Development of depolymerization methods of carbonaceous resources utilizing reduction reactions by formic acid

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Introduction

1. Coal and its efficient utilization

Coal is the most abundant fossil fuel in the world with a 1,074,108 million tons reserve, which would last for 139 years if production were to continue at the current rate while petroleum would last for 53 years and natural gas for 49 years.[1] However, increasing fossil fuel consumption in recent years has led to concern about the emission of greenhouse gas.[2] As it is known to all, CO_2 is the main source of greenhouse gas, which is mainly evolved in fossil fuels combustion. The energy-related CO_2 emissions grew to 37.1 Gt in 2021, which is a record-high value[3] overall. At the Paris climate conference (COP21) in December 2015, 196 parties adopted the goal to "limit global warming to well below 2, preferably to 1.5 degree Celsius" for the first time.[4] According to a model developed by International Energy Agency,[5] to limit the temperature increase within 2 °C by 2050, the CO_2 levels should not exceed 15 Gt annually.

Huge amount of CO_2 emissions from burning coal as fuel. As shown in figure 1, CO_2 emissions from coal increased rapidly since 1990 and reached 15 Gt in 2021,[6] which is markable and urgent to be decreased. Thus, the non-fuel use of coal which does not utilize coal as fuel but as raw materials for carbon materials or chemical products is now attracting more attention.

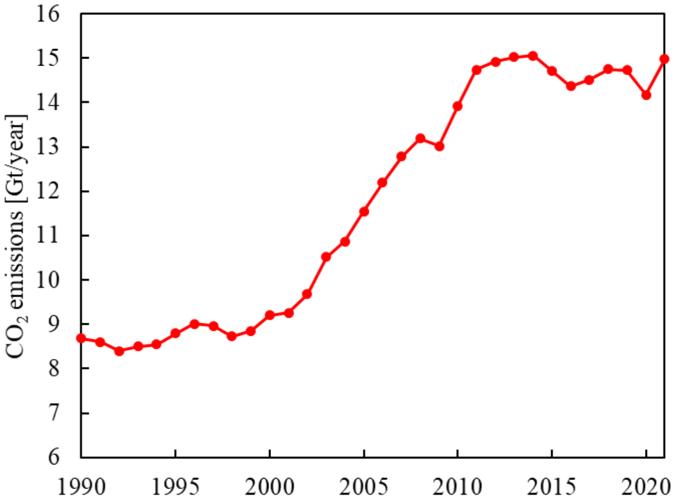


Figure 1. World CO_2 emissions from coal[3]

The similar chemical structure between coal and petroleum makes coal more favorable for chemical and carbon materials and not only for electric generation and transport[6]. By using coal in a “non-fuel” way, the coal would become more valuable, and the amount of CO_2 emissions would decrease as well.

As shown in figure 2, low-rank coal lack of low-molecular-weight compounds (LMWC) can only be burned as fuel while high-rank coal with abundant LMWC can be prepared into metallurgical coke due to its good thermoplasticity. Meanwhile, the LMWC in coals such as tar, pitch, and extracts produced by coking, pyrolysis, and extraction, can become raw materials of value-added products like specialty carbon materials such as graphite, carbon black, and carbon fibers as well as aromatic chemicals.[7,8] Thus, depolymerization which can increase the LMWC in coal, is the key to utilizing coals more efficiently as materials not only as fuels, and also is the goal of this dissertation.

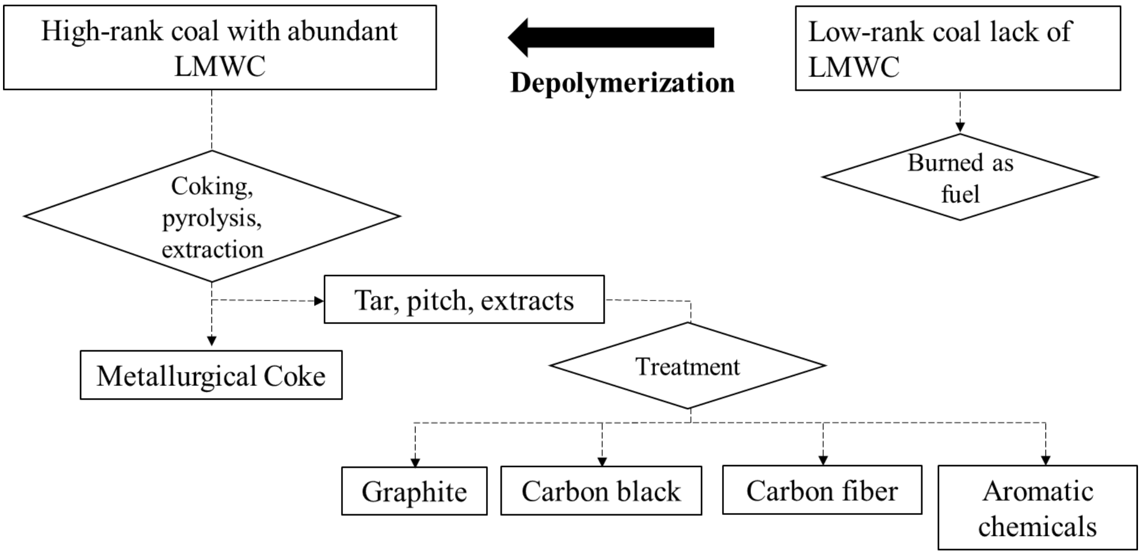


Figure 2. Examples of value-added utilization of coal

2. Coal for metallurgical coke production and its situation

Metallurgical coke is a macroporous carbon material of high strength produced by carbonization of coals of specific rank or coal blends at temperatures up to 1400 K. The coke in the blast furnace (figure 3) plays three major roles: fuel, chemical reducing agent, and permeable support. As the only solid material in the furnace supports the iron-

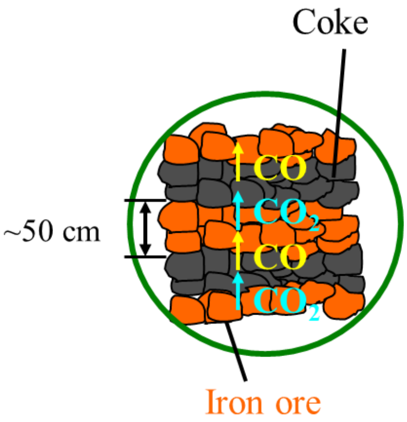


Figure 3. A schematic diagram of coke in the blast furnace

bearing the burden and making sure the route for hot gases to pass upwards into the stack,[9] the high mechanical strength of coke was required.

Coking coals show thermoplasticity between around 400 °C and 550 °C, which is required for producing high mechanical strength coke.[10] The thermoplasticity of coking coal is believed to be related to its abundant LMWC.[11] Low-rank coals such as brown coals and sub-bituminous coals, on the other hand, have no thermoplasticity upon being heated in an inert gas atmosphere, suggesting the LMWC in low-rank coal is extremely lacked.[10] One of the reasons that can be considered is the cross-linking reaction or so-called polymerization would occur under 400 °C, between O–H groups or C–O groups which are more abundant in low-rank coals.[12–14]

Figure 4 shows the world coal production in 2014. High-rank coking coal only had a 13 % share of all the coal produced, which is likely to be depleted. Figure 5 shows the average price of coal each year. The price of coking coal has been keeping higher than thermal coal in recent years. Therefore, in the future, low-rank coal with poor coking properties must be used mainly as a coke feedstock.

Various methods have been developed to increase the percentage of low-rank coals used in the coke feedstock. Increasing the packing density of coking coals in coke production is effective, the Stamp Charging Technology[15] and the Formed Coke Manufacturing Process[16] are processes that take advantage of this effect. SCOPE21 (Super Coke Oven for Productivity and Environmental enhancement toward the 21st century) is a process for modifying low-rank coals through pretreatment, which has been commercialized in Japan.[17] In SCOPE21, the softening and melting properties of low-rank coals can be improved by rapidly heating raw materials containing low-rank coals to about 350 °C. While such physical and thermal treatments are in practical use, the treatment of coal using chemicals has mainly been used for demineralization,[18] and few processes to upgrade low-rank coals have been developed.

