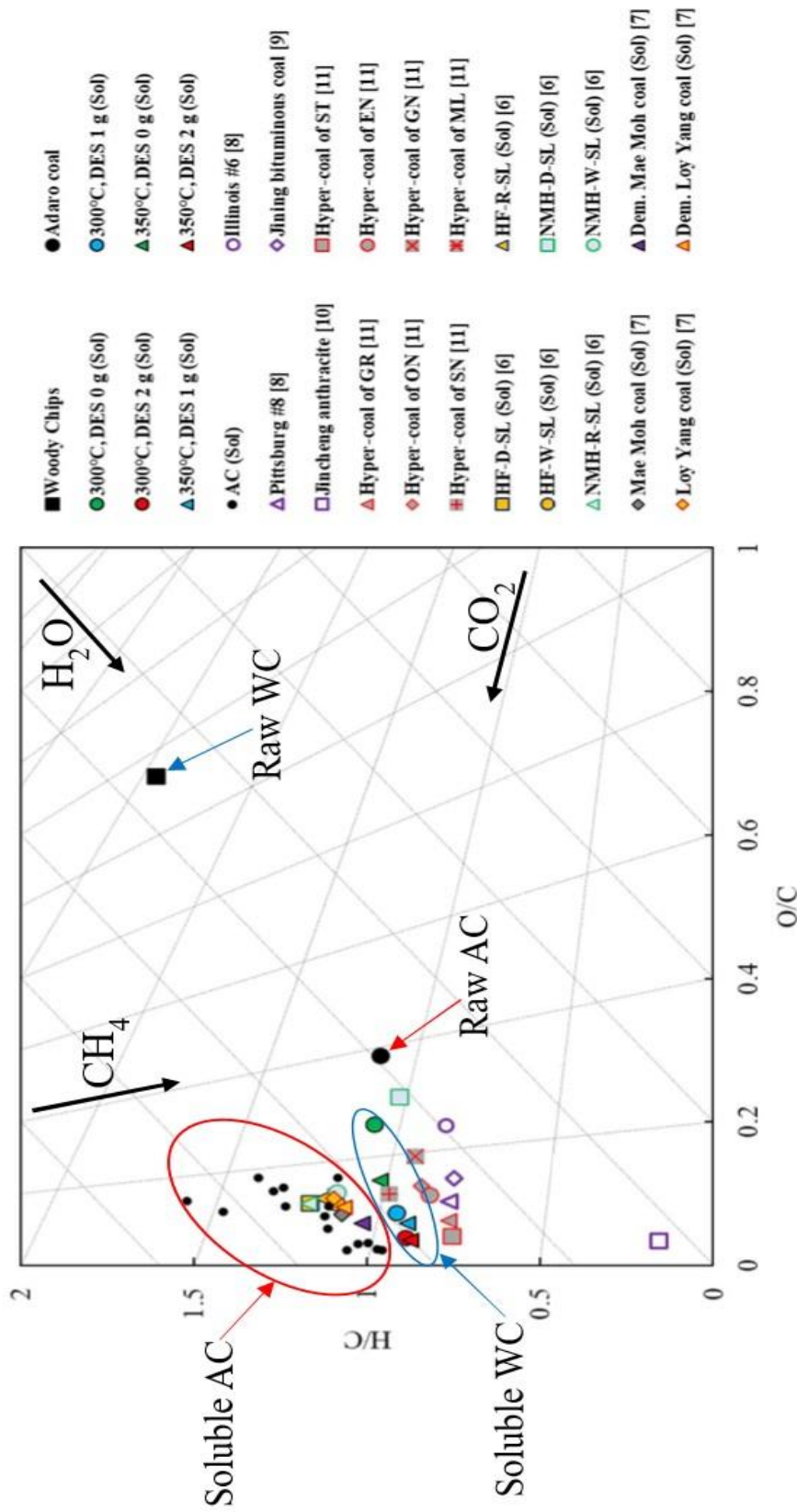
**Fig. 3.6** Relationship between H/C and O/C atomic ratios for WC, Soluble, Residue, various coals and Hyper-coal. Illinois #6 and Pittsburg #8 as bituminous coal [8], Jining bituminous coal [9] and Jincheng anthracite [10], Hyper coal (at 350°C and 0.05–0.5 MPa in 1-MN) [11], and HF-SL and NMH-SL were Soluble of HF (HF-SL) and NMH (NMH-SL) (R: Raw coal, D: Dried coal, W: Coal containing 30 wt% of moisture) (at 350°C and 0.2 MPa for 60 min in 1-MN) [6], Soluble of Mae Moh coal and Loy Yang coal (Dem.: demineralization) (at 350°C and 3–5 MPa for 60 min in 1-MN) [7].

Fig. 3.7 shows the carbon and oxygen balance in Soluble and Residue at 300-350 °C for 90 min, respectively. Unlike low-rank coal, the oxygen present in the Soluble decreased with increasing the reaction temperature and the amount of DES added, while the oxygen present in Residue increased. It was considered that the carbon-rich components produced by the decomposition of Residue were extracted as Soluble even for biomass.
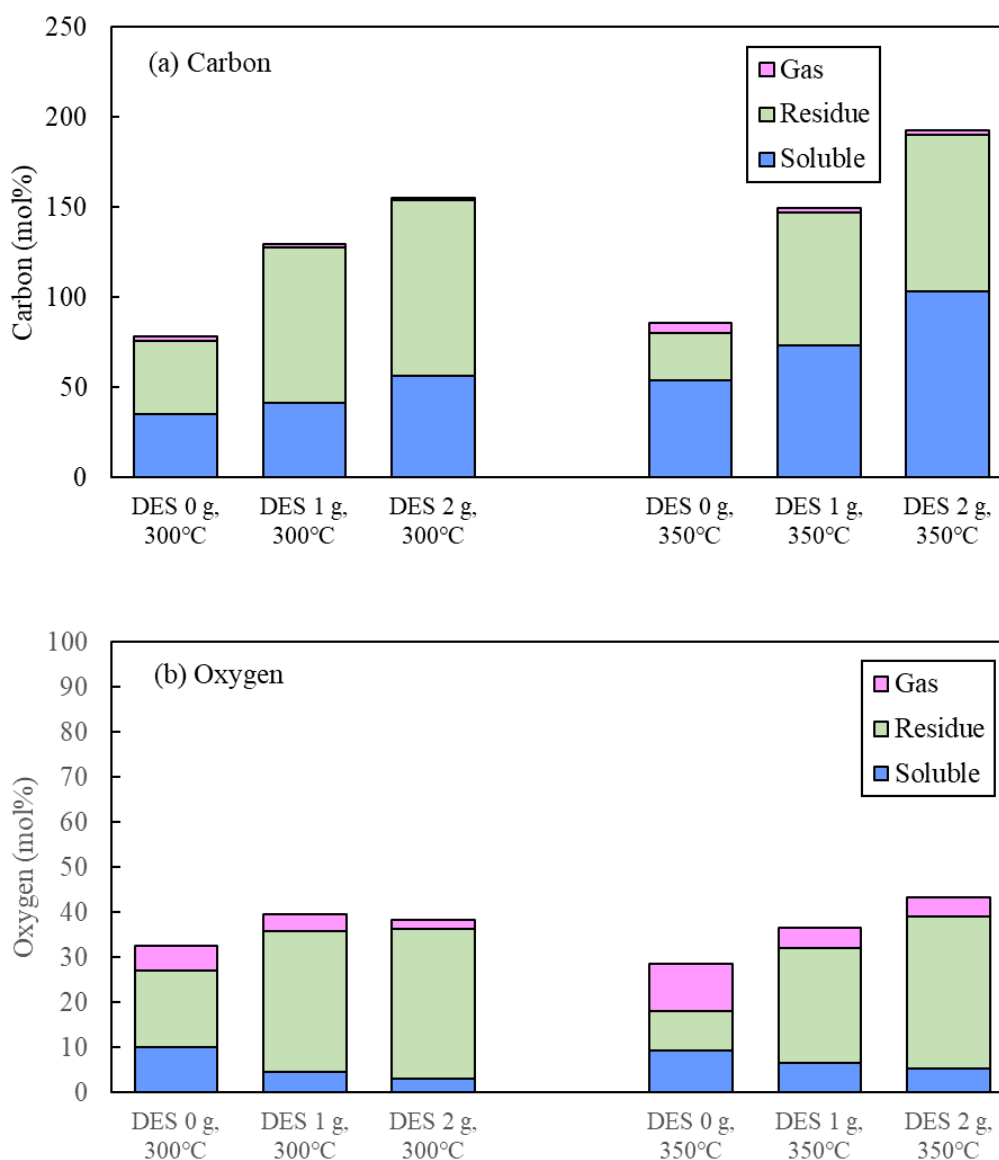


**Fig. 3.7** (a) Carbon and (b) oxygen balance in the degradative solvent extraction of WC.

### 3.3.2 Structural characterization of Soluble and Residue

The TG profiles of Soluble and Residue at 300-350 ℃ for 90 min and the results of TG differential (DTG) profiles are shown in Fig. 3.8 (a–d). The weight for WC began to decrease

at approximately 200 °C and remained 10 wt% at 900 °C (Fig. 3.8 (a)). Similar to AC, the thermal decomposition temperature of the Soluble for WC lowered with increasing the addition amount of DES. This suggested that the increase in the addition amount of DES promoted to produce the low-molecular-weight Soluble. However, it can be seen that the decomposition temperature of Soluble is the same as or slightly higher than that of WC. This result indicates that Soluble obtained from WC has almost the same molecular-weight component as WC. Unlike the case of AC, the Residue is found to be more difficult to decompose than the raw WC, indicating that the Residue has high-molecular-weight components.
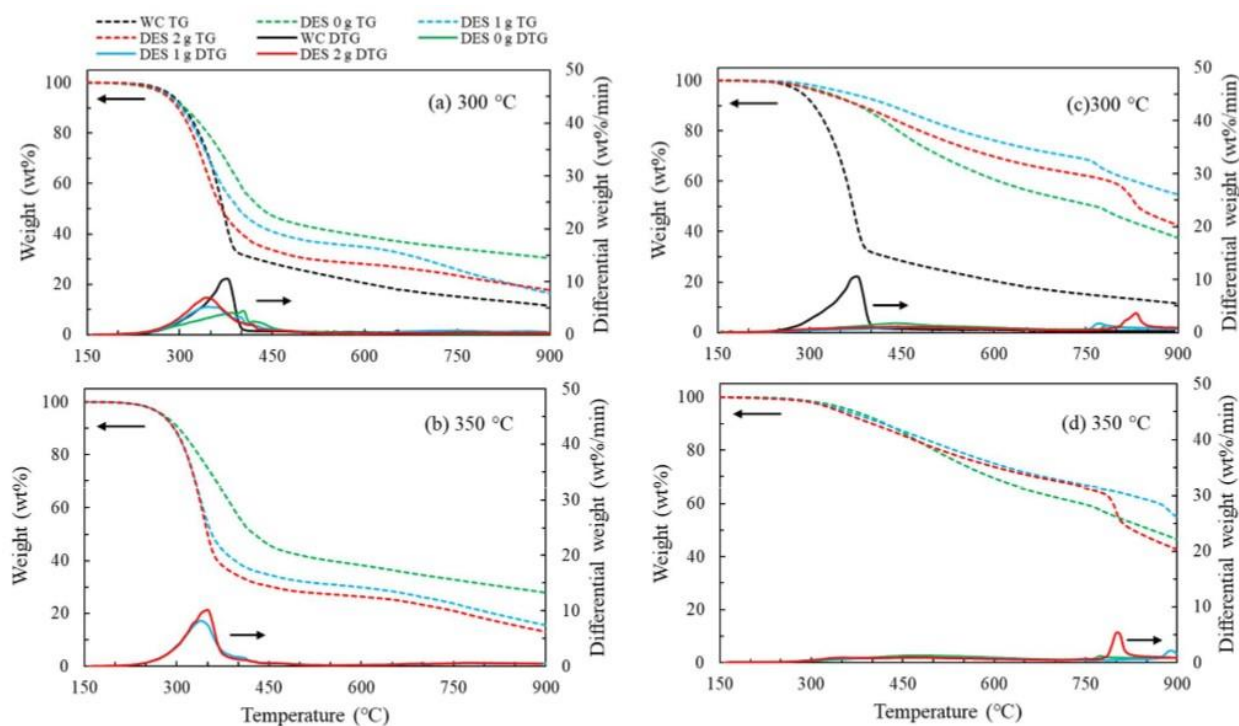


**Fig. 3.8** TG and DTG profiles of the Soluble obtained at (a) 300 °C and (b) 350 °C, and Residue at (c) 300 °C and (d) 350 °C for 90 min.

