

**Effect of Solvent on the Degradative Solvent Extraction of
Low Rank Coal and Examination of Propensity to
Spontaneous Heating of
the Solvent Treated Coal and Residue**

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Chapter 1

Introduction

1.1 Background

It is without question that coal is a valuable resource used not only as fuels but also as chemical feedstock in this century. However, the minable reserve of high grade coal, bituminous coal, has been depleting very rapidly due to the rapid increase of worldwide coal consumption. This inevitably requests us to utilize low rank coals, brown coal/lignite, and sub-bituminous coal, instead of the high grade coal, because the minable reserve of the low-rank coals is as large as that of the high grade coal. 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. Brown coals, for example, contain a large amount of water (~60%) and oxygen functional groups in general, 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 coals for their effective utilization. Here upgrading means the treatment which not only increase the heating value but suppress the propensity to spontaneous heating of the low rank coals.

1.2 Coal Upgrading Technologies

Various methods have been proposed for dewatering and/or upgrading low rank coals by many researchers as reviewed by Katalambula ^[1]. When coal is subjected at elevated temperatures, it will produce gaseous, liquid, and solid products. Most of works have focused on the attention of treated coal as solid fuel. General coal upgrading involves

drying of low rank coal by thermal drying which evaporates using huge amounts of energy. Approaches for conversion of low rank coal are pyrolysis, liquefaction, and solvent extraction.

Pyrolysis is thermal decomposition at elevated temperatures in the absence of air. The product from pyrolysis process termed char consists of largely carbon and smaller amount of hydrogen and oxygen. During the thermal decomposition of coal, coal occasionally does not release any volatile matters but it is considered accurately removal of moisture under 300 °C in an inert stream ^[2]. Char can be utilized through gasification or combustion in reducing or oxidizing atmosphere. Due to the need of carbon sources to supplement crude oil or natural gas, it is focused on low rank coal as one of suitable candidate. Abundant low rank coal can be converted to solid products with high calorific value ^{[1], [3]}.

Gasification is a partial process of oxidation that can be conducted with air, H₂O or steam, and CO₂. It is occurrence of oxygen insufficient. There are mainly two steps of gasification. First one is the reactions that require heat. Coal can be decomposed into hydrocarbon gas components (mainly CH₄ and other hydrocarbons), H₂, CO, CO₂, H₂O, and tar at elevated temperatures lower than 600 °C ^[2]. The remaining products after the treatment are char and ash content. Second step is performed char with oxygen, steam, and hydrogen at the higher temperatures. The typical final products of gasification are heat, combustible gas. The synthesis gases generally utilize for thermal and electrical applications such as electricity generation application with some specific equipment.

Combustion of coal refers to the higher temperature than gasification. Combustion is required excess or sufficient oxygen to fulfill completely reactions ^{[4], [5]}. Combustion is the burning of coal or dried coal to generate heat in a form of steam for such as a boiler or steam engine use. Combustion usually requires low moisture content of feedstock. At early stage of combustion, moisture is removed by heating and drying. The combustion process forms gas products of H₂, CO, CO₂, CH₄, and hydrocarbons at desired temperatures. After that, char, CO₂ and H₂O are formed to completely oxidize at the end of combustion.

Another upgrading process is liquefaction which is operated under elevated temperatures and pressures. Liquefaction refers to the conversion of solid coal into liquid fuel. The principle purpose of coal liquefaction are liquid or synthetic oil and gases for industrial as feedstock. Liquefaction process involves the hydrogenation of coal and catalysts ^[5]. The possibility of catalyst recovery to obtain clean derived products can be also reduced the cost of catalyst and prepared in a commercial aspect ^[6].

However, most of the works on low rank coal dewatering and upgrading are aiming at using the treated coals as solid fuel. If we think of the low-rank coals as the feedstock of chemicals and carbon materials, we might have to develop methods that enable to effectively extract precursors of chemicals and/or carbon materials from low-rank coals in addition to develop the methods for dewatering and/or upgrading ^[7-9]. Solvent extraction of coal may be one of the promising methods for the purpose. However, solvent extraction cannot upgrade but just extract low-molecular-weight compounds from the coals. Furthermore, the extraction yield is very low at room temperature when using nonpolar solvents from practical viewpoint. Using strong polar solvents increases

the extraction yield, but it makes the separation of the extract from solvent difficult ^[10],
[11].

Overcoming these drawbacks, Miura *et al.* have recently proposed a degradative solvent extraction method which treats carbonaceous resources in a non-hydrogen donor at around 350 °C, under pressure, using a batch autoclave to dewater without phase change, to remove oxygen functional groups, and to produce low-molecular-weight compounds [12], [13]. The core concept underlying this method involves exposing the entire sample to thermal reactions in a nonpolar solvent at around 350 °C. The anticipated thermal reactions under these conditions include deoxygenation reactions consisting of dehydration and decarboxylation without primary decomposition reactions accompanying the disruption of C–C bonds. The products formed during the thermal reactions at around 350 °C are then filtrated at the same temperature to recover the extract and residue (the latter is termed Residue in this thesis). The extract is further separated into two fractions at room temperature: the fraction that precipitates as a solid (Deposit) and the soluble fraction (Soluble). The soluble fraction is also finally recovered as a solid by removing the solvent. When the method was applied to 8 low rank coals using a nonhydrogen donor solvent, 1-methylnaphthalene, the carbon based yields of the three solid fractions were 19.4–31.2% as Solubles, 4.2–16.8% as Deposits, and 54.7–69.2% as Residues ^[14]. Overall, more than 94.4% of carbon was recovered as solid fractions. Meanwhile 30.5–54.9% of oxygen was removed as either H₂O or CO₂. The interesting findings were the Solubles and Deposits obtained from all of the coals were respectively very close to each other in elemental composition, chemical structure, molecular weight distribution, thermal decomposition behavior, and thermoplastic behavior. Elemental compositions of Solubles were C = 81.8–84.8 wt %, H = 7.5–8.1 wt %, and O = 6.5–10.2

wt %, which were rather close to the elemental composition of bituminous coal. Therefore, the degradative solvent extraction method was found to be effective in converting various types of low-rank coals into residues and compounds having very similar chemical and physical properties without losing heating values ^[15]. This method was also successfully applied to dewater and upgrade various biomass wastes ^[16]. It was worthy to note that the properties of Solubles and Deposits were almost independent of raw materials. This means that almost same Solubles and Deposits are obtained from both low rank coals and biomass wastes. The peculiarities of the degradative solvent extraction method are summarized in **Figure 1.1**. The method is well expected to contribute to effective utilization of both low rank coals and biomass wastes.

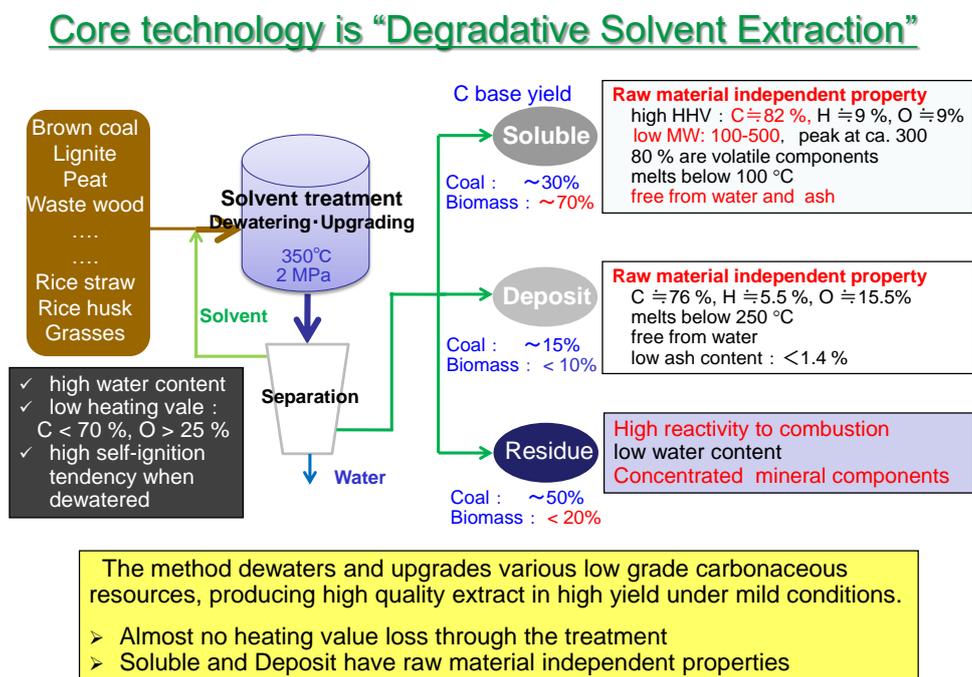
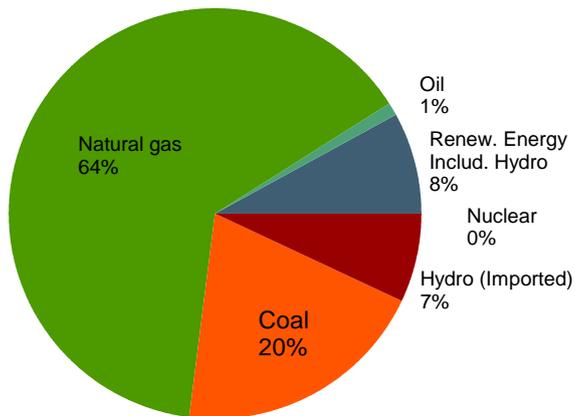


Figure 1.1. The peculiarities of the degradative solvent extraction method.

Share of Energy Generation by 2014



Share of Energy Generation by 2036 (PDP 2015)

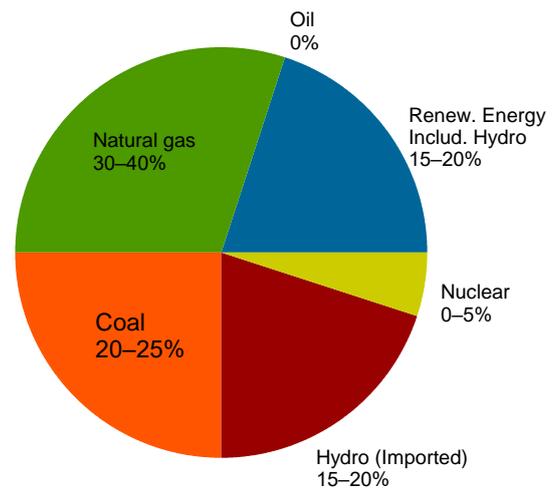


Figure 1.2. The share of energy generation by 2014 and 2036 in Thailand ^[18].

1.3 Present and future of coal utilization in Thailand

In Thailand, coal has been used as fuel for heat and power generation in power plants and other manufacturing industries. About 19.8 Mt of lignite were produced and 23.0 Mt of steam coal were imported in 2015, and the coal accounts for about 15 % of primary energy consumption of Thailand ^[17]. The share of coal is also expected to grow in Thailand in the next few decades, especially in power generation sector, following the Thai government’s Power Development Plan (PDP) 2015 shown in **Figure 1.2** ^[18]. The share of coal in power generation sector is estimated to increase from 20 % in 2014 to 20–25% in 2036 with the future coal-fired power plants installation of 7,390 MW.

Low rank coals, however, have several disadvantages as compared with high rank coals as stated above. The disadvantages make it economically unfeasible to transport the coals. Furthermore, the utilization of these low rank coals generally brings about high CO₂ emission. It is therefore very important for Thailand to utilize the low rank coals more effectively and environmentally friendly. Hence, pretreatment consisting of dewatering, cleaning, and upgrading is essential in Thailand also. In addition, low rank coals are expected to be valuable resources for chemicals in this century. However, since low rank coals contain a large amount of ash (10–30 %) and since their oxygen contents are very huge, it is very difficult to isolate valuable chemicals as well as to produce carbonaceous materials from low rank coals ^[19]. Research and development to improve both technical and economical feasibility in this interested area is therefore important.

Another source of fuels abundant in Thailand is biomass from agricultural wastes and agricultural processing waste. Over 140 Mt/year of biomass generation is estimated ^[20]. A large energy production has been realized from the source *via* combustion technology. However, the utilization of biomass as fuels has several drawbacks due to its low heating value, high alkali content, high chlorine content, difficulty in handling, etc. ^{[21], [22]}. Since most of drawbacks that biomass has typically are similar to those low rank coal has, the technologies developed for effective utilization of low rank coal is believed to be successfully applied to effective utilization of biomass.

1.4 A Japan–Thailand SATREPS project

SATREPS is an abbreviation of a collaborative research program that is called Science and Technology Research Partnership for Sustainable Development. This program is supported by the Japan Science and Technology Agency (JST) and Japan International Cooperation Agency (JICA) to promote international joint research in which both Japanese research institutions and those of recipient countries work together based upon the social needs in recipient countries. Its aims are to obtain new knowledge and to utilize research outcomes to the benefit of the society with a viewpoint to resolving global issues such as the environment and energy, biological resources, disaster prevention, and infectious diseases. In conjunction with this, it also aspires to improve the development of human resources and research capabilities in recipient countries by conducting joint research.

In 2013, a research group of Kyoto University (KU) and the Joint Graduate School of Energy and Environment (JGSEE)/King Mongkut’s University of Technology Thonburi (KMUTT) initiated a joint research entitled “**Development of clean and efficient utilization of low rank coals and biomass by solvent treatment**” in collaboration with the research teams of Akita University (AU), Central Research Institute of Electric Power Industry (CRIEPI), Kobe Steel Co., Ltd. and PTT public Co., Ltd. under the SATRPES program. The collaborative research project is aimed at exploring the novel technology to overcome the technical drawbacks of utilization of low rank coals and biomass based on the degradative solvent extraction technology developed by the Kyoto University group. Within the scope of the project, four parallel research tasks (outcomes) were proposed. **Figure 1.3** shows the schematic illustration of the outline of this project.

Structure of Research and Development

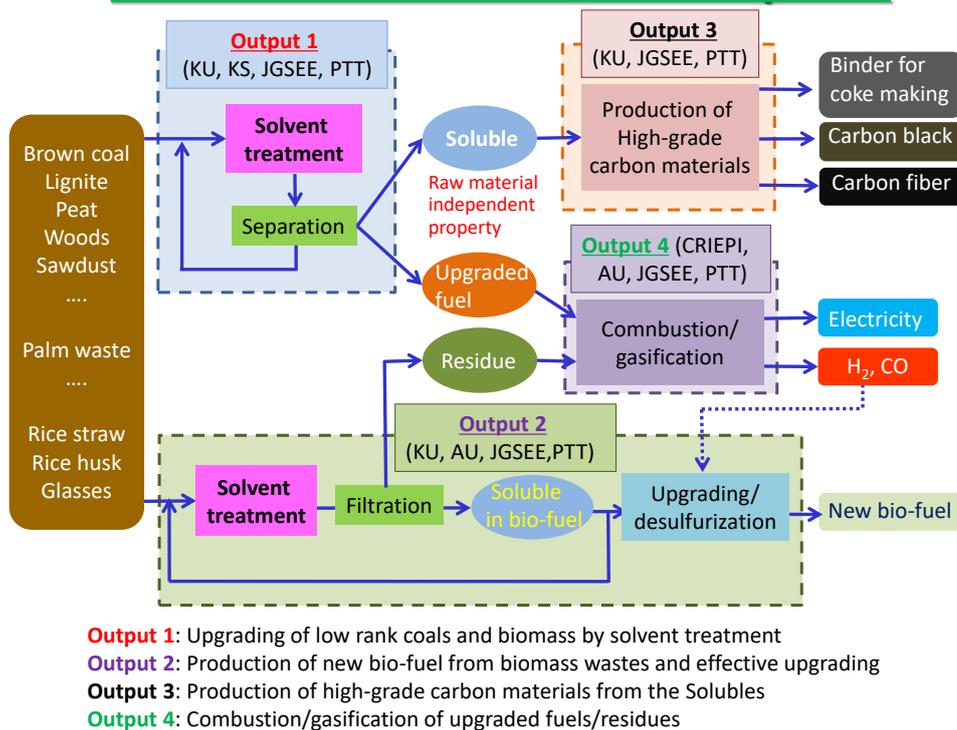


Figure 1.3. A schematic illustration of the outline of the project.

1.5 Content of the thesis

I, myself, have been recruited as a PhD candidate by the Japanese Government as a part of this SATREPS project framework. My role has been participating in this SATREPS project through performing several research subtopics. Then this thesis is focused on two subtopics. First one is related to the examination of the effect of solvent on the yield distribution of Soluble, Deposit, and Residue and the examination of the possibility of preparing solvent treated coal (abbreviated to STC) ^[23] in the framework of the output 1. STC is expected to be a high quality of solid fuel. Second one is the examination of propensity to spontaneous heating of Residue and STC, which are expected to be high

quality solid fuels, in the framework of the output 4. For the second subtopic, some index evaluating the propensity to spontaneous heating is essential ^{[24], [25]}. This work focuses on the role of adsorption of water vapor in addition to the oxidation by air to define one of such indices. Therefore, this thesis summarizes the works of two research subtopics.

Chapter 1 is the introduction and states about the background and the purposes of this thesis. Chapter 2 and 3 are the main body of this thesis. The purpose of each the three chapters is as follows:

Chapter 2:

This chapter aims at examining the effect of solvent on the product yield distributions, characteristics of each fraction and the yield and the properties of STCs prepared from two lignites. 1-methylnaphthalene (1-MN), kerosene, and 1 to 1 mixture of 1-MN and kerosene are used as the solvents. Kerosene is employed as a candidate of a practical solvent for preparing STC. The products were characterized by elemental compositions, molecular weight distributions, and thermal characteristics in addition to yields.

Chapter 3:

The purposes of this chapter are to measure the heat of desorption of water during the thermal drying of as-received coal at a temperature of 107 °C and to clarify the role of adsorption of water vapor in relative to coal-oxygen interaction at 107 °C from the viewpoint of examining propensity to spontaneous heating of dried coal. To do so, a TG-DSC analyzer which measures weight change and heat flow in moist atmosphere was used ^[26]. Using the TG-DSC analyzer, the heat flow is straightforwardly related to the weight change. This enabled us to estimate accurately the heats of adsorption/desorption of water directly at such a high temperature.

Chapter 4:

To evaluate the potential of Residue, and STC as high quality solid fuels, estimation of their propensity to spontaneous heating is essential in addition to the evaluation of their heating values and rates of combustion and/or gasification. In chapter 3, it was demonstrated that the weight change and the heat generation rate measured at 107 °C in both dry air and wet air can be an index to estimate the propensity to spontaneous combustion. This chapter applies the method to estimate the propensity to spontaneous heating of Residue and STC prepared from two low rank coals. The propensity to spontaneous heating of the parent coals and chars prepared in an inert atmosphere at 350 °C is also examined for comparison purpose.

Chapter 5:

Finally, the last chapter, Conclusions and Recommendations summarizes the results of this thesis and purposes several recommendations for effective utilization of low rank coals and for the development of the degradative solvent extraction in Thailand.

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Chapter 2

Effect of Solvent on the Degradative Solvent Extraction of Low-rank Coal

2.1 Introduction

Our research group of Kyoto University has recently presented the degradative solvent extraction method for dewatering and upgrading of low-rank coals and biomasses at 350 °C by using 1-methylnaphthalene (1-MN) as a solvent ^{[1],[2]}. In this process, the solvent is expected not to take part in chemical reactions with a sample but to act simply as a dispersant for the sample. Low-rank coals and biomasses were not only dewatered but also upgraded by the selective removing of oxygen functional groups in the form of either H₂O or CO₂ during the treatment. The upgraded product was fractionated into three solid fractions: Soluble, Deposit, and Residue. The carbon based yield of Soluble reached as high as 70 % for some biomass wastes. Solubles were free from water and mineral matters and their physical and chemical properties were almost independent of raw materials. Solubles having such unique properties were expected to be utilized as raw materials of value added products. On the other hand, Residues produced from low-rank coals in 50 % yields were expected to be used as high quality solid fuels. However, there are still several problems to be solved for the practical application of the proposed extraction method. One of the examinations required is the effect of solvent on the yields and properties of three solid extracts.

In this chapter, the possibility of using a practical solvent for this extraction method was examined. Kerosene, which is easily obtained and has lower boiling point than 1-MN, was selected as the practical solvent. Solvent having lower boiling point expected to be easily separated and recovered from the upgraded product. 1-MN and the 1 to 1 mixture of 1-MN and kerosene were also used for comparison purpose. The three upgraded fractions, Soluble, Deposit, and Residue, were characterized in detail. If we intend to

convert the low-rank coals to just high quality solid fuels, it is not necessary to separate the solvent treated product into three fractions. Then we also prepared “Solvent treated coal” (abbreviated to STC) under the same condition but without separating the upgraded coal into 3 fractions ^[3]. Since STC is a mixture of Soluble, Deposit, and Residue in principle, STC is almost completely dewatered and its carbon content is as high as 78 to 80 %. This showed that STC can be well utilized as a high quality solid fuel from the viewpoint of heating value. STC was also characterized in detail as was done for the three fractions.

2.2 Experimental

2.2.1 Materials and solvent used

Two low-rank coals, an Australian brown coal, Loy Yang (abbreviated to LY) and an Indonesian lignite, Pendopo (PD) were used as samples. Their analyses are shown in **Table 2.1**. The appearance of LY is shown to give an image of brown coal in **Photo 2.1**. The coals were ground without drying and sieved to have a diameter less than 0.2 mm before serving to the experiments. Three kinds of solvents were selected in this study. A common liquid fuel, kerosene (abbreviated to Kerosene), which obtained from PTT Company (Thailand) was used as a practical solvent. A non-polar solvent, 1-methylnaphalene (1-MN) purchased from Tokyo Chemical Industry Company was selected as a model solvent. The 1 to 1 mixture of 1-MN and kerosene (abbreviated to 1-MN/Kerosene) was also used for comparison purpose. The boiling points of solvents used were respectively 110, 120 and 160 °C for Kerosene, 1-MN/Kerosene, 1-MN.



Photo 2.1. Picture of coal used (Loy Yang coal).

2.2.2 Experimental procedure

Photo 2.2 shows the experimental apparatus used for the degradative solvent extraction experiment. The major parts of the extraction system consist of a stainless steel autoclave reactor (130 mL in volume), a reservoir (130 mL in volume), a stainless steel filter (65 mm O.D, 0.5 μm opening) equipped at the bottom of the autoclave reactor, and an electric furnace. The autoclave reactor was connected with the reservoir by a ball valve. On each run, about 5 g (d.a.f) of coal and 80 mL of solvent were carefully charged into the autoclave reactor with the connecting valve closed. Prior to starting the experiment, both of the autoclave reactor and the reservoir were purged by 0.5 MPa of He for several times to ensure that the oxygen inside the reactor was completely removed. Then the sample was heated up to 350 °C at a constant heating rate of 5 K/min. An impeller magnetically connected to the agitator stirred the content of autoclave throughout the experiment. After 60 min of treatment at 350 °C, the connecting valve was opened, allowing the extract together with the solvent moving to the reservoir by a pressure difference. The extraction residue remaining in the autoclave is called Residue (see **Photo 2.3 (a)**) in this study. Cooling down the mixture of the extract and solvent to room temperature precipitates a

part of extract as solid. It was firstly separated by a vacuum filtration using PTFE filter (0.5 μm opening). The solid extract above this filter was called Deposit in this study (see **Photo 2.3 (b)**). Another extract dissolving in the solvent was also recovered as solid by removing the solvent using a rotary evaporator. It is called Soluble (see **Photo 2.3(c)**) in this study. Residue, Deposit, and Soluble were dried at 160 °C for 8 h by using a vacuum oven. An example of Soluble after drying is shown in **Photo 2.3 (d)**. The experiment separating the upgraded product into fractions is abbreviated to “Fractionation scheme” hereinafter.

To prepare the solvent treated coal (STC), the extraction apparatus was operated without the reservoir as shown in **Figure 2.1**. The experiment was performed by following the exactly same procedure as the above experiment until the end of treatment at 350 °C. After 60 min of treatment at 350 °C, the autoclave was cooled down to room temperature, and then all the content in the autoclave was carefully collected. The solvent treated coal was recovered by only removing the solvent from the content by the rotary evaporator and by additional drying in the vacuum oven. An example of STC is shown in **Photo 2.3 (e)**. The experiment recovering STC by just removing the solvent from the upgraded product is abbreviated to “Non-fractionation scheme” hereinafter.

All the gaseous products were also collected in a gas bag at room temperature by purging the reactor and reservoir with pressurized He before collecting the extracts. The purging of He was performed several times until the concentration of the product gas in the whole system will be reduced to less than 1%. Then the gas was analyzed and quantified by a gas chromatography.