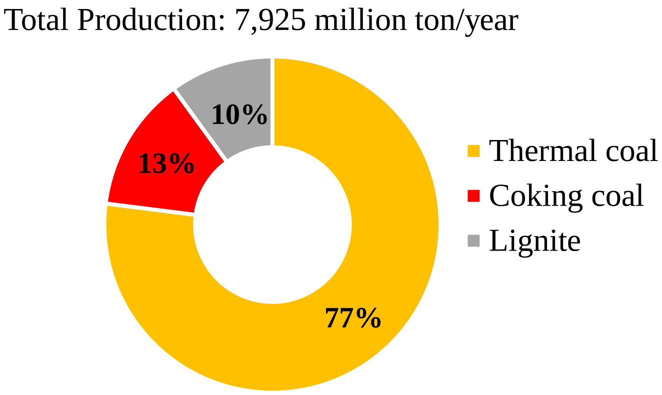


Figure 4. **World coal production in 2014**[19]

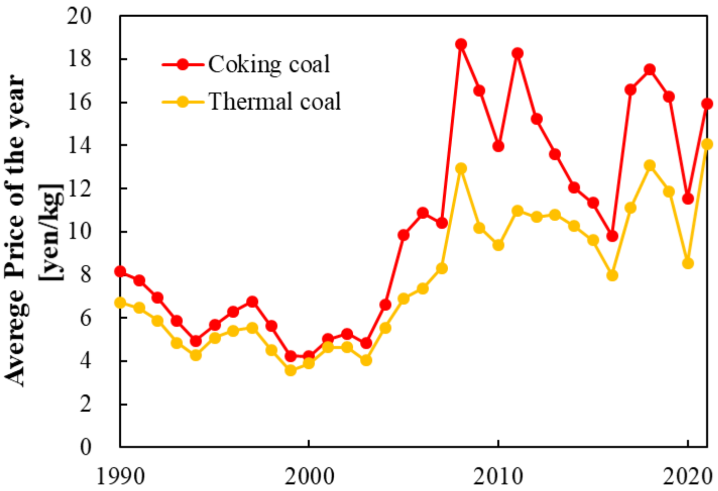


Figure 5. **The average price of coal each year**[20]

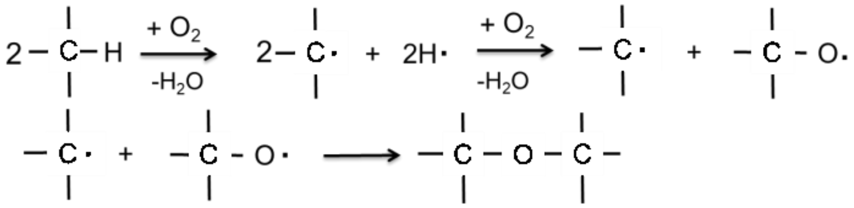


Figure 6. An example of the mechanism for coal weathering proposed by Liotta *et al.*[21]

The oxidative weathering of the coking coal can also diminish the coal in value for the coke produced with weathered coal which was of poorer quality. The mechanism of coal weathering is shown in figure 6. The ether cross-linking reaction is the main reaction in the weathering process which polymerizes and destroys the thermoplasticity of coking coals.[21]

Since coking coals are usually stored exposed to air for months before being used to produce coke, the weathering that occurs during that time would lead to a decrease in coke properties prepared from coking coal. Thus, it is also necessary to revive the weathered coal for restoring the coke property.

3. Solvent extraction method for valuable extracts in coal

The solvent extraction method can extract valuable LMWC from coal. When combining the depolymerization method of coal with the solvent extraction method, the valuable LMWC can be obtained easily at a higher yield. There have been several methods for solvent extraction of coal. Pyridine,[22] one of the strong polar solvents, and CS_2-NMP,[23] one of the binary solvents were used to investigate the structure of coal. The strong interaction between coal and solvents makes it difficult to separate the solvent from coal. The fractionation solvent extraction method which uses a flowing stream of a non-polar solvent such as tetralin or 1-methylnaphtalene under 10 MPa at temperatures lower than 350 °C[24–26] was applied to extract and quantified LMWC of coal in this study to quantify the amount of LMWC of raw and treated coal. The coal was separated into several fractions having different molecular weights without decomposition,[27] unextractable high-molecular-weight compounds ‘residue’ (>1000 g/mol), extractable low-molecular-weight compounds ‘deposit’ (400–1000 g/mol), and ‘soluble’ (<500 g/mol).[28] Each fraction has almost the same properties such as elemental compositions, FT-IR spectral, molecular weight distribution, thermomechanical analysis results, and thermogravimetric analysis results even from the different coal sources.[29] The fractionation solvent extraction method is also advantageous compared to other solvent extraction methods because a large amount of thermally released molecules can be dissolved in a non-polar solvent and the coal and solvent can be easily separated.[30] Thus, the total yield of the deposit and soluble was used as one of the standards to evaluate the degree of depolymerization of coal in this study. The higher yield of deposit and soluble is obtained, the higher degree of depolymerization of the coal is.

The extracts have the excellent coal properties, such as no ash, no water, and a high-calorie density. Okuyama and co-authors[31] developed the process to produce ash-free coal (Hyper-coal) using the extracts. Li and co-authors[32] prepared the carbon fiber by using the extracts obtained by this method as the precursor and obtained similar carbon fibers to those of commercial carbon fibers. Thus, the increase of the yield of LMWC by the depolymerization method means the increase of valuable extracts in the fractionation solvent extraction method for value-added products.

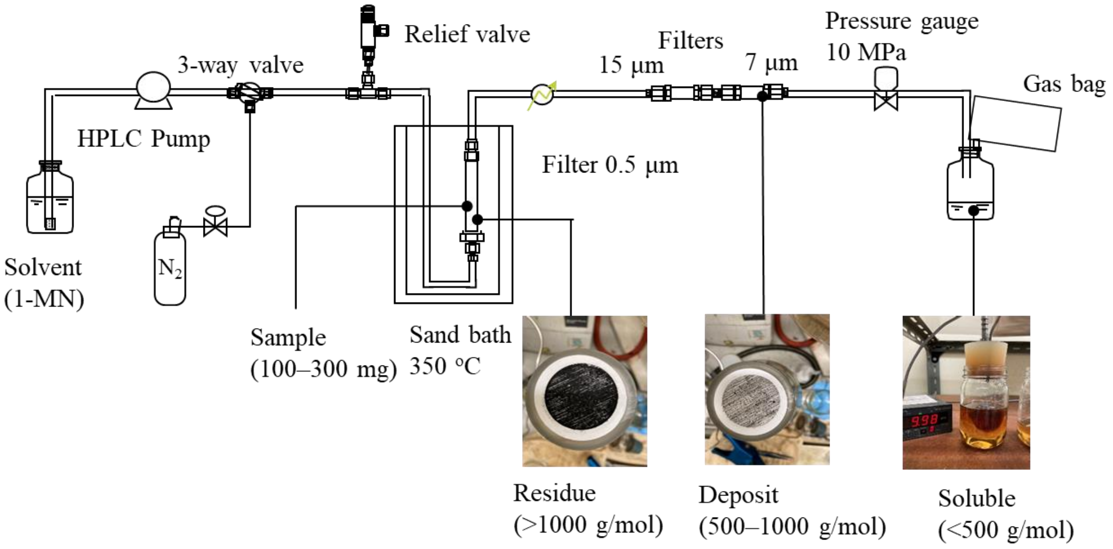


Figure 7. A schematic diagram of experimental apparatus used for extraction in a flowing stream of a non-polar solvent[27]

4. The relationships between the thermoplasticity and LMWC of coals

The thermoplasticity of coal is thought to be deeply related to the LMWC inherent existed in coal, γ compounds[33] and the LMWC evolved in thermal pyrolysis.[34-36] Takanohashi and co-authors[37] extracted the coals using CS_2-NMP at around 400 °C, and found the fluidity of coal and the yield of the extracts are correlated well. Kumagai and co-authors[38] monitored the mobile compounds of coals by using in-situ ^1H-NMR in the softening and melting stage of coals and found the thermoplastic behavior had a good correlated relationship with the yield of the mobile compounds. It suggested that the amount of LMWC in coals would influence their thermoplasticity. The thermoplasticity of coals was measured by thermomechanical analysis (TMA-50/60, Shimadzu) in this study.