Figs. 3.9 and 3.10 show the FTIR spectra of Soluble and Residue at 300-350 °C for 90 min. In WC spectrum, the peaks at 3600-3400 cm$^{-1}$ and 1630 cm$^{-1}$ were attributed to O-H and C=O stretching vibrations, respectively. Additionally, the bands observed at 2930-2850 cm$^{-1}$ and 1500-1350 cm$^{-1}$ were attributed to aliphatic C-H stretching and bending vibrations, respectively. For Soluble, the peaks attributed to the aromatic and aliphatic C-H stretching vibrations were observed at 3100-3050 cm$^{-1}$ and 2950-2800 cm$^{-1}$. As was described in 2.3.6, the peaks observed at 1850-1550 cm$^{-1}$, 1450-1300 cm$^{-1}$, 1300-1000 cm$^{-1}$ and 830-750 cm$^{-1}$ were attributed to the C=O stretching, C-H bending, C-O stretching (derived from esters,

ethers, and alcohols) and aromatic nucleus C-H bending vibrations, respectively [12-18]. The aliphatic C-H stretching vibrations in the Soluble tended to decrease with increasing the addition amount of DES. Soluble is considered to be a substance containing relatively low-molecular-weight aromatic components. However, similar to the case of AC, there is no significant difference in the structure of Residue. Residue is considered to be a substance containing components that are more difficult to decompose than raw WC.
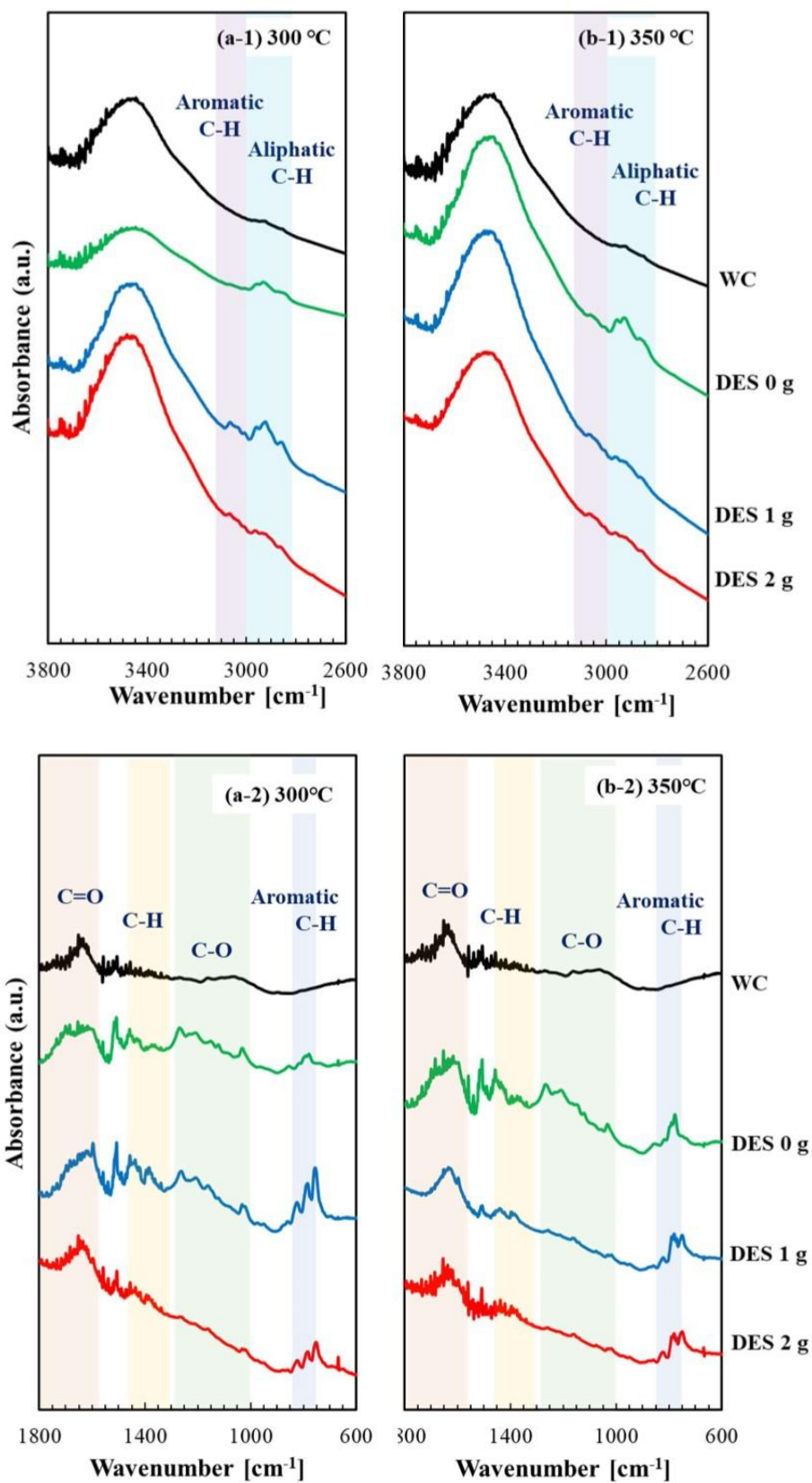
**Fig. 3.9** FT-IR spectra of Soluble obtained at (a) 300ºC and (b) 350ºC for 90 min.
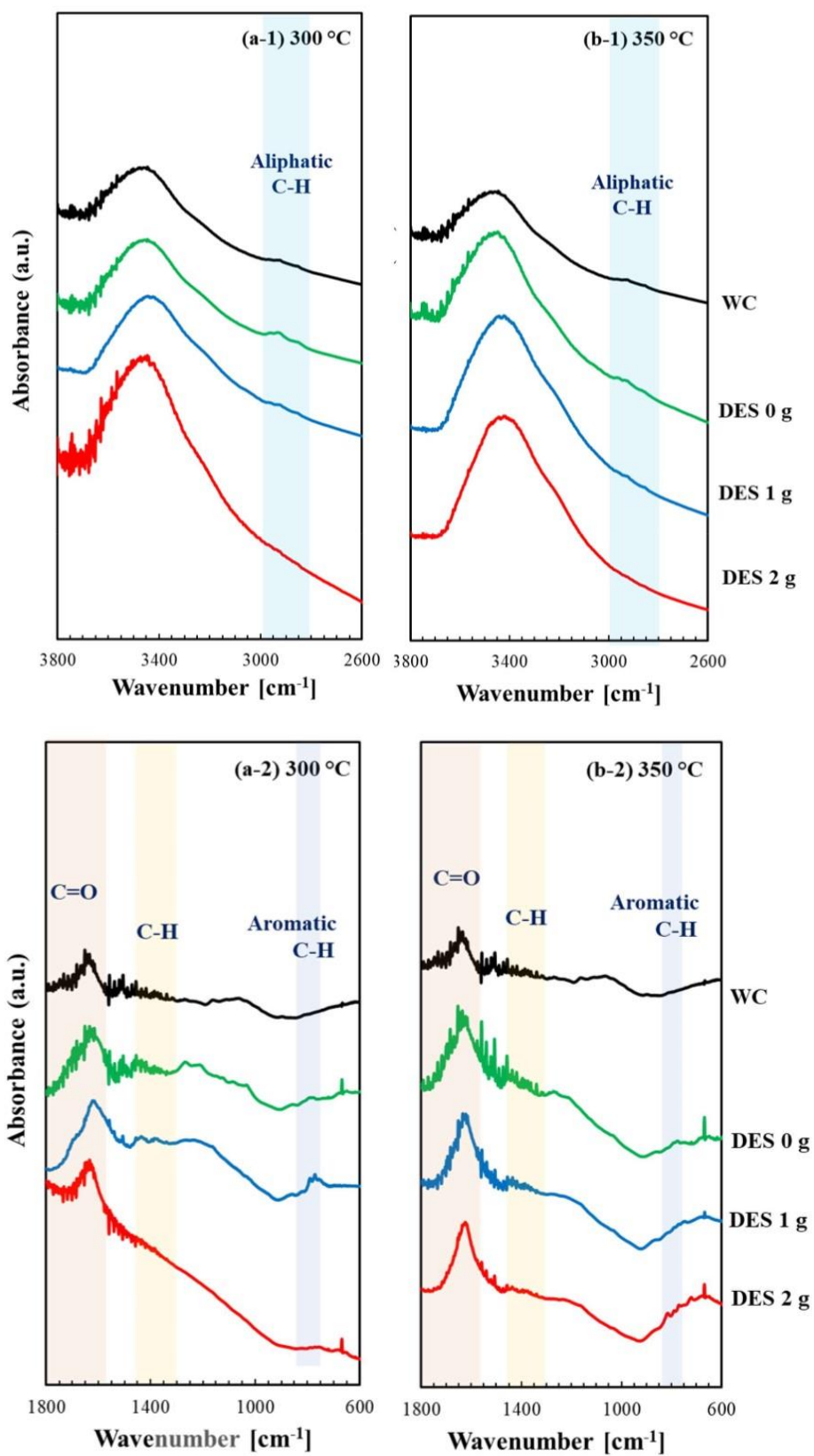
**Fig. 3.10** FT-IR spectra of Residue obtained at (a) 300ºC and (b) 350ºC for 90 min.

### 3.3.3 Calorific value of Soluble

The higher heating value (HHV) of raw WC is 18 MJ/kg, lower than AC. The HHV of Soluble is higher than the HHV of raw AC (Table 2.5). The same tendency of AC was verified in the degradative solvent extraction of WC. However, the HHV increased with increasing DES amount in all conditions of degradative solvent extraction of WC.

### 3.4 Conclusion

Degradative solvent extraction of woody chips (WC) as biomass using DES was performed in 1-MN.

➢ Similar to the case of AC, the Soluble yield increased and the oxygen content decreased with increasing reaction temperature and DES amount. The molecular weight of Soluble became large without DES, but small with DES. The aromaticity in the Soluble increased with DES;

➢ The dehydration took place by the degradative solvent extraction and the DES addition;

➢ The HHV of Soluble was higher than raw WC. On the other hand, the HHV of Soluble obtained by WC was lower than that of Soluble obtained by AC.

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**Chapter 4 Role of deep eutectic solvent on degradative solvent extraction of low-rank coal and woody biomass**

### 4.1 Introduction

The use of DES in the degradative solvent extraction has various advantages that include the higher extraction efficiency, less time duration, low solvent requirement as compared to conventional extraction methods with organic solvents [1]. As described in Chapters 2 and 3, it was found that the addition of DES in the degradative solvent extraction of low-rank coal (AC) and biomass (WC) increased the yield of Soluble with high carbon content. In addition, the decomposition temperature of the Soluble from WC was not significantly different from that of raw WC, whereas the Soluble from AC consisted of lower molecular weight components than raw AC. On the other hand, the Residues from AC and WC were decomposed at a higher temperature than raw AC and WC, suggesting that they became higher molecular weight components during the degradative solvent extraction.

Woody biomass is composed of cellulose, hemicellulose and lignin shown in Fig. 3.1. In order to clarify the role of DES in the degradative solvent extraction of WC, it would be very useful to discuss the effect of DES on the degradative solvent extraction of constituents such as cellulose, hemicellulose and lignin. In addition, as shown in Fig. 2.2, low-rank coal has a structure in which 1-3 condensed aromatic ring units are connected by aliphatic chains via covalent bonds or hydrogen bonds. The structure of this low-rank coal is very similar to that of lignin shown in Fig. 3.1. Therefore, a detailed investigation of the degradative solvent extraction of lignin may also help understand the degradative solvent extraction mechanism of low-rank coal.

The purpose of this chapter is to discuss the role of DES on the degradative solvent extraction of low-rank coal and woody biomass by comparing the results of the degradative solvent extraction of cellulose and lignin, with those of AC and WC.

### 4.2 Experimental

#### 4.2.1 DES preparation and samples

DES was prepared in the same way as already described in subsection 2.2.1.

The organosolv lignin (Sigma-Aldrich) and cellulose powder (Nacalai Tesque) were used in this chapter. Table 4.1 shows the elemental analysis and higher heating value of lignin and cellulose.