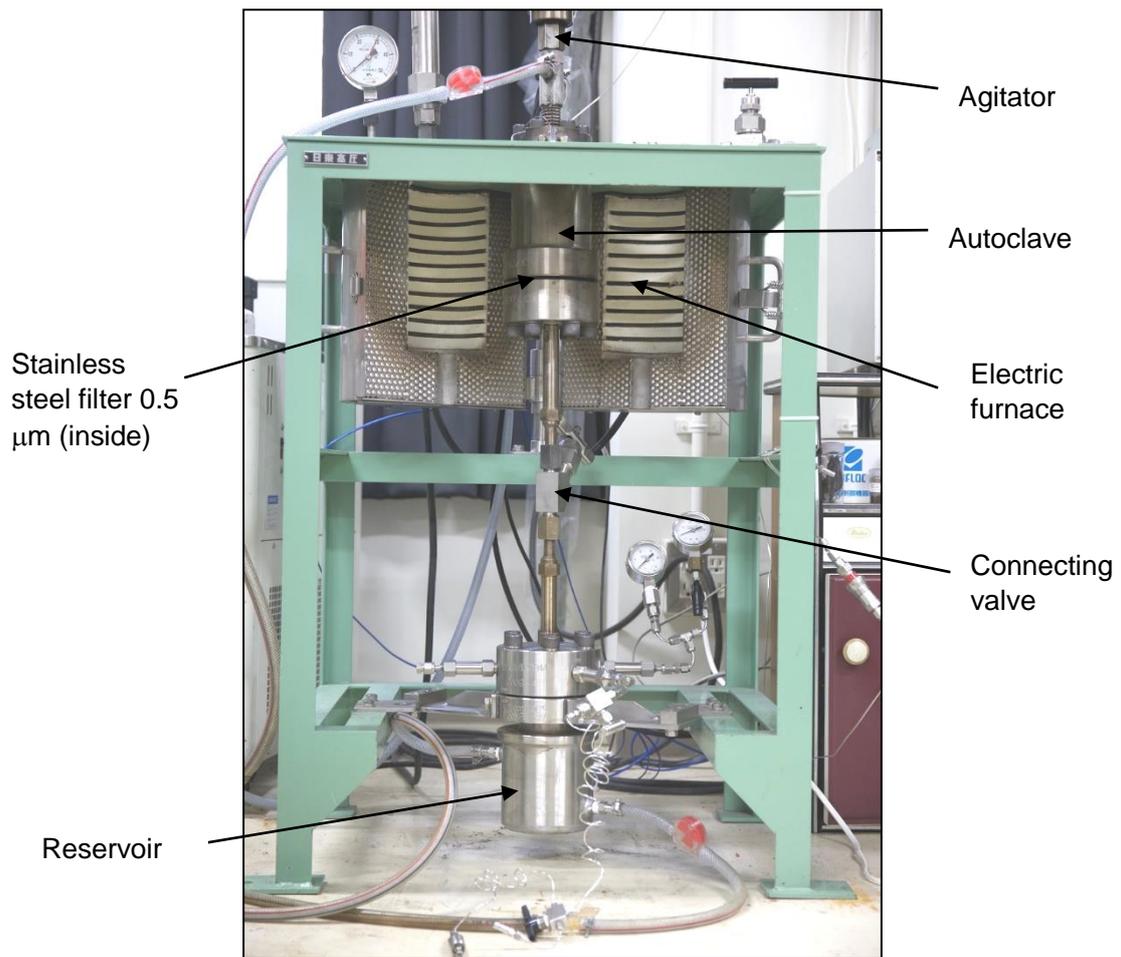


Photo 2.2. Degradative solvent extraction apparatus used for a separation experiment.

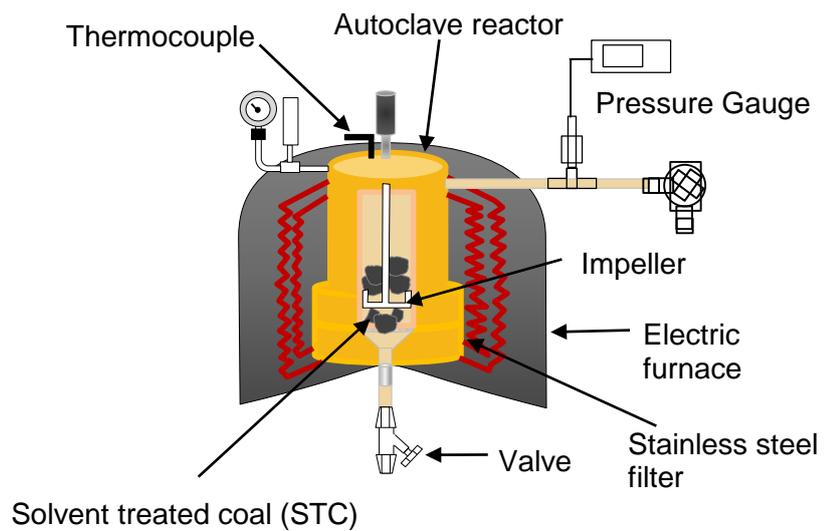


Figure 2.1. Degradative solvent extraction apparatus used for preparing a solvent treated coal (STC).

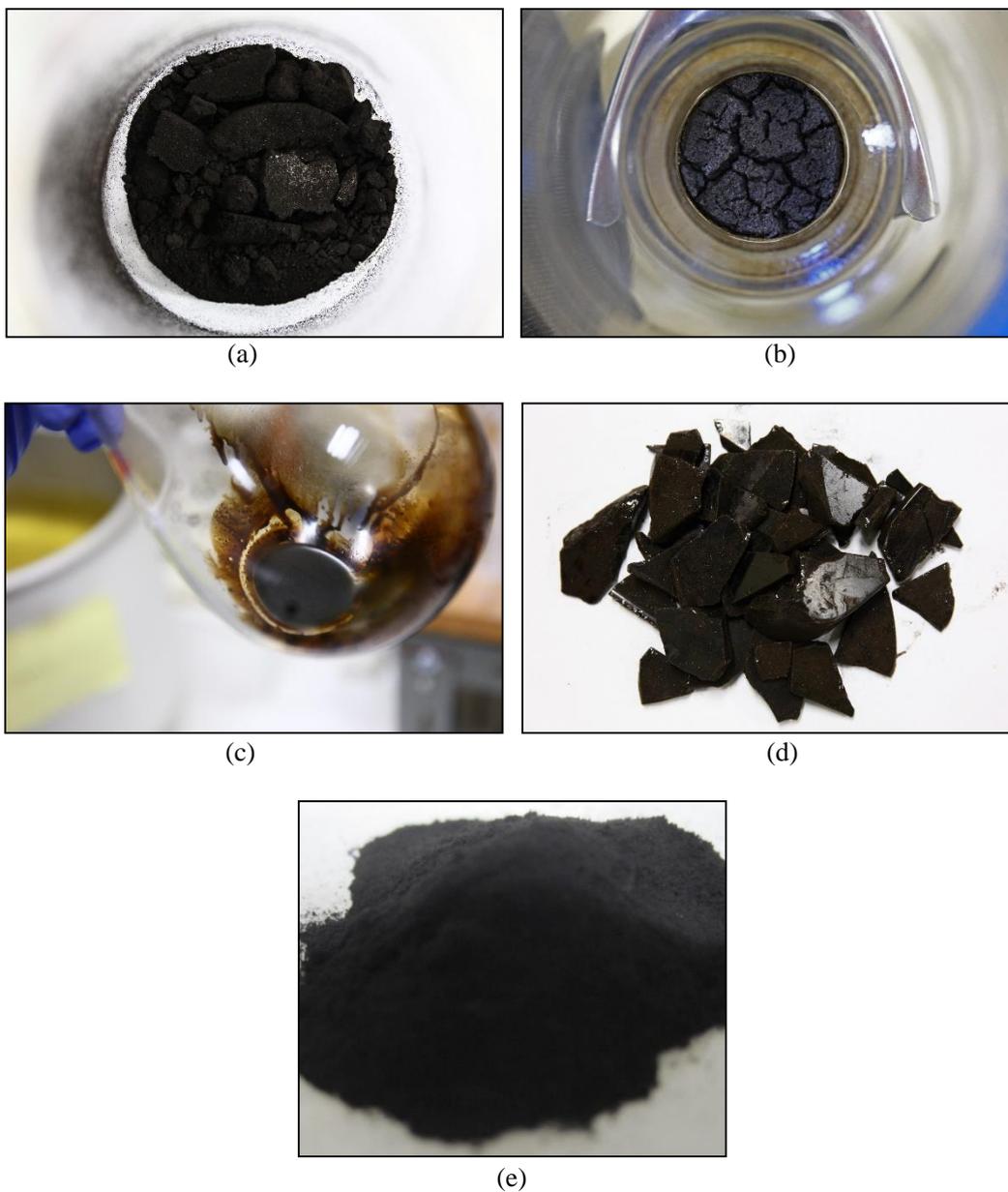


Photo 2.3. Pictures of solvent treated products: (a) Residue, (b) Deposit, (c) Soluble after removing solvent by rotary evaporator, (d) dried Soluble, (e) solven treated coal (STC).

2.2.3 Characterizations of upgraded products

Soluble, Deposit, and Residue obtained by Fractionation scheme and STC obtained by Non-fractionation scheme were carefully characterized by several techniques. First, each of their yields was estimated from its weight. The sum of the product yields, the sum of the yields of Soluble, Deposit, Residue, and gaseous product for Fraction scheme, and the sum of the yields of STC and gaseous product for Non-fraction scheme, were less than 1 for most of experiments. The difference is named “Liquid” and it was assumed to consist of the fraction of smallest molecular weight compounds that were not separated from the solvent. The proximate and the ultimate analyses of the solid products were performed respectively by using a thermogravimetric analyzer (Shimadzu, TGA 50) and a CHN corder (Yanaco, CHN MT-6M). The thermoplastic behavior was investigated by using a thermomechanical analyzer (Shimadzu, TMA 50). The molecular weight distribution was analyzed by a laser desorption/ionization time-of-flight mass spectrometry (Shimadzu/Kratos, KOMPACT-MALDI-II).

2.3 Results and Discussion

2.3.1 Product yields and element balances

Table 2.1 lists the yields of Residue, Deposit, and Soluble for Fractionation scheme and the yield of STC for Non-fractionation scheme obtained using 1-MN, 1-MN/Kerosene, and Kerosene, respectively, for both LY and PD. The proximate analyses, elemental composition, atomic ratios including the higher heating values (HHVs) are also listed in the table. **Figures 2.2** and **2.3** compare the product yield distributions including gaseous

product and Liquid between Fractionation scheme and Non-fractionation scheme respectively for LY and PD. We assume that the effect of solvent on this degradative solvent extraction method should be examined from two viewpoints. The first one is if solvent affects the degradation reaction at 350 °C. The second one is how solvent affects the product distribution. Of course, discussion from the second viewpoint should be made after definite answer to the first viewpoint. Answer to the first viewpoint can be made by comparing the yields of gaseous product. For PD, the yields of gaseous product were almost same for all the solvents as shown in Fig. 2.3. For LY, the yields of gaseous product were almost same for 1-MN and Kerosene as shown in Fig. 2.2. These results suggest that solvent did not affect the decomposition reaction at 350 °C.

Based on the conclusion on the first viewpoint, the product distributions and the properties of each fraction were examined. Let us focus on the yields of Residue, Soluble, and Liquid to make discussion simple. It was found the extraction with 1-MN gave the highest yield of both Soluble and smallest yields of Residue and Liquid, and Kerosene gave the smallest yield of Soluble and highest yields of both Residue and Liquid for both coals. Meanwhile, as expected, the extracts yield lied between the two solvents when using 1-MN/Kerosene. In more details, the yields of Residue obtained from 1-MN extraction was 63.9 % and around 71.2 % from Kerosene for LY coal. The yields of Soluble obtained from 1-MN, 1-MN/Kerosene, and Kerosene extractions were, respectively, 20.0 %, 12.0 %, and 4.8 % for LY. These yield values indicate that Liquid obtained from Kerosene must contain low-molecular-weight compound that could not be separated from Kerosene. It was rather easy to remove Kerosene from either the mixture of Soluble and Solvent or STC and Solvent, but Kerosene inevitably accompanied small molecular weight compounds of Soluble fraction when it evaporates at rather high rate.

Then the difference in the distributions of the three fractions among the three solvents can be well explained by the difference of solubilities of the solvents. 1-MN showed strongest affinity to the upgraded product and Kerosene showed weakest affinity to the upgraded product. The yield of STC obtained using 1-MN was 84.6 %, which was higher than the 77.1 % of STC yield obtained using kerosene. Since the sum of the yields of three fractions for Fractionation scheme is almost equal to the yield of STC for Non-fractionation scheme for every combination of soluble and coal, the smaller STC yield obtained using Kerosene comes from the loss of smaller molecular weight compounds to Liquid. The carbon contents of Residue obtained from 1-MN, 1-MN/Kerosene, and Kerosene extractions were 77.1 %, 78.9 %, and 77.7 %, and those of STC obtained from 1-MN, 1-MN/Kerosene, and Kerosene extractions were 78.2 %, 80.1 %, and 75.2 %, respectively. This shows that both Residue and STC prepared are really upgraded coals from the viewpoint of heating value, and they may be utilized as high quality solid fuels.

For PD, the yields of Residue obtained from 1-MN, 1-MN/Kerosene, and Kerosene extractions were 54.3 %, 59.7 %, and 60.7 %, and the yields of STC obtained from 1-MN, 1-MN/Kerosene, and Kerosene were 81.3 %, 76.3 %, and 72.6 %, respectively. The carbon contents of Residue obtained from 1-MN, 1-MN/Kerosene, and Kerosene extractions were 76.5 %, 77.4 %, and 74.3 %, and those of STC obtained from 1-MN, 1-MN/Kerosene, and Kerosene extractions were 78.7 %, 79.4 %, and 76.5 %, respectively. These results show that the above discussion for LY is also valid for PD.

Table 2.1. Analyses of coals used and their extract products.

Coal	Yield [wt %, d.a.f.]	Ultimate analysis [wt %, d.a.f. ^a]				Proximate analysis [wt %, d.b. ^b]			Atomic ratio (-)		HHV [MJ/kg, d.a.f.]
		C	H	N	O (diff.)	VM	FC	ash	O/C	H/C	
Loy Yang (LY)		66.6	4.5	0.5	28.4	50.0	47.8	2.2	0.32	0.81	23.9
<i>Extraction in 1-MN</i>											
Residue	63.9	77.1	4.2	0.8	18.0	35.1	59.6	5.3	0.17	0.65	28.9
Deposit	7.2	76.8	5.1	0.9	17.2	40.6	58.6	0.8	0.17	0.79	30.2
Soluble	20.0	82.2	7.7	0.5	9.6	76.3	23.7	0.1	0.09	1.13	37.2
STC	84.6	78.2	4.9	0.9	14.0	42.4	55.7	1.9	0.12	0.73	30.9
<i>Extraction in mixture of 1-MN and kerosene (mixed solvent)</i>											
Residue	67.1	78.9	4.2	0.8	16.1	32.2	65.6	2.2	0.15	0.64	29.9
Deposit	8.1	74.8	5.7	0.8	18.8	49.4	49.9	0.7	0.19	0.91	30.1
Soluble	12.0	80.5	8.7	0.3	10.5	83.0	16.9	0.1	0.10	1.30	37.9
STC	83.2	80.1	5.0	0.9	14.0	41.2	56.6	2.1	0.13	0.75	31.8
<i>Extraction in kerosene</i>											
Residue	71.2	77.7	4.2	1.7	16.5	30.6	67.2	2.2	0.16	0.65	29.3
Deposit	1.8	75.2	6.1	1.7	16.9	70.7	28.8	0.5	0.17	0.97	31.2
Soluble	4.8	84.9	10.7	0.4	4.0	89.0	10.9	0.1	0.04	1.51	43.4
STC	77.1	75.2	4.7	0.7	19.4	37.6	59.9	2.6	0.19	0.75	28.7
<hr/>											
Pendopo (PD)		67.5	5.1	0.8	26.6	49.4	38.0	12.6	0.30	0.91	25.4
<i>Extraction in 1-MN</i>											
Residue	54.3	76.5	4.5	1.2	17.7	40.1	42.4	17.4	0.15	0.71	29.2
Deposit	4.1	81.1	5.4	1.5	12.0	44.8	54.2	0.9	0.11	0.80	33.0
Soluble	23.2	83.8	7.6	0.7	7.9	76.3	23.4	0.3	0.07	1.09	37.9
STC	81.3	78.7	5.1	1.2	15.0	41.6	45.8	12.5	0.14	0.78	31.3
<i>Extraction in mixture of 1-MN and kerosene (mixed solvent)</i>											
Residue	59.7	77.4	4.4	1.3	16.9	30.1	53.8	16.1	0.16	0.68	29.4
Deposit	4.8	76.7	5.7	1.2	16.5	49.3	50.0	0.7	0.16	0.89	31.2
Soluble	15.9	80.5	8.5	0.4	10.6	87.1	11.8	0.6	0.10	1.27	37.6
STC	76.3	79.4	5.2	1.2	14.2	38.3	49.2	12.5	0.14	0.79	31.8
<i>Extraction in kerosene</i>											
Residue	60.7	74.3	4.3	1.2	20.2	31.6	57.5	11.1	0.20	0.69	27.3
Deposit	2.0	78.6	7.3	0.9	13.2	69.6	30.2	0.2	0.13	1.11	34.7
Soluble	8.9	83.6	10.3	0.3	5.7	94.7	5.2	0.1	0.05	1.48	42.1
STC	72.6	76.5	5.6	1.0	16.8	44.0	44.3	11.7	0.16	0.88	30.9

^aDry, ash-free. ^bDry basis.

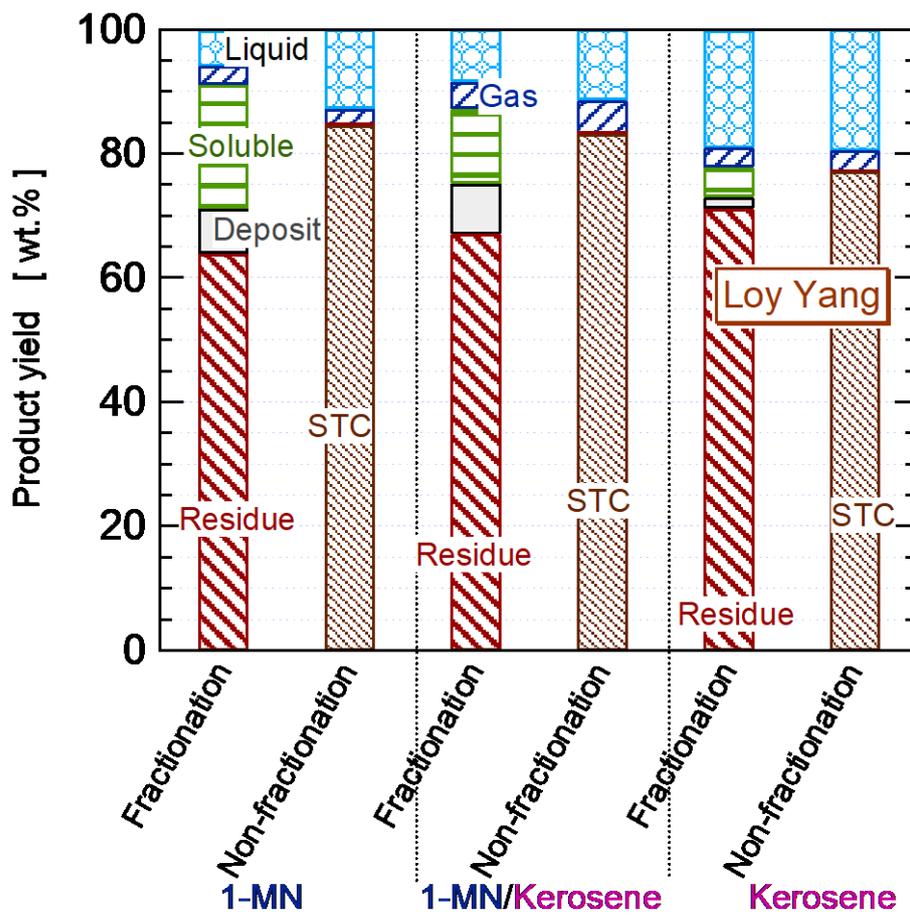


Figure 2.2. Comparison of the product yield distributions between Fractionation scheme and Non-fractionation scheme for LY.

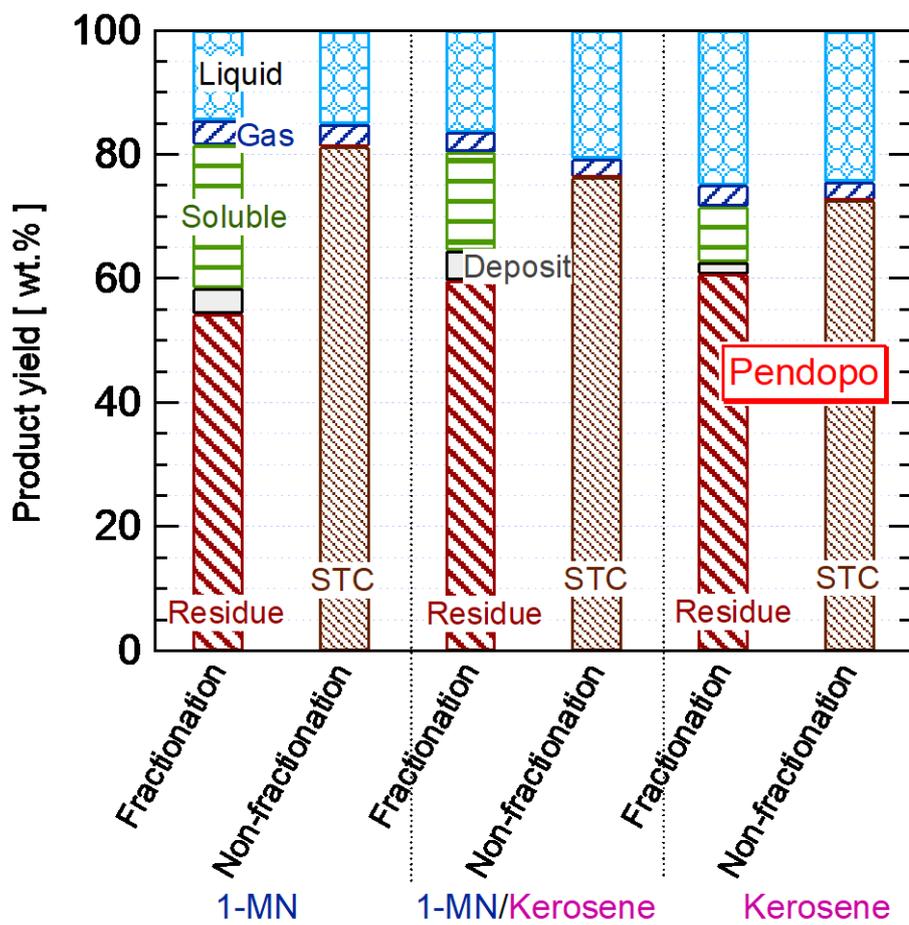


Figure 2.3. Comparison of the product yield distributions between Fractionation scheme and Non-fractionation scheme for PD.

2.3.2 Molecular weight distributions of raw coals and its products

Figure 2.4 compares the molecular weight distributions (MWD) of Soluble prepared using three different solvents for LY. **Figure 2.5** shows similar comparison for PD. The LDI-TOFMS measurement used small amounts but almost same amounts of samples for different samples. Then the intensities obtained are multiplied by the yields of Soluble to construct the figures. This was done so as to make the comparison among the three solvents rather quantitative. Let focus on the MWDs of Solubles prepared using 1-MN and Kerosene for LY first. The MWD obtained from Kerosene extraction is well incorporated in the MWD obtained from 1-MN extraction in either the intensity or the range of molecular-weights. The MWD obtained from Kerosene extraction misses both the lower molecular-weight compounds and higher molecular weight-compounds from the MWD obtained from 1-MN extraction. This is also the case for PD as the MWDs of Solubles in Fig. 2.5 shows. The missing of the higher molecular weight-compounds can be explained by the difference in solubility between 1-MN and Kerosene, and the missing of the lower molecular-weight compounds is due to the loss of those compounds with Kerosene during the evaporation process of Kerosene as discussed above. Thus the MWD measurement well supports the above discussion based on the yield distribution. The MWDs of all Soluble ranged from 200 to 600 in molecular weight with a peak molecular weight at around 300, indicating that Solubles can be utilized as precursors as some value added products including carbon fiber.

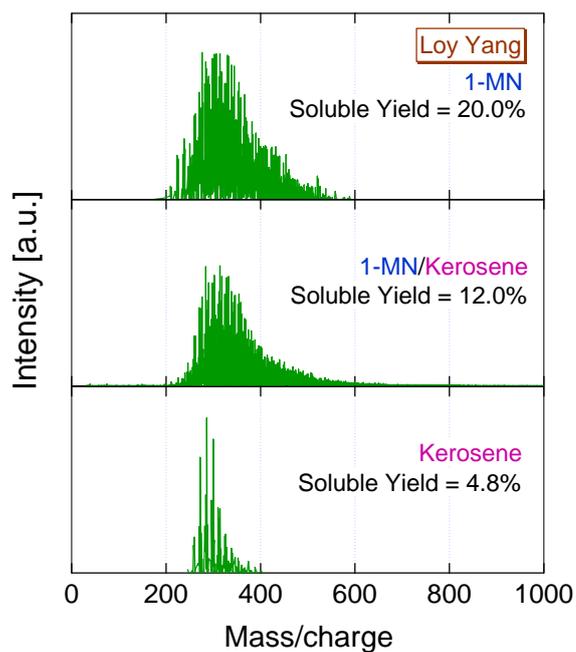


Figure 2.4. Molecular weight distributions of Solubles prepared using three solvents for LY.

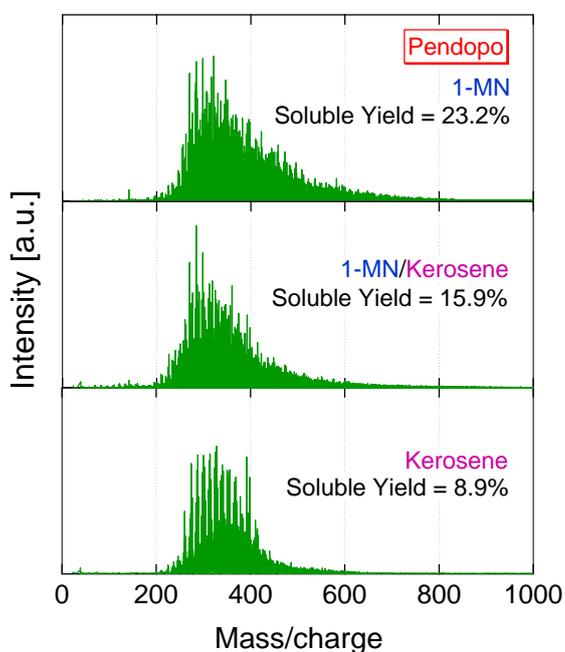


Figure 2.5. Molecular weight distributions of Solubles prepared using three solvents for PD.