Figure 8 shows the schematic diagram of the TMA used in this study. The samples were stacked about 1 mm thick in a platinum cell with an inner diameter of 5.3 mm, and heated to 900 °C in nitrogen at a temperature increase rate of 10 °C/min while applying a 0.098 N load with a 4.3 mm diameter rod, and the change in position from the initial rod position was monitored and recorded. The position was normalized by the initial thickness of the sample bed to obtain 'normalized displacement' data. The sample would have better thermoplasticity if it has a lower average molecular weight, and the lowest normalized displacement before the resolidification would be smaller.

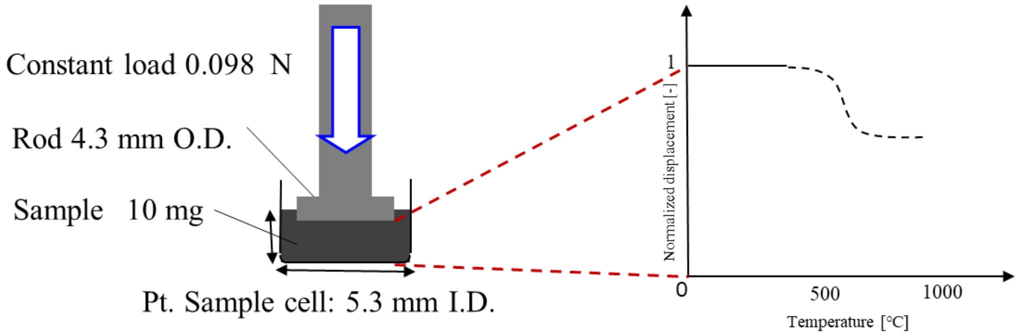


Figure 8. A schematic diagram of the Thermomechanical analysis

Ashida and co-authors[29] investigated the relationships between the thermoplasticity and the yields of the extracts extracted by the solvent fractionation method mentioned before and found that when the ratios of the three fractions (residue, deposit, soluble) were determined, the sample would have the same shape of the TMA curves no matter the source of the coals, and the resolidification temperature and maximum fluidity of the sample were also decided. In other words, the TMA curves would be an efficient method to measure the degree of the depolymerization of coal conveniently. In this study, the minimum relative displacements of the TMA curves were applied to evaluate the thermoplasticity of the sample.

5. Structure of carbonaceous resources

To depolymerize the carbonaceous resources, it is necessary to understand their structures. figures 9–11 show the models of different types of coal. Figure 8 shows the structure of bituminous coal proposed by Wiser *et al*.[39] The abundant polycyclic aromatic hydrocarbon in the bituminous coal is related to ether C–O or C–C bonds to form a large net-shaped structure. Figure 9 shows the structure of a kind of brown coal from Germany proposed by Hüttinger *et al*.[40] The aromatic hydrocarbons with 2–3 rings in the brown coal were connected by aliphatic C–H chains or ether C–O groups. Figure 10 shows the lignin structure proposed by Rahimi *et al*.[41] Monocyclic aromatic hydrocarbons were also connected with ether C–O or C–C bonds. It is noticed when the ether C–O bonds or aliphatic C–H bonds are cleaved with the formed radicals stabilized, the LMWC of carbonaceous resources can be increased. Also, because oxygen in the coal and biomass can be the cross-linking reaction sites as mentioned, the removal of oxygen from carbonaceous resources can increase their degree of depolymerization indirectly.

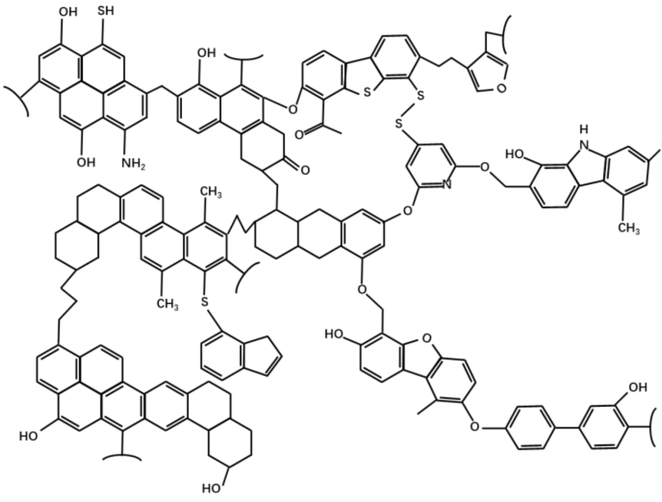


Figure 9. A schematic model for a type of bituminous coal proposed by Wiser *et al.*[39]

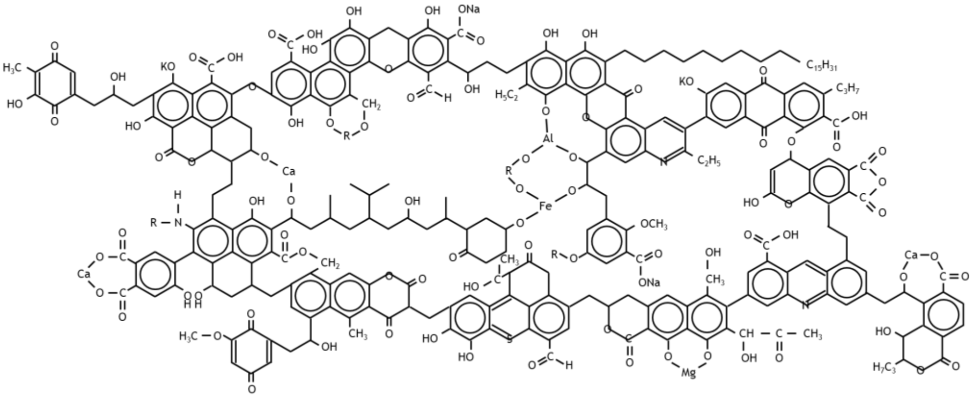


Figure 10. A schematic model for brown coal proposed by Hüttinger *et al.*[40]

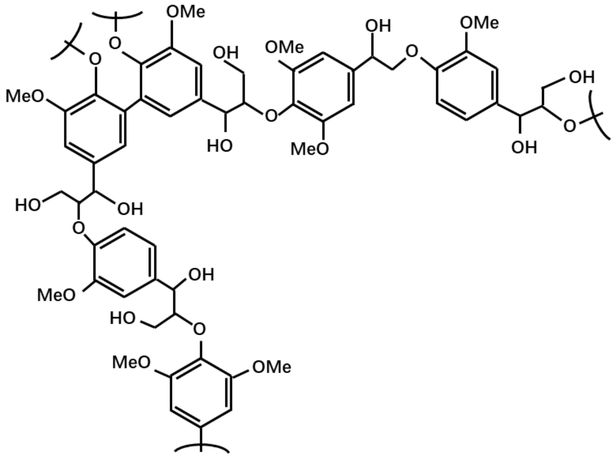


Figure 11. A schematic model for lignin proposed by Rahimi *et al.*[41]

6. Previous studies about depolymerization of carbonaceous resources

There are many attempts to increase the LWMC in coal or biomass by the cleavage of C–O and C–C bonds.

Pyrolysis, involved in liquefaction, gasification, and combustion, is one of the most important coal conversion processes.[42] The coal liquefaction process depolymerizes coal by the cleavages of ether and methylene bridges, but the conditions are usually extremely severe.[43] A typical liquefaction process, the NEDOL process, applied at 450 °C, 17 MPa, metal catalyst and hydrogen supplier solvent to achieve a 50 % yield of coal-liquefied oil.[44] The cost of the heat energy and plant device is too high to be commercialized for the process.[45] Pyrolysis in relatively mild conditions was also tried to depolymerize coals.

Liang and co-authors[46] depolymerized two kinds of low-rank coals and the tar yields increased from 3.6 % to 5 % and 7.8 % for Neimeng coal, from 8.1 % to 11.4 % and 10.9 % for Xinjiang coal after the addition of Mo and Fe based catalysts in a batch reactor at 550 ^{o}C. Liu and co-authors[47] increased the organic liquid products of coal from 0.2 % to 1.6 % by adding 1 wt. % iron-based catalyst in a Gray-King assay reactor from 150 to 600 ^{o}C. These works did not apply so high pressure like liquefaction, but the yield of LMWC increased only a little, and conditions were still hard making it not suitable for coal depolymerization process.