**Table 4.1** Ultimate analysis and higher heating value of lignin and cellulose.

| Sample | C | H | N | O (diff) | HHV [MJ/kg] |
|---|---|---|---|---|---|
| Lignin | 65.7 | 5.93 | 0.084 | 28.3 | 25.7 |
| Cellulose | 42.3 | 6.30 | 0.046 | 51.4 | 14.1 |

### 4.2.2 Degradative solvent extraction of lignin and cellulose

The degradative solvent extraction of lignin and cellulose was performed in the same way as subsection 2.2.3 and the equipment and methods used were the same as those for low-rank coal (Fig. 2.3). First, 5 g of sample (lignin or cellulose), 100 mL of 1-MN and 1.0-2.0 g of DES were added in custom autoclave. After the nitrogen purge three times, the pressure in the reactor was set to 0.2 MPa. The temperature was raised to 300-350 ℃, and the reaction was performed for 90 min with agitation at 300 rpm. The separation operation after extraction has the same as subsection 2.2.4. The yields of Soluble and Residue were calculated by the Eq. (4.1). The characterization of extracts was carried out by FT-IR, TG and elemental analysis.

$$\text{Yields (wt\%)} = \frac{\text{Recovery amount of Soluble or Residue}}{\text{Amount of sample (5 g)} + \text{Amount of DES}} \times 100 \qquad (4.1)$$

### 4.3 Results and discussion

### 4.3.1 Degradative solvent extraction of lignin and AC

The product yields in the degradative solvent extraction of lignin and AC with and without DES are summarized in Fig. 4.1 and Tables 4.2, 4.3. The results of AC were already shown in Tables 2.4 and 2.5. The total yield of Soluble and Residue in Fig. 4.1 (a, b) did not reach 100%, and this shortfall is considered to be a liquid product such as water. In the absence of DES, the yield of Soluble from lignin at 300 °C was 49 wt%, which was higher than the yield of Soluble from AC of 12 wt%. As shown in Fig. 3.1, this is considered to be because lignin contains a large amount of aromatic components which is easily extracted into 1-MN. On the other hand, AC has few aromatic components than that of lignin (see Fig. 2.2). When the reaction temperature was raised to 350 °C, the yields of Soluble from lignin and AC slightly increased to 54 and 22 wt%, respectively. The effect of DES addition was significantly different between lignin and AC: the yield of Soluble from lignin decreased to 26 wt% (300 °C) and 45 wt% (350 °C), whereas the yield of Soluble from AC increased to 20 wt% (300 °C) and 39 wt% (350 °C). The yields of Residue from lignin increased by DES addition, while the yields of Residue from
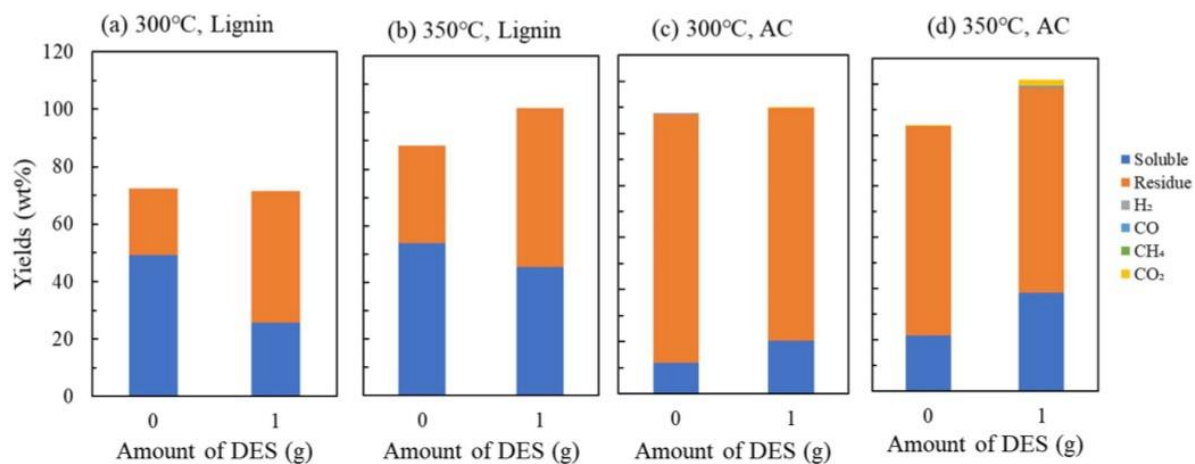
AC decreased by DES addition.



**Fig. 4.1** Product yield distribution of degradative solvent extraction of lignin at (a) 300 ℃ and (b) 350 ℃, and AC at (c) 300 ℃ and (d) 350 ℃ with and without DES for 90 min.

**Table 4.2** Yield and ultimate analysis of Soluble obtained by the degradative solvent extraction of lignin.

| Temperature (°C) | Time (min) | DES (g) | Yield (wt%) | Ultimate Analysis (wt%, d.b.) | | | | HHV (MJ/kg) |
|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | O (diff.)* | |
| 300 | 90 | 0.0 | 49.2 | 73.1 | 6.2 | 0.0 | 20.7 | 30.0 |
| 300 | 90 | 1.0 | 25.8 | 80.7 | 6.3 | 0.1 | 12.9 | 34.1 |
| 350 | 90 | 0.0 | 54.0 | 79.2 | 6.4 | 0.0 | 14.4 | 33.4 |
| 350 | 90 | 1.0 | 45.3 | 91.4 | 6.7 | 0.0 | 1.9 | 40.3 |

* "O (diff)" indicates oxygen amount because there is no ash in Soluble.

**Table 4.3** Yield and ultimate analysis of Residue obtained by the degradative solvent extraction of lignin.

| Temperature (°C) | Time (min) | DES (g) | Yield (wt%) | Ultimate Analysis (wt%, d.b.) | | | | HHV (MJ/kg) |
|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | O (diff.)** | |
| 300 | 90 | 0.0 | 23.2 | 71.4 | 4.8 | 0.1 | 23.6 | 26.9 |
| 300 | 90 | 1.0 | 45.6 | 70.6 | 3.7 | 0.7 | 25.1 | 24.7 |
| 350 | 90 | 0.0 | 34.2 | 77.6 | 4.6 | 0.2 | 17.6 | 29.7 |
| 350 | 90 | 1.0 | 56.3 | 70.1 | 3.0 | 0.7 | 26.3 | 23.3 |

** "Other (diff)" indicates that it mainly composed of oxygen and ash.

Fig. 4.2 shows the carbon and oxygen balance in the degradative solvent extraction of lignin

and AC. As described above, since the total carbon content exceeds 100 mol%, only the oxygen balance was considered in this study. The oxygen content in Soluble from lignin decreased with increasing in the reaction temperature and the addition of DES, while the oxygen content in Residue from lignin did not change except for 1 g of DES at 300 °C. For AC, the oxygen content in Soluble was almost the same as approximately 5 mol%, while that in Residue decreased with increasing in the reaction temperature and the addition of DES.
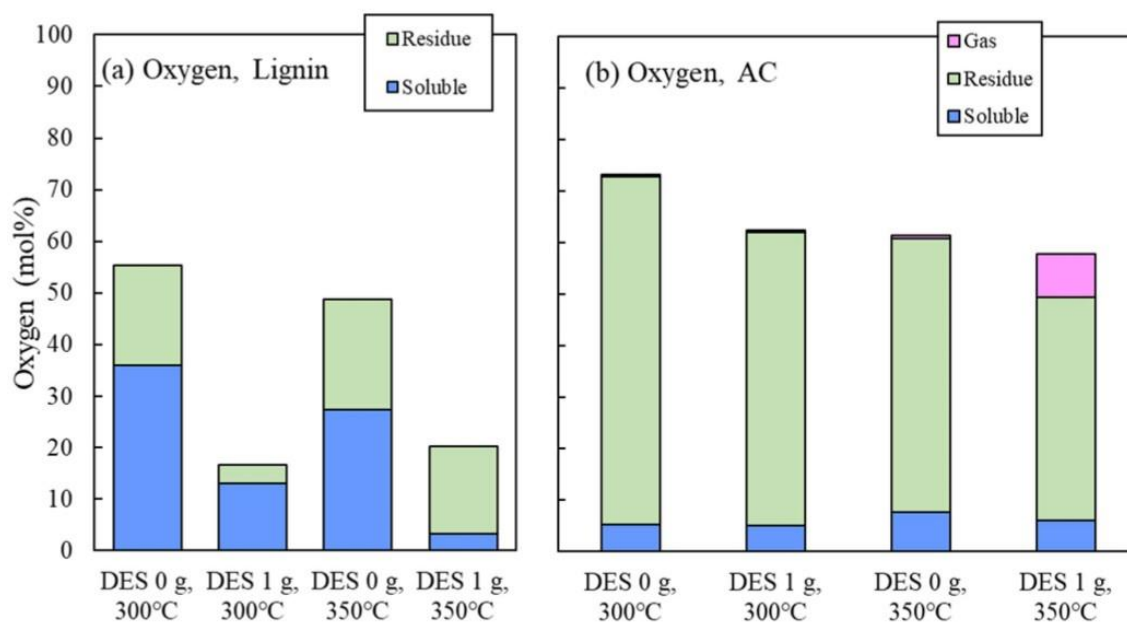


**Fig. 4.2** Oxygen balance in the degradative solvent extraction of (a) lignin and (b) AC.

The elemental compositions of Soluble obtained from lignin and AC at different reaction temperatures and DES contents were investigated. Fig. 4.3 shows the plot of the carbon and oxygen contents as a function of the Soluble yield. This figure also shows the results of AC and other studies [2,3]. The carbon contents of lignin and AC were 65.7 wt% and 67.5 wt%, and oxygen contents of lignin and AC were 28.3wt% and 26.1 wt%, respectively. In the Soluble obtained by the degradative solvent extraction of AC, with increasing Soluble yield, the carbon content increased from 80 wt% to 89 wt%, and the oxygen content decreased from 12 wt% to 4 wt%. The Soluble yield and elemental compositions for lignin was not similar to those for AC. Even if the Soluble yield was high, a large amount of oxygen remained in the Soluble. This suggests that lignin contains oxygen that is difficult to remove.
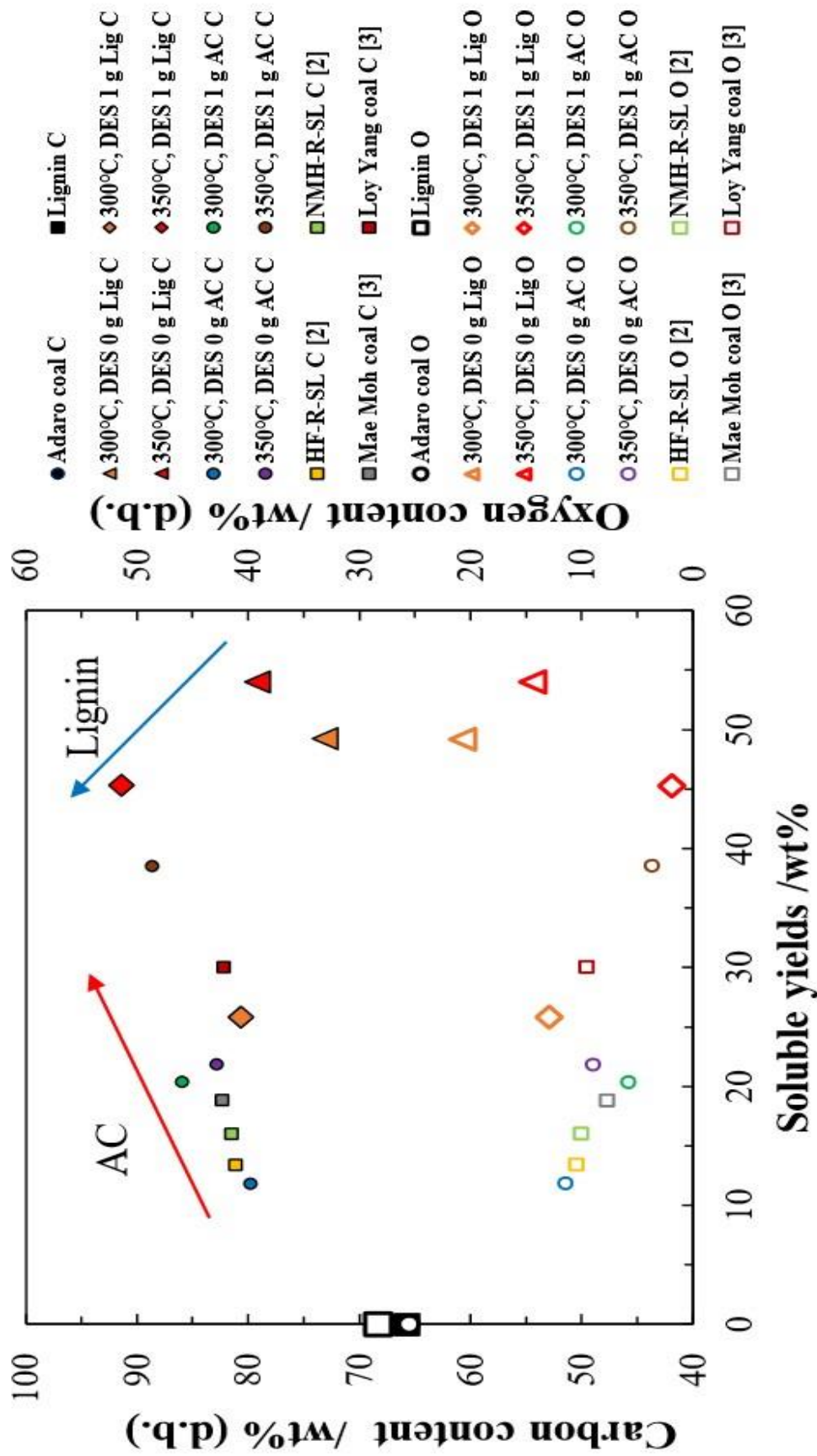
**Fig. 4.3** Relation between carbon/oxygen contents in Soluble and Soluble yields. This figure also shows the results of Lignin, AC and other studies [2, 3].