2.3.3 The higher heating values (HHVs) of raw coals and its products

Table 2.1 summarizes the higher heating values (HHVs) of three solid fractions and STC obtained from all solvents used. In this study, the higher heating values in dry-ash-free basis of samples were calculated by using the Dulong equation ^[4] below:

$$\text{HHV (MJ/kg, d.a.f.)} = (338.1C + 1441.8H - 180.2O)/1000 \quad (1)$$

where C, H, and O represent the weight percentage of carbon, hydrogen, and oxygen, respectively.

It was found that the sample basis HHVs of Soluble, Deposit, Residue, and STC were all much higher than those of corresponding raw coals. The HHVs of Soluble and Deposit were estimated to be respectively as high as 37.2 to 43.4 MJ/kg, and 30.1 to 31.2 MJ/kg for LY. The HHVs of Soluble and Deposit were respectively as high as 37.6 to 42.1 MJ/kg, and 31.2 to 34.7 MJ/kg for PD. The HHVs of Residue were respectively 28.9 to 29.9 MJ/kg and 27.3 to 29.2 MJ/kg for LY and PD. The HHVs of STC were respectively as high as 28.7 to 31.8 MJ/kg and 30.9 to 31.8 MJ/kg for LY and PD. These HHVs well corresponds to the HHVs of subbituminous or bituminous coals on dry-ash-free basis.

One of the purposes of upgrading technologies of low-rank coal is to increase the heating value of the upgraded product. In this sense the HHVs given above show the validity of the proposed degradative solvent extraction method. However, the heating value recovered in the solid products from raw coal is more informative from the practical viewpoint. It can be examined by using the HHVs converted to the unit weight of raw material by using the yield values and HHVs given in Table 2.1. Then **Figures 2.6** and **2.7** show the HHVs converted to the values per dry-ash-free of 1 kg-raw coal respectively for LY and PD. The heating values recovered were almost equal to the heating values of the raw coals for most of solvent-coal combinations. The smallest recovery ratio was around 80 % for Kerosene-PD combination. Thus, the proposed degradative extraction method was found to be effective not only to produce clean and high heating value product, but to transfer the heating value of the raw coals to the solid products very effectively. This shows that the method is effective even when the solid product is simply utilized as fuel.

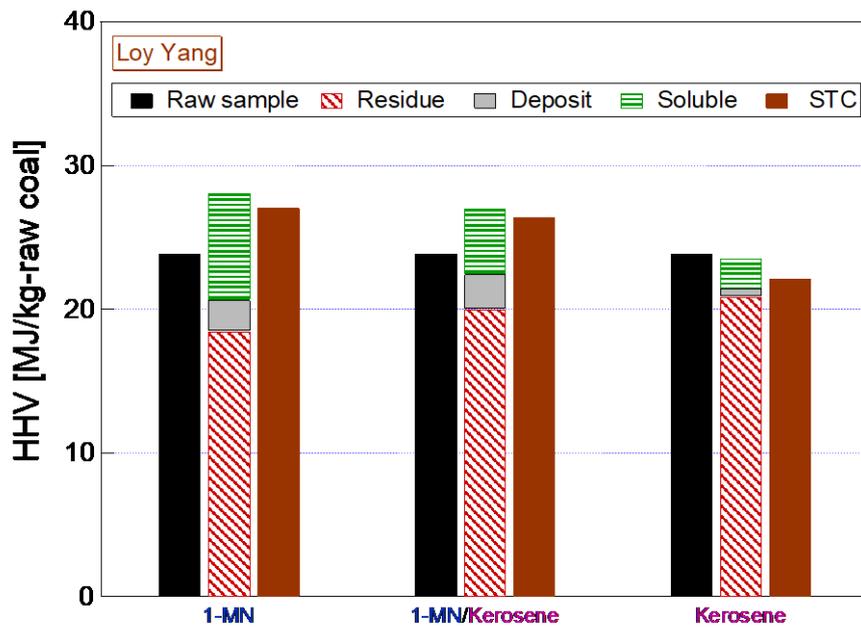


Figure 2.6. Comparison of HHVs among raw coal, solid extracts, and STC for LY on raw coal basis.

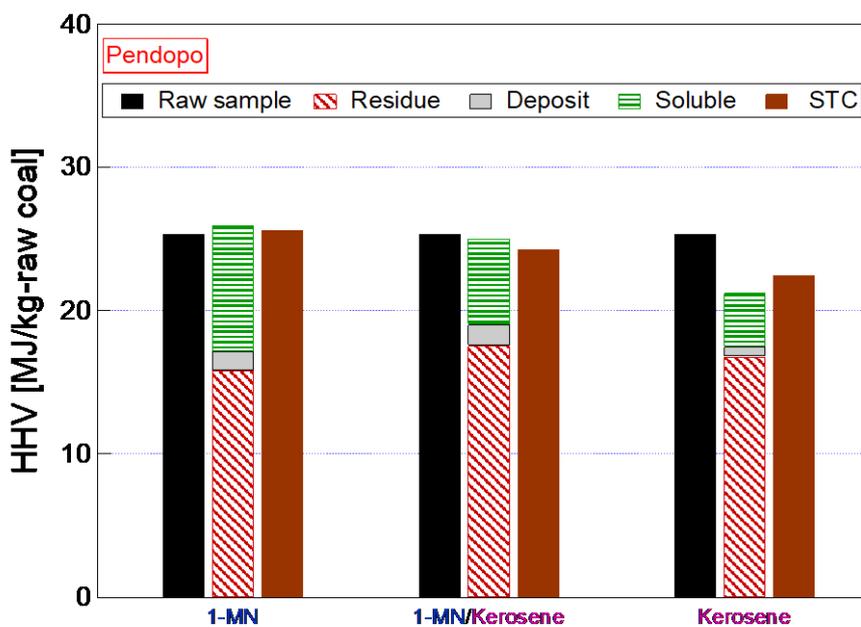


Figure 2.7. Comparison of HHVs among raw coal, solid extracts, and STC for PD on raw coal basis.

2.3.4 Thermal properties of Soluble and STC

The potential utility of the solid products as raw materials for carbon materials was evaluated using thermal analyses. **Figures 2.8** and **2.9** compare the thermogravimetric (TG) curves of raw coal, Solubles, and STCs, respectively, for LY and PD. The solid lines are the TG curves on sample basis and the broken lines are the TG curves on raw coal basis. First we will focus on the TG curves of Solubles. The content of volatile matters is largest for the Soluble prepared from Kerosene and smallest for the Soluble prepared from 1-MN as expected. The TG curves shown on sample basis (solid lines) may be misleading, but the TG curves shown on raw coal basis (broken lines) clearly show that the Soluble prepared from Kerosene can be regarded as a part of the Soluble prepared from 1-MN both for LY and PD. It is also worthy to note that the TG curves of STCs on raw coal basis (broken lines) are so close each other above 400 °C for different solvents. These results again show that solvent did not affect the degradation reaction at 350 °C.

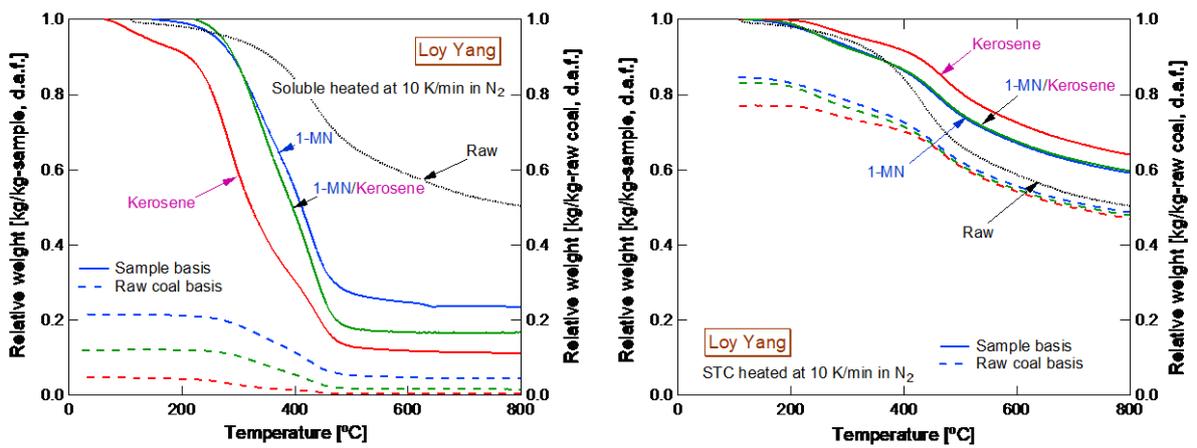


Figure 2.8. TG curves of solid products and raw coal for LY. The solid line shows results on sample basis while the broken line shows the results on raw coal basis.

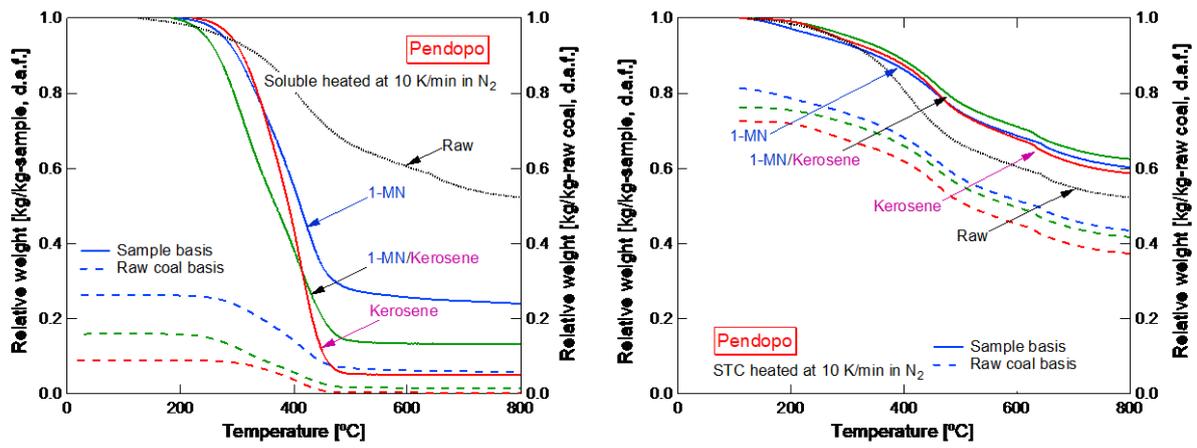


Figure 2.9. TG curves of solid products and raw coal for PD. The solid line shows results on sample basis while the broken line shows the results on raw coal basis.

Figures 2.10 and **2.11** compare the melting behaviors of Solubles for LY and PD, respectively. Since all STCs did not show any melting behaviors, their results are not shown. From the figure, the TMA profiles were rather similar among the Solubles obtained from different solvents. Soluble obtained using 1-MN shows the highest melting point whereas Soluble obtained using kerosene shows the rather low melting point as was expected. In addition, TMA profiles of all Solubles reached -1 , showing their complete melting at less than $200\text{ }^{\circ}\text{C}$. The discussion suggests that solvent may adjust thermoplastic properties so as to meet the requirement of specific use of Soluble.

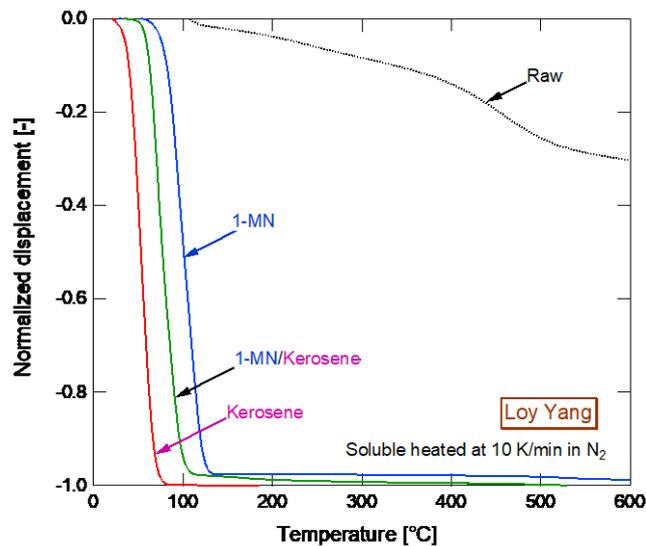


Figure 2.10. TMA profiles of Solubles and raw coal for LY.

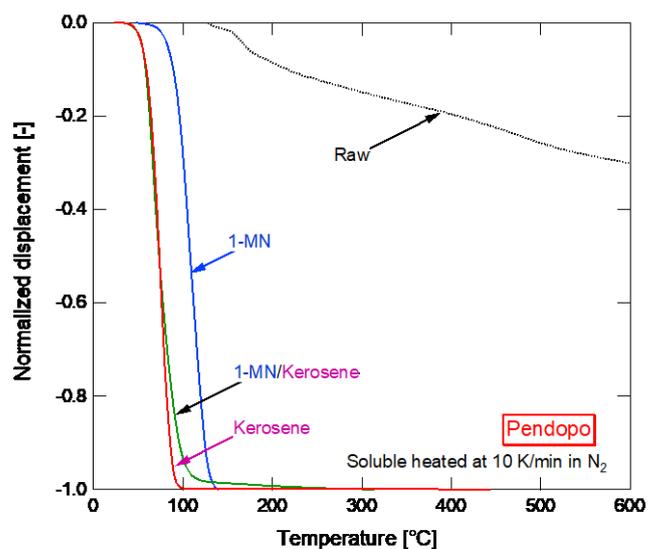


Figure 2.11. TMA profiles of Solubles and raw coal for PD.

2.3.5. Discussion on the role of solvents for coal extraction

We assumed that the effect of solvent on this degradative solvent extraction method should be examined from two viewpoints as stated above. The first one is if solvent affects the degradation reaction at 350 °C. The second one is how solvent affects the product distribution. In other words, the assumption regards that solvent has two roles in the proposed solvent extraction method. Its first role is a media to disperse raw material during the solvent treatment at 350 °C and hence it is not expected to react with the raw material. The second role is to act as extraction solvent to dissolve decomposed and upgraded product by its solubility at 350 °C. Therefore, the product distribution, the yield ratios of Residue, Deposit, and Soluble, are dependent on the kinds of solvent in principle. Then the first question is how solvent affects the product distribution. For both

coals, the Soluble yield was highest using 1-MN, and smallest using Kerosene as expected. Next question is how solvent affects the total solid yield. The sum of the yields of Residue, Deposit, and Soluble was used to examine the effect of solvent. For both coals, the total solid yield was largest using 1-MN, and smallest using Kerosene as shown in Figs. 2.2 and 2.3.

Finally, it was examined which solvent is best to recover STC easily and in high yield. In principle the sum of the yields of Residue, Deposit, and Soluble must be equal to the yield of STC if only solvent and the extraction product can be perfectly separated. It was the case for both LY and PD as shown in Figs. 2.2 and 2.3., but the yield treated by the three solvents as Fig. 2.1. However, it was not the case for PD. The sum of the yields of Residue, Deposit, and Soluble (\cong the yield of STC) obtained using Kerosene was smallest. This was judged to come from the difficulty in removing Kerosene selectively from either Soluble or STC. Some low molecular-weight was judged to be removed with Solvent during the solvent removing process due to high volatility of Kerosene.

Preparation of STC was intended to convert low-rank coal to high quality solid fuel. The properties of STC are little affected by the treating solvent as shown in Table 2.1. The carbon contents of STC prepared using Kerosene were as high as 75.2 to 76.5 %, and therefore their calorific value were as high as 28.7 to 30.9 MJ/kg on d.a.f. basis. Since Kerosene has advantages such as cheap and common practical solvent and the easiness of separation from the upgraded product, it can be a candidate of a practical solvent for preparing STC from low-rank coal.

2.4 Conclusions

In this chapter, the effects of solvent on the degradative solvent extraction of two low-rank coals, Loy Yang (LY) and Pendopo (PD), were examined by using three solvents: 1-MN, Kerosene, and the 1 to 1 mixture of 1-MN and Kerosene. It was judged that solvent does not affect the degradation reaction at 350 °C, and hence the performance of this degradative solvent extraction method such as selective deoxygenation and effective dewatering is realized by all the solvents used. The yield distributions of extracted products were dominated by the solubility of solvent used as expected. 1-MN, showing highest solubility, gave the largest yield of Soluble followed by the mixed solvent, and kerosene (the practical solvent). The preparation of STCs from different solvents also gave the yields close to the sum of the yields of Soluble, Deposit, and Residue for all solvents used. Most of the heating values of solid products were over 29 MJ/kg and rather close to subbituminous coal. All Solubles were found to melt completely at rather low temperature and their behaviors were also similar even using different solvents. Kerosene, having advantages such as cheap and common practical solvent and the easiness of separation from the upgraded product, was expected to be a candidate of a practical solvent for preparing STC from low-rank coal.

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Chapter 3

TG-DSC Study to Measure Heat of Desorption of Water during the Thermal Drying of Coal and to Examine the Role of Adsorption of Water Vapor for Examining Spontaneous Heating of Coal over 100 °C

3.1 Introduction

Many researchers have examined water forms in low-rank coal and/or the interaction of water and low-rank coal. The study of Allardice *et al.* ^[1] and the current review of Yu *et al.* ^[2], for example, well sum up the present state of fundamental researches and drying/dewatering technologies.

From practical viewpoints, examinations of water forms and water-coal interaction have at least two aspects: first one is those examination for as-received coal and the second one is the examinations for dried or partially dried coal. The first one is important for developing advanced drying or dewatering systems. This examination must be performed under the conditions close to those of target drying/dewatering processes. The second one will be significant for effective utilization of dried coals, one of which is the examination of the contribution of adsorption of water vapor to spontaneous heating of coal. The dried coal is known to adsorb water vapor very rapidly from moist air ^[3]. Bhattacharyya ^[4], for example, stated, *“In a humid atmosphere when simultaneous sorption of water vapour and oxygen takes place, the rate of heat generation in coal due to the sorption of water vapor becomes the rate-determining factor. For a given coal, this rate of heating has been found to reach the maximum within a few hours of the start of the process, and to increase with the increase in the equilibrium deficiency of the coal. In the absence of total heat dissipation any increase in the coal temperature accelerates its rate of oxidation, thus producing more heat. This gradual acceleration of oxidation may eventually start the actual combustion.”* In previous papers Miura has also shown that the rate of adsorption of water vapor on dried coal is very rapid even from the ambient atmosphere and showed experimentally that the large amount of heat generated

by the adsorption of water vapor raises the coal temperature significantly and instantly [5], [6].

From the above two aspects, the author has reviewed the literature and has realized that most of the results are not directly utilized for the practical applications. Pioneering works to examine water forms and isosteric heat of adsorption of water vapor in as-received coal by Allardice *et al.* [7], [8] were performed using elaborate measurements of desorption isotherms during the drying stage at 30 to 60 °C. Relatively new two methods, proton nuclear resonance (NMR) spectroscopy and differential scanning calorimetry (DSC), measure proton mobility and heat of congelation, respectively, at a temperature range of 220 to 330 K [9–12]. Most of these examinations were performed to categorize the water in as-received coal to “bound water” and “non-freezable water”. The above cited paper of Bhattacharyya [4] measuring the rates of heat generation in coal due to the sorption of water vapor and coal-oxygen interaction was carried out using a calorimeter at 30 °C. The thermal drying of as-received coal will be conducted over 100 °C and measurement of the rates of heat generation in coal due to the sorption of water vapor and coal-oxygen interaction at higher temperatures at which the rate of heat generation by the oxidation of coal is large enough to lead to self-ignition will be more important when examining the propensity to spontaneous heating of coal.

In this chapter, the objectives are to measure the heat of desorption of water during the thermal drying of as-received coal at a temperature of 107 °C and to clarify the role of adsorption of water vapor in relation to coal-oxygen interaction at 107 °C from the viewpoint of examining propensity to spontaneous heating of dried coal. A TG-DSC analyzer which measures weight change and heat flow in moist atmosphere was used for

the purposes. By using the TG-DSC analyzer, the heat flow is directly related to the weight change. Therefore, this enables to estimate the heats of adsorption/desorption of water directly at such a high temperature.

3.2 Experimental

3.2.1 Materials

Three coals, two Indonesian lignites (Pendopo, abbreviated to PD, and coal A), and an Australian brown coal (Loy Yang, LY), were used in this chapter. The properties of the three coals used are listed in **Table 3.1**. As-received coal A was ground into fine particles of less than 150 μm in diameter and stored in small airtight bags, about 100 g in each bag, to prevent the oxidation in ambient atmosphere. As-received LY coal was stored in a pail with airtight lid. As-received Pendopo coal was stored in a 1 L airtight bin. For coal A, the airtight bag was opened just before the experiment and the remaining coals were carried to airtight bin and stored in a refrigerator. For Pendopo and LY, small amount of sample was taken out either from the pail or the bin and pulverized to fine particles in an agate mortar just before the experiments.

Table 3.1. Analyses of coals used.

coal	ultimate analysis [wt%, d.a.f. ^a]				proximate analysis [wt%, d.b. ^b]		
	C	H	N	O+S (diff)	VM	FC	ash
Loy Yang (LY)	66.6	4.5	0.5	28.4	50.0	47.8	2.2
Pendopo (PD)	67.5	5.1	0.8	26.6	49.4	38.0	12.6
Coal A	73.1	5.1	1.1	20.7	50.0	48.0	2.0

^aDry, ash-free. ^bDry basis.



Photo 3.1. TG-DSC analyzer used for simultaneous measurement of weight and heat flow during oxidation of coals.

3.2.2 Experiment procedure

As shown in **Photo 3.1**, a TG-DSC analyzer (NETZSCH, STA 449F3 Jupiter) was used for simultaneous measurements of weight change and heat flow. The analyzer with a platinum furnace was carried out for the drying and subsequent oxidation of coal in a dry air. The analyzer with a water vapor furnace was carried out for the water vapor adsorption from a saturated air and a saturated nitrogen on the dried coal, and desorption of adsorbed water from the coal adsorbing water in a nitrogen stream. For both experiments, about 15 mg (on dry basis) of coal sample placed in a PtRh crucible (6.8mm ϕ x 3 mmH) was set on the sample probe and an identical empty PtRh crucible was set on the reference probe. The sample crucible and the reference crucible were heated at the heating rate of 10 °C /min to 107 °C at which they were kept 20 min in a 100 mL/min of N₂ stream to evaporate water adsorbed on coal. The weight change and heat flow of this pretreatment stage measured with the platinum furnace were conducted for examining the heat required for drying of coal. For the subsequent oxidation of the dried coal in a dry air, the gas stream was changed to 100 mL/min of dry air stream and kept 30 min at 107 °C. After 30 min of oxidation, the gas stream was switched back to N₂ to terminate the oxidation and to check the base line of heat flow. For the water vapor adsorption on the dried coal and desorption of adsorbed water experiments, the nitrogen stream was changed to either an air stream or a nitrogen stream saturated with water vapor at 60 °C (pressure of water vapor, $p_{\text{H}_2\text{O}} = 19.92$ kPa) and kept 30 min to complete the adsorption. Then the gas stream was switched back to the N₂ stream at 107 °C and kept for 30min to examine the desorption behavior of the adsorbed water vapor. The saturated air and the saturated nitrogen were supplied from a steam generator separately designed. The line connecting the steam generator and the TG-DSC analyzer was heated over a temperature of 80 °C to prevent the water vapor from condensation.

For coal A, the water vapor adsorption experiments from air saturated with water vapors at 40 °C ($p_{\text{H}_2\text{O}} = 7.375$ kPa), 50 °C ($p_{\text{H}_2\text{O}} = 12.34$ kPa), and 80 °C ($p_{\text{H}_2\text{O}} = 47.36$ kPa) were also performed to examine the effect of pressure of water vapor. For LY coal, the water vapor adsorption experiment from a nitrogen saturated with water vapor at 60 °C was also performed at 90 °C to examine the effect of temperature on the adsorption of water vapor.

3.3 Results and Discussion

3.3.1 Drying of as-received coal in a nitrogen stream and the oxidation of dried coal in a dry air

Figure 3.1 shows typical data obtained through the drying in N_2 stream and oxidation in dry air for LY coal. The big weight decrease and accompanying big endothermic peak were clearly observed during the drying stage. The relative weight to dried coal was calculated by assuming that all inherent water was removed by keeping coal for 20 min at 107 °C. About 60 % of water evaporated during the heating up stage and the rest of water evaporated at the final temperature of 107 °C. The weight change and the heat generation rates after switching the gas stream from the N_2 stream to the dry air are much smaller than those during the drying stage, but some changes were clearly observed.