Oxidation is wildly studied for coal depolymerization. Kappo with co-authors[48] and Bimmer with co-authors[49] attempted to oxidize coals with oxygen in a NaOH solution under the mild conditions of 110 °C to 270 °C and 4.0 MPa to 7.5 MPa. They achieved gathering the water-soluble organics at 50 % yield on a carbon basis. However, O_2 oxidation converts 50 % of the carbon into CO_2 in the treatment, which is not suitable for the coal depolymerization process either.

For the depolymerization of other carbonaceous resources like biomass, hard conditions were also applied. Lavoie and co-authors[50] applied 5 wt. % of NaOH aqueous solution to pretreat softwood and hemp lignin at the temperature between 300 to 350 ^{o}C, Roberts and co-authors[51] applied a similar base-catalyzed treatment for commercial organosolv lignin at 300 ^{o}C and 25 MPa for the depolymerization, they obtained 10 % monomers, 60 % dimers and trimers but the conditions are even harder than that of coal liquefaction.

The previous methods for depolymerization of carbonaceous resources mostly needed high temperature and high pressure for the purpose to study their structures. The severe conditions cost a lot for the energy and the device, and lead to high yields of undesirable by-products like CO_2. Moreover, since the solution was introduced in most of the methods, the separation of the solution and solid samples also costs a lot. Thus, treatment methods to increase the LMWC of carbonaceous resources under milder conditions at a low cost are required.

7. Proposed depolymerization method in this dissertation

The traditional depolymerization method for coals focuses on the cleavage of the C–C or C–O bonds under severe conditions such as high temperatures and high pressures, few studies concentrate on the stabilizing of coal inherent radicals which can succeed under mild conditions. The stabilization of radicals can inhibit the cross-linking reactions between LMWC so that more LMWC can be reserved. It is known that radicals are present in coal not only when heated but also originally[52, 53], and it has been reported that radicals can be removed by reduction treatment using chemical substances[54]. Larsen and co-authors reported that the pyrolysis behavior of immature kerogen was significantly altered by removing the inherent radicals[55, 56]. Radicals originally present in low-rank coals may recombine upon heating and become cross-linking points for molecules in the coal. In this study, the polymerization reaction caused by the recombination of radicals was focused on, and the radicals of the LMWC were stabilized before the recombination happened so that more LMWC can be reserved.

Predtechenskii and co-authors[57] found that when adding 10 % formic acid (FA) in supercritical water to treat noncaking coal at around 600 ^{o}C, the single-axis compression strength of the formed agglomerates increased from 5-10 kg/cm^2 to 45 kg/cm^2, indicating the effectiveness of FA in improving the caking properties of coals under supercritical water conditions. However, few studies are using FA to treat coal under mild conditions at 60–250 ^{o}C and 0.1 MPa. In this study, FA is proposed as the reducing agent to stabilize the radicals in coals under mild conditions. FA has the advantage such as does not introduce inorganic impurities to the solid coal after the treatment and is relatively cheap. Also, FA would become CO_2 gas after reduction and can be easily separated from coal. Formic acid has almost the equal boiling point as water and can be supplied as a vapor even at temperatures below 100 °C. When gaseous formic acid is used, both the reactant (FA) and product (CO_2) of the reductant are gaseous, and considering separation and the reasons mentioned above, the process should be suitable for treating solid coal and biomass to depolymerize them at low cost.

Table 1. The property of formic acid[58]

Chemical Formula	CH_2O_2
Price	360–390 yen/kg (76 %)
Boiling point	100.75 ^{o}C
Density	1.22 kg/m^3

8. Dissertation objective and outline

The traditional depolymerization method for the carbonaceous resources required severe conditions such as 4–17 MPa, and 110–600 °C, which leads to the high cost. This study aims to develop several methods to increase the low-molecular-weight compounds in carbonaceous resources by depolymerization under mild conditions only under 60–250 °C and 0.1 MPa, which can contribute to the wide non-fuel utilization of the carbonaceous resource and decrease of CO_2 emission as well at a low energy cost.

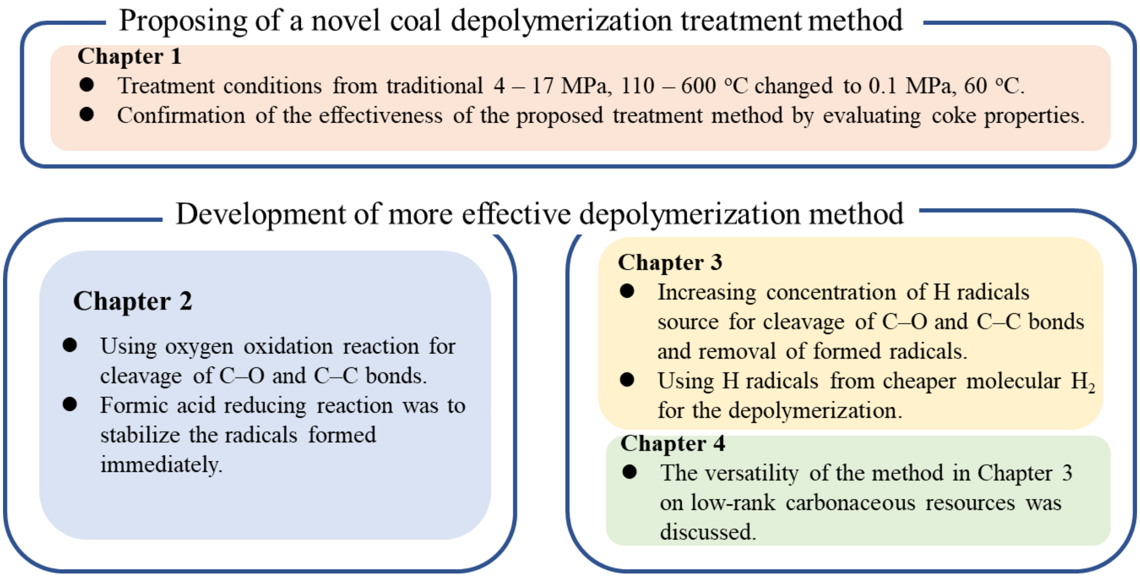
Based on the purpose and the mechanism of depolymerization, the four kinds of research topics are investigated and summarized in this study. The outline is described below.

Chapter 1 is dedicated to the improvement of the thermoplastic behavior of coal and the enhancement of the mechanical strength for coke production. The inherent radicals of low-rank coals and weathered coals were designed to be stabilized under mild reducing reactions so that the recombination reactions between the radicals of the low-molecular-weight compounds can be prevented and more low-molecular-weight compounds can be reserved. Formic acid, a reducing agent which can provide H radicals for stabilization was first proposed. The treatment under 60 °C and 0.1 MPa with both aqueous and gas formic acid was found to be able to increase the coking properties of treated coals and increase the tensile strength of the resulting coke.

Since the amount of the inherent radicals in coal is limited, the depolymerization method proposed in Chapter 1 has a limitation. In Chapter 2, to enhance the depolymerization degree of coal, a novel coal treatment method that combines oxygen oxidation reaction and gaseous formic acid reduction reaction to treat a bituminous coal under mild conditions (>90 °C, 0.1 MPa) is proposed. The oxidation reaction was found to cleave the C–O bonds in coals and H radicals from formic acid stabilized the formed radicals instantly. The method proposed in Chapter 2 proved to be more effective compared to the method proposed in Chapter 1.

Because the mole fraction of formic acid has a limitation, the H radicals sources are also limited in the previous 2 chapters. To solve this issue, in Chapter 3, another coal treatment method aimed at more efficient depolymerization is proposed using co-existing gaseous FA and H_2 to treat the same bituminous coal in Chapter 2 under mild conditions (90–110 °C, 0.1 MPa). The much higher H radicals concentration made it possible to cleave C–O or C–C bonds without bringing changes to coal structures using oxidation or pyrolysis. Also, the co-existing of formic acid and hydrogen gas made it possible to use formic acid as a catalyst to transport H radicals from cheaper hydrogen gas, which could decrease the cost of the treatment more.