Fig. 4.4 shows the relationship between H/C and O/C atomic ratios calculated from the elemental analysis of Soluble obtained by degradative solvent extraction of lignin and AC. In this figure, the H/C and O/C of Soluble from other samples [2-7] are also shown. The H/C of lignin and AC were 1.08 and 0.96, and O/C of lignin and cellulose were 0.32 and 0.29, respectively; both H/C and O/C of lignin were very similar to those of AC. The slight decrease in H/C and O/C of lignin by degradative solvent extraction may be caused by the evolution of a small amount of $CO_2$ and $H_2O$. This figure also shows that the dehydration progressed with increasing DES amount, which is consistent with the result of oxygen balance (Fig. 4.2). As already described in chapter 2, in the case of AC, dehydration and decarboxylation were promoted with increasing DES amount.
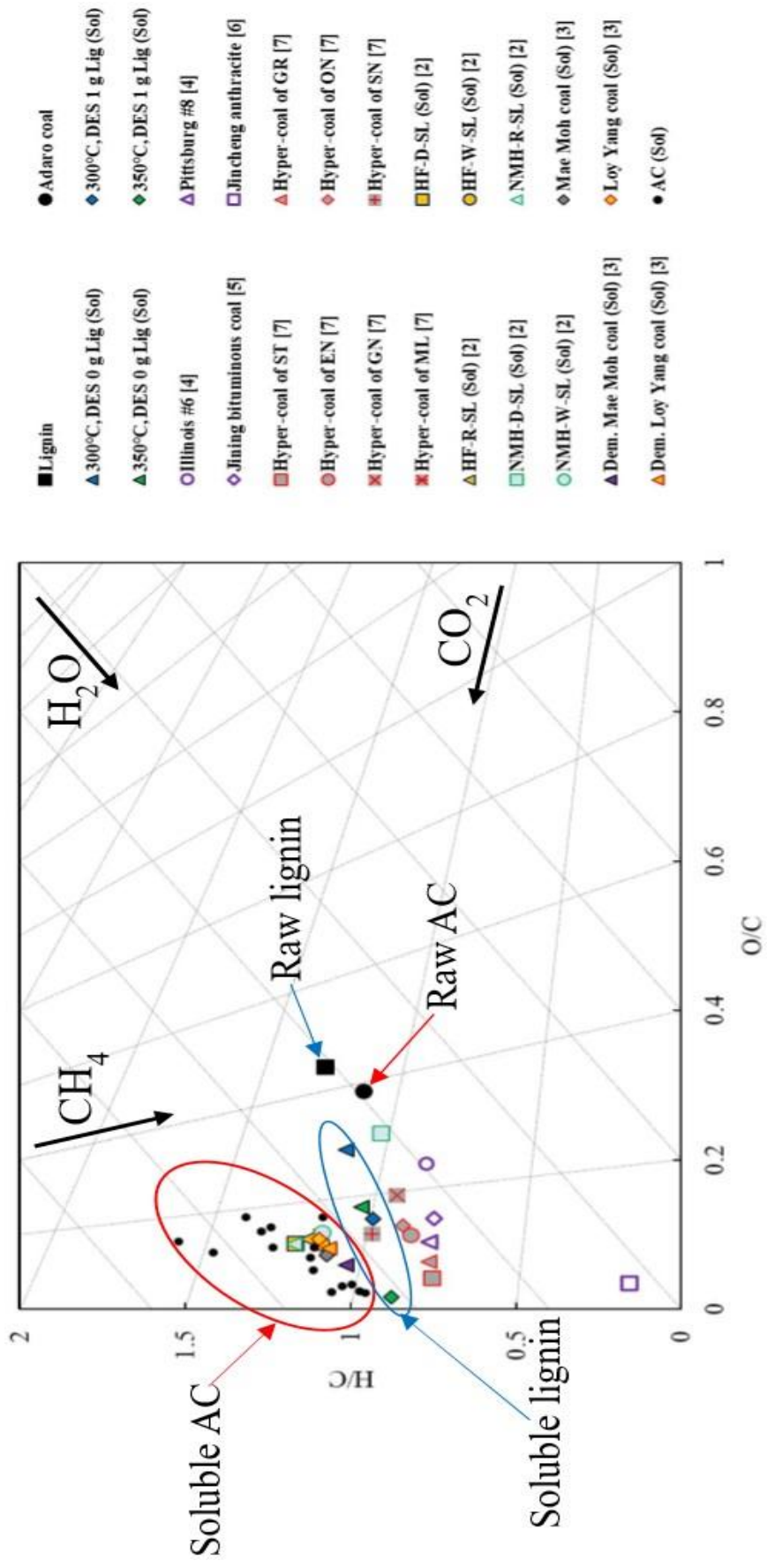
**Fig. 4.4** Relationship between H/C and O/C atomic ratios for raw samples (lignin, AC), Soluble and other samples [2-7].

**4.3.2 Structural characterization of Soluble and Residue from lignin and AC**

Fig. 4.5 and 4.6 shows the TG and DTG profiles of Soluble and Residue obtained from lignin and AC. Lignin began to decompose at around 200 °C and lost around 60 wt% of its weight by around 900 °C. The decomposition temperature of Soluble obtained in the presence of DES was lower than that of raw lignin, indicating that the molecular weight of Soluble became lower. TG and DTG profiles of Soluble obtained by degradative solvent extraction of lignin were very similar to those of AC On the other hand, the molecular weight of Residue from lignin was higher than that of raw lignin due to the shift of the decomposition temperature to the higher temperatures. The TG profiles of Residue obtained by degradative solvent extraction of AC are almost the same as raw AC. As referred to in chapter 2, this may be because the structure of Residue does not differ much from that of the raw AC, although Residue contains a large amount of oxygen.
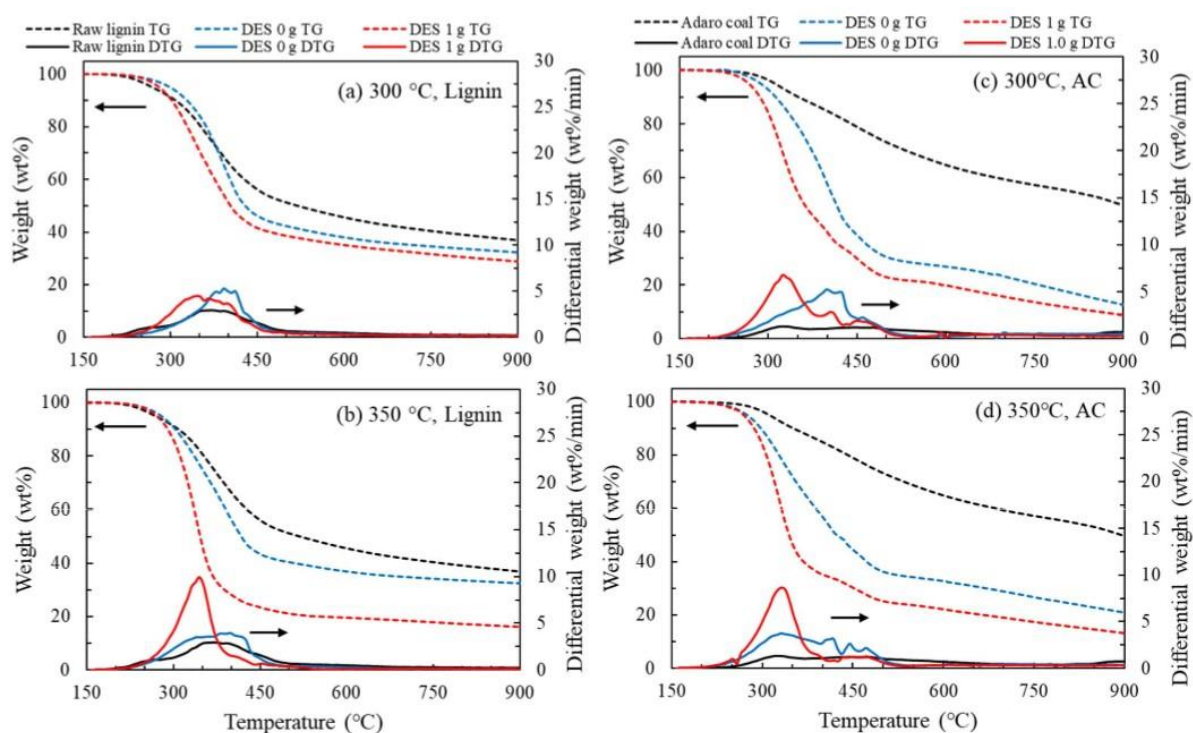


**Fig. 4.5** TG and DTG profiles of Soluble obtained by lignin at (a) 300 ℃ and (b) 350 ℃, and Soluble obtained by AC at (c) 300 ℃ and (d) 350 ℃.
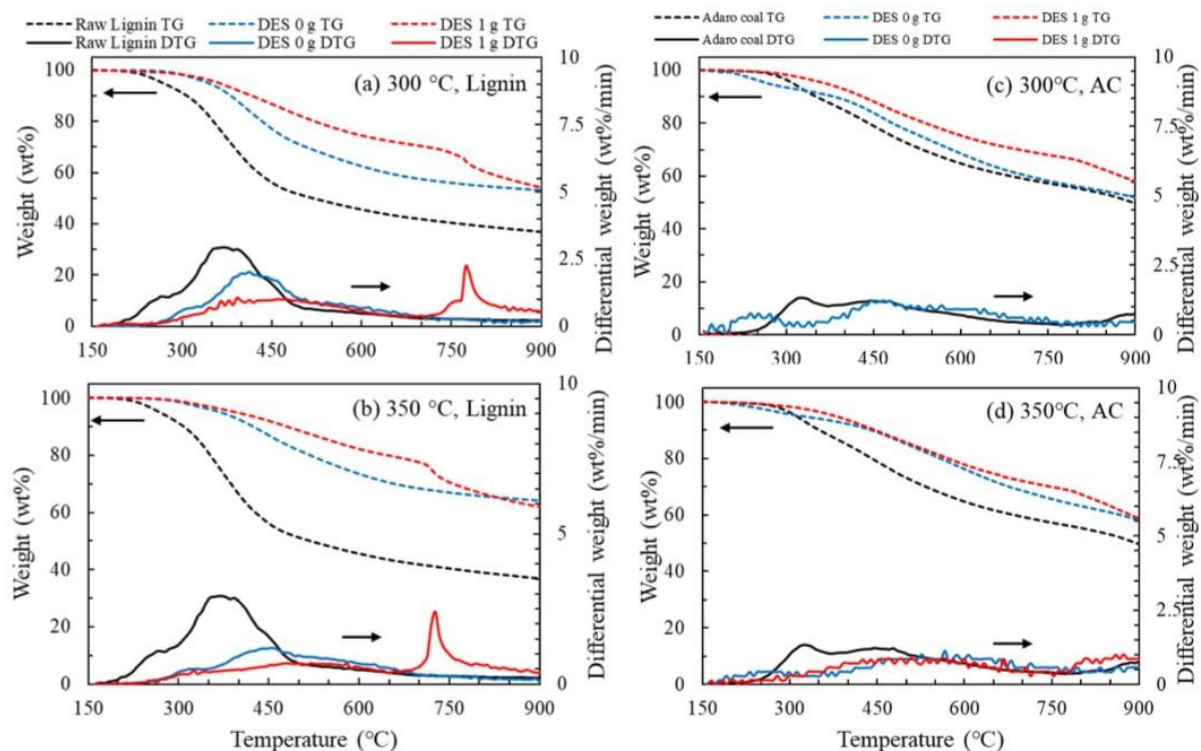
**Fig. 4.6** TG and DTG profiles of Residue obtained by lignin at (a) 300 ℃ and (b) 350 ℃, and Residue obtained by AC at (c) 300 ℃ and (d) 350 ℃.