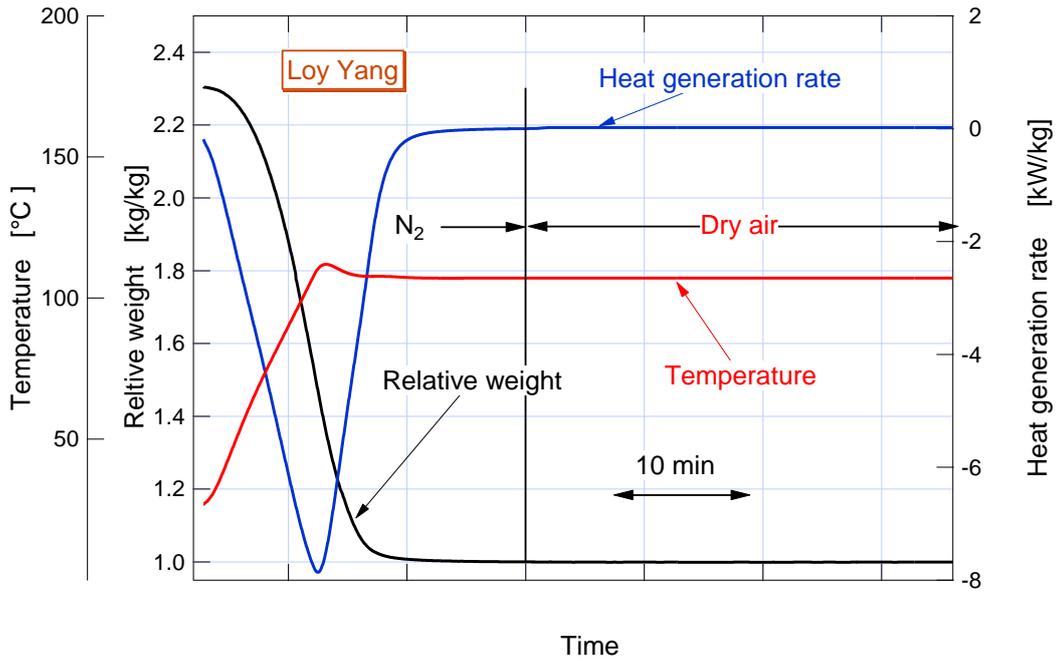


Figure 3.1. Typical data obtained during drying in N₂ stream and oxidation in dry air.

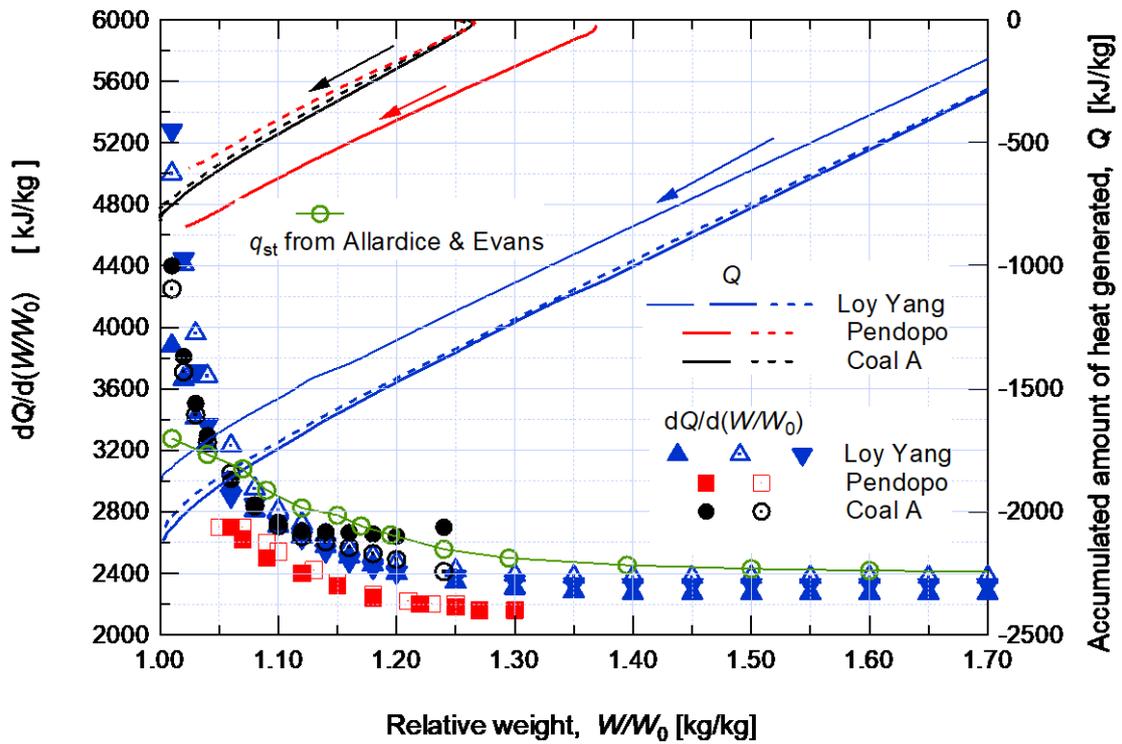


Figure 3.2. Heats of vaporization of water during drying of as-received coals in N₂ stream. Multiple data for same coal are results of duplicate experiments.

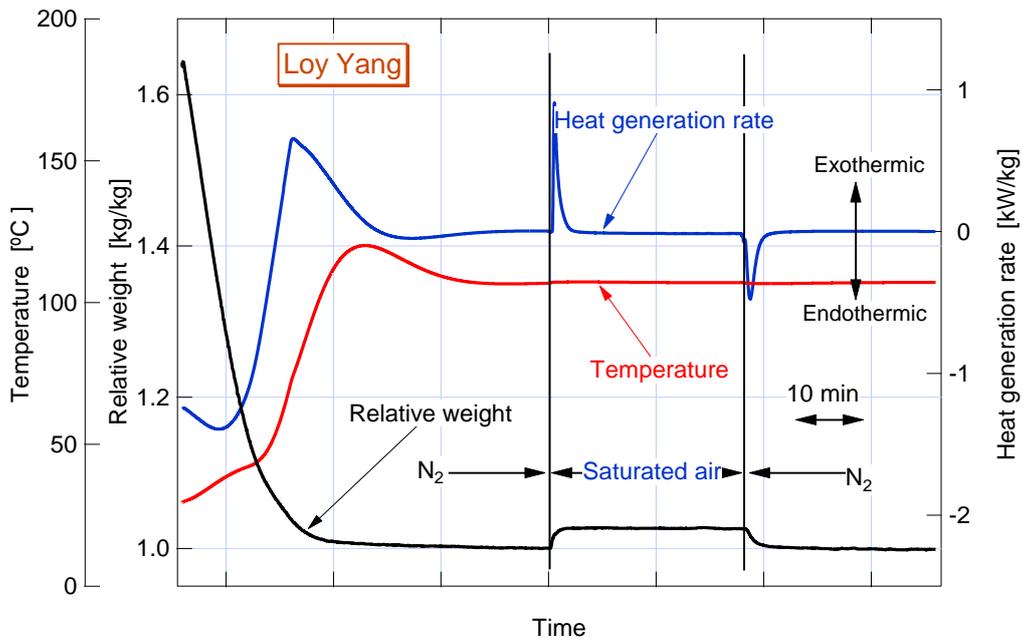


Figure 3.3. Typical data obtained by an experiment where dried coal is contacted with air containing water vapor (Saturated air at 60 °C) at 107 °C and subsequent desorption of water in N₂ stream.

The heat generation rate data during the drying stage were integrated to estimate the amount of heat generated, Q , and plotted against the relative weight, W/W_0 , (> 1), in **Figure 3.2**. Results of all duplicate runs are shown together in the figure. The Q values during the heating up stage inevitably involve the contribution of endothermic heat used to heat up the coal and adsorbed water, but its contribution was neglected in this chapter because it is difficult to separate its contribution from total heat generation and because its contribution is null after reaching 107 °C, and mainly because the contribution is much smaller than the heat required to evaporate water. The Q vs. W/W_0 relationships are not exactly linear but their slopes clearly gradually increase with decreasing W/W_0 . The slopes of the Q vs. W/W_0 relationships, $dQ/d(W/W_0)$, represent the amount of heat needed to evaporate water at the corresponding W/W_0 value. The values of $dQ/d(W/W_0)$ were estimated by graphically differentiating the Q vs. W/W_0 relationships and shown as the keys in Fig. 3.2. The $dQ/d(W/W_0)$ values for LY coal were almost constant of 2300 to 2350 kJ/kg until W/W_0 decreases to 1.35. With further decrease of W/W_0 , the $dQ/d(W/W_0)$ values increased further to reach 5000 kJ/kg or so at $W/W_0 \cong 1$. Pendopo and Coal A showed similar trends, although the initial water contents of the coals were less than 0.35 kg/kg. The isosteric heats of adsorption of water vapor measured by Allardice and Evans^[8], q_{st} by their notation, are shown in Fig. 3.2 for comparison purpose. The q_{st} values were obtained from desorption isotherms measured at 30, 40, 50, and 60 °C for as-received Yallourn coal. The values were 10.3 kcal/mol (= 2392 kJ/kg) for $W/W_0, > 1.5$ and they increased steeply with decreasing W/W_0 to reach 14.0 kcal/mol (= 3251 kJ/kg) at $W/W_0 = 1.025$. The heat of vaporization of water, ΔH_{vap} , given in a steam table is 2406.9 kJ/kg at 40 °C, 2344.0 kJ/kg at 70 °C, and 2238.1 kJ/kg at 107 °C. The q_{st} values for $W/W_0, > 1.5$ almost exactly coincides with ΔH_{vap} at around 40 °C and the $dQ/d(W/W_0)$ values of LY for $W/W_0 > 1.35$ almost exactly coincides with ΔH_{vap} at 70 to 107 °C. This shows

that the TG-DSC measurement of this work is accurate enough to estimate the heat of vaporization as accurate as the thermodynamics measurement performed by Allardice and Evans. The big merit of the TG-DSC measurement is just one measurement can give similar results as were obtained by elaborate experiments of Allardice and Evans. In addition, the $dQ/d(W/W_0)$ values obtained will be directly utilized to examine the heat needed in practical coal drying process.

There may be a question on as high as 5000 kJ/kg of $dQ/d(W/W_0)$ at $W/W_0 \approx 1$ for LY coal. Allardice and Evans^[8] stated, by mentioning the 14.0 kcal/mol (= 3251 kJ/kg) of q_{st} at $W/W_0 = 1.025$, that “*These results do not imply that there is no strongly chemisorbed water associated with the brown coal. In fact, earlier work by the authors established that some water is so strongly bound to the coal that it can be desorbed only by thermal treatment.*” This may not exclude high $dQ/d(W/W_0)$ value of 5000 kJ/kg for LY coal as observed in this work.

3.3.2 Adsorption of water vapor on dried coal and desorption of adsorbed water at 107 °C

Fig. 3.3 shows typical data obtained using the TG-DSC analyzer with the water vapor furnace for the water vapor adsorption on the dried coal and desorption of adsorbed water at 107 °C for LY coal. The programmed heating profile before changing the gas flow from N₂ gas to the air containing water vapor at 107 °C is exactly same as that for the drying and air oxidation experiment shown in Fig. 3.1. The actual temperature profile shown as the red solid line in **Figure 3.3** did not exactly follow the programmed temperature profile, resulting in rather complicated change especially in heat generation rate. This comes from the difficulty in precise temperature controlling at low temperature

region using the water vapor furnace which has rather big heat capacity. After reaching and being stabilized at 107 °C, however, temperature is exactly kept at 107 °C and the signals of weight change and heat flow were so smooth and can well represent the changes coming from adsorption and desorption of water and some oxygen-coal interaction involved when the adsorption experiment is performed in saturated air stream.

The data typically shown in Fig. 3.3 were replotted by choosing the time when the gas flow was changed from N₂ gas to either air or nitrogen containing water vapor as 0. The plotted results for LY, PD, and coal A are respectively shown in **Figures 3.4, 3.5, and 3.6**. In each figure the upper graph shows the relative weight, W/W_0 , and the lower graph shows the heat generation rate, dQ/dt , and the accumulated amount of heat generated, Q , which was obtained by integrating dQ/dt over time. The data for the oxidation in dry air, which were typically shown in Fig. 3.1, are also included in each figure. For LY coal, the result of the water vapor adsorption experiment from a saturated nitrogen stream performed at 90 °C is included in Fig. 3.4. For coal A, the results of the water vapor adsorption from airs saturated with water vapors at 40 °C, 50 °C, and 80 °C are also included in Fig. 3.6.

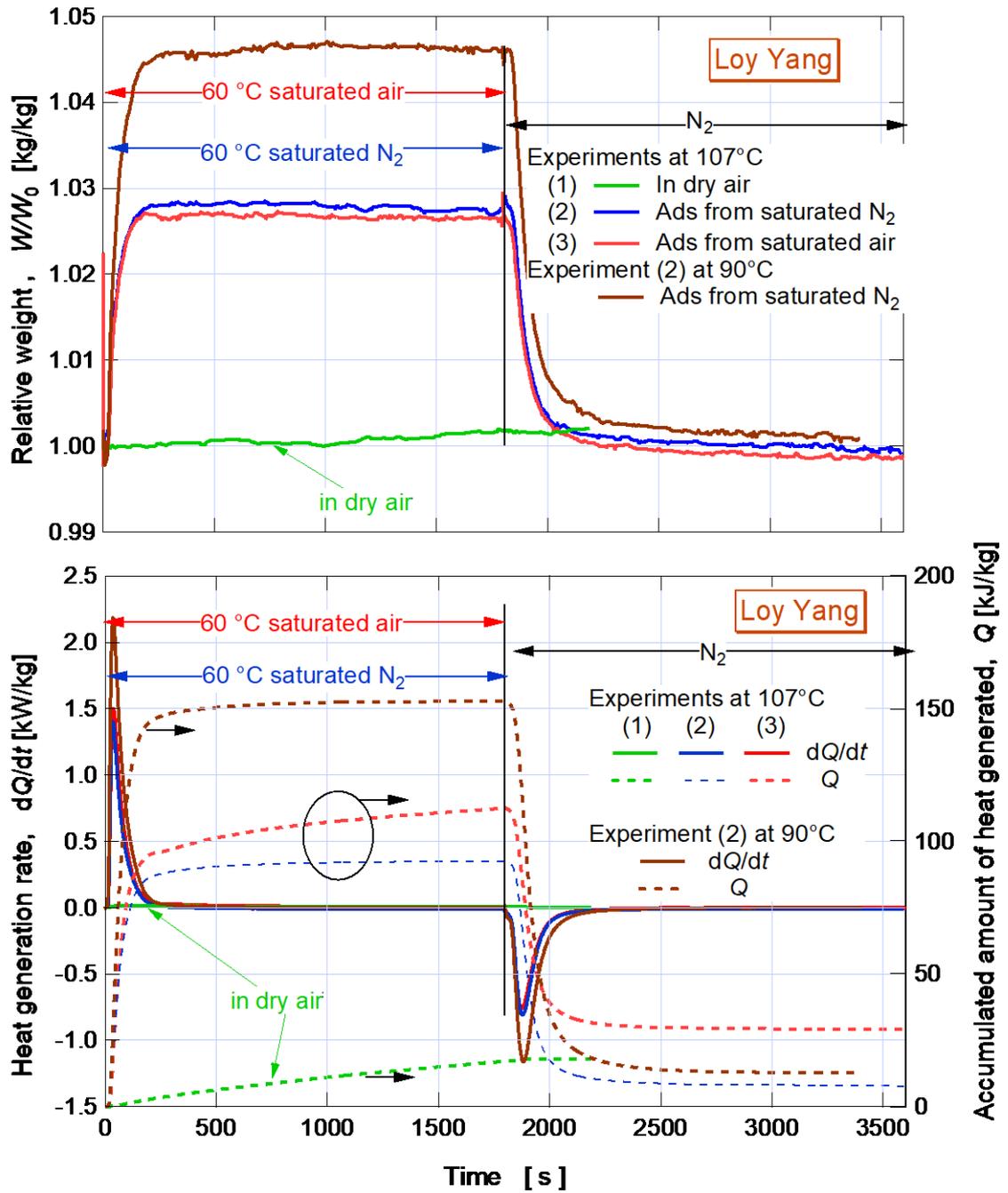


Figure 3.4. Changes of relative weight (upper graph) and heat generation rate, dQ/dt , and amount of heat accumulated, Q , for Loy Yang.

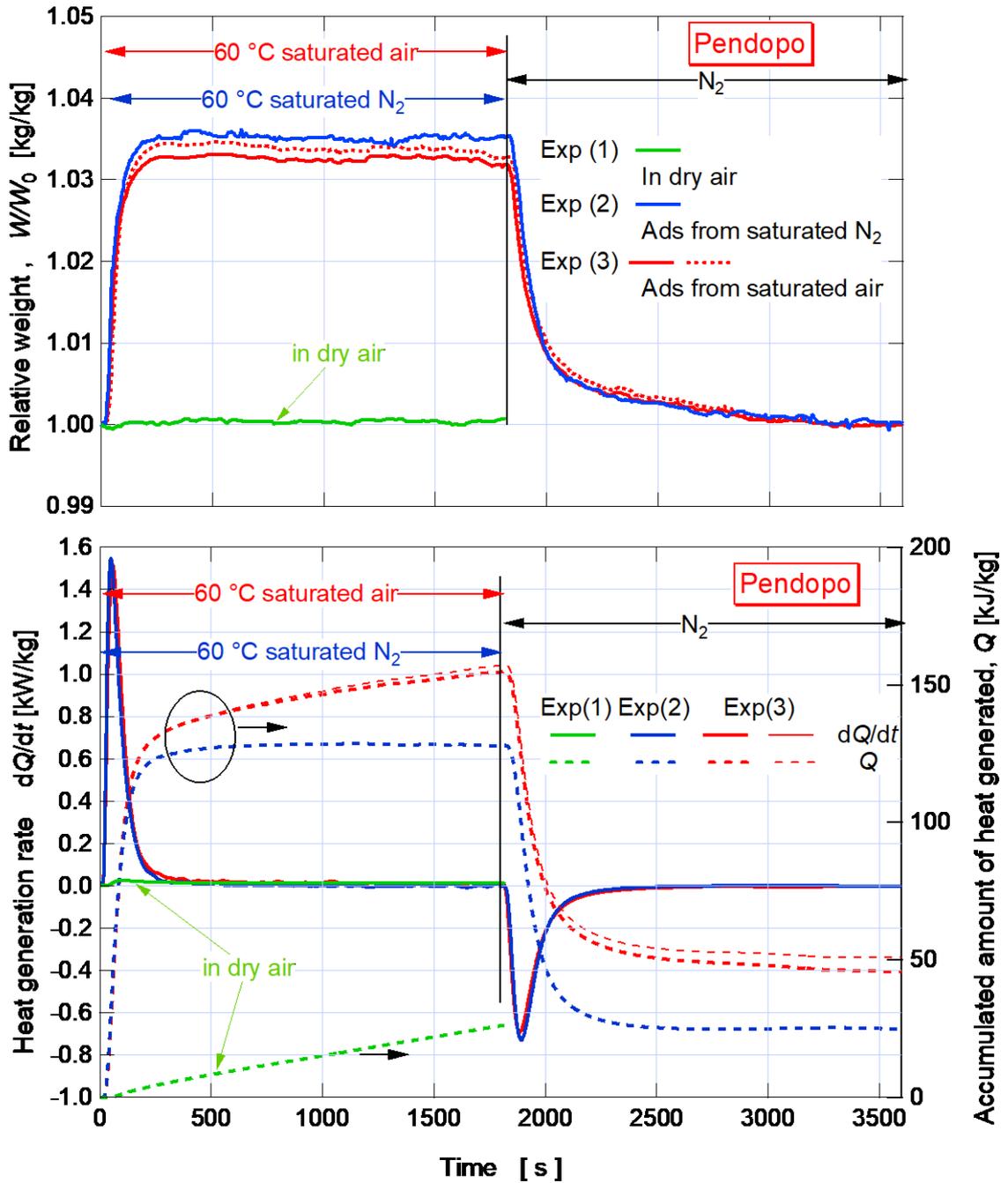


Figure 3.5. Changes of relative weight (upper graph) and heat generation rate, dQ/dt , and amount of heat accumulated, Q , for Pendopo. Multiple data for same experiment are results of duplicate runs.

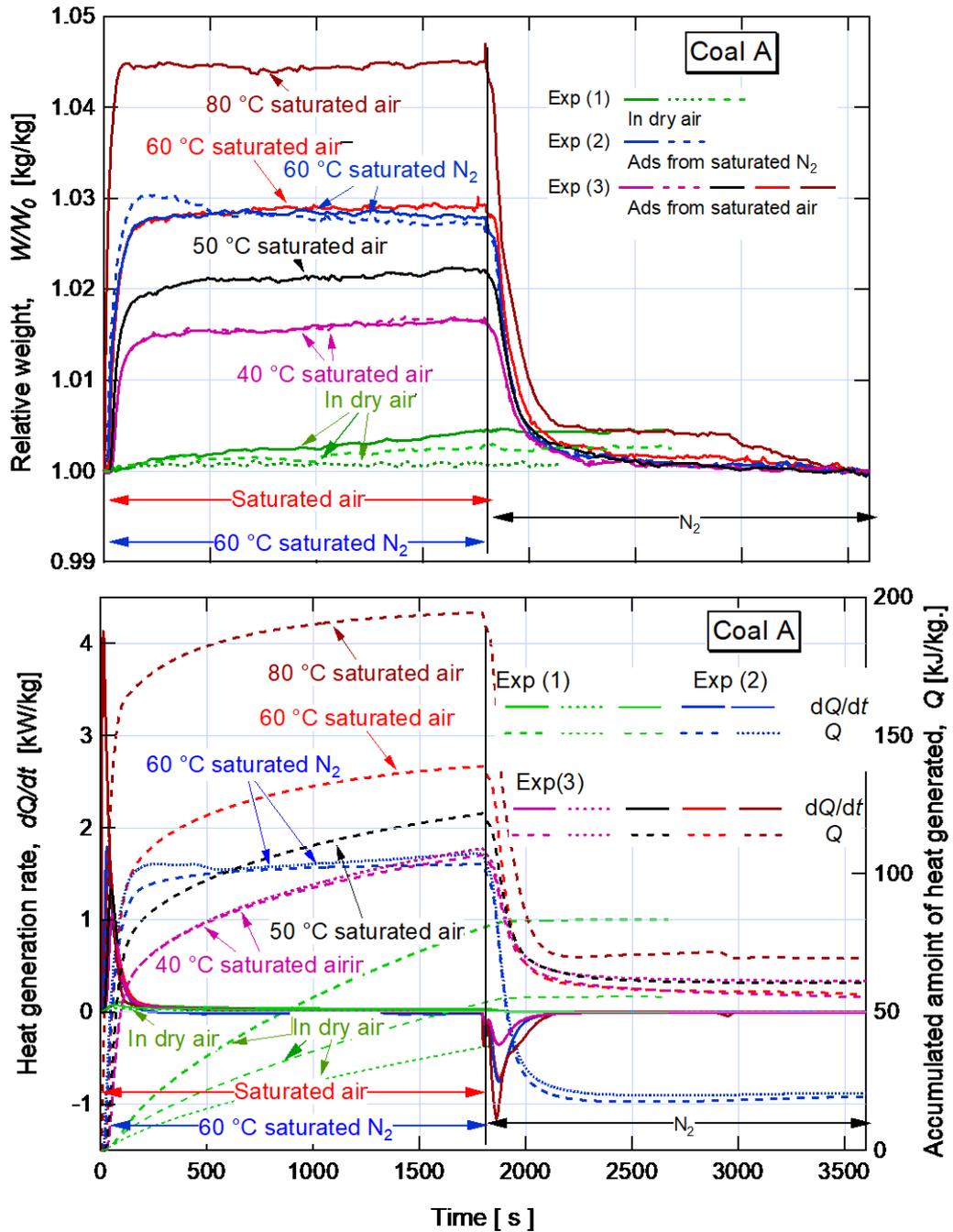


Figure 3.6. Changes of relative weight (upper graph) and heat generation rate, dQ/dt , and amount of heat accumulated, Q , for coal A. Multiple data for same experiment are results of duplicate runs.

One of our concerns when examining propensity of coal to spontaneous heating is the relative magnitude of heat generation between water vapor adsorption and oxidation by dry air at a temperature as high as 107 °C. It can be examined by comparing three experiments: (1) oxidation in dry air, (2) adsorption of water vapor from water vapor containing N₂, and (3) adsorption of water vapor from water vapor containing air. Experiment (1) solely examines the coal-oxygen interaction, experiment (2) is expected to solely examine the adsorption of water vapor, and experiment (3) examines the combined effects among coal, oxygen, and water vapor. First, let us focus on Fig. 3.4 which shows the comparison of three experiments at 107 °C for LY. Experiment (1) shows that the relative weight, W/W_0 , gradually increases with time but it was only 1.002 even after 30 min of reaction. Some amount of heat was generated and the accumulated amount of heat generated, Q , reached 17 kJ/kg after 30 min of reaction. Experiment (2) shows that W/W_0 rapidly increased on changing the gas stream from the N₂ to the N₂ containing water vapor to reach 1.028 in 2 min or so and shows no further appreciable change. Heat was also generated rapidly in parallel to the change of W/W_0 and the Q value finally reached 92.4 kJ/kg in 30 min. Experiment (3) shows that W/W_0 rapidly increased on changing the gas stream from the N₂ to the air containing water vapor to reach 1.027 in 2 min or so and shows no further distinct change. The heat generation rate, dQ/dt , rapidly increased to reach a peak of 1.5 kW/kg at 40 s and then decreased rapidly, and the Q value reached 85 kJ/kg in 2 min and finally reached 112.5 kJ/kg in 30 min. These results clearly show that the contribution of the adsorption of water vapor on coal from the atmosphere containing water vapor by as low as 19.92 kPa of p_{H_2O} (= vapor pressure at 60 °C) is much more significant than the action of dry air on coal even at 107 °C. The Q value as large as 90 kJ/kg is large enough to raise coal temperature by more than 60 °C under adiabatic conditions. Since the adsorption of water vapor is completed

in several minutes, it is well expected that coal temperature will be raised instantly if dried coal contacts with the steam vapor.