In Chapter 4, the versatility of the proposed method in Chapter 3 is studied further by testing 3 types of coals and one biomass, lignin. The effects of the proposed treatment method on different carbonaceous resources are examined. The possibility of the proposed method to depolymerize various types of carbonaceous resources is investigated.



Proposing of a novel coal depolymerization treatment method

Chapter 1

- Treatment conditions from traditional 4 – 17 MPa, 110 – 600 °C changed to 0.1 MPa, 60 °C.
- Confirmation of the effectiveness of the proposed treatment method by evaluating coke properties.

Development of more effective depolymerization method

Chapter 2

- Using oxygen oxidation reaction for cleavage of C–O and C–C bonds.
- Formic acid reducing reaction was to stabilize the radicals formed immediately.

Chapter 3

- Increasing concentration of H radicals source for cleavage of C–O and C–C bonds and removal of formed radicals.
- Using H radicals from cheaper molecular H_2 for the depolymerization.

Chapter 4

- The versatility of the method in Chapter 3 on low-rank carbonaceous resources was discussed.

Figure 12. The outline of the dissertation

Table 2. The targets and H radicals sources in each chapter

Sources of H radicals	Removal of inherent radicals	Cleavage of C–O and C–C bonds and removal of formed radicals
Formic acid	Chapter 1	Chapter 2
Hydrogen (with FA)	Chapters 3 & 4	

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Chapter 1–Improvement of coking property of low-rank coals by mild reduction treatment

1. 1. Introduction

Coke has a role in the blast furnace as a reductant to reduce iron ore, a fuel to maintain high temperatures, and a spacer to secure distribution paths for gas and molten iron.[1] In general, to produce coke with a certain level of mechanical strength, the coal must be softened and melted by heating, which is named coking coal.

The amount of the high-rank coking coal used in the production of coke for steelmaking is only about 10 % of the total available coal reserves and is feared to be depleted.[2] Therefore, in the future, low-rank coal with poor coking properties must be used mainly as a coke feedstock. The thermoplasticity of coking coal is believed to be related to its abundant low-molecular-weight compounds (LMWC).[3] Low-rank coals lack LMWC so the coke produced from them has poor mechanical strength and cannot serve as a spacer. Thus, it is necessary to increase the LMWC in low-rank coal for coke production.

Traditional coal depolymerization methods which focus on the cleavage of C–C or C–O bonds of coals and the stabilization of the formed radicals usually applied severe conditions of high temperatures and high pressures, and also applied solvent which increased the separation process cost.[4-9] Solvent refined coal (SRC) method was a typical coal depolymerization method for coke production which applied the conditions of 400 ^{o}C, 7 MPa of hydrogen, and under wet process.[10] On the other hand, few studies concentrate on the stabilizing of coal inherent radicals which can succeed under mild conditions and reserve more LMWC of treated coals. It is known that radicals are present in coal not only when heated but also originally,[11, 12] and it has been reported that radicals can be removed by reduction treatment using chemical substances.[13] When the inherent radicals of LMWC in coals are stabilized, the cross-linking reactions between them would be inhibited, so that more LMWC can be reserved and the degree of depolymerization of coal is also enhanced.

Formic acid (FA), which can provide H radicals under mild conditions was first proposed as the reducing agent in this study. Since the purpose is to stabilize the inherent radicals of coals, the treatment conditions were only 60 ^{o}C and 0.1 MPa which were much milder compared to the traditional methods. Meanwhile, since FA could be supplied in vapor and the product of the reducing reaction is only gaseous CO_2 from the following equation (1.1), there is no need for the separation cost for solid coals.

$$HCOOH \rightarrow CO_2 + 2H^+ + 2e^- \qquad (1.1)$$

In this study, different types of low-rank coals and accelerated weathered coal are treated in FA aqueous solution or FA gas atmosphere, and the thermoplasticity of treated coal and indirect tensile strength of the coke prepared with the treated coals are investigated to demonstrate the proposed treatment method.

1. 2. Experimental

1. 2. 1 Sample

Two types of low-rank coals A, B, and a coking coal C were used. The elemental compositions of these coals measured by CHN Corder (MT-6M, Yanaco) are shown in Table 1.1. The coals were ground to less than 1 mm before use.

Table 1.1. Elemental compositions of the samples used in this study

Coal	Ultimate analysis [wt. %, d.a.f.]				Atomic ratio[–]		Ash (wt.%, d.b.)
	C	H	N	O [diff.]	H/C	O/C	
A	79.8	5.6	1.3	13.3	0.83	0.13	14.8
B	83.2	5.0	1.0	10.9	0.71	0.10	8.8
C	86.9	4.5	0.8	7.8	0.62	0.07	4.7

d.a.f. : dry-ash-free, d.b. : dry basis, diff. : differential

1. 2. 2 FA aqueous solution treatment

Figure 1.1 shows the apparatus for the FA aqueous solution treatment. In an Erlenmeyer flask, 5 g of raw coal and 250 cm^3 of 0.5 mol/L formic acid aqueous solution were mixed and the flask was immersed in a water bath kept at 60 °C. After 6 hours, the flask was taken out of the water bath and the solution and coal were separated by filtration using a PTFE filter paper (ADVANTEC, H050A047A) of which pore size was 0.5 μm.

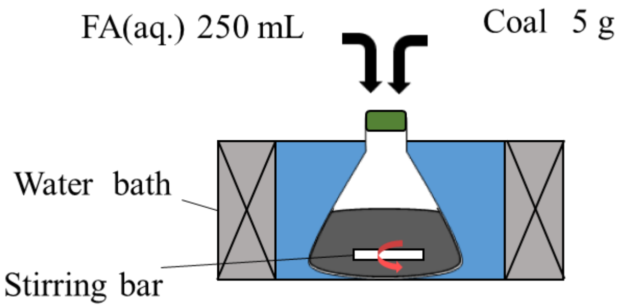


Figure 1.1. Apparatus for the FA aqueous solution treatment

1. 2. 3 FA vapor treatment

Figure 1.2 shows the apparatus for the FA vapor treatment. In a closed 250 cm^3 glass container, 2.5 g of raw coal and 7 g of formic acid in a sample tube bottle were separately placed, and the volatilized formic acid and raw coal were in contact with each other at 60 °C for 2 or 6 hours using the water bath.

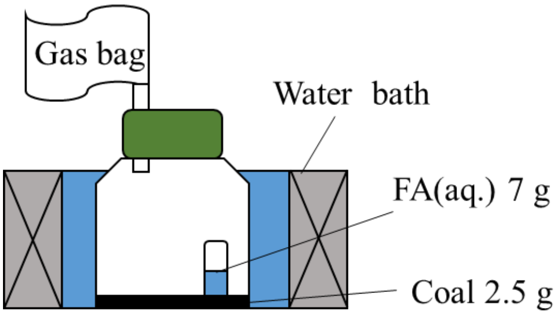


Figure 1.2 apparatus for the FA vapor treatment

1. 2. 4 Analyses of the products

The gases produced during the treatment were collected in a gas bag and analyzed by a gas chromatograph (GC-12A, Shimadzu, Colume: Porapak Q, 200 ^{o}C, Detector: FID, 220 ^{o}C).

The yield of the treated coal was calculated as follows:

Yield = M_f/M_s x 100 %
M_s is the weight of coal used (on dry basis).
M_f is the weight of treated coal after the treatment (on dry basis).

The treated coals were subjected to elemental analysis (CHN Corder MT-6M, Yanaco) and thermomechanical analysis (TMA-50, Shimadzu). As mentioned before, the TMA which measures the thermoplasticity of coal was applied as a convenient method to evaluate the degree of depolymerization of coals.[14] The resolidification of coals would happen in the carbonization in TMA where the normalized displacement would have a minimum value, which was focused on to evaluate the thermoplasticity of coals in this study. The solvent fractionation extraction method was applied to quantify the amount of low-molecular-weight compounds (LMWC) of raw and treated coal. The detail of this method is mentioned before.