Fig. 4.7 shows FT-IR spectra of Soluble obtained from lignin and AC, respectively. Raw lignin had large absorption peaks of aliphatic C-H stretching, C=O stretching and C-O stretching vibrations, whereas these absorption peaks decreased and aromatic C-H stretching vibrations were conspicuous in the Soluble from lignin. Especially when the degradative solvent extraction was carried out with 1g of DES, the aromatic C-H peaks appeared remarkably. These results indicate that the aromatization proceeded during the degradative solvent extraction of lignin and AC and the aromatic components were extracted as Soluble.
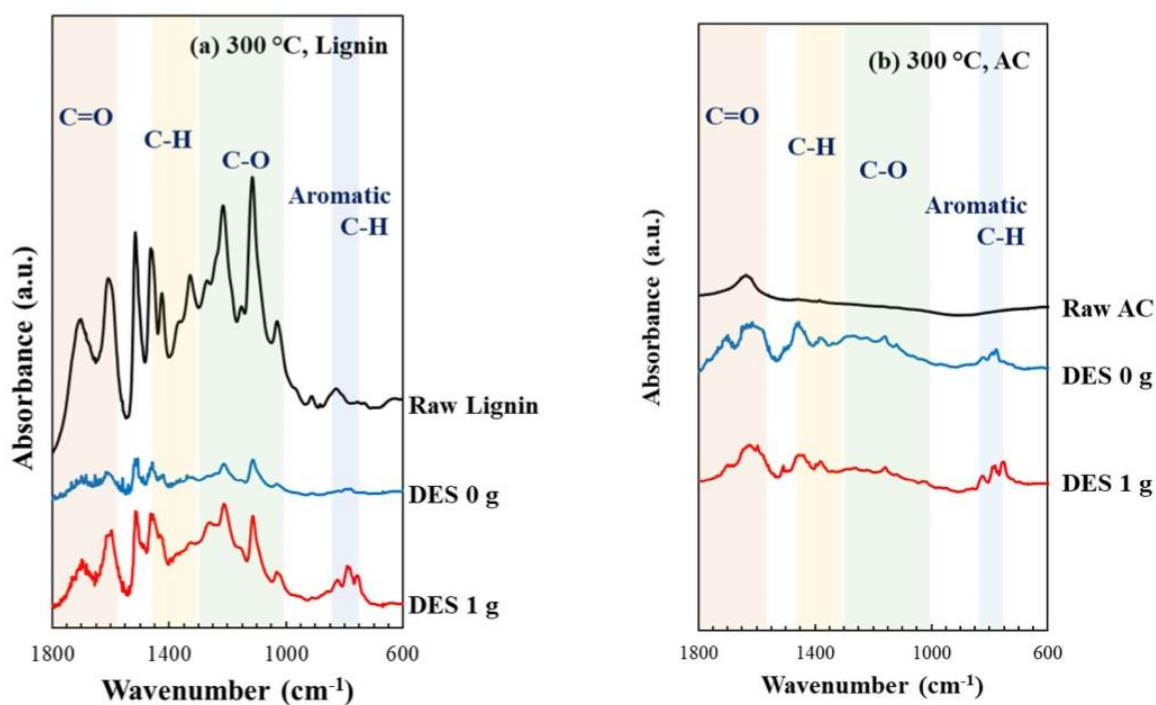
**Fig. 4.7** FT-IR spectra of Soluble obtained from (a) lignin and (b) AC at 300 ℃ for 90 min.

### 4.3.3 Role of DES for degradative solvent extraction of lignin

The Main results of the degradative solvent extraction of lignin are summarized as follows:

➢ The Soluble yield of lignin decreased with increasing DES;

➢ Oxygen content in Soluble decreased by dehydration and aromatization was promoted with DES;

➢ Molecular weight of Soluble slightly decreased.

Previous studies describe that the degradative solvent extraction method is able to upgrade low-rank coal and biomass through the selective removal of oxygen functional groups in the form of $H_2O$ or $CO_2$ [8,9]. The Soluble fraction obtained in this way has a high carbon content, a low oxygen content, and is almost completely free from ash. The main reactions in the degradative solvent extraction process have been identified as thermal extraction, deoxygenation, decarboxylation, and aromatization. To identify structural components of products and to understand the reaction process of degradative solvent extraction, it is necessary to analyze the composition of the solid and gas states of the initial reactants and final products. However, since the degradative solvent extraction process involves thermal decomposition, the reaction process and products are complex. Fig. 4.8 shows the schematic postulated for the reaction process of the degradative solvent extraction of rice straw [8]. The

authors described that the degradative solvent extraction process was divided by temperature range into three stages: From 200 to 300 °C, from 300 to 350 °C (0 min), and during the prolonged residence time of 60 min at 350 °C. In the first stage, the hydrogen bonds were cleaved by dehydration and aromatic compounds started to appear. In the second stage, $H_2O$, CO and $CO_2$ were evolved by dehydration and decarboxylation and the aromatization reaction proceeded. In the final stage, the further aromatization and dehydration reactions occurred. This indicates that intramolecular reactions were the predominant mechanism for dehydration in the degradative solvent extraction of RS. This also signifies that polymerization of RS during the degradative solvent extraction process was suppressed and that the final product is composed of smaller molecular compounds.
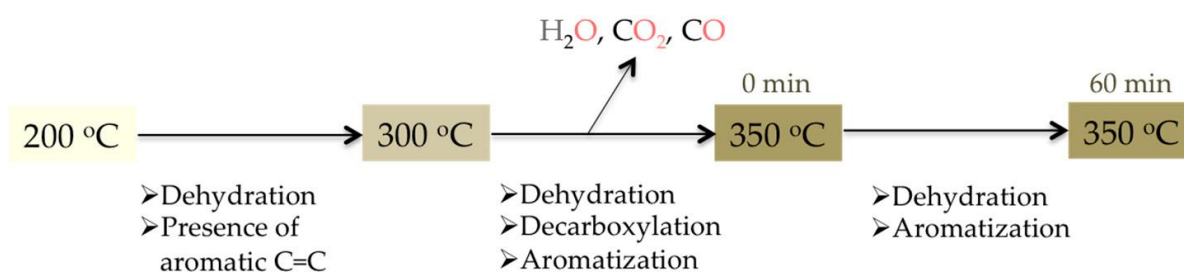


**Fig. 4.8** Schematic postulated for the reaction process of the degradative solvent extraction of rice straw [8].

Zhu et al. proposed the conversion process of the degradative solvent extraction of biomass (sawdust). The process was divided into two stages. The first stage took place at heating up stage from 250 to 350 °C and the beginning of the isothermal stage at 350 °C. At first stage, the thermal extraction, deoxygenation and aromatization reactions of the raw biomass occurred significantly. The main product was Deposit, which is dissolved in 1-MN at the extraction temperature but is deposited at the room temperature. At the second stage, the Deposit was further deoxygenated and converted into Soluble. In this stage, the Deposit underwent complex reactions, such as the cleavages of oxygen containing cross-links and aromatization reactions. The oxygen was mainly removed as $H_2O$ at the second stage. During the whole extraction process, the extracts (Soluble and Deposit) were well dispersed in the solvent. The reactions in this process were mainly intramolecular. [10].

In the case of lignin, the yield of Soluble increases with increasing temperature, and the Soluble with low oxygen content and high aromaticity are obtained. And the molecular weight of this Soluble became lower. In addition, the yield of Residue and its molecular weight

increased. On the other hand, the addition of DES decreased the Soluble yield. From these results, the following reaction mechanism (Fig. 4.9) is proposed. Since lignin originally contains many aromatic components, the Soluble yield is high. Degradative solvent extraction without DES cleaves hydrogen bonds and hydroxy groups, so that the low-molecular-weight components with a large amount of oxygen are eluted as Soluble. At the same time, the small fragments are released as $CO_2$ and $H_2O$. The addition of DES in the degradative solvent extraction promotes to cleave the ether bonds as well as some bonds with low binding energy, resulting in the yields of Soluble containing a small amount of oxygen increases. On the other hand, Residue may be combined with another Residue to form a macromolecule. This is considered to be the reason why the molecular weight of Residue increased.
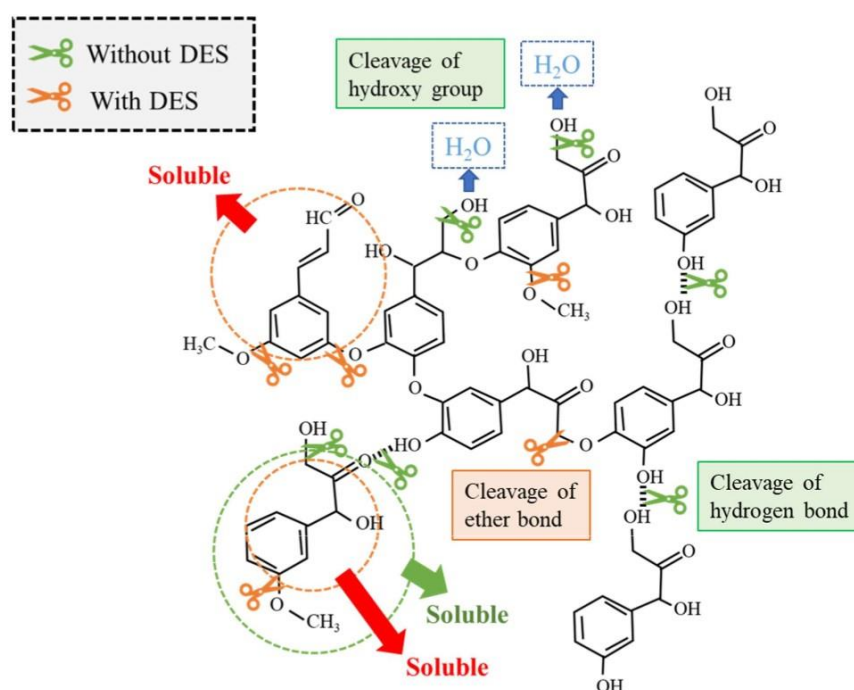


**Fig. 4.9** Proposed mechanism of degradative solvent extraction for lignin.

### 4.3.4 Role of DES for degradative solvent extraction of low-rank coal

The Main results of the degradative solvent extraction of low-rank coal are summarized as follows:

➢ The Soluble yield of AC increased with increasing DES amount;

➢ The amount of oxygen in Soluble was almost the same independent of the experimental conditions, but decarboxylation, dehydration and aromatization progressed with DES added;

➢ Molecular weight of Soluble decreased.

These effects are very similar to the effects of DES on lignin. Fig. 4.10 shows the proposed mechanism for the degradative solvent extraction of low-rank coal. Without DES, the hydrogen bonds and the carboxy groups were cleaved by degradative solvent extraction to form Soluble and $CO_2$, respectively. With DES, cleavage of the ether bonds together with decarboxylation and dehydration took place during degradative solvent extraction. On the other hand, the high-molecular-weight components together with oxygen remains in the Residue.
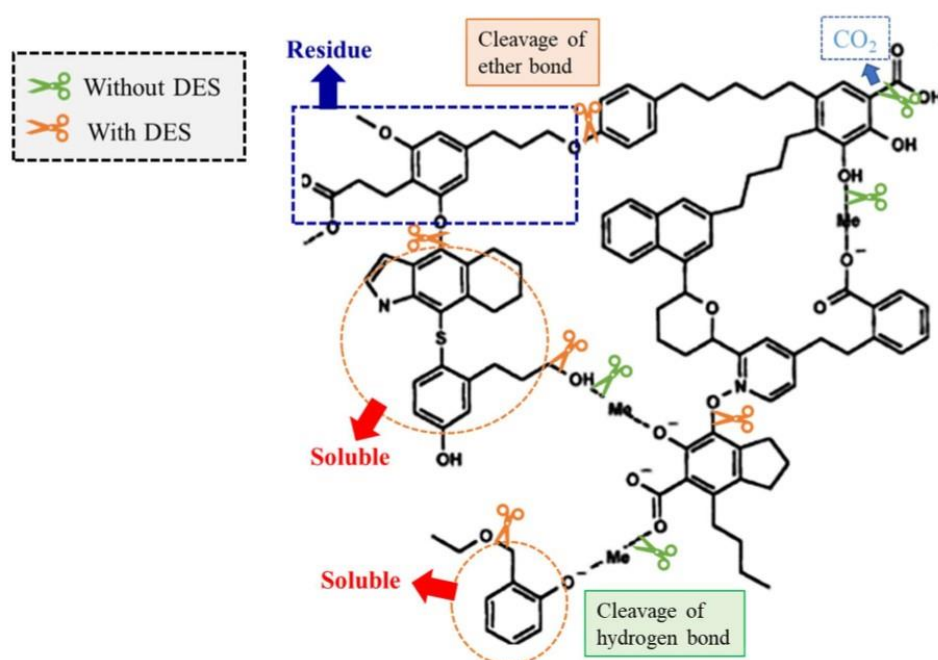