Another concern is if the coal-oxygen interaction and water vapor adsorption on coal are independent events or not. If we focus on the heat generation, the two events are judged to be independent and parallel because the Q vs. time relationship of experiment (3) is well equated to the sum of the Q vs. time relationships of experiments (1) and (2). It was not exactly the case for the weight change. Experiment (2) showed slightly larger weight increase than experiment (1), but the difference was rather small. The discussion suggests that the coal-oxygen interaction and water vapor adsorption on coal can be treated as independent events from practical viewpoint for LY coal.

The results shown for PD in Fig. 3.5 show almost similar trends in the changes of both relative weight and heat generation as for LY except that the dried PD coal adsorbed 0.035 kg/kg of water. Results of duplicated experiments for both experiments (2) and (3) well show the accuracy of the experiments of this work.

Fig. 3.6, showing the results for coal A, involves the experiments performed with airs saturated with water vapors at 40 °C ($p_{\text{H}_2\text{O}} = 7.375$ kPa), 50 °C ($p_{\text{H}_2\text{O}} = 12.34$ kPa), and 80 °C ($p_{\text{H}_2\text{O}} = 47.36$ kPa). The results of several duplicate runs performed are also included in the figure. The duplicate runs for experiments (2) and (3) showed excellent reproducible results. However, duplicate runs of experiment (1), oxidation in dry air, were not so reproducible. Preliminary studies showed that coal A is very reactive in dried air, which means that even the as-received coal containing water by more than 30 % is oxidized rather quickly in ambient atmosphere. The experiment performed by using the

coal from a newly opened airtight bag gave the largest oxidation rate. Using the coal stored in a refrigerator after opening the airtight bag showed smaller oxidation rate. Then it was judged that the slight differences in the degree of oxidation in ambient atmosphere during the storage affected the results. However, it was not the case for either LY or PD. It was also not the case for either experiment (2) or (3) for coal A as just discussed above.

By taking into account the high reactivity of coal A to dried air, the relative magnitude of heat generation between water vapor adsorption and oxidation by dry air at temperatures was examined by focusing on experiments (2) and (3) performed with the gas stream saturated with water vapor at 60 °C and experiment (1) performed with dry air. Experiment (1) shows that the relative weight, W/W_0 , gradually increases with time to reach 1.0007 to 1.0048 after 30 min of reaction. Fairly large amount of heat was generated accompanying the weight change and the accumulated amount of heat generated, Q , reached as high as 37.3 to 79.8 kJ/kg after 30 min of reaction. Experiment (2) shows that W/W_0 rapidly increased to reach 1.027 to 1.030 in 2 min or so and showed no further change. Heat was generated rapidly in parallel to the change of W/W_0 and the Q value finally reached 102 to 108 kJ/kg in 30 min. Experiment (3) shows that W/W_0 rapidly increased to reach 1.027 in 2 min or so and showed gradual increase with increasing time to reach 1.029 in 30 min. The Q value reached over 100 kJ/kg in 2 min and finally reached 139.2 kJ/kg in 30 min. Next we focused on experiment (3) performed with air saturated with different levels of water vapors. Both the W/W_0 and Q values increased in parallel to the increase of the water vapor pressure. The W/W_0 value reached a plateau in 5 min or so, indicating that the adsorption of water vapor is finished in 5 min or so for every level of water vapor. The Q value increased rapidly initially and gradually

increased after 5 min or so. The Q vs. time relationships look almost parallel after 5 min where coal-oxygen interaction dominates.

Comparison of experiments (2) and (3) with the atmosphere saturated with water vapor at 60 °C indicates that the weight increase at the time of 500 s can be equated to the equilibrium weight of water adsorbed. Assuming that this is the case for other experiments (3) performed with different water vapor pressures of $p_{\text{H}_2\text{O}}$, the Q values at the time of 500 s were plotted against corresponding W/W_0 values as the key \odot in **Figure 3.7**. The results of experiments (2) and (1) are also included, respectively, as the keys \odot and \bullet . The slope of the smoothly connected Q vs. W/W_0 relationship gives the heat of adsorption at the corresponding W/W_0 value. The slope of the line connecting 3 data points for smaller $p_{\text{H}_2\text{O}}$ values is 2920 kJ/kg and the slope of the line connecting two data points for larger $p_{\text{H}_2\text{O}}$ values is 2550 kJ/kg. Since the heat of vaporization of water, ΔH_{vap} , is 2238.1 kJ/kg at 107 °C, the estimated values of the heat of adsorption are slightly larger than ΔH_{vap} . This clearly shows that the increases of both Q and W/W_0 with increasing $p_{\text{H}_2\text{O}}$ value solely come from the adsorption of water. It is also suggested that the Q vs. W/W_0 relationship extrapolated to $W/W_0 \cong 1$ gives the contribution of the coal-oxygen interaction. The Q value at $W/W_0 \cong 1$ is estimated to be around 20 kJ/kg, which is close to the difference between the Q values of experiments (3) and (2) for $p_{\text{H}_2\text{O}} = 19.92$ kPa (atmosphere containing water vapor saturated at 60 °C). These examinations showed that the contribution of adsorption of water is larger than that of coal-oxygen interaction even at the relative humidity of as low as 0.057 (= 7.375 kPa /129.47 kPa) at as high as 107 °C, and the contribution of the adsorption of water vapor increases with increasing relative humidity of the air and will be almost 10 times larger than the contribution of coal-oxygen interaction at the relative humidity of 0.366 ($p_{\text{H}_2\text{O}} = 47.36$ kPa). It is also

well assumed that the contribution of coal-oxygen interaction and water vapor adsorption on coal are independent as the first approximation for coal A.

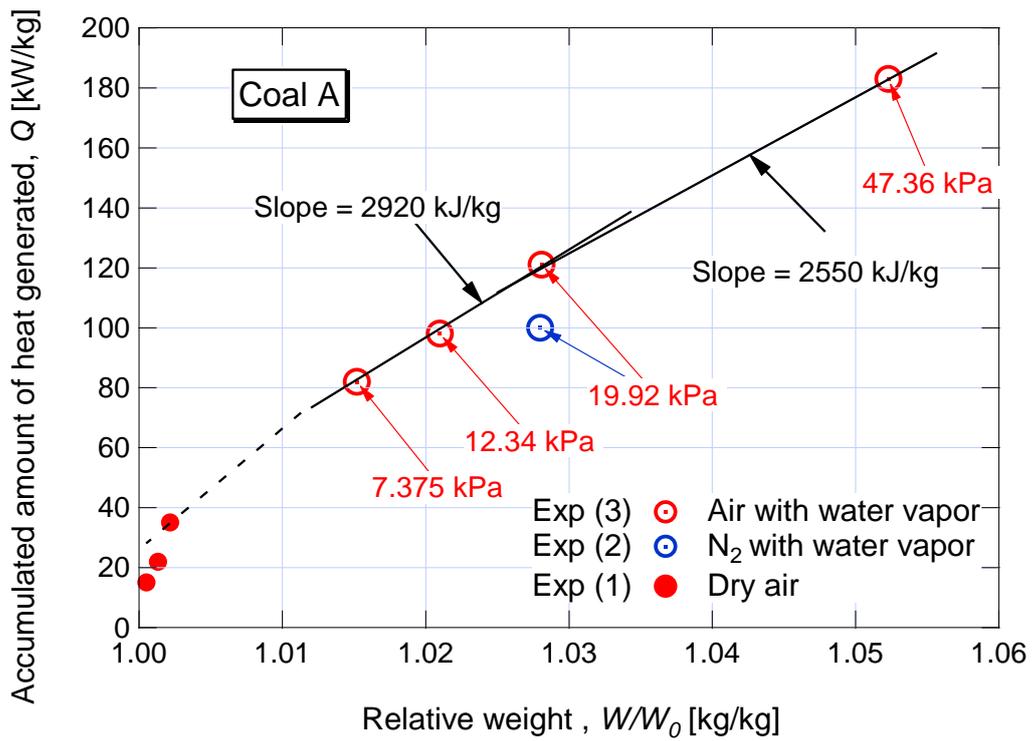


Figure 3.7. Estimation of heat of adsorption, ΔH_{ads} , from experiment (3) performed at different water vapor pressures for coal A.

3.3.3 How can we estimate the contribution of water vapor adsorption at 107 °C

One of next questions is how we can estimate the amount of water adsorbed from the pressure of steam vapor, $p_{\text{H}_2\text{O}}$, or the relative humidity ($= p_{\text{H}_2\text{O}}/p_s$) of the atmosphere at as high as 107 °C. Then it was tried to estimate the adsorption isotherm at 107 °C from the adsorption isotherm measured at 30 °C for the dried coal A using a volumetric adsorption apparatus. The adsorption isotherms at 30 °C is shown in Fig. 3.8 by the black line with + markers. The Clausius-Clapeyron equation applied to adsorption of vapor allows to estimate the isosteric heat of adsorption from the adsorption isotherms measured at two different temperatures by

$$\ln\left(\frac{p_{\text{H}_2\text{O},2}}{p_{\text{H}_2\text{O},1}}\right) = -\frac{q_{\text{st,av}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (1)$$

where T_1 and T_2 are the temperatures, $p_{\text{H}_2\text{O},1}$ and $p_{\text{H}_2\text{O},2}$ are the equilibrium vapor pressures at a same amount of adsorbed of the two adsorption isotherms, R is the gas constant, and $q_{\text{st,av}}$ is the average isosteric heat of adsorption between T_1 and T_2 . This equation can be used to estimate the adsorption isotherm at T_2 from the adsorption isotherm at T_1 by assuming $q_{\text{st,av}}$ value. By choosing $T_1 = 303.15$ K and $T_2 = 380.15$ K, the adsorption isotherm at 107 °C were estimated for three $q_{\text{st,av}}$ values of 2500, 2750 and 3000 kJ/kg as shown by the blue lines with markers in **Figure 3.8**. The equilibrium water contents adsorbed obtained above for four $p_{\text{H}_2\text{O}}$ values are plotted as the key \odot in Fig. 3.8. It is surprising to find that the 3 data points for smaller $p_{\text{H}_2\text{O}}$ values lie on the adsorption isotherm estimated using $q_{\text{st,av}} = 2750$ kJ/kg, and the data point for $p_{\text{H}_2\text{O}}/p_s = 0.366$ ($p_{\text{H}_2\text{O}} = 47.36$ kPa) lie slightly above the isotherm estimated using $q_{\text{st,av}} = 2750$

kJ/kg. This indicates that the $q_{st,av}$ value for the data point is slightly smaller than 2750 kJ/kg. Allardice and Evans ^[8] estimated $q_{st,av}$ values of dried Yallourn brown coal between 30 to 60 °C from the adsorption isotherms measured at 30, 40, 50, and 60 °C. They slightly increased from 2418 kJ/kg at the equilibrium water content of 0.15 kg/kg to 2464 kJ/kg at the equilibrium water content of 0.045 kg/kg with decreasing equilibrium water content. Assuming that these $q_{st,av}$ values for coal A are same as those for Yallourn brown coal, the $q_{st,av}$ for the three smaller p_{H_2O} values can be roughly calculated as

$$q_{st,av} \cong (2464+2920)/2 = 2692 \text{ kJ/kg}$$

This value is surprisingly so close to 2750 kJ/kg.

The above discussion clarified that the TG-DSC measurement used in this work is so accurate and that the adsorption of water vapor on coal at as high as 107 °C can well be treated in the framework of classical thermodynamics.

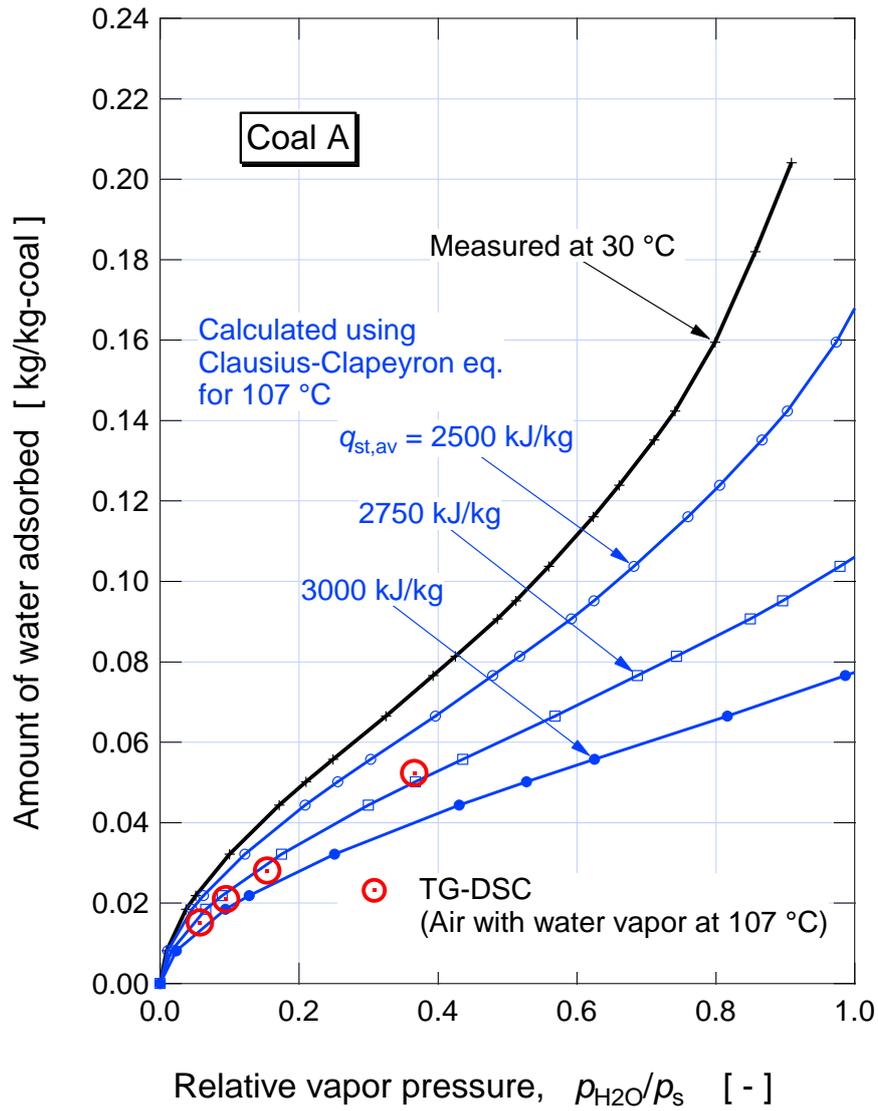
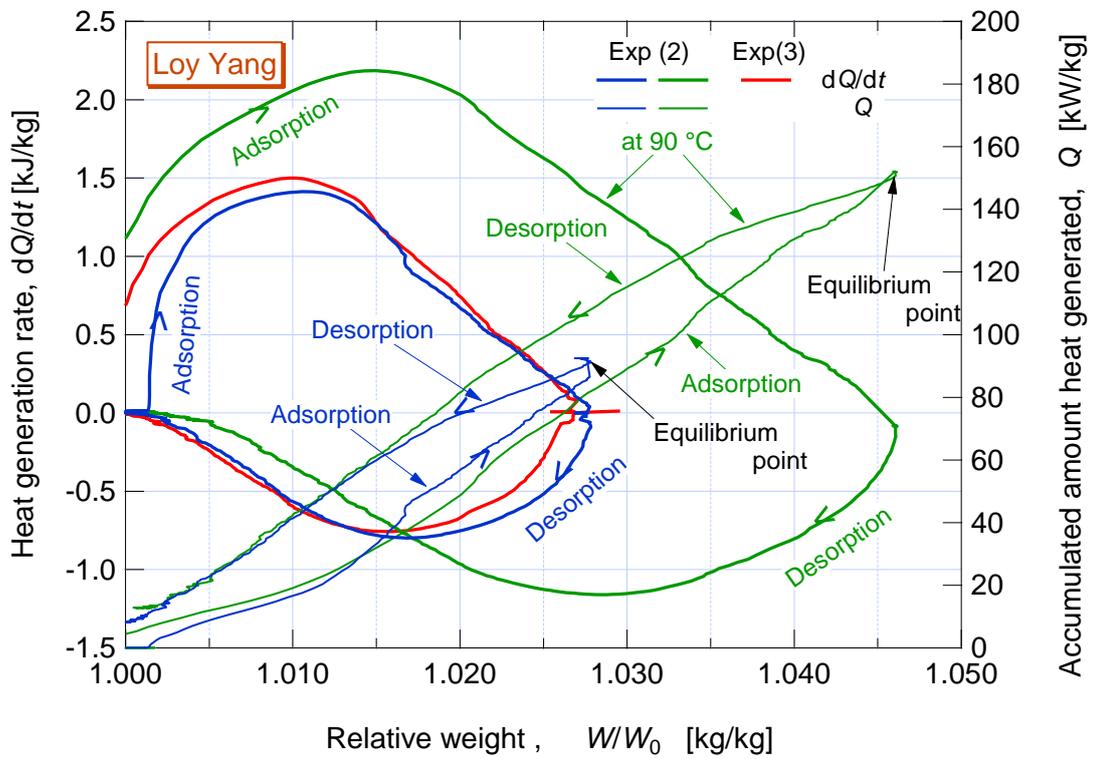


Figure 3.8. Estimation of amount of water vapor adsorbed at 107 °C using the Clausius–Clapeyron equation from the adsorption isotherm measured at 30 °C.

3.3.4 Non equilibrium heats of adsorption of water vapor on dried coal and desorption of adsorbed water at 107 °C

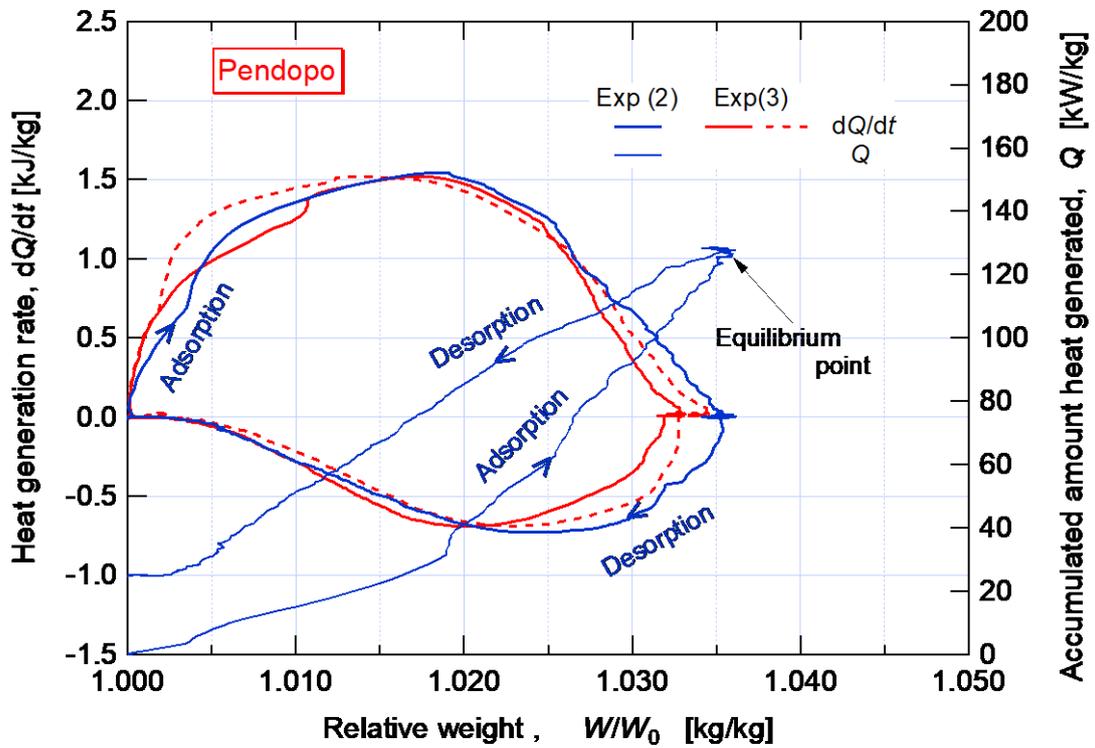
Discussion in the sections 3.3.2 and 3.3.3 focused on the equilibrium water content and the equilibrium heat of adsorption/desorption. The TG-DSC measurement of this work gives very accurate weight change and heat flow during the process to reach the equilibrium as shown in Figs. 3.4 to 3.6. It was then intended to estimate the heats of adsorption of water vapor on the dried coal during the process approaching to equilibrium and the heats of desorption of water during the process evaporating the water from the equilibrium state to dried coal. These heat values are practically important for detailed examination of temperature increase caused by water vapor adsorption and they are interesting from fundamental viewpoint examining water-coal interaction at high temperature also. To do so, the results obtained from experiment (2), which solely examine the adsorption of water vapor and desorption of the adsorbed water, were used. Then the results of experiment (2) shown in Figs. 3.4 to 3.6 were replotted as the relationships of dQ/dt vs. W/W_0 (> 1) and Q vs. W/W_0 in **Figure 3.9** for all of the coals. Those relationships obtained from experiment (3) are also shown for comparison purpose for all of the coals. Figure **3.9a**, showing the results for LY coal, includes the result of experiment (2) performed at 90 °C. For LY coal, the dQ/dt value for experiment (2) at 107 °C (shown by the blue thick solid line) increased rapidly on changing the gas flow from N_2 to the N_2 containing water vapor to reach a maximum of 1.4 kW or so at $W/W_0 \cong 1.012$ and then decreased to reach 0 to reach an equilibrium at $W/W_0 \cong 1.028$. On switching back the gas stream the N_2 containing water vapor to N_2 , the dQ/dt value decreased rather rapidly to reach a minimum of -0.6 kW or so at $W/W_0 \cong 1.017$ and then returned to zero when the desorption was finished. The dQ/dt value for experiment (3) (red thick solid line) showed more rapid increase on changing the gas flow from N_2 to

the air containing water vapor than experiment (2) to reach a maximum of 1.5 kW or so at $W/W_0 \cong 1.012$. This is due to the additional contribution of the coal-oxygen interaction. The dQ/dt value then decreased to reach 0. On switching back the gas stream from the air containing water vapor to N_2 , the dQ/dt value decreased rather rapidly to reach a minimum of -0.65 kW or so at $W/W_0 \cong 1.017$. After that the dQ/dt value followed almost exactly the path of experiment (2). This shows that there is no effects of coal-oxygen interaction during the desorption stage for experiment (3). The dQ/dt value for experiment (2) at 90 °C (green thick solid line) showed similar changing trends although the equilibrium W/W_0 value reached $\cong 1.047$. The results for both PD coal and coal A respectively shown in Figs. **3.9b** and **3.9c** showed similar changing trends of dQ/dt vs. W/W_0 , although the equilibrium W/W_0 values are slightly different among the coals.



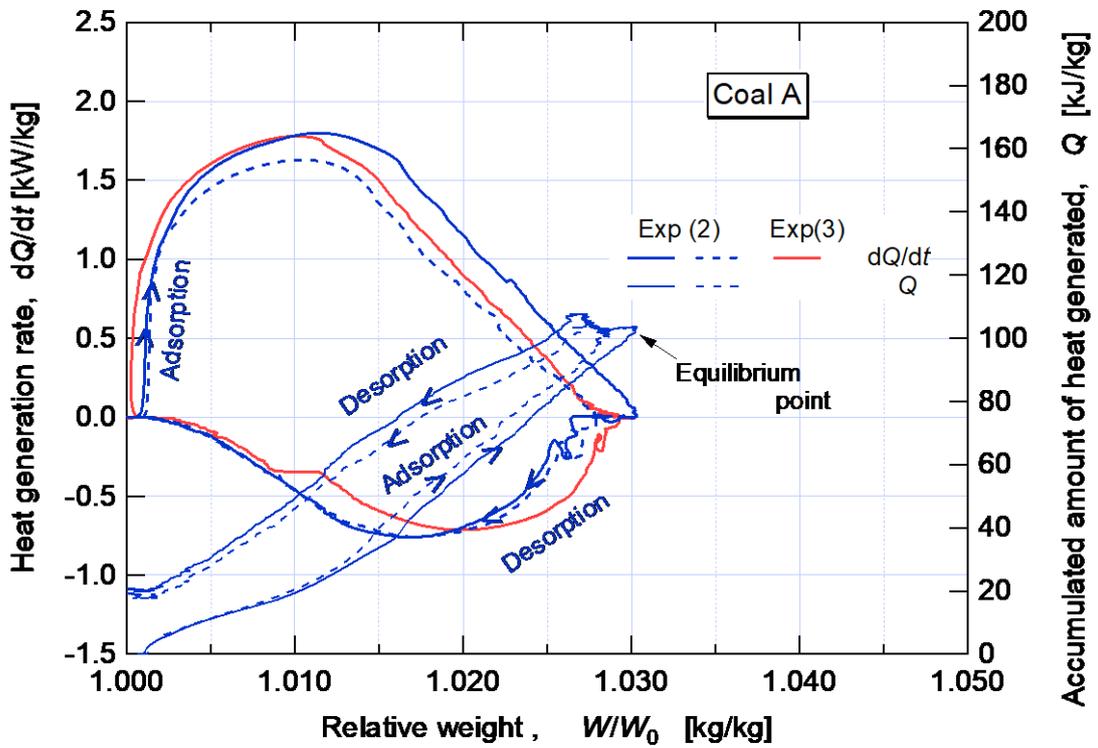
3.9a. Loy Yang.

Figure 3.9. Changes of heat generation rate, dQ/dt , and amount of heat accumulated, Q , during the adsorption and desorption experiments of experiment (2).



3.9b. Pendopo, Multiple data for same experiment are results of duplicate runs.

Figure 3.9. Changes of heat generation rate, dQ/dt , and amount of heat accumulated, Q , during the adsorption and desorption experiments of experiment (2).



3.9c. Coal A, Multiple data for same experiment are results of duplicate runs.

Figure 3.9. Changes of heat generation rate, dQ/dt , and amount of heat accumulated, Q , during the adsorption and desorption experiments of experiment (2).