1. 2. 5 Preparation and evaluation of coke

Raw coal and treated coals were made into coke, and the indirect tensile strength was measured. Approximately 2 g of coking coal or treated coal was charged into a stainless steel tube with an inner diameter of 16.8 mm, heated to 900 °C at 10 °C /min in nitrogen, and held for 30 minutes to prepare the coke.[15] Indirect tensile strength tests (AGS-10kNJ, Shimadzu) were performed on the resulting cylindrical coke to evaluate the strength of the coke. Figure 1.3 shows the process of the indirect tensile strength test. The cylinder shape coke was set on the platform, then the lord of pressure was added to the coke at a constant rate of 0.2 mm/s in the direction of the cylinder diameter. The coke received the pressure stress and the tensile stress at the same time. Since the coke had high density, it can bear more pressure stress than other stress.[16] Finally, when the load at failure reached, the cylinder of coke was broken by simple tension fracture, and the tensile strength was calculated indirectly by the following formula:[17]

$$\sigma = \frac{2P}{\pi DL} \tag{1.2}$$

(σ: Indirect tensile strength, D: diameter of the cylinder, L: Length, P: Load at failure)

The indirect tensile strength test is one of the most convenient tests in terms of sample preparation, testing requirements, and availability of appropriate standards.[17]

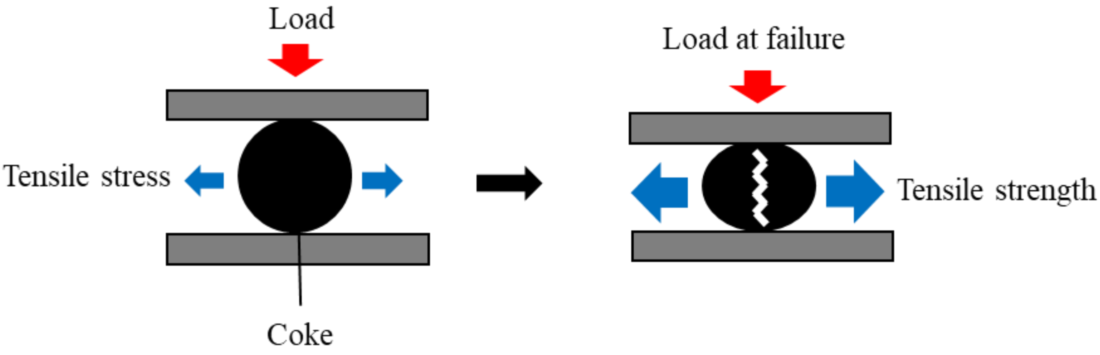


Figure 1.3.　A schematic diagram of the indirect tensile strength analysis

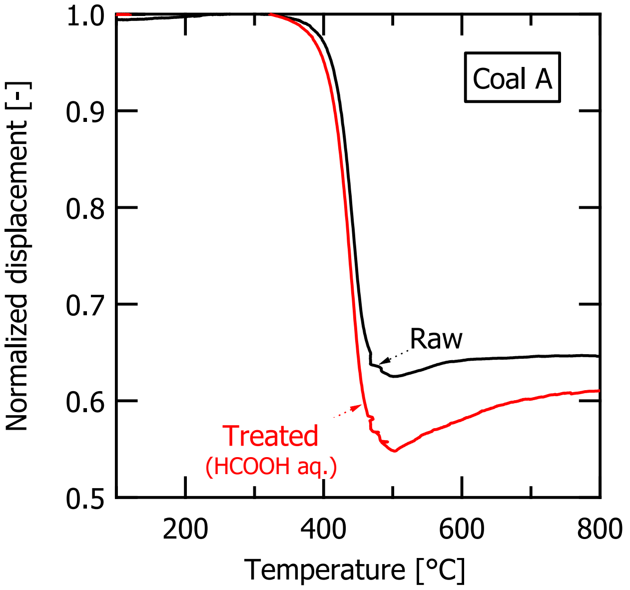
1. 3. Results and discussion

1. 3. 1 Results of formic acid aqueous solution treatment

Table 1.2 shows the yields of treated coals when coal A or coal B was treated with formic acid aqueous solution or hydrochloric acid at 60 °C. The yields of treated coals were almost 100 %. Figure 1.4 shows the thermomechanical analysis curves of the raw coal and formic acid aqueous solution treated coal. The rod position changed more significantly for the formic acid-treated coals than for the raw coals at around 400 °C and reached a lower value of normalized displacement, where softening and melting occurs, indicating that the treatment clearly improved the thermoplasticity of the treated coals.

Table 1.2. Yields of coals treated in formic acid aqueous solution (HCOOH aq.) or hydrochloric acid (HCl aq.)

Coal	Yield [wt. %, d.b.]	
	HCOOH aq.	HCl aq.
A	95.5	97.6
B	96.1	98.4



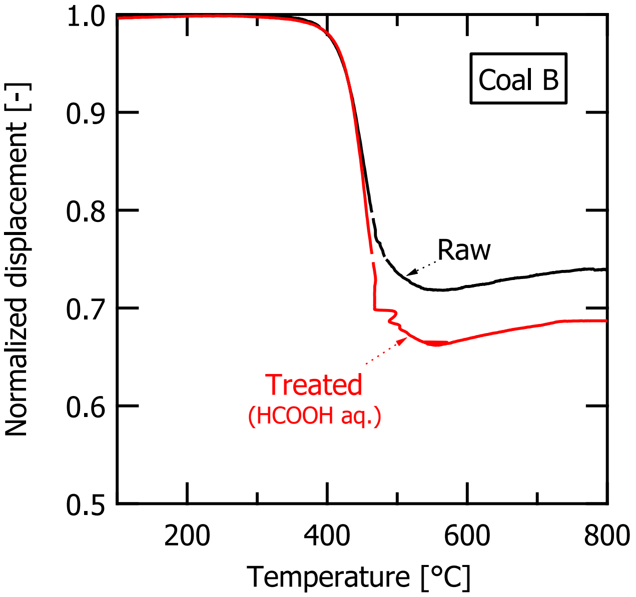


Figure 1.4. TMA curves of the raw coals and coals treated in formic acid aqueous solution (HCOOH aq.)

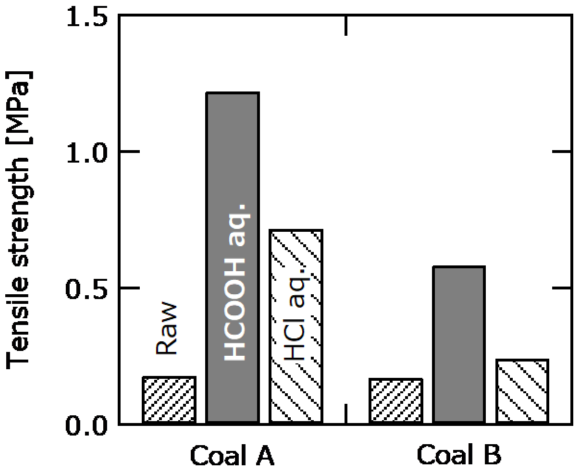


Figure 1.5. Strength of coke prepared from coals treated in formic acid aqueous solution (HCOOH aq.) or hydrochloric acid (HCl aq.)

Table 1.3. The apparent density of coke prepared from coals treated in formic acid aqueous solution or hydrochloric acid (HCl aq.)

	Apparent density [kg/m^3]
Coal A Raw	668.5
Coal A HCOOH aq.	713.8
Coal A HCl aq.	704.2
Coal B Raw	793.2
Coal B HCOOH aq.	772.8
Coal B HCl aq.	787.1

Figure 1.5 shows the indirect tensile strength of coke prepared from raw coal and formic acid aqueous solution treated coal. The strength of coke increased after the treatment with formic acid aqueous solution regardless of the coal type, indicating the effectiveness of formic acid aqueous solution treatment. The strength-enhancing effect of the coke in the proposed method could be attributed to the improved thermoplasticity mentioned earlier. Since formic acid is both a reducing agent and an acid, it is possible that the strength was increased by acid-induced demineralization. Therefore, a similar treatment with hydrochloric acid was performed with the same acidity as the formic acid solution used and compared the strength of the coke. Figure 1.5 shows that the strength increased more when treated with formic acid solution than when treated with

hydrochloric acid, which confirmed the effectiveness of the reducing effect of formic acid in the treatment. Table 1.6 shows the apparent density of each coke. The density of each coke did not change so much, indicating that the increase in tensile strength of coke is not mainly due to the change of porosity in the FA aqueous solution treatment.