**Fig. 4.10** Proposed mechanism of degradative solvent extraction for low-rank coal.

### 4.3.5 Degradative solvent extraction of cellulose and WC

The product yields in the degradative solvent extraction of cellulose and WC with and without DES are summarized in Fig. 4.11 and Tables 4.4 and 4.5. The results of WC were already shown in Tables 3.4 and 3.5. The total yield of Soluble and Residue in Fig. 4.11 did not reach 100%, and this shortfall is considered to be a liquid product such as water. In the absence of DES, the yield of Soluble from cellulose at 300 °C was 18 wt%, which was lower than the yield of Soluble from WC of 23 wt%. As shown in Fig. 3.1, cellulose has no aromatic components, but the presence of components soluble in 1-MN means that aromatic components were produced during the degradative solvent extraction. When the reaction temperature was raised to 350 °C, the yields of Soluble from cellulose and WC slightly increased to 24 and 33

wt%, respectively. The effect of DES addition on degradative solvent extraction of cellulose was similar to that of WC. The Soluble yields of cellulose and WC increased with increasing the DES amount and the reaction temperature. The yields of Residue from cellulose and WC increased by the reaction temperature and the DES addition.
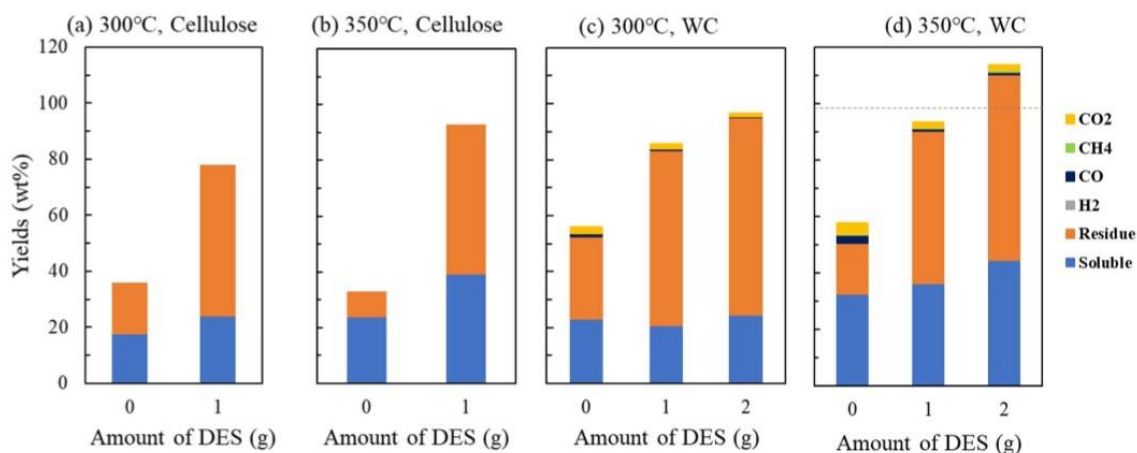


**Fig. 4.11** Product yield distribution of degradative solvent extraction of cellulose at (a) 300 ℃ and (b) 350 ℃, and WC at (c) 300 ℃ and (d) 350 ℃ with and without DES for 90 min.

**Table 4.4** Yield and ultimate analysis of Soluble obtained by the degradative solvent extraction of lignin and cellulose.

| Temperature (°C) | Time (min) | DES (g) | Yield (wt%) | Ultimate Analysis (wt%, d.b.) | | | | HHV (MJ/kg) |
|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | O (diff.)* | |
| 300 | 90 | 0.0 | 17.6 | 77.4 | 5.8 | -0.1 | 16.9 | 31.5 |
| 300 | 90 | 1.0 | 23.8 | 81.9 | 5.8 | 0.5 | 11.8 | 34.0 |
| 350 | 90 | 0.0 | 23.8 | 83.7 | 6.3 | -0.1 | 10.1 | 35.6 |
| 350 | 90 | 1.0 | 39.0 | 90.8 | 6.3 | 0.2 | 2.8 | 39.2 |

* "O (diff)" indicates oxygen amount because there is no ash in Soluble.

**Table 4.5** Yield and ultimate analysis of Residue obtained by the degradative solvent extraction of cellulose.

| Temperature (°C) | Time (min) | DES (g) | Yield (wt%) | Ultimate Analysis (wt%, d.b.) | | | | HHV (MJ/kg) |
|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | O (diff.)** | |
| 300 | 90 | 0.0 | 18.2 | 68.0 | 4.5 | 0.1 | 27.5 | 24.5 |
| 300 | 90 | 1.0 | 54.1 | 58.2 | 2.9 | 0.4 | 38.5 | 16.9 |
| 350 | 90 | 0.0 | 9.2 | 72.9 | 3.8 | 0.1 | 23.2 | 26.0 |
| 350 | 90 | 1.0 | 53.8 | 62.2 | 3.0 | 0.4 | 34.3 | 19.1 |

** "Other (diff)" indicates that it mainly composed of oxygen and ash.

Fig. 4.12 shows the oxygen balance in the degradative solvent extraction of cellulose and WC. The amount of oxygen present in the Soluble obtained by cellulose and WC slightly decreased with increasing the reaction temperature and the DES added, while that in Residue showed no systematic changes.
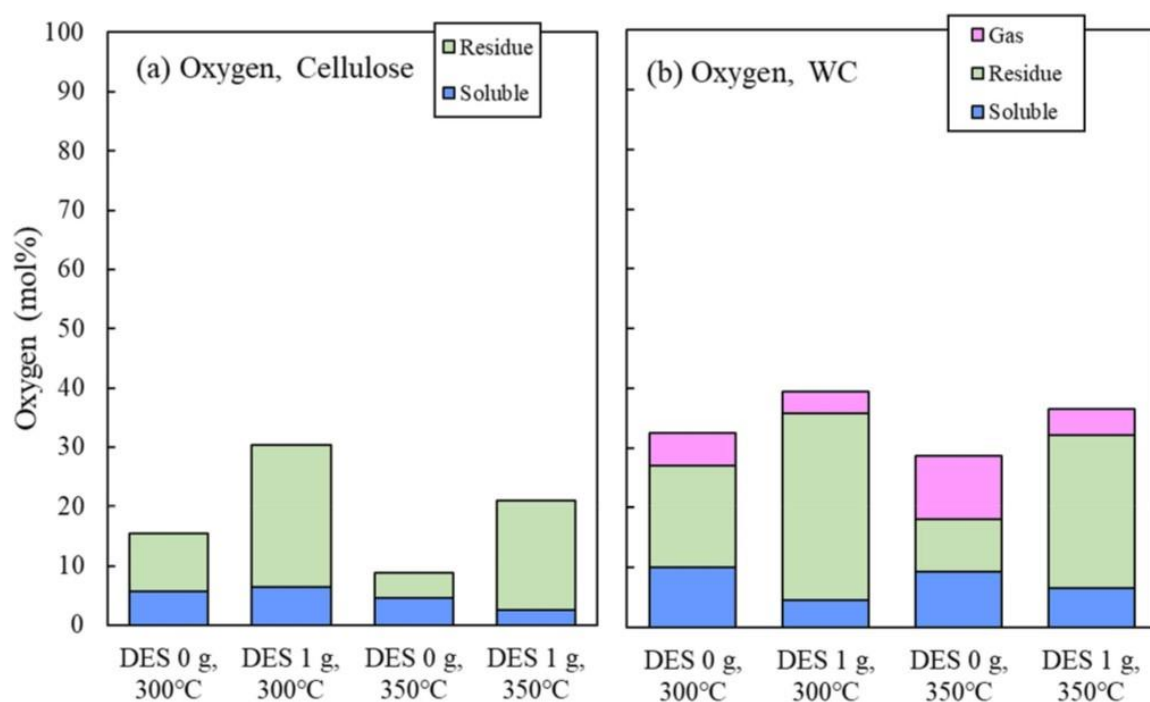


**Fig. 4.12** Oxygen balance in the degradative solvent extraction of (a) cellulose and (b) WC.

The elemental compositions of Soluble obtained from cellulose and WC at different reaction temperatures and DES contents were investigated. Fig. 4.13 shows the plot of the carbon and oxygen contents as a function of the Soluble yield. This figure also shows the results of other studies [2,3]. The carbon contents of cellulose and WC were 42.3wt% and 49.1 wt%, and oxygen contents of cellulose and WC were 51.4 wt% and 44.0 wt%, respectively. In the Soluble obtained by the degradative solvent extraction of cellulose, with increasing Soluble yield, the carbon content increased from 77 wt% to 91 wt%, and the oxygen content decreased from 17 wt% to 3 wt%. The relationship between Soluble yield and elemental compositions for cellulose was similar to that for WC.
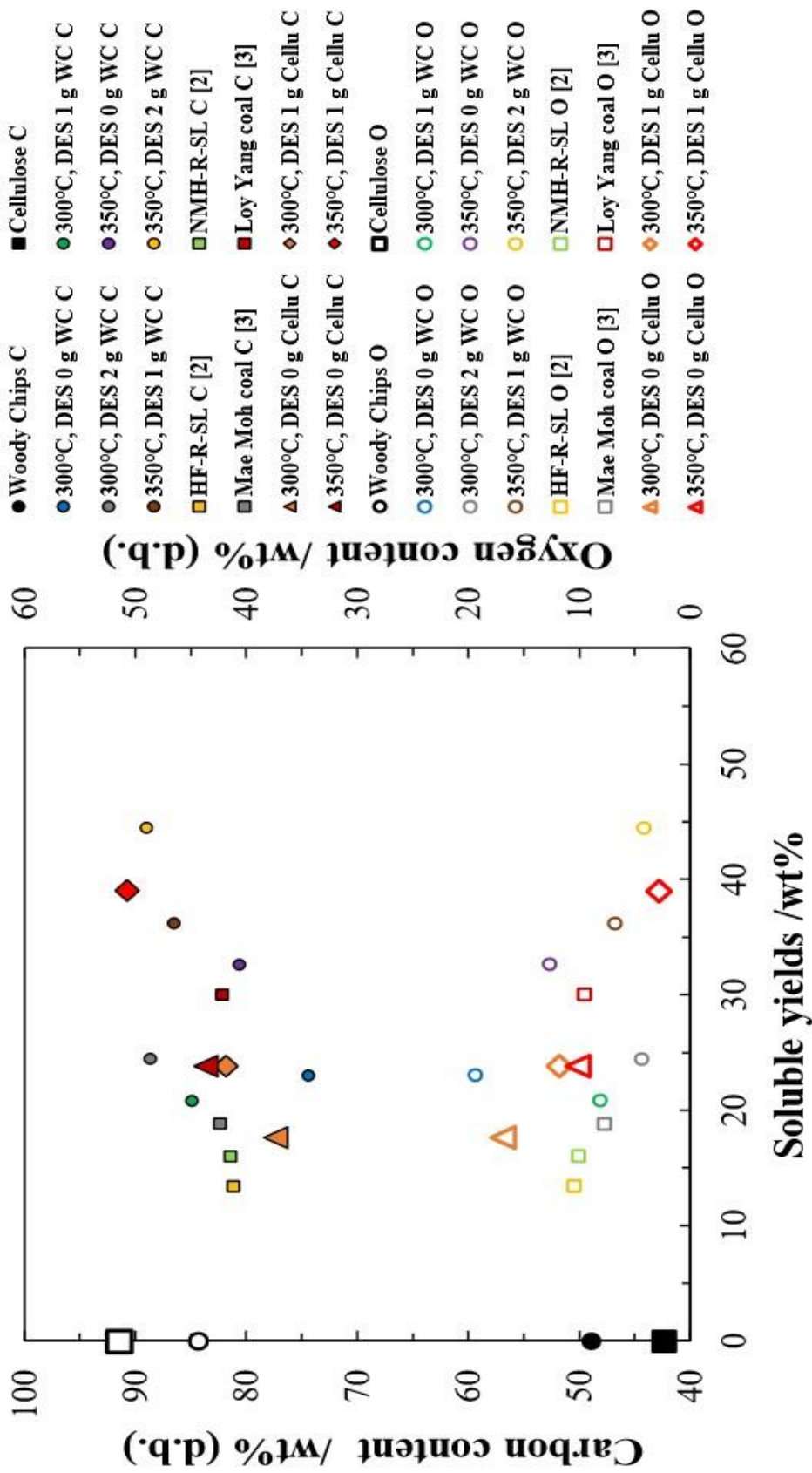
**Fig. 4.13** Relation between carbon/oxygen contents in Soluble and Soluble yields. This figure also shows the results of cellulose, WC and other studies [2, 3].