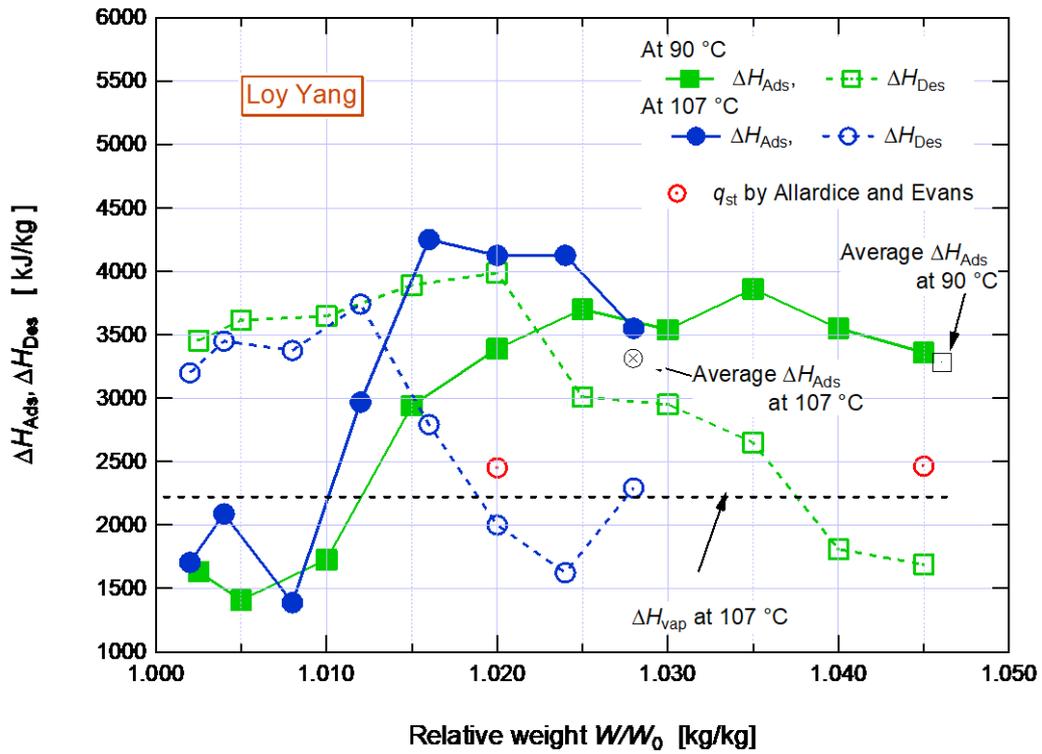
Reflecting the changing trends of dQ/dt vs. W/W_0 , the Q vs. W/W_0 relationships for experiment (2) showed the different paths for adsorption stage and the desorption stage for all of the coals as shown by the blue and green thin lines in Figs. 3.9a to 3.9c. The slopes of the Q vs. W/W_0 relationships, $dQ/d(W/W_0)$, give the heat of adsorption, ΔH_{Ads} , or the heat of desorption, ΔH_{Des} , at the corresponding W/W_0 value. First glance of the Q vs. W/W_0 relationships clearly shows that the Q vs. W/W_0 relationships are not linear, and hence the values of ΔH_{Ads} and ΔH_{Des} are expected to be dependent on W/W_0 . Then the values of ΔH_{Ads} and ΔH_{Des} were estimated by graphically differentiating the Q vs. W/W_0 relationships and shown as the keys in **Figure 3.10** for all of the coals. For LY, Fig. **3.10a** the ΔH_{Ads} value was as low as 1500 kJ/kg at the initial stage of adsorption, increased rapidly to reach over 4000 kJ/kg at $W/W_0 \cong 1.015$ and decreased to 3500 kJ/kg when the equilibrium was attained at $W/W_0 = 1.0276$. The average ΔH_{Ads} value between $W/W_0 = 0$ and 1.0276 was calculated to be 3350 kJ/kg ($\cong 92.4$ kJ/kg/0.0276 kg/kg). On the other hand, the ΔH_{Des} value at the beginning of desorption was obviously smaller than the heat of vaporization, ΔH_{Des} , increased rapidly to 3700 kJ/kg at $W/W_0 \cong 1.010$, reached 3150 kJ/kg at $W/W_0 \cong 1.0025$. The changing trends of both ΔH_{Ads} and ΔH_{Des} at 90 °C were similar as those at 107 °C. The average ΔH_{Ads} value between $W/W_0 = 0$ and 1.0461 at 90 °C was calculated to be 3300 kJ/kg ($\cong 152.1/$ kJ/kg/0.0461 kg/kg) which was slightly smaller than the value at $W/W_0 = 1.0276$ and 107 °C.

Water adsorption on dried low rank coal has been investigated extensively at around room temperature. It is well accepted that water molecules adsorb on coal by forming hydrogen bonds with oxygen functional groups such as carboxylic and hydroxylic groups [13], [14]. If we follow the work of Charrière and Behra [15], which may not be precise but gives a clear intuitive image of adsorption of water on coal, the water adsorption process

on a French lignite at 25 °C is divided into four processes: process 1: adsorption on the primary sites, i.e., oxygen containing functional groups for $0.05 < p_{\text{H}_2\text{O}}/p_s < 0.25$, process 2: adsorption on the secondary sites, i.e., water molecules for $0.30 < p_{\text{H}_2\text{O}}/p_s < 0.45$, process 3: beginning of formation of water clusters at $p_{\text{H}_2\text{O}}/p_s = 0.50$, and process 4: micropore filling of water clusters and capillary condensation for $0.55 < p_{\text{H}_2\text{O}}/p_s < 0.95$. If we assume that this discussion is valid at 107 °C, ΔH_{Ads} and ΔH_{Des} estimated here are for the process 1. Then the strength of hydrogen bonds between water molecules and the oxygen functional groups decide the values of ΔH_{Ads} and ΔH_{Des} . It is believed that there are several types of hydrogen bonds which have different strengths not only between the oxygen functional groups and water molecules but among the oxygen functional groups in coal^[16]. The small ΔH_{Ads} value at the initial stage of adsorption probably comes from the adsorption of H₂O on the free oxygen functional groups. With the progress of adsorption, some hydrogen bonds among the oxygen functional groups in coal must be released before water molecule can adsorb the oxygen functional groups. The process may lead to larger ΔH_{Ads} value.

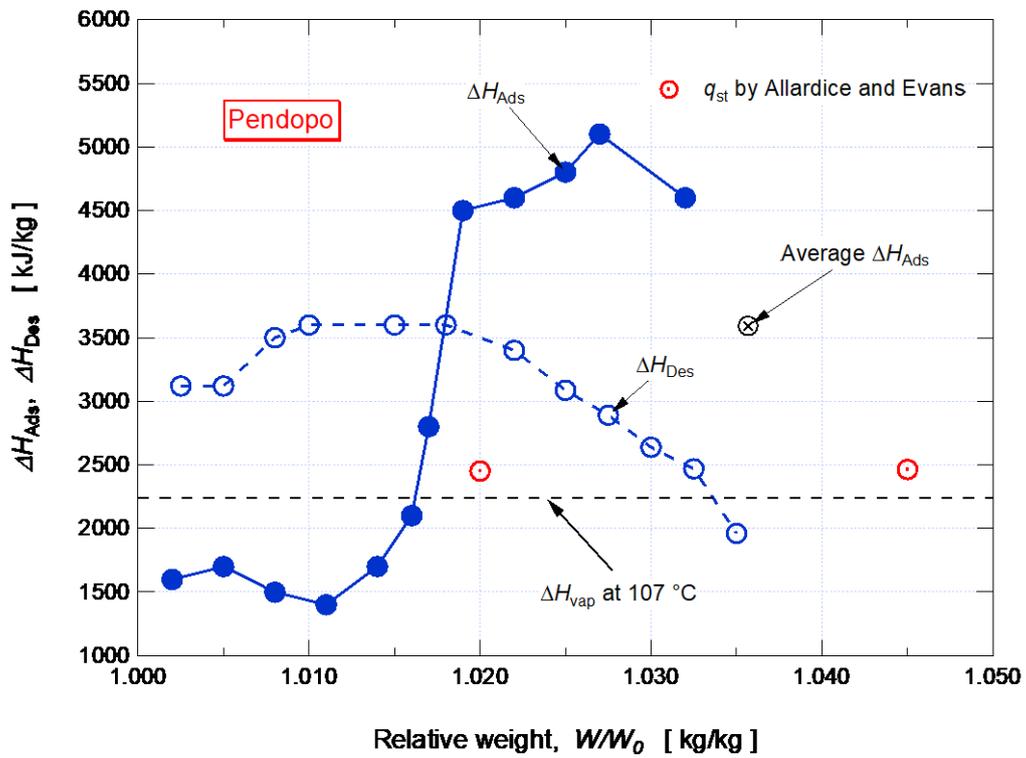
The changing trends of both ΔH_{Ads} and ΔH_{Des} for PD coal and coal A, which are respectively shown in Figs. **3.10b** and **3.10c**, are similar to those for LY coal, although the absolute values are slightly different. The average ΔH_{Ads} value between $W/W_0 = 0$ and $W/W_0 = 1.0350$ was 3670 kJ/kg ($\cong 128.3 \text{ kJ/kg}/0.0350 \text{ kg/kg}$) for PD coal and the value between $W/W_0 = 0$ and $W/W_0 = 1.0350$ was 3710 kJ/kg ($\cong 103.6 \text{ kJ/kg}/0.0279 \text{ kg/kg}$) for coal A. In sections 3.3.2 and 3.3.3 we have estimated that the isosteric heat of adsorption for coal A is around 2920 kJ/kg at $W/W_0 = 1.0276$. The difference between the average ΔH_{Ads} and the isosteric heat of adsorption comes from the difference of the definition of heat of adsorption. The isosteric heat of adsorption is the heat generated

when unit amount of H₂O is adsorbed on the system in equilibrium between the adsorbed H₂O and water vapor at a specified amount of adsorbed of H₂O. On the other hand, the average ΔH_{Ads} estimated in this section is the average heat generated during the process in which dried coal ($W/W_0 = 1$), contacting with a water vapor of a constant $p_{\text{H}_2\text{O}}$, reaches an equilibrium state. The average ΔH_{Ads} value bigger than the isosteric heat of adsorption when compared at a same W/W_0 comes from the big ΔH_{Ads} values at $W/W_0 = 1.015$ to 1.02 before reaching equilibrium as discussed above. The results obtained here will surely be useful when examining the contribution of adsorption of water vapor to the spontaneous heating of coal over 100 °C.



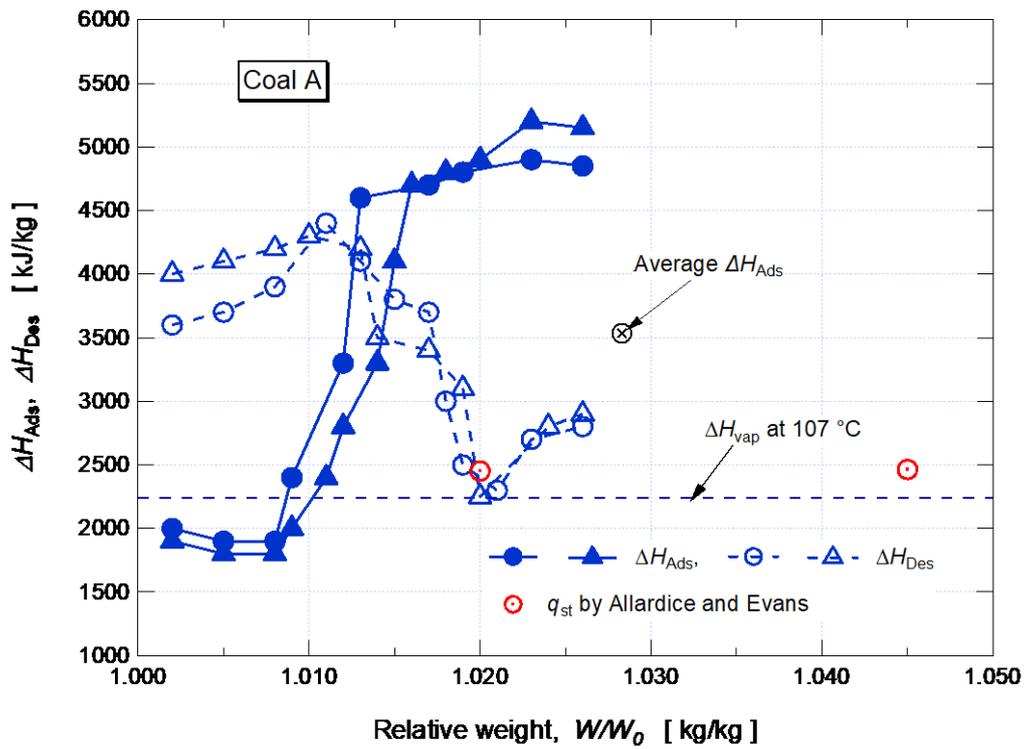
3.10a. Loy Yang experiment at 107 °C and 90 °C.

Figure 3.10. Changes of heat of adsorption of water vapor, ΔH_{Ads} , and heat of desorption of water vapor, ΔH_{Des} , during the adsorption and desorption experiments of experiment (2).



3.10b. Pendopo.

Figure 3.10. Changes of heat of adsorption of water vapor, ΔH_{Ads} , and heat of desorption of water vapor, ΔH_{Des} , during the adsorption and desorption experiments of experiment (2).



3.10c. Coal A, Multiple data are results of duplicate runs.

Figure 3.10. Changes of heat of adsorption of water vapor, ΔH_{Ads} , and heat of desorption of water vapor, ΔH_{Des} , during the adsorption and desorption experiments of experiment (2).

3.4 Conclusions

This chapter examined the coal-water interaction over 100 °C to estimate the heat of desorption of water from as-received coal and heat of adsorption/desorption of water on dried coal from the viewpoint of examining propensity to spontaneous heating of the dried coal. To do so a sensitive TG-DSC which measures weight change and heat flow in moist atmosphere was used. The heats of desorption were almost constant of 2300 to 2350 kJ/kg until water content decreases to 0.35 kg/kg-dried coal, close to heat of vaporization, and increased gradually to reach 5000 kJ/kg or so at the completion of drying at 107 °C for two low-rank coals. For the three coals tested, the heat generated by the adsorption of water vapor from the moist air of 0.15 of relative humidity were 90 to 130 kJ/kg-dried coal in 30 min and were 1.2 to 4 times larger than the heats generated by the coal-oxygen interaction even at 107 °C, suggesting that adsorption of water vapor plays an important role for the spontaneous heating of coal even over 100 °C. The transient changes of heats of adsorption/desorption of water on the way to reach equilibrium were also successfully estimated and discussed in relation to isosteric heat of adsorption/desorption and heat of vaporization of water.

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Chapter 4

Examination of Interactions of Solvent
Treated Coal with Oxygen and Water
Vapor at over 100 °C using TG-DSC
for Examining Propensity to
Spontaneous Heating of
the Solvent Treated Coal

4.1 Introduction

It is without question that low-rank coals such as brown coal/lignite and sub-bituminous coal will be used worldwide in this century, because they are widely distributed and their minable reserve is huge. However, low-rank coals are presently utilized just for power generation near coal mines. This is because brown coals, for example, contain a large amount of water (~60%) and oxygen functional groups in general, resulting in low calorific value and causing various problems for storage and transportation, one of which is the high propensity to spontaneous heating. It is therefore essential to develop the technologies that can not only dewater but upgrade the low rank coals so as to utilize them more effectively. According to the review published by Katalambula *et al.* [1], various methods have been proposed for dewatering and/or upgrading low-rank coals by many researchers.

Miura *et al.* have recently proposed a degradative solvent extraction method which treats carbonaceous resources in a non-hydrogen donor at around 350 °C under pressure using a batch autoclave to dewater without phase change, to selectively remove oxygen functional groups as either H₂O or CO₂, and to produce low-molecular-weight compounds [2-4]. The core concept underlying this method involves exposing the entire sample to thermal reactions in a nonpolar solvent at around 350 °C. The anticipated thermal reactions under these conditions include deoxygenation reactions consisting of dehydration and decarboxylation without primary decomposition reactions accompanying the disruption of C–C bonds. The products formed during the thermal reactions at around 350 °C are then filtrated at the same temperature to recover the extract and residue (the latter is termed Residue in this chapter). The extract is further separated

into two fractions at room temperature: the fraction that precipitates as a solid (Deposit) and the soluble fraction (Soluble). The soluble fraction is also finally recovered as a solid by removing the solvent. When eight low-rank coals were treated by the proposed method, the Soluble yields were as high as 18.3 to 27.2 % and the Deposit yields were 3.5 to 16.9 % on dry and ash free basis. Both Solubles and Deposits were free from water and ash, and the carbon contents of Solubles reached as high as 81.8 to 84.0 wt%. Most noteworthy finding was that Solubles and Deposits were respectively very close to each other in elemental composition, chemical structure, molecular weight distribution, thermal decomposition behavior, and thermal plastic behavior. Thus, the degradative solvent extraction method was found to be effective in converting wide range of low-rank coals into compounds having very similar chemical and physical properties in rather high yields under mild conditions.

The degradative solvent extraction method produced simultaneously Residues by the yields of as high as 49.7 to 63.6 %. However, the carbon contents of Residues were as high as 77 to 79 wt% for 6 coals tested, and the ash contents were as low as 2.3 to 5.7 wt % except 2 high ash content coals. The gasification rates of the Residues prepared were higher than or comparable to those of the parent coals ^[5]. These examinations suggested that Residue can be used as a high quality solid fuel. If we intend to convert the low-rank coals to just high quality solid fuels, it is not necessary to separate the solvent treated product into three fractions. Then we also prepared “Solvent treated coal” (abbreviated to STC) under the same condition but without separating the upgraded coal into 3 fractions ^[6]. Since STC contains Soluble, Deposit, and Residue in principle, STC is almost completely dewatered and its carbon content was as high as 78 to 80 %. This

showed that STC can be well utilized as a high quality solid fuel from the viewpoint of heating value.

To evaluate the potential of Residue, and STC as high quality solid fuels, estimation of their propensity to spontaneous heating is essential in addition to the evaluation of their heating values and rates of combustion and/or gasification. Since researchers at Kyoto University tried to estimate the propensity to spontaneous heating of Residue and STC from their weight increases on exposure to dried air at 65 °C ^[6]. The estimation method was simple and quite reliable. The studies have been shown the importance of adsorption of water vapor as a source of heat generation leading to spontaneous heating ^{[7], [8]}. In Chapter 3, the author have proposed the weight change and the heat generation rate measured at 107 °C in both dry air and wet air can be an index to estimate the propensity to spontaneous heating ^[9]. From this investigation, the aim of this chapter is to apply the method for estimation of the propensity to spontaneous heating of Residue and STC prepared from two low rank coals. The propensity to spontaneous heating of the parent coals and chars prepared in an inert atmosphere at 350 °C are also examined for comparison purpose.

4.2 Experimental

4.2.1 Raw coals and preparation of Residue, STC, and Stabilized char

An Australian brown coal, Loy Yang (abbreviated to LY), and an Indonesian lignite, Pendopo (PD), were used as low-rank coal samples. The properties of the two coals used are listed in **Table 4.1**. The coals were subjected to the degradative solvent extraction at 350 °C using 1-methylnaphthalene as the solvent to produce solvent treated coal (STC) as well as Residue. A fully procedure of the degradative solvent extraction was detailed in our previous papers ^[2-4] and in the chapter 2. The apparatus of the extraction method is shown in **Figure 4.1**. The procedure is in short as follows: The coals were ground and sieved to less than 0.2 mm as the particle size and served to experiments without drying. Experimental setup includes an autoclave reactor (130 mL in volume), a reservoir (130 mL in volume), and an electric furnace. The autoclave reactor was made of stainless steel. A stainless filter (65 mm O.D., 0.5 µm opening) was equipped at the bottom end of the autoclave. The autoclave and the reservoir were connected by a valve. The autoclave was loaded with about 5 g (d.a.f.) of raw sample and 80 mL of 1-methylnaphthalene. After purging the autoclave with 0.5 MPa of helium gas, the autoclave was heated up to 350 °C at the rate of 5 K/min and held for 60 min at 350 °C. By opening the valve connecting the autoclave and the reservoir, Residue was recovered in the autoclave, and Soluble and Deposit with solvent were transferred to the reservoir to be cooled down to room temperature. Deposit, precipitated as solid, was recovered by filtration using a PTFE filter (0.5 µm opening). Soluble was separated from the solvent by a rotary evaporator. Liquid, consisting largely of water, was also recovered from the solvent. Gaseous products were collected in a gas bag and quantified by a gas chromatograph. STC was

prepared under the same procedure but without separating the product into fractions. The Residue and STC were inevitably exposed to ambient atmosphere during the collecting and drying process removing the solvent, and hence they might have been oxidized during the process. Since it is hard to avoid the oxidation, however, the Residue and STC obtained by the above procedure and stored in bins at room temperature were regarded as target products.

Heat treatment at around 300 °C in an inert atmosphere, called mild pyrolysis or torrefaction, is believed to be an upgrading method of low grade carbonaceous materials. Then coals heat treated at 350 °C were prepared for comparison purpose. To do so, the coals were heated up to 350 °C at the rate of 5 K/min in a nitrogen stream and kept 20 min at 350 °C. Then they were cooled down to room temperature in the N₂ stream and stored in a bin with airtight lid for more than 2 months to prepare the samples which we call “stabilized chars”. The stabilized chars were characterized as were done for Residue and STC and were served to the experiments estimating the propensity to spontaneous heating. The stabilized chars were prepared to compare their properties with those of Residue and STC on a same basis. Their product yields and analyses are also given in Table 4.1. For comparison purpose, heat treated coal which is not exposed to air, which we call “Fresh char”, was also prepared by the procedure given below and served to the experiments estimating the propensity to spontaneous heating.

Table 4.1. Yields of Residue, STC, and Stabilized char and their analyses.

Sample	Yield [wt%, d.a.f. ^a]	Ultimate analysis [wt%, d.a.f.]				Proximate analysis [wt%, d.b. ^b]			HHV [MJ/kg, d.a.f.]
		C	H	N	O+S	VM	FC	Ash	
Loy Yang (LY)	-	66.6	4.5	0.5	28.4	50.0	47.8	2.2	23.9
Residue	63.9	77.1	4.2	0.8	18.0	35.1	59.6	5.3	28.9
STC	84.4	78.2	4.9	0.9	14.0	42.4	55.7	1.9	30.9
Stabilized Char	85.5	70.6	4.3	0.6	24.5	-	-	-	25.7
Pendopo (PD)	-	67.5	5.1	0.8	26.6	49.4	38.0	12.6	25.4
Residue	54.3	76.5	4.5	1.2	17.7	40.1	42.4	17.4	29.2
STC	81.3	78.7	5.1	1.2	15.0	41.6	45.8	12.5	31.3
Stabilized Char	81.2	70.2	4.5	0.9	24.4	-	-	-	25.9

^aDry, ash-free. ^bDry basis.

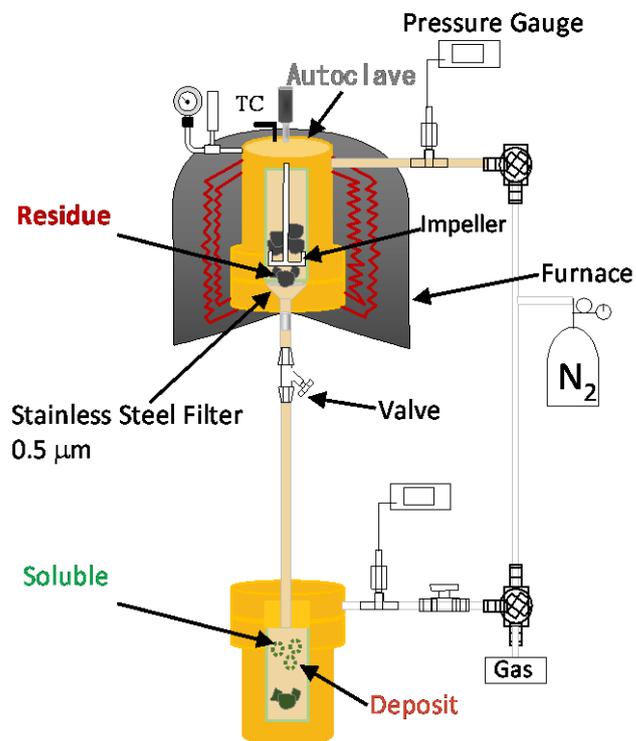


Figure 4.1. Degradative solvent extraction apparatus used for a separation experiment.

4.2.2 Characterization of Raw coal, STC, Residue, and Stabilized char

Raw coal, STC, Residue, and Stabilized char were characterized by elemental compositions using a CNH analyzer (J-Science, JM10) and functional groups using FTIR spectrometer (JEOL, JIR-WINSPEC50) as shown in **Photo 4.1**. The KBr pellet method was used for the measurement of functional groups. About 1.25 mg of dried sample was mixed with 500 mg of dried KBr and ground into fine particles. About 200 mg of the fine particles were pressed for 10 min under a constant load of 8 ton in vacuum to obtain transparent 13 mm ϕ of disk. The absorbance spectra of the samples was measured and collected with a resolution of 4 cm⁻¹ and the acquisition of 150 scans.



Photo 4.1. FTIR spectrometer set (JEOL, JIR-WINSPEC50) used for analysis of functional groups.