1. 3. 2 Results of formic acid vapor treatment

Table 1.4 shows the yields of treated coals when coal A or B was treated with formic acid vapor at 60 °C for 2 or 6 hours. As in the case of the formic acid aqueous solution treatment, the yield of the treated coals was almost 100 %.

Figure 1.6 shows the thermomechanical analysis curves of the raw coal and formic acid vapor treated coal. For the 2 h treated coal A and the 2 h and 6 h treated coal B, the rod position changed more significantly for the formic acid vapor treated coals than for the raw coals at around 400 °C, where softening and melting occurs, indicating that the treatment clearly improved the thermoplasticity. For the 6 h treated coal A, unlike the other treated coals, a rod drop was observed even by 200 °C, and the drop around 400 °C was not much different from that of the raw coal. Table 1.3 shows that only in the case of the 6 h treatment of coal A, the yield of the treated coal was slightly higher than 100 %. This suggests that there may have been physical or chemical adsorption of formic acid on the coal under this treatment condition, and that the rod drops to 200 °C in TMA may occur as the adsorbed formic acid was desorbed. This adsorption and desorption of formic acid may have negatively affected the thermoplasticity of coal A. This behavior was not observed in the 2 h treatment of coal A and the 2 h and 6 h treatments of coal B, which have improved thermoplasticity of the both coals.

Table 1.4. Yields of coals treated by formic acid vapor

Coal	Yield [wt. %, d.b.]	
	2 h	6 h
A	99.2	108.3
B	97.8	99.5

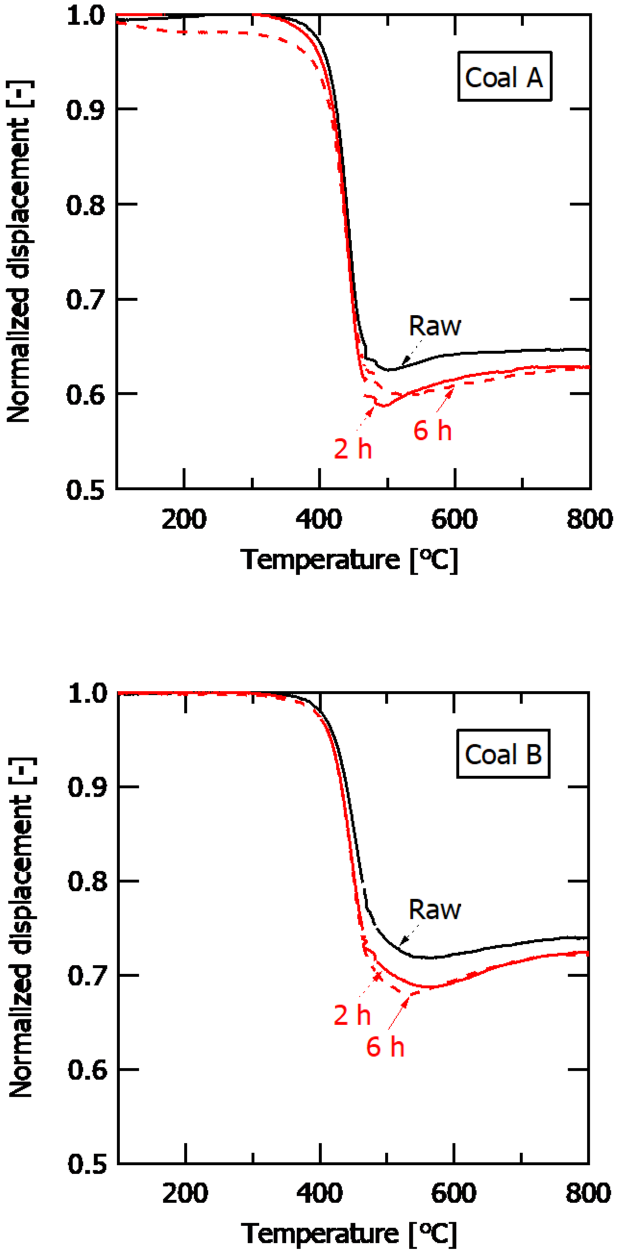


Figure 1.6. TMA curves of the raw coals and coals treated by formic acid vapor

Figure 1.7 shows the indirect tensile strength of coke prepared from the raw coal and formic acid vapor treated coals. Even with formic acid vapor treatment, which is a simpler process than the wet treatment, the strength of coke increased regardless of coal type, indicating the effectiveness of formic acid vapor treatment. For coal B, coke strength increased with treatment time, and after 6 h of treatment, the strength was more than six times higher than that of the raw coal coke. For coal A, treatment for 2 h increased the strength to 5 times that of the raw coal coke, but when the treatment time was extended to 6 h, the coke strength decreased a little. These results are in good agreement with the results of the thermomechanical analysis, which showed that the thermoplasticity was improved for the treated coals except for the 6 h treated coal A. Table 1.5 shows the apparent density of each coke. The apparent density of coke prepared from coal B changed little after the treatment while that of coke prepared from coal A coal had a higher density after the treatment. The decrease of the porosity in the coke from coal A can be another reason for the increase in tensile strength.

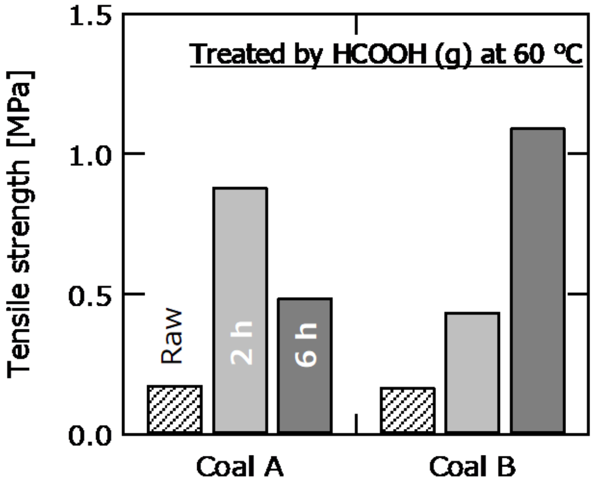


Figure 1.7. Strength of coke prepared from coals treated by formic acid vapor

Table 1.5. The apparent density of coke prepared from coals treated by formic acid vapor

	Apparent density [kg/m^3]
Coal A Raw	668.5
Coal A 2h	806.7
Coal A 6h	812.4
Coal B Raw	793.2
Coal B 2h	841.6
Coal B 6h	800.7

1. 3. 3 The structural change of coals through the treatment

To examine the changes that occurred in the coal as a result of the treatment, elemental compositions were analyzed and the results are shown in Table 1.6. Formic acid solution treatment slightly increased the carbon content in both coals, but there was no significant difference in elemental composition before and after the treatment.