Fig. 4.14 shows the relationship between H/C and O/C atomic ratios calculated from the elemental analysis of Soluble obtained by cellulose and WC. In this figure, the H/C and O/C of Soluble from other samples [2-7] are also shown. The H/C of cellulose and WC were 1.77 and 1.61, and O/C of cellulose and WC were 0.91 and 0.68, respectively; both H/C and O/C of cellulose were higher than those of WC. In Soluble from cellulose, H/C and O/C decreased significantly with increasing reaction temperature and DES content, indicating that a large amount of water produced from cellulose by the degradative solvent extraction.
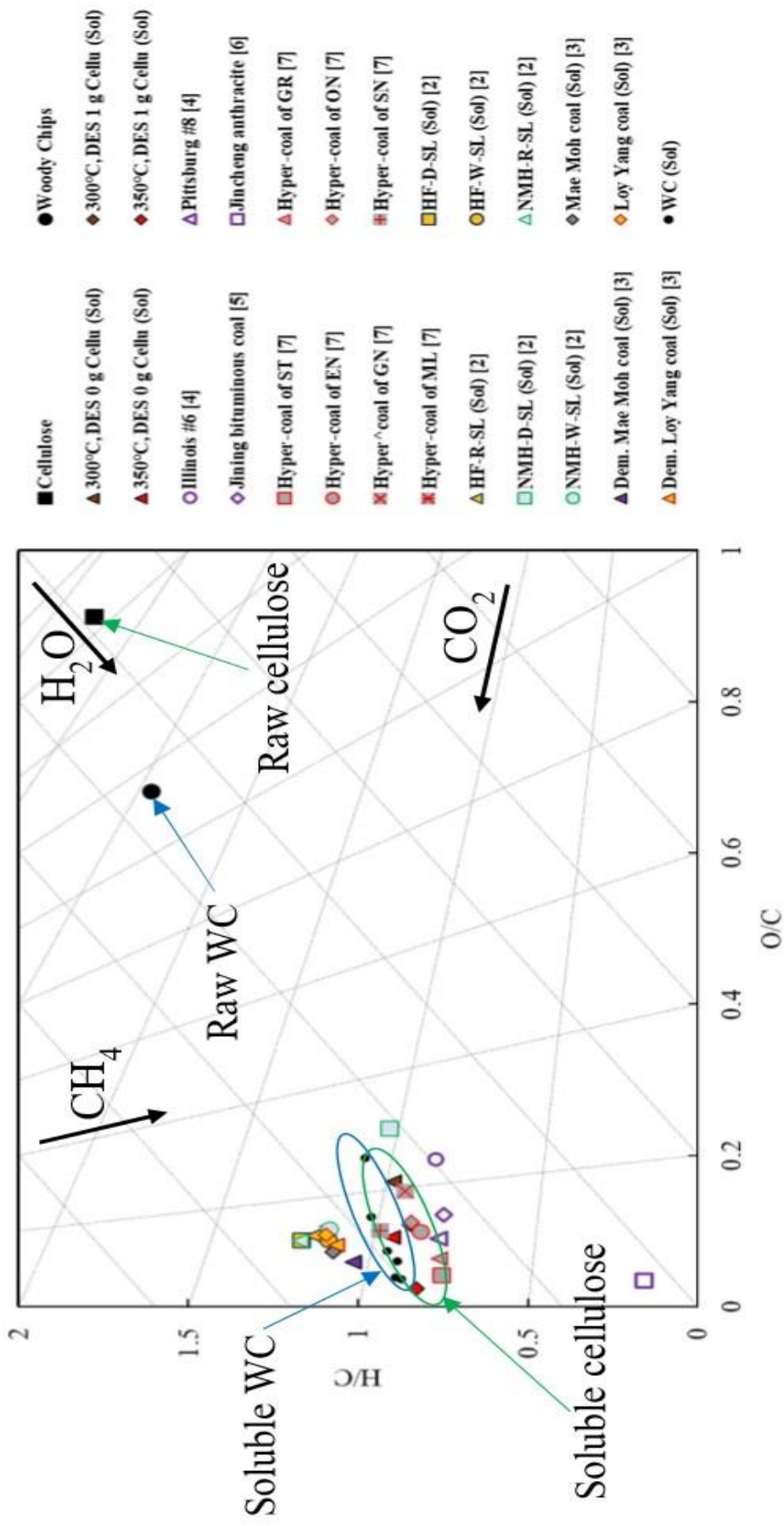
**Fig. 4.14** Relationship between H/C and O/C atomic ratios for raw samples (cellulose and WC), Soluble and other samples [2-7].

**4.3.6 Structural characterization of Soluble and Residue from cellulose and WC**

Fig. 4.15 and 4.16 shows the TG and DTG profiles of Soluble and Residue obtained from cellulose and WC. Weight of cellulose decreased to about 26 wt% in the vicinity of 340ºC. The decomposition temperature of Soluble obtained at 300°C is higher than that of cellulose, indicating that the Soluble is composed of higher molecular weight components than cellulose. The thermal decomposition behaviors of cellulose and the Soluble obtained by adding DES at 350ºC do not seem to differ much except for slightly lowering the decomposition temperature. TG profiles showed significantly different behaviors between cellulose and Residue. Residue has a structure containing many high-molecular-weight components, and this tendency is further enhanced by the addition of DES. The decomposition temperature of Soluble and Residue obtained by cellulose was similar for that of WC.
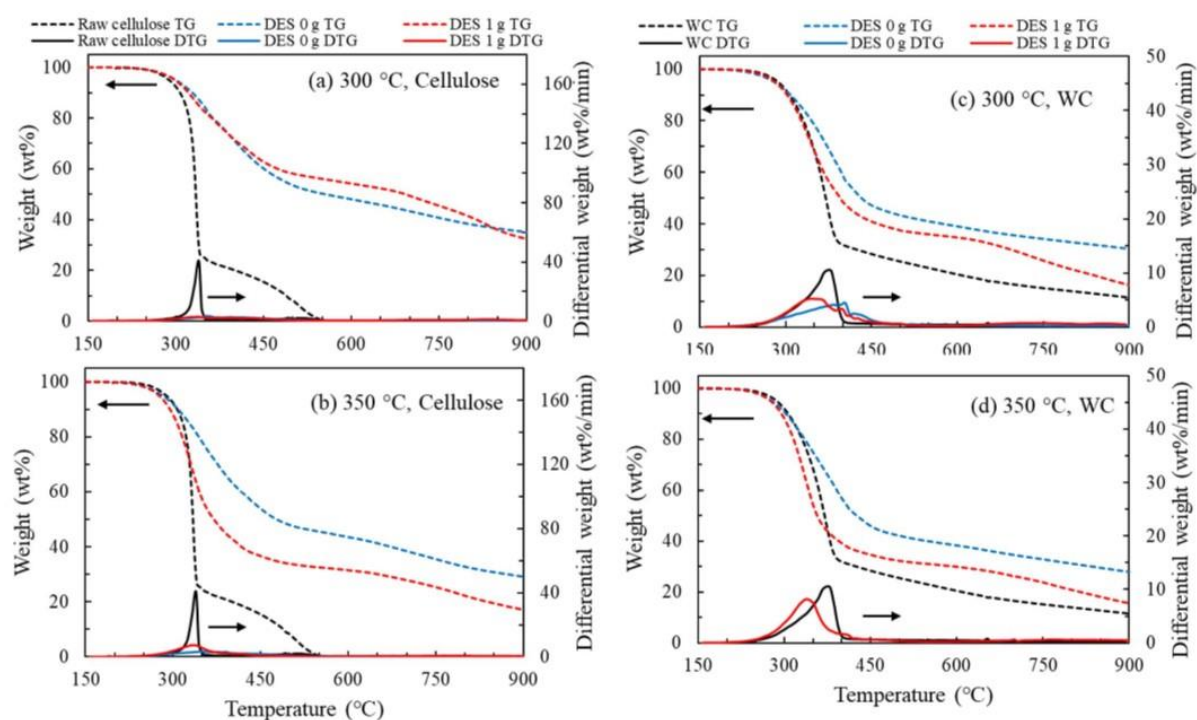


**Fig. 4.15** TG and DTG profiles of the Soluble obtained by cellulose at (a) 300 ºC and (b) 350 ºC, and Soluble obtained by WC at (c) 300 ºC and (d) 350 ºC for 90 min.
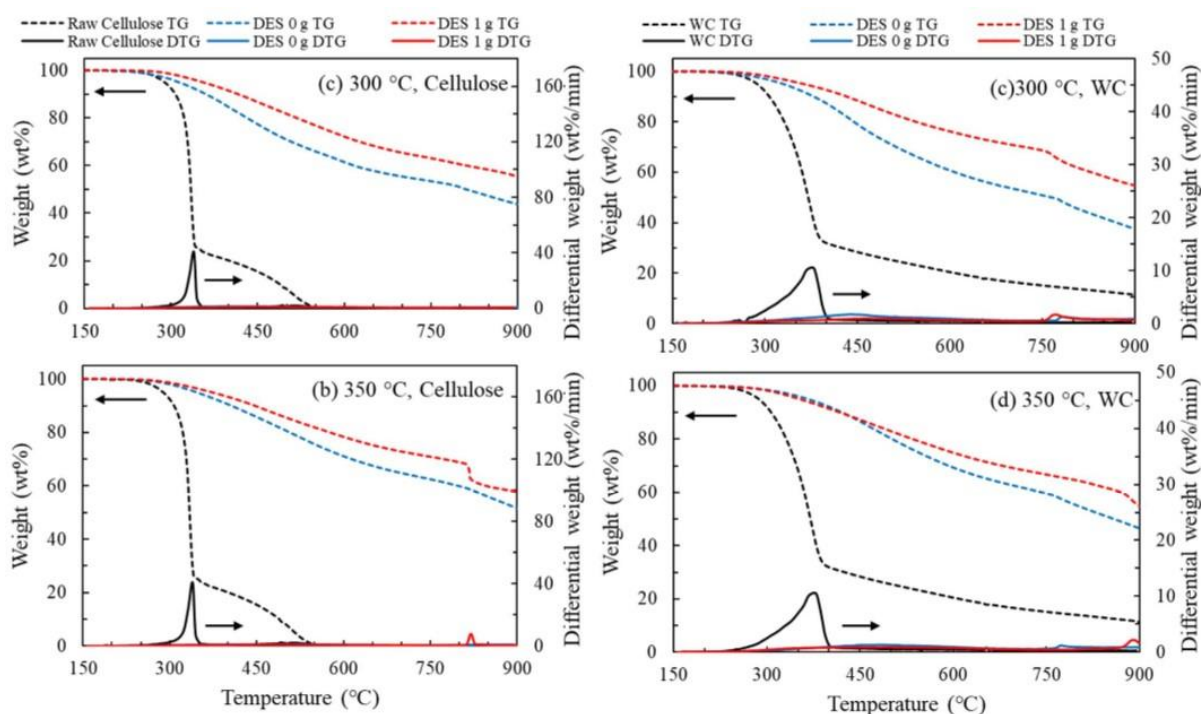
**Fig. 4.16** TG and DTG profiles of the Residue obtained by cellulose at (a) 300 ℃ and (b) 350 ℃, and Residue obtained by WC at (c) 300 ℃ and (d) 350 ℃ for 90 min.

Fig. 4.17shows FT-IR spectra of Soluble obtained from cellulose and WC, respectively. The strong absorption at 1000-1230 cm^{-1} shown in the cellulose is attributed to an ether bond of the pyranose ring, which is the basic skeleton of the monosaccharide in cellulose [11,12]. The pyranose ring in Soluble with and without DES was almost eliminated, and the absorption peak of aromatic C-H stretching vibration appeared similar to the case of Soluble from WC. These results indicate that the aromatization proceeded during the degradative solvent extraction of cellulose and WC and the aromatic components were extracted as Soluble. From the FT-IR spectra of Residue from cellulose and WC, it can be seen that the features disappeared with the increase in the addition amount of DES.
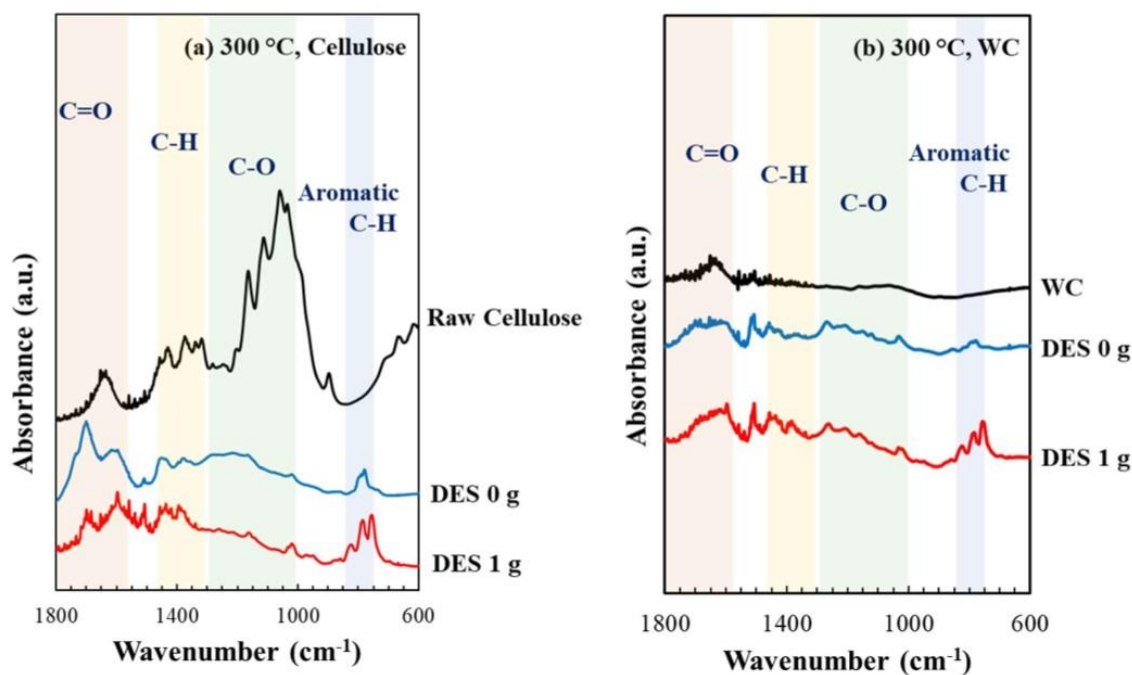
**Fig. 4.17** FT-IR spectra of Soluble obtained from (a) cellulose and (b) WC at 300 ℃ for 90 min.