4.2.3 Measurement of propensity to spontaneous heating

Propensity to spontaneous heating of every sample was estimated by following the procedure described in the previous chapter ^[9]. Weight change and heat generation rates accompanying the oxidation of the sample and the adsorption of water vapor on the sample at 107 °C were measured using a TG-DSC analyzer (NETZSCH, STA 449F3 Jupiter). The analyzer with a platinum furnace was used for the oxidation of sample in a dry air. The analyzer with a water vapor furnace was used for examination of interaction of sample with an air saturated with water vapor at 60 °C (pressure of water vapor, $p_{H_2O} = 19.92$ kPa), which we simply call “wet air” in this work. For both experiments, about 15 mg (on dry basis) of sample placed in a PtRh crucible (6.8mm ϕ x 3 mmH) was set on the sample probe and an identical empty PtRh crucible was set on the reference probe. The sample crucible and the reference crucible were heated at the rate of 10 K/min to 107 °C at which they were kept for 20 min in a 100 mL/min of N₂ stream to evaporate water adsorbed on the sample. To start the oxidation of the sample in a dry air, the gas stream was changed to 100 mL/min of dry air stream and kept 30 min at 107 °C. For examination of interaction of sample with the wet air, the nitrogen stream was changed to the wet air and kept for 30 min at 107 °C. The wet air was supplied from a steam generator separately designed. The line connecting the steam generator and the TG-DSC analyzer was heated over 80 °C to prevent the water vapor from condensation.

The experiment estimating the propensity to spontaneous heating of the above mentioned “Fresh char” was performed as follows. About 15 mg (on dry basis) of raw coal was heated at the rate of 10 K/min to 107 °C at which it was kept for 20 min in a 100 mL/min of N₂ stream to evaporate water adsorbed on the coal. Then the dried coal was heated at

the rate of 5 K/min to 350 °C at which they were kept for 20 min. The heat treated coal, fresh char, was cooled at the rate of 10 K/min to 107 °C in the N₂ stream and kept for 15 min to stabilize the temperature. Then the gas stream was changed to either the dry air or the wet air and kept for 30 min as was done for the other samples. The experiment to oxidize the fresh char at 30°C in the dry air was also performed by cooling down the fresh char prepared at 350 °C to 30°C at the rate of 10 K/min and by exposing it to the dry air for 30min. This experiment was performed to estimate the rate of oxidation of Fresh char in ambient atmosphere.



Photo 4.2. Apparatus used for the direct measurement of temperature increase.

4.2.4 Direct measurement of temperature increase of propensity to spontaneous heating

Experiments exposing dried Raw coal, STC, and Residue to saturated and stagnant atmospheres were also performed using the experimental setup shown in the paper^[8] to directly measure temperature increase of the sample materials caused by water vapor adsorption and oxidation by air. The apparatus of this measurement is shown in **Photo 4.2**. In short, the experimental procedure is as follows. Around 1 to 1.5 g (on dry basis) of samples wrapped by SUS mesh with opening of 400 Tyler mesh was dried in a N₂ stream at 107 °C and cooled down to \cong 80 °C. Then the sample was promptly transferred to a 5 L desiccator in which air is saturated with liquid water charged at the bottom of the desiccator at a regulated temperature. Water vapor in the desiccator instantly adsorbs on the sample and air will also interact with the sample, which raises the sample temperature. A thermocouple embedded in the sample records the temperature increase. The desiccator was regulated to be 80 °C, but the actual measurement showed that the temperature inside desiccator was kept at 82 °C during the experiment.

4.3 Results and Discussion

4.3.1 Characterization of STC, Residue, and Stabilized char

Table 4.1 gives yield, elemental analysis, proximate analysis, and higher heating value calculated by the Dulong equation^[10] for every sample prepared. The yields of Residue were 63.9 % and 54.3 %, the yields of STC were as high as 84.4 % and 81.3 %, and the yields of Stabilized char were 85.5 % and 81.2 %, respectively, for LY and PD. The carbon contents of Residue were 77.1 % and 76.5 %, and those of STC were 78.2 % and 78.7 %, respectively, for LY and PD. These high carbon contents of the Residue and the STC come from selective elimination of oxygen from coal as either H₂O or CO₂ during the degradative solvent extraction. On the other hand, the carbon contents of Stabilized char were 70.6 % and 70.2 % in spite of that the yields of Stabilized char were almost same as those of STC. Reflecting the elemental composition, the HHV values for Residue were 28.9 MJ/kg and 29.2 MJ/kg, those for STC were 30.9 MJ/kg and 31.3 MJ/kg, and those for Stabilized char were 25.7 MJ/kg and 25.9 MJ/kg, respectively, for LY and PD. The HHV values of STC on the raw coal basis can be calculated to be 26.1 MJ/kg (= 0.844 × 30.9 MJ/kg) and 25.4 MJ/kg (= 0.813 × 31.3 MJ/kg), respectively, for LY and PD. This means that the degradative solvent extraction does not lose the heating value through the treatment, indicating that it is a very effective upgrading technology from the viewpoint of energy efficiency. This was realized by selective elimination of oxygen from coal as either H₂O or CO₂ as stated above. The discussion suggests the importance of examination of propensity to spontaneous heating of Residue and STC as an additional index for evaluating the property of solid fuel.

4.3.2 Oxidation behavior of STC, Residue, and Stabilized char in dry air

Figures 4.2 and 4.3 show the results of oxidation of each sample in dry air at 107 °C, respectively, for LY and PD. In each figure the upper graph shows the relative weight, W/W_0 , and the lower graph shows the heat generation rate, dQ/dt , and the accumulated amount of heat generated, Q , which was obtained by integrating dQ/dt over time.

Fig. 4.2, which compares the oxidation behaviors among STC, Residue, Stabilized char, and Raw coal for LY. The relative weights of Raw coal, STC, and Stabilized char gradually increased with time but they were respectively only $\cong 1.002$, $\cong 1.0015$, and $\cong 1.003$ after 30 min of reaction. The relative weights of Residue increased gradually to reach a maximum of $\cong 1.001$ and then decreased to reach $\cong 0.999$ after 30 min of reaction. The weight changes during the oxidation in dry air are very small, and it is impossible to discuss the differences of the oxidation rate among the samples from the weight changes only. On the other hand, the heat generation rates were clearly different among the samples. The dQ/dt value of Stabilized char instantly increased on changing the gas stream from N_2 to dry air to reach a maximum of $\cong 0.065$ kW/kg at 1 min or so and decreased gradually with progress of oxidation. The dQ/dt value of Raw coal showed similar changing trends but the value at a peak was $\cong 0.018$ kW/kg. The dQ/dt values of both Residue and STC were clearly smaller than the dQ/dt value of Raw coal. The accumulated amounts of heat generated after 30 min of reaction, Q_{30} , were respectively $\cong 29$ kJ/kg, $\cong 17$ kJ/kg, $\cong 16$ kJ/kg, and $\cong 9$ kJ/kg for Stabilized char, Raw coal, Residue, and STC. The discussion clearly shows that the heat generation rates in dry air of both STC and Residue are smaller than the heat generation rate of Raw coal, indicating that the degradative solvent extraction is also effective to decrease the oxidation rate in dry

air. The heat generation rates of both STC and Residue are also much smaller than the heat generation rate of Stabilized char which was tested for comparison purpose.

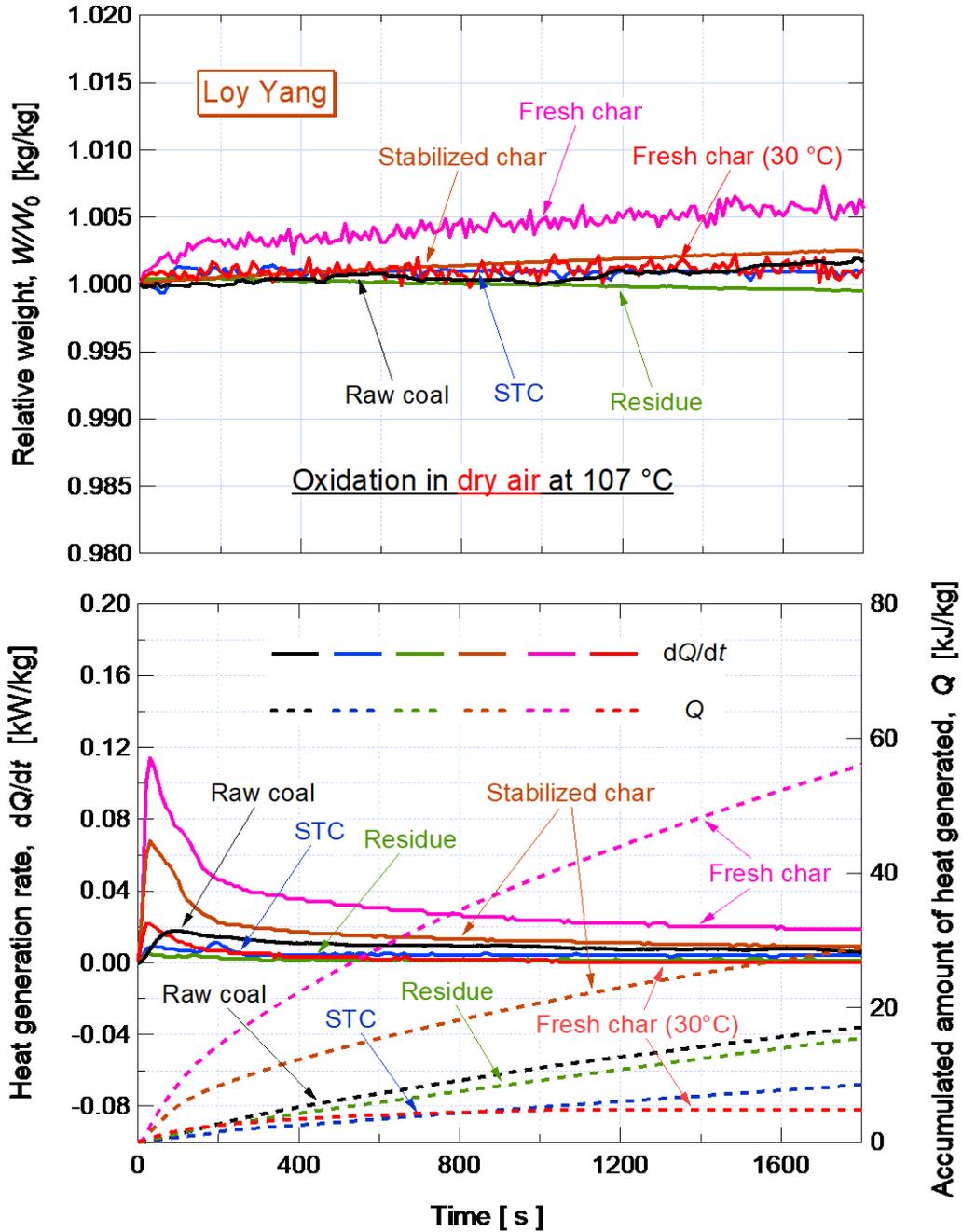


Figure 4.2. Changes of relative weight (upper graph) and heat generation rate, dQ/dt , and accumulated amount of heat generated, Q , (lower graph) during the oxidation of each sample in dry air at 107 °C for Loy Yang.

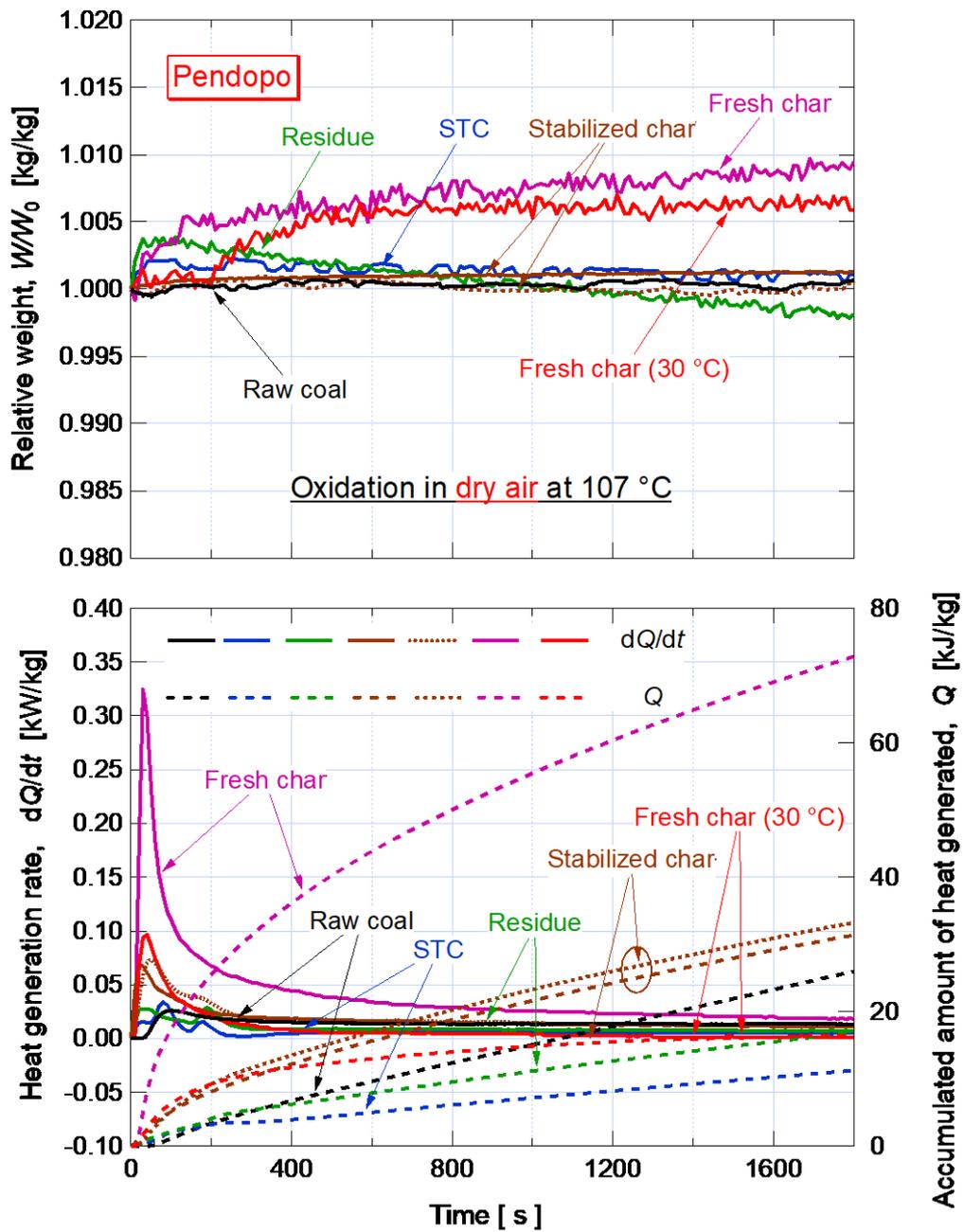


Figure 4.3. Changes of relative weight (upper graph) and heat generation rate, dQ/dt , and accumulated amount of heat generated, Q , (lower graph) during the oxidation of each sample in dry air at 107 °C for Pendopo. Multiple data for same experiment are results of duplicate runs.

Fig. 4.3 compares the oxidation behaviors among STC, Residue, Stabilized char, and Raw coal for PD. The changing trends and the order of magnitudes among the samples are similar to those for LY. The changes of relative weights of Raw coal, STC, and Stabilized char were very small and were respectively only 1.001 to 1.002 after 30 min of reaction. The relative weights of Residue increased gradually to reach a maximum of $\cong 1.004$ and then decreased to reach $\cong 0.998$ after 30 min of reaction. The Q_{30} values were respectively $\cong 31$ to 32 kJ/kg, $\cong 25$ kJ/kg, $\cong 17$ kJ/kg, and $\cong 11$ kJ/kg for Stabilized char, Raw coal, Residue, and STC. The heat generation rates in dry air of both STC and Residue are smaller than the heat generation rate of Raw coal and are much smaller than the heat generation rate of Stabilized char.

The largest Q_{30} value was $\cong 31$ to 32 kJ/kg for Stabilized char prepared from PD. The Q_{30} values for STC and Residue were respectively 9 to 11 kJ/kg and 16 to 17 kJ/kg which will raise the sample temperature only by around 7 to 13 °C (heat capacity of sample was assumed to be 1.35 kJ/(kg·K)) in 30 min under adiabatic conditions.

4.3.3 Examination of interaction of STC, Residue, and Stabilized char with the wet air

Figures 4.4 and 4.5 show the results examining the interaction of each sample and the wet air at 107 °C, respectively, for LY and PD. First, let focus on Fig. 4.4 which compares the results among STC, Residue, Stabilized char, and Raw coal for LY. The W/W_0 values for both Raw coal and Stabilized char rapidly increased on changing the gas stream from the N_2 to the wet air to reach $\cong 1.027$ in 2 min and showed no further appreciable changes. Heat was also generated rapidly in parallel to the changes of W/W_0 and the Q_{30} values reached respectively $\cong 129$ kJ/kg and $\cong 119$ kJ/kg for Raw coal and Stabilized char. The W/W_0 values for STC and Residue also increased rather rapidly on changing the gas stream from the N_2 to the wet air to reach $\cong 1.008$ in 10 min and the W/W_0 value for STC showed no further appreciable changes but the W/W_0 value for Residue decreased gradually. Heat was also generated in parallel to the changes of W/W_0 and the Q_{30} values reached respectively $\cong 32$ kJ/kg and $\cong 36$ kJ/kg for STC and Residue. These results clearly show that the contribution of the adsorption of water vapor on the sample from the wet air containing water vapor by as low as 19.92 kPa of p_{H_2O} (= vapor pressure at 60 °C) is much more significant than the action of dry air on the sample even at as high as 107 °C. The Q_{30} value as large as 129 kJ/kg for Raw coal is large enough to raise coal temperature by more than 90 °C under adiabatic conditions. Since the adsorption of water vapor is completed in several minutes, it is well expected that coal temperature will be raised instantly if dried coal contacts with the wet air. The Q_{30} values of both Residue and STC were only one quarter of the Q_{30} value of either Raw coal or Stabilized char.

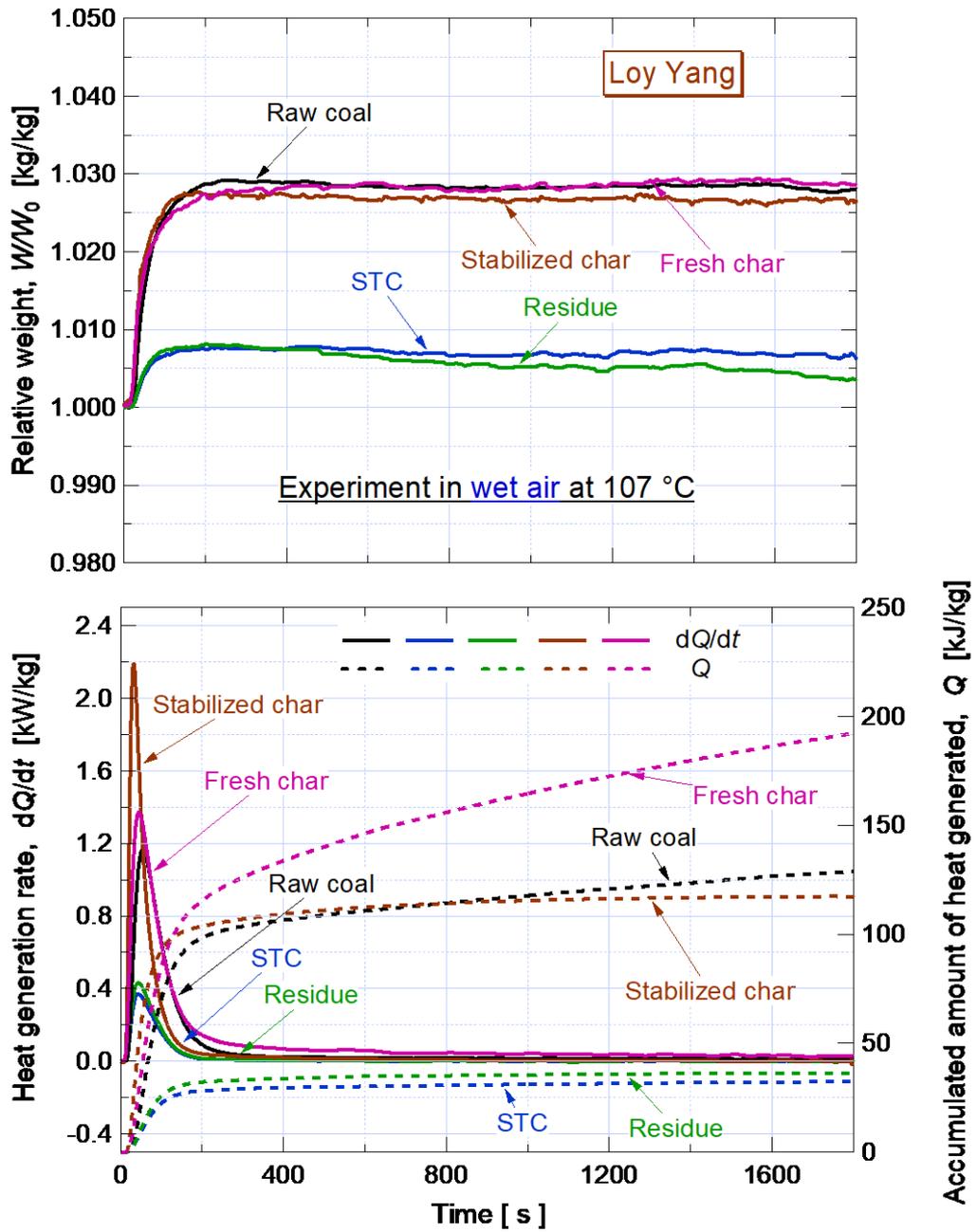


Figure 4.4. Changes of relative weight (upper graph) and heat generation rate, dQ/dt , and accumulated amount of heat generated, Q , (lower graph) during the interaction of each sample and the wet air at 107 °C for Loy Yang.

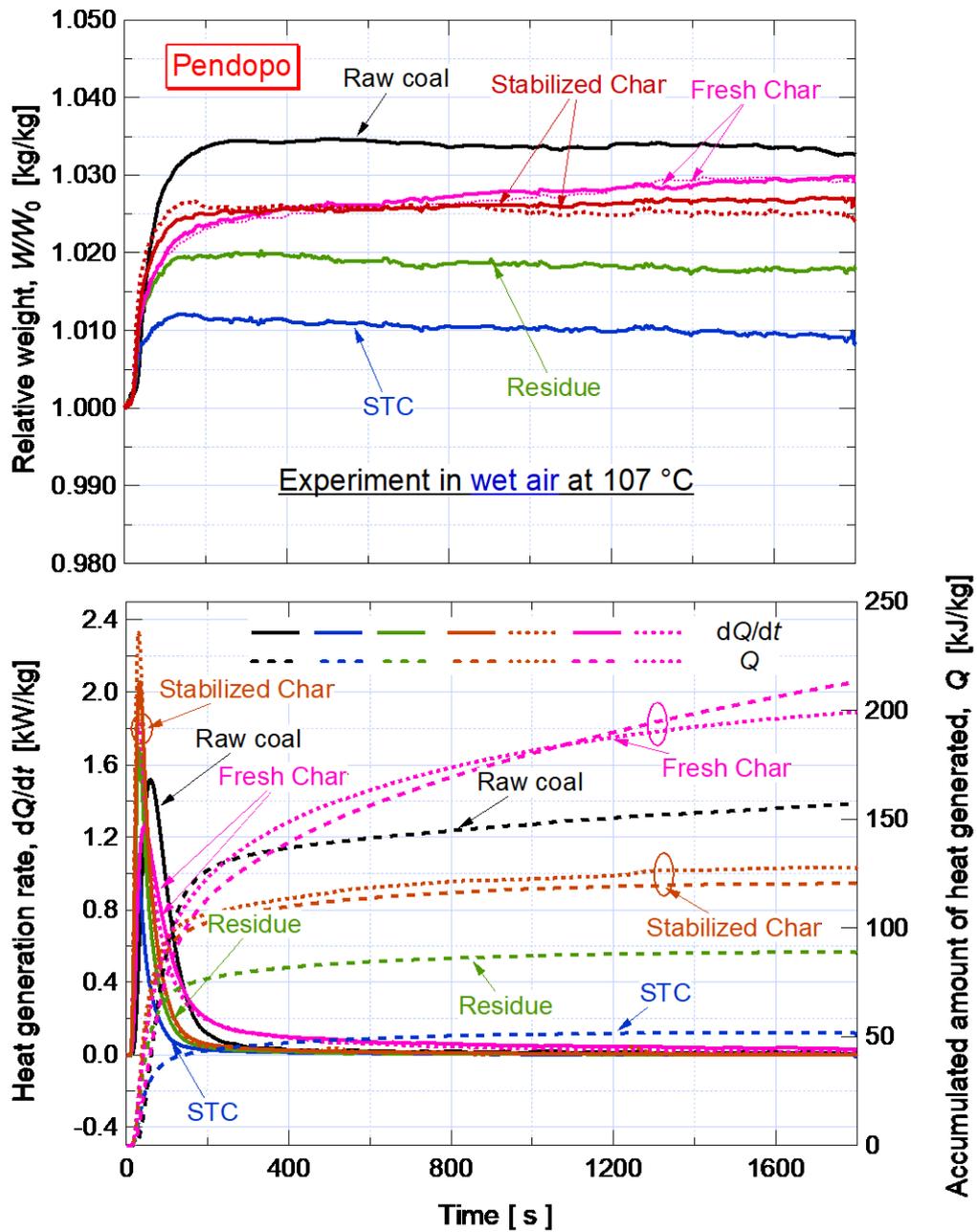


Figure 4.5. Changes of relative weight (upper graph) and heat generation rate, dQ/dt , and accumulated amount of heat generated, Q , (lower graph) during the interaction of each sample and the wet air at 107 °C for Pendopo. Multiple data for same experiment are results of duplicate runs.