Table 1.6. Elemental compositions of raw coals and coals treated in formic acid solution

Coal	Ultimate analysis [wt%, d.a.f]				Atomic Ratio [-]		Ash
	C	H	N	O (diff.)	H/C	O/C	[wt%, d.b.]
A raw	79.8	5.6	1.3	13.3	0.83	0.13	14.8
A treated	80.4	5.6	1.3	12.7	0.83	0.12	7.5
B raw	83.2	5.0	1.0	10.9	0.71	0.10	8.8
B treated	83.9	5.1	1.0	10.0	0.73	0.09	7.3

d.a.f. :dry ash-free, d.b. : dry basis, diff. : differential

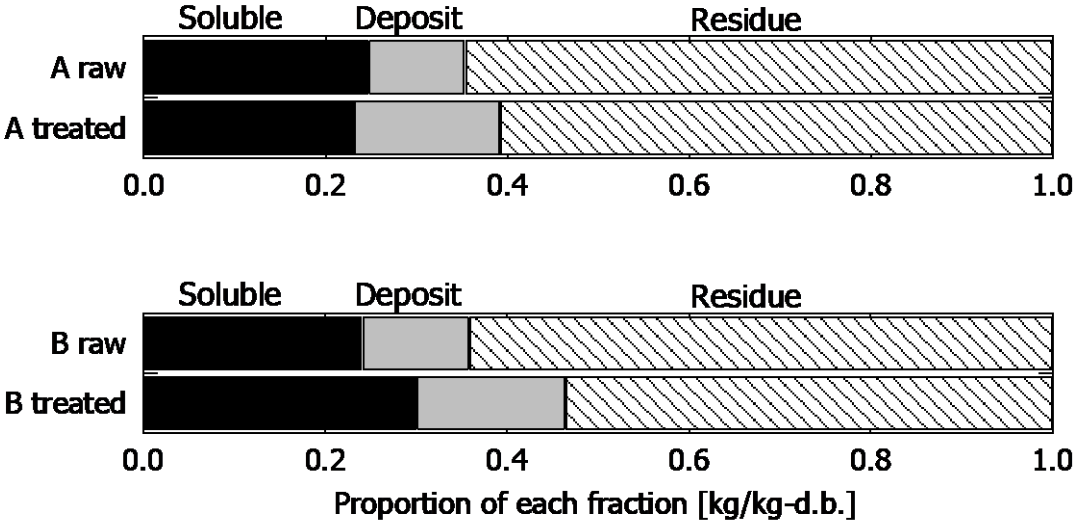


Figure 1.8. Yield of each fraction obtained through solvent extraction from the raw coals and 2 h formic acid vapor treated coals

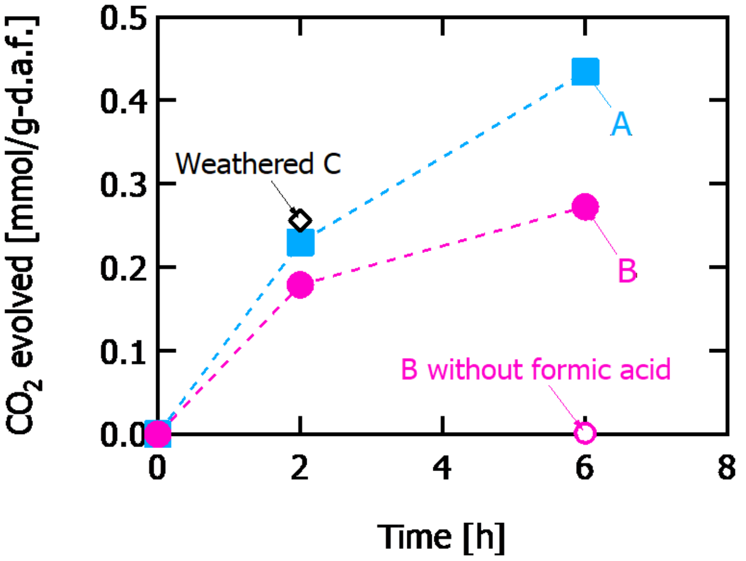


Figure 1.9. **CO_2 amount formed in the formic acid vapor treatment**

Figure 1.8 shows the fractionation solvent extraction results for the raw coals and 2 h formic acid vapor treated coals. The yield of extractable fractions (soluble and deposit) of the raw coal A was 35 %, while the formic acid vapor treatment increased the extractable fractions to 39 %. The yield of extractable fractions of the raw coal B was 36 %, but the extractable fractions increased significantly to 46 % after formic acid vapor treatment. These results are consistent with the TMA results that the 2 h formic acid vapor treatment improved the thermoplasticity of the coals.

Figure 1.9 shows the change over time of CO_2 amount formed in the formic acid vapor treatment. Since the amount of produced CO_2 was negligible when the control experiment using only coal or only formic acid was performed, it can be said that the CO_2 produced during the treatment was due to the reaction between coal and formic acid. When formic acid reacts as a reducing agent, it produces CO_2 as expressed in equation (1.1),

$$HCOOH \rightarrow CO_2 + 2H^+ + 2e^- \quad (1.1)$$

Therefore, considering that the CO_2 produced during the treatment was derived from formic acid, the amount of formic acid that reacted during the 2 h treatment was 0.23 mmol/g-coal for coal A and 0.18 mmol/g-coal for coal B. Even if formic acid-derived H is added to the coal according to equation (1.1), the hydrogen content increases by only about 0.4 mmol/g-coal, or about 0.04 wt. %, and it is difficult to detect these increases with the accuracy of elemental analysis.

The fact that the treatment increased the extraction yield of coal despite the little amount of reduction by formic acid is verified below by approximate estimation. Assuming an average molecular weight of 500 g/mol of coal, the number of molecules per gram of coal is 2 mmol. If the amount of CO_2 formed from formic acid is 0.2 mmol/g-coal, the H radical donation by equation (1.1) is 0.4 mmol/g-coal, which stabilizes a number of radicals equivalent to 20 % of the 2 mmol molecules per 1 g of coal. Since one cross-link is formed by two radicals, the number of suppressed cross-links is 10 % of the total number of molecules in this case. There are three types of cross-linkings as follows:

1. Cross-linking between two low molecular weight compounds, resulting in the disappearance of two low molecular weight compounds.
2. Cross-linking between low and high molecular weight compounds, resulting in the loss of one low molecular weight compound.
3. Cross-linking between two high molecular weight compounds, or intramolecular cross-linking, with no loss of low molecular weight compounds

If the average number of LMWC lost through crosslink formation is hypothetically one per crosslink, the treatment can increase the number of low molecular weight compounds by 10 % by preventing the cross-linking reactions, which is close to the increase of LMWC in coal B. Based on the above estimates, it could be said that even a reduction with formic acid of about 0.2 mmol/g-coal is sufficient to increase the extraction yield of coal.

1. 3. 4 Application of the proposed method for weathered coking coal

The applicability of the proposed method to weathered coking coal was examined. The simulated weathered coal was prepared by oxidizing coking coal C at 130 °C for 90 minutes in an air stream at a flow rate of 125 cm^3/min, and the simulated weathered coal was treated with formic acid vapor at the same process as coals A and B at 60 °C for 2 hours. As shown in Figure 1.6, the amount of CO_2 produced during formic acid vapor treatment was 0.26 mmol/g-coal, which was similar to that produced during the treatment of coals A and B. Figure 1.10 shows the strength of coke made from the raw C coal, simulated weathered coal, and simulated weathered coal treated with formic acid vapor, respectively. Although weathering reduced the strength of the coke by about half, formic acid vapor treatment restored the strength to the same level as that of the raw coal coke. The proposed method was also shown to be effective in reviving weathered coking coal.

Figure 1.11 shows the thermomechanical analysis curves of the raw coal C, simulated weathered coal, and simulated weathered coal treated with formic acid vapor. Weathering reduced the rod drop and thermoplasticity of coal, but formic acid vapor treatment restored the rod drop to the same level as that of the original coal. These results correspond well with the coke strength results shown in Figure 1.10. Table 1.7 shows the apparent density of each coke. The apparent density of each coke only changed a little, and the higher density did not result in higher tensile strength, indicating that the porosity was not the dominant factor of the tensile strength for the coke prepared from coal C in the treatment.

Table 1.7. The apparent density of the raw coal C, simulated weathered coal, and simulated weathered coal treated with formic acid vapor

	Apparent density [kg/m^3]
Coal C Raw	910.6
Coal C Weathered	944.6
Coal C Weathered, then HCOOH(g) treated	850.1

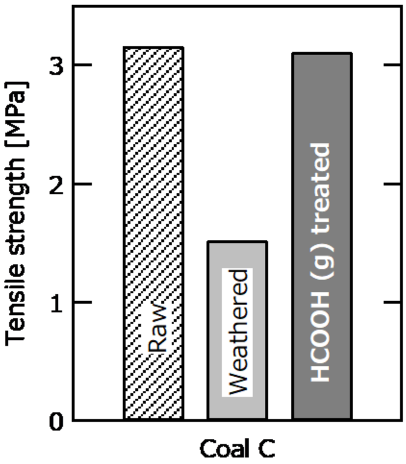


Figure 1.10. Strength of coke made from the raw coal C, simulated weathered coal, or simulated weathered coal treated with formic acid vapor