### 4.3.7 Role of DES for degradative solvent extraction of cellulose and WC

The Main results of the degradative solvent extraction of cellulose and woody biomass are summarized as follows:

➢ The Soluble yield increased with increasing the DES amount and reaction temperature;

➢ Oxygen content in Soluble decreased by dehydration;

➢ The increase of the DES amount and reaction temperature promotes the cleavage of C=O and C-O bonds and aromatization;

➢ The molecular weight become large by degradative solvent extraction, but low with DES, while Residue has high-molecular-weight components containing large amounts of oxygen.

Fig. 4.18 shows the proposed reaction mechanism of cellulose. The yield of Soluble increases with increasing temperature, and the Soluble with low oxygen content and high aromaticity are obtained. In addition, the yield of Residue and its molecular weight increased also as WC. Degradative solvent extraction without DES cleaves hydrogen bonds and elutes low-molecular-weight components, so that they become Soluble. In addition, some bonds with low bond energies are cleaved and forming $CO_2$ and $H_2O$. The addition of DES on degradative solvent extraction promotes to cleave the C-O bonds and hydroxy groups as well as some bonds

with low binding energy, resulting in increases of the yields of Soluble. On the other hand, Residue may be combined with another Residue to form a macromolecule forming high-molecular-weight components.
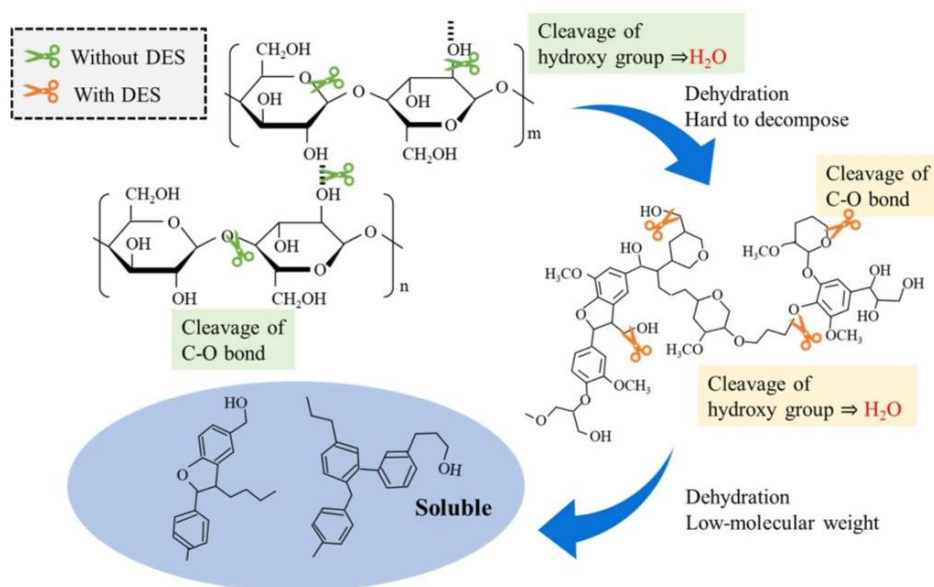


**Fig. 4.18** Proposed mechanism of degradative solvent extraction for cellulose.

## 4.4 Conclusion

The corresponding reaction mechanism of degradative solvent extraction for AC and WC at 300 or 350 ℃ with DES for 90 min are shown in Fig. 4.19. DES is considered to play a role in cleaving oxygen-containing bonds such as ether bonds in the Residue. As a result, the decarboxylation and dehydration took place and the aromatic low-molecular-weight components not containing oxygen were extracted as Soluble, while the oxygen remained in Residue with large-molecular-weight components.
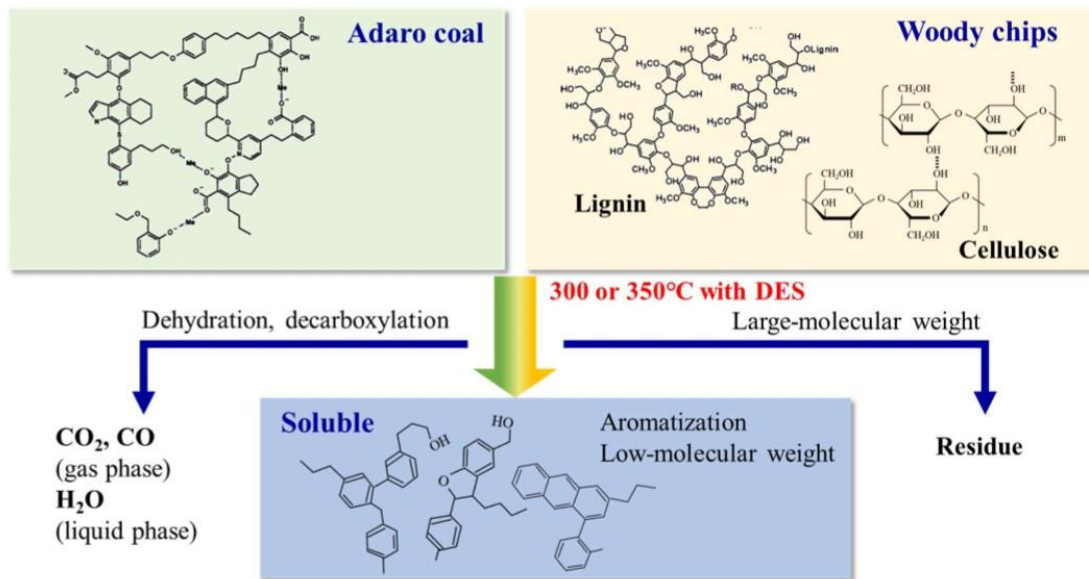
**Fig. 4.19** Reaction mechanism of AC and WC.

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**Chapter 5 Conclusions**

**5.1 Conclusions**

<u>Chapter 2</u>

Degradative solvent extraction of AC using DES was performed in 1-MN.

◆ The Soluble yield increased and the oxygen content decreased with increasing reaction temperature and DES amount;

◆ The decarboxylation took place by the degradative solvent extraction and the decarboxylation and dehydration took place by the DES addition;

◆ The HHV of Soluble were higher than raw AC.

<u>Chapter 3</u>

Degradative solvent extraction of WC using DES was performed in 1-MN.

➢ The Soluble yield increased and the oxygen content decreased with increasing reaction temperature and DES amount;

➢ The dehydration mainly took place by the DES addition;

➢ The HHV of Soluble was higher than raw WC. On the other hand, the HHV of Soluble obtained by WC was lower than that of Soluble obtained by AC.

<u>Chapter 4</u>

❖ The role of DES is to promote the dehydration and decarboxylation, and then the aromatization.

**5.2 Future prospects**

Mozambique has high-rank coal and low-rank coal reserves. Fig. 5.1 shows the Mozambique map.

Ncondezi Coal Fired Power Plant, Mozambique, is a company that:

➢ It is planned in Tete, Mozambique;

➢ Is a power development company that integrates power plant and mine to produce and supply electricity to the Mozambican market;

➢ The project is expected to enter into commercial operation in 2024. The offtake capacity is expected to be 300 MW.

Soluble obtained by degradative solvent extraction of low-rank coal and biomass will be

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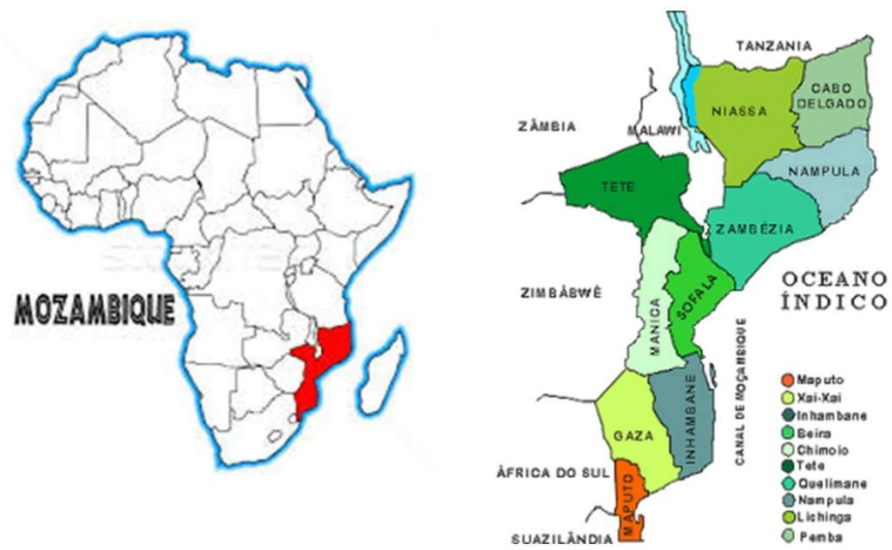
expected to use as the fuels required in fired power plants.



**Fig. 5.1** The Mozambique map.

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Pedro Domingos DAUCE

**Peer-Reviewers Journal Papers related to this thesis**

(1) <u>Pedro Domingos Dauce</u>, Ayano Nakamura, Kenji Murakami

"Extraction of fuel with high calorific value from biomass by degradative solvent extraction using deep eutectic solvent"

Global Journal of Engineering Science and Research Management, in press

(Corresponding to chapter 3 and 4)


(2) <u>Pedro Domingos Dauce</u>, Ryo Suzuki, Ayano Nakamura, Kenji Murakami, Degradative solvent extraction of subbituminous coal with deep eutectic solvent and effect of reaction conditions on products, *Carbon Resources Conversion* 6 (2023) 43–50

(Corresponding to chapter 2 and 4)

**Papers presented at domestic conferences related to this thesis**

(1) <u>Pedro Domingos Dauce</u>, Ayano Nakamura, Kenji Murakami

"Liquid fuel production with high calorific value from biomass by degradative solvent extraction using deep eutectic solvent"

The 57th Annual conference on Coal Science (2020, Kagawa, Online)

(Corresponding to chapter 3 and 4)

(2) <u>Pedro Domingos Dauce</u>, Ayano Nakamura, Kenji Murakami

"Extraction of Fuel from woody biomass degradative solvent extraction using deep eutectic solvent"

Regional Meeting of the Society of Chemical Engineers of Japan (2021, Akita, Online)

(Corresponding to chapter 3 and 4)

(3) Ayano Nakamura, <u>Pedro Domingos Dauce</u>, Kenji Murakami

"Extraction of fuel from biomass by degradative solvent extraction using choline chloride and $FeCl_3$ based deep eutectic solvent"

The 5th International Symposium on Fuel and Energy (2021, Hiroshima, Online)

(Corresponding to chapter 3 and 4)

(4) <u>Pedro Domingos Dauce</u>, Ayano Nakamura, Kenji Murakami

"Solid fuel production with high calorific value from low-rank coal by degradative solvent extraction using deep eutectic solvent"

The 58th Annual conference on Coal Science (2021, Sendai, Online)

(Corresponding to chapter 2 and 4)

(5) Ryo Suzuki, <u>Pedro Domingos Dauce</u>, Ayano Nakamura, Kenji Murakami

"Effect of reaction temperature and deep eutectic solvent on degradative solvent extraction of woody biomass"

Joint Meeting of the Tohoku Area Chemistry Societies (2022, Iwate)

(Corresponding to chapter 3 and 4)

⑹ Ayano Nakamura, Ryo Suzuki, <u>Pedro Domingos Dauce</u>, Kenji Murakami

"Role of deep eutectic solvent in degradative solvent extraction of low-rank coal"

The 59th Annual conference on Coal Science (2022, Hokkaido)

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