Fig. 4.5 compares the results examining the interaction of each sample and the wet air for PD. Results of duplicated experiments for Stabilized char show the accuracy of the experiments of this work. Again the changing trends and the order of magnitudes among the samples are similar to those for LY. The W/W_0 values for Raw coal and Stabilized char rapidly increased on changing the gas stream from the N_2 to the wet air to reach respectively $\cong 1.034$ and $\cong 1.026$ in 3 min for Raw coal and Stabilized char and showed no further appreciable changes. Heat was also generated rapidly in parallel to the changes of W/W_0 and the Q_{30} values reached respectively $\cong 157$ kJ/kg and $\cong 116$ to 117 kJ/kg for Raw coal and Stabilized char. The W/W_0 values for STC and Residue also increased rather rapidly to reach respectively $\cong 1.012$ and $\cong 1.019$ in 3 min for STC and Residue and the both W/W_0 values decreased gradually to reach respectively $\cong 1.009$ and $\cong 1.018$ in 30 min for STC and Residue. Heat was also generated in parallel to the changes of W/W_0 and the Q_{30} values reached respectively $\cong 52$ kJ/kg and $\cong 89$ kJ/kg for STC and Residue. The Q_{30} value as large as 157 kJ/kg for Raw coal is large enough to raise coal temperature by more than 120°C under adiabatic conditions. The Q_{30} value of STC was less than one thirds and the Q_{30} value of Residue was a half of the Q_{30} value of Raw coal. The above discussion clearly shows that the heat generation rates in the wet air of both STC and Residue are smaller than the heat generation rates of either Raw coal or Stabilized char which was tested for comparison purpose for both LY and PD. Heat generation related to spontaneous heating of the sample comes from oxygen-sample interaction and adsorption of water vapor on the sample as stated above. The examinations in this work showed that the heat generation rates in the wet air were much larger than those in dry air even at 107°C . In addition, there was little difference in the heat generation rates among the samples in dry air. This means that the degrees of propensity to spontaneous heating of the samples are judged to be estimated by the

differences in the heat generation rates in the wet air. Then, we can conclude that the degrees of propensity to spontaneous combustion of both Residue and STC are much lower than the Raw coals, indicating that the proposed solvent treatment method is effective not only to upgrade raw grade carbonaceous material but to suppress the propensity to spontaneous heating of the upgraded product.

4.3.4 Direct measurement of temperature increase on exposure to a stagnant saturated air

The big heat generation by the adsorption of water vapor has the potential to raise the temperature well over the critical temperature. Then the temperature increase of dried Raw coal, Residue, and STC on exposure to the saturated air at 82 °C was directly measured for LY samples as shown in **Figure 4.6**. The temperature of Raw coal reached a maximum temperature of as high as 130 °C in less than 1 min and then gradually decreased, whereas the temperatures of Residue and STC reached maxima of 112 °C and 105 °C respectively and the temperatures never exceeded the temperature of Raw coal. These results well support the above discussion. The saturated air at 82 °C which contains water vapor by 81.33 kPa of pressure was chosen arbitrarily from the limitation of experimental setup in this work. Then the question may be if the sample will actually contact such stagnant atmosphere. This can happen when run-of-mine low-rank coal is in stockpile. Dried coal in a certain position in the stock pile will contact surrounding coal still containing a large amount of water. The stagnant air in the stockpile will easily be saturated with the water vapor coming from the surrounding coal. The dried coal will easily adsorb the water vapor and its temperature will increase instantly. This, however,

will not happen practically for both STC and Residue, because STC and Residue contain little water and hence water is supplied from neither STC nor Residue in stockpile. In this sense, STC and Residue may be safer in stockpile than Raw coal, because both STC and Residue do not encounter such situation in the stockpile.

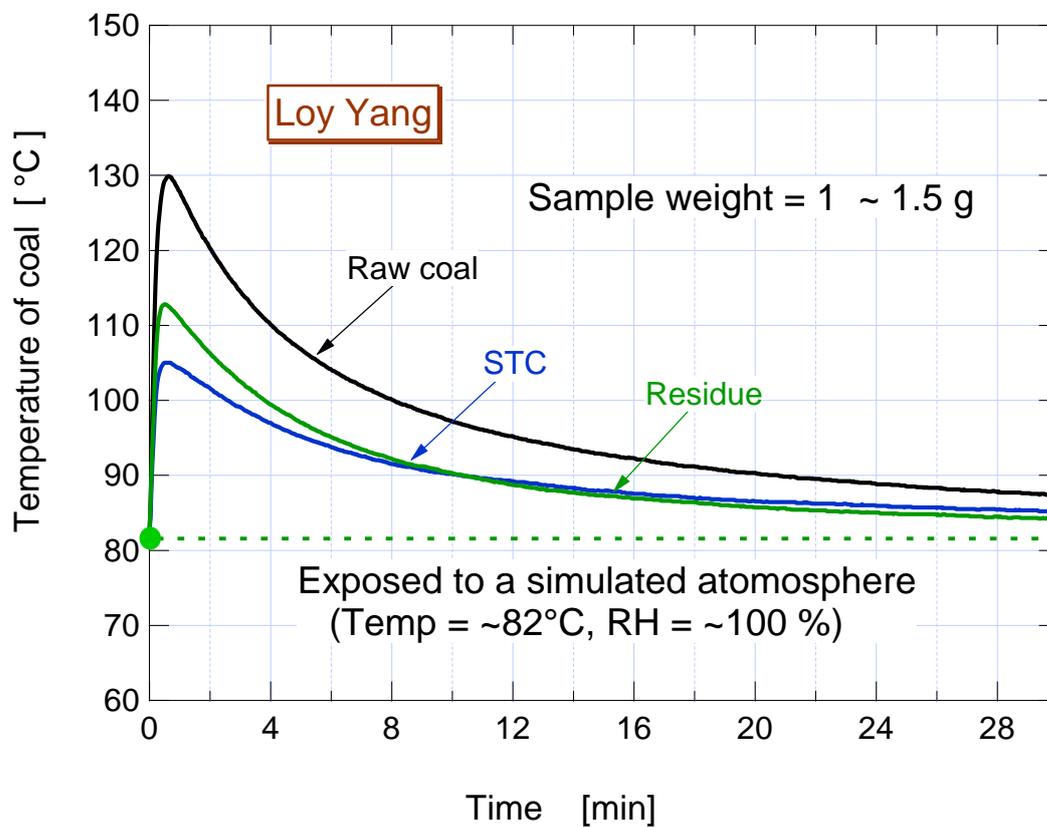


Figure 4.6. Temperature increase of dried Raw coal, Residue, and STC on exposure to the saturated air at 82 °C for LY samples.

4.3.5 Some discussion on the mechanism of air oxidation and adsorption of water vapor

The propensity to spontaneous heating of Residue and STC was judged to be reduced mainly because the water vapor adsorption capacity was significantly reduced by the degradative solvent extraction. The water vapor adsorption capacity is well related to the amount of oxygen functional groups ^{[11], [12]}. The ultimate analyses in Table 4.1 show that the oxygen contents of STC and Residue are much smaller than those of Raw coal and Stabilized char. To examine the differences of oxygen functional groups among the samples, FTIR analysis was made for Raw coal, Residue, STC, and Stabilized char, and the results are shown in **Figure 4.7**. It is clearly shown that the intensities of the adsorption bands associated with –OH groups at 3100-3600 cm⁻¹ and the adsorption bands associated with –COOH at 1690 and 1696 cm⁻¹ of Residue and STC are much smaller than the corresponding intensities of either Raw coal or Stabilized char for both LY and PD. This was realized by selective elimination of oxygen from coal as either H₂O or CO₂ as repeatedly stated above.

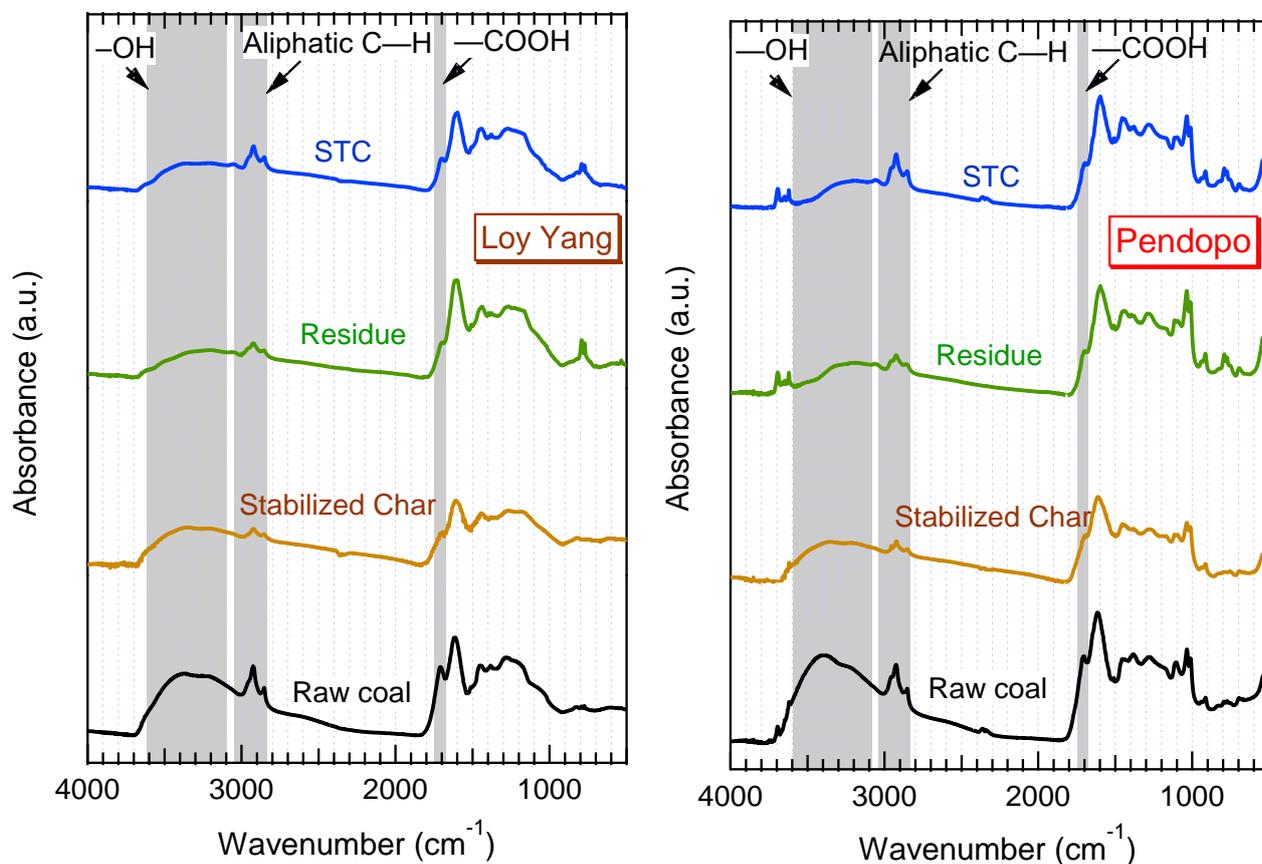


Figure 4.7. FTIR analyses for Raw coal, Residue, STC, and Stabilized char for Loy Yang (left) and for Pendopo (right).

The intensities of the adsorption bands associated with aliphatic C-H groups at 2950-3000 cm^{-1} do not show big differences among the samples. It is generally accepted that the aliphatic carbon moieties are main reactants of the oxidation of coal at low temperatures. The aliphatic carbons are first oxidized to form peroxides, and then the peroxides are further oxidized to form oxygen-containing functional groups, such as aldehydes, carboxyls, esters, and anhydrides, with simultaneous formation of H_2O and CO_2 [13-16]. This suggests that the interaction between oxygen and sample will be similar among the samples if the oxidation mechanism can be applied to STC, Residue, and Stabilized char also. The results shown in Figs. 4.2 and 4.3 actually showed that the differences in both weight changes and heat generation rates among Raw coal, Residue, STC, and Stabilized char are small in the dry air for both LY and PD. However, the heat generation rate of Stabilized char was clearly larger than the heat generation rates of the other samples for both LY and PD. This seemed to suggest the existence of additional mechanisms for the interaction of oxygen and heat treated coal. The existence of additional mechanisms may be examined by oxidizing the “Fresh char” in dry air.

Figs. 4.2 and 4.3 include the results performed using “Fresh char”. It is clearly shown that the oxidation rate of Fresh char is much larger than the oxidation rates of the other samples at 107 °C. The W/W_0 values rapidly increased on changing the gas stream from the N_2 to dry air and to reach respectively $\cong 1.006$ and $\cong 1.009$ after 30 min of reaction for LY and PD. The dQ/dt value instantly increased on changing the gas stream from N_2 to dry air to reach a maximum of respectively $\cong 0.11$ kW/kg and $\cong 0.32$ kW/kg at less than 1 min for LY and PD and decreased gradually but was much larger than the dQ/dt values of the other samples through the whole course of the oxidation. The Q_{30} values were respectively as large as $\cong 56$ kJ/kg and $\cong 73$ kJ/kg for LY and PD. The Q_{30} values

are large enough to raise the temperature of Fresh char by 40 to 54 °C in 30 min by only the oxidation reaction. Since the big differences of heat generation rates between Raw coal and Fresh char cannot be explained by the amount of aliphatic groups, the heat treatment in N₂ atmosphere at 350 °C must have created some active sites for oxidation such as free radicals [17–19]. Fresh char was also subjected to the oxidation at 30 °C as shown by the red lines in Figs. 4.2 and 4.3. It is surprising to notice that the dQ/dt value for Fresh char at 30 °C is comparable to or even larger than the dQ/dt value for Raw coal at 107 °C for both LY and PD. This clearly shows that the reactive sites in Fresh char were created during the heat treatment and that Fresh char is very reactive to oxygen. In other words, Fresh char is weathered rather quickly when exposed to ambient atmosphere and will be stabilized to the state of Stabilized char, although Stabilized char is still more reactive to oxygen than Raw coal.

Next, the effect of the heat treatment on the capacity of adsorption of water vapor was also examined by referring to the results shown for Fresh char in Figs. 4.4 and 4.5. For LY, the W/W_0 vs. time relationship for Fresh char was rather close to the relationships of both Stabilized char and Raw coal. If the comparison was made on the basis of raw coal, however, the W/W_0 values of Fresh char and Stabilized char are smaller than the W/W_0 value of raw coal by $\cong 15\%$. For PD, the W/W_0 value for Fresh char was rather close to that of Stabilized char but was a little smaller than that of Raw coal during the whole course of experiment. The heat generation rate of Fresh char, on the other hand, was largest of all of the samples for both LY and PD. The Q_{30} values were respectively as large as $\cong 192$ kJ/kg and $\cong 200$ to 220 kJ/kg for LY and PD. The differences in the Q_{30} values between Fresh char and Stabilized char come from the differences in the Q_{30} values in the dry air. These results show that the capacity of adsorption of water vapor is

reduced by only through the heat treatment. The weathering of Fresh char will reduce the oxidation rate in dry air but will not change the capacity of adsorption of water vapor. In summary, it can safely conclude that the degradative solvent extraction is an effective method not only to upgrade low-rank coal but to suppress the propensity to spontaneous heating of the upgraded product mainly through reducing the capacity of adsorption of water vapor.

4.4 Conclusions

This chapter shows the propensity to spontaneous heating of Residue and STC prepared from two low rank coals by the degradative solvent extraction were examined in comparison with the propensity to spontaneous heating of the parent coals and chars prepared in an inert atmosphere at 350 °C. The weight change and the heat generation rate measured at 107 °C in both dry air and wet air were used as an index to estimate the propensity to spontaneous heating. It was found that the degree of propensity to spontaneous heating of Residue and STC is much less than that of the corresponding parent coal and chars, because the heat generation rates of Residue and STC in the wet air are much smaller than those of the corresponding parent coal and chars. This was realized because the degradative solvent extraction decomposes selectively the oxygen functional groups of parent coal. Thus the degradative solvent extraction is found to be an effective method not only to upgrade low-rank coal but to suppress the propensity to spontaneous heating of the upgraded product. The coal-oxygen interaction even at 107 °C, suggesting that adsorption of water vapor plays an important role for the spontaneous heating of coal even over 100 °C. The transient changes of heats of adsorption/desorption of water on the way to reach equilibrium were also successfully estimated and discussed in relation to isosteric heat of adsorption/desorption and heat of vaporization of water.

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Chapter 5

Conclusions and Recommendations

5.1 Conclusions

The present dissertation tackled the two important research subtopics raised in the Japan-Thailand SATREPS project entitled *Development of clean and efficient utilization of low rank coals and biomass by solvent treatment*. The project intends to develop several technologies for effective utilization of low-rank coal and biomass waste based on a core technology called “Degradative Solvent Extraction”. The first subtopic tackled was related to the examination of the effect of solvent on the yield distribution of Soluble, Deposit, and Residue and the examination of the possibility of preparing solvent treated coal (abbreviated to STC) in the framework of the degradative solvent extraction method. The second subtopic was the examination of propensity to spontaneous heating of Residue and STC, which are expected to be high quality solid fuels. For the second subtopic, some index evaluating the propensity to spontaneous heating was essential. The outcomes of the examination were shown in Chapters 2 to 4 in this dissertation. They are summarized as follows:

In chapter 2, the effects of solvent on the degradative solvent extraction of two low-rank coals, Loy Yang (LY) and Pendopo (PD), were examined by using three solvents: 1-MN, Kerosene, and the 1 to 1 mixture of 1-MN and Kerosene. It was judged that solvent does not affect the degradation reaction at 350 °C, and hence the performance of this degradative solvent extraction method such as selective deoxygenation and effective dewatering is realized by all the solvents used. The yield distributions of extracted products were dominated by the solubility of solvent used as expected. 1-MN, showing highest solubility, gave the largest yield of Soluble followed by the mixed solvent, and Kerosene (the practical solvent). The preparation of STCs from different solvents also

gave the yields close to the sum of the yields of Soluble, Deposit, and Residue for all solvents used. Most of the heating values of solid products were over 29 MJ/kg and rather close to the heating value of subbituminous coal. All Solubles were found to melt completely at rather low temperature and their behaviors were also similar even using different solvents. Kerosene, having advantages such as cheap and common practical solvent and the easiness of separation from the upgraded product, was expected to be a candidate of a practical solvent for preparing STC from low-rank coal.

Chapter 3 examined the coal-water interaction over 100 °C to estimate the heat of desorption of water from as-received coal and heat of adsorption/desorption of water on dried coal from the viewpoint of examining propensity to spontaneous heating of the dried coal. To do so a sensitive TG-DSC which measures weight change and heat flow in moist atmosphere was used. The heats of desorption were almost constant of 2300 to 2350 kJ/kg until water content decreases to 0.35 kg/kg-dried coal, close to heat of vaporization, and increased gradually to reach 5000 kJ/kg or so at the completion of drying at 107 °C for two low-rank coals. For the three coals tested, the heat generated by the adsorption of water vapor from the moist air of 0.15 of relative humidity were 90 to 130 kJ/kg-dried coal in 30 min and were 1.2 to 4 times larger than the heats generated by the coal-oxygen interaction even at 107 °C, suggesting that adsorption of water vapor plays an important role for the spontaneous heating of coal even over 100 °C. The transient changes of heats of adsorption/desorption of water on the way to reach equilibrium were also successfully estimated and discussed in relation to isosteric heat of adsorption/desorption and heat of vaporization of water.

In chapter 4 the propensity to spontaneous heating of Residue and STC prepared from two low-rank coals by the degradative solvent extraction were examined in comparison with the propensity to spontaneous heating of the parent coals and chars prepared in an inert atmosphere at 350 °C. The weight change and the heat generation rate measured at 107 °C in both dry air and wet air were used as an index to estimate the propensity to spontaneous heating. It was found that the degree of propensity to spontaneous heating of Residue and STC is much less than that of the corresponding parent coal and chars, because the heat generation rates of Residue and STC in the wet air are much smaller than those of the corresponding parent coal and chars. This was realized because the degradative solvent extraction decomposes selectively the oxygen functional groups of parent coal. Thus the degradative solvent extraction is found to be an effective method not only to upgrade low-rank coal but to suppress the propensity to spontaneous heating of the upgraded product.

5.2 Recommendations

Research activities in the framework of the Japan-Thailand SATREPS project have been developing various technologies for effective use of low-rank coal and biomass waste. Unfortunately, however, most of researches including this dissertation are rather fundamental. There seem to exist several drawbacks to be overcome for practical applications of the degradative solvent extraction technology. One of the drawbacks is the selection of solvent that meets a specific purpose. 1-methylnaphthlene is believed to be a best solvent to prepare Soluble suitable for preparation of carbon fiber in high yield. However, 1-methylnaphthlene is so expensive to be practically employed. In this

dissertation kerosene was proposed as a candidate solvent for preparing just STC, but it is not used if carbon fiber is the target product. More extensive studies are essential to find solvents applicable for various practical purposes.

This dissertation employed the weight change and the heat generation rate measured at 107 °C in both dry air and wet air as an index to estimate the propensity to spontaneous heating based on the works published our research group. The index is, however, is not directly utilized to predict actual temperature increase of coal stockpile. The works to formulate the index as rate equations that can be used in practical stockpile are essential. Elaborate and careful experiments covering wide ranges of temperature, oxygen pressure, and relative humidity will be required for the purpose.

Propensity to spontaneous heating of STC and Residue was examined using the “stabilized” STC and Residue due to experimental difficulty of preparing “fresh” Soluble and Residue. Results and discussion in Chapter 4 will surely suggest that the degree of propensity to spontaneous heating of “fresh” Soluble and Residue are less than that of “fresh char”. However, some trials to examine the propensity to spontaneous heating of “fresh” STC and Residue may be requested. In relation to this discussion, this dissertation examined the propensity to spontaneous heating of only “stabilized” and “fresh” chars. Since chars are widely prepared as high quality solid fuels from various coals, it may be interesting to examine the propensity to spontaneous heating of char under various operating conditions.

LIST OF PUBLICATIONS

List of first authorship publications

Journal publications

“TG-DSC Study to Measure Heat of Desorption of Water during the Thermal Drying of Coal and to Examine Role of Adsorption of Water Vapor for Examining Spontaneous Heating of Coal over 100 °C”

Trairat Muangthong-on, Janewit Wannapeera, Hideaki Ohgaki, and Kouichi Miura.

Energy Fuels, ACS Publications, Publish after minor revisions.

“Examination of Interactions of Solvent Treated Coal with Oxygen and Water Vapor at over 100 °C using TG-DSC for Examining Propensity to Spontaneous Heating of the Solvent Treated Coal”

Trairat Muangthong-on, Janewit Wannapeera, Hideaki Ohgaki, and Kouichi Miura.

Energy Fuels, ACS Publications, Publish after minor revisions.

“Effect of Solvent on the Degradative Solvent Extraction of Low Rank Coal”

Trairat Muangthong-on, Janewit Wannapeera, Supachai Jadsadajerm, Nakorn Worasuwanarak, Hideaki Ohgaki, and Kouichi Miura.

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“TG-DSC Study to Measure Heat of Desorption of Water during the Thermal Drying of Coal and Heat of Adsorption/Desorption of Water on Dried Coal over 100 °C”

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“Examination of Propensity to Spontaneous Heating of the Solvent Treated Coal”

Trairat Muangthong-on, Janewit Wannapeera, Hideaki Ohgaki, and Kouichi Miura.

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“Examination of Spontaneous Combustibility of Solvent Treated Coal and Biomass using Differential Scanning Calorimetry”

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Trairat Muangthong-on, Janewit Wannapeera, Hideaki Ohgaki, and Kouichi Miura.

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List of contributed publications

Journal publications

“Proposal of Liquid Membrane-FTIR Spectroscopy to Investigate Soluble Fraction of Degradative Solvent-Extraction”

Watcharakorn Ketren, Trairat Muangthong-on, Janewit Wannapeera, Heishun Zen, Toshiteru Kii, Kouichi Miura, and Hideaki Ohgaki.

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“Pyrolysis and Gasification Characteristics of Upgraded Products by Degradative Solvent Treatment of Low Rank Coal and Biomass”

Hiroyasu Fujitsuka, Trairat Muangthong-on, Hideaki Ohgaki, Ryuichi Ashida and Kouichi Miura.

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“Pyrolysis and Gasification Characteristics of Upgraded Products Obtained by Degradative Solvent Treatment of Low Rank Coal and Biomass”

Hiroyasu Fujitsuka, Trairat Muangthong-on, Hideaki Ohgaki, Ryuichi Ashida and Kouichi Miura.

The 12nd Eco-Energy and Materials Science and Engineering (12th EMSES), 2015, Krabi, Thailand.

“Examination of Rates of Oxidation Reaction and Water Vapor Adsorption at Low Temperatures”

Kouichi Miura, Trairat Muangthong-on, Janewit Wannapeera and Hideaki Ohgaki.

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“Proposal of Liquid Membrane-FTIR Spectroscopy for Investigation of Soluble Fraction of Degradative Solvent-Extraction”

Watcharakorn Ketren, Trairat Muangthong-on, Janewit Wannapeera, Heishun Zen, Toshiteru Kii, Kouichi Miura, and Hideaki Ohgaki.

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“The Liquid Membrane FTIR Spectroscopy for examination of Soluble Fraction of Degradative Solvent Extraction”

Watcharakorn Ketren, Trairat Muangthong-on, Janewit Wannapeera, Heishun Zen, Toshiteru Kii, Kouichi Miura, and Hideaki Ohgaki.

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“Measurement of Air Oxidation Rate of Coal at 60 to 80 °C”

Kouichi Miura, Hiroyasu Fujitsuka, Janewit Wannapeera, Trairat Muangthong-on, and Hideaki Ohgaki.

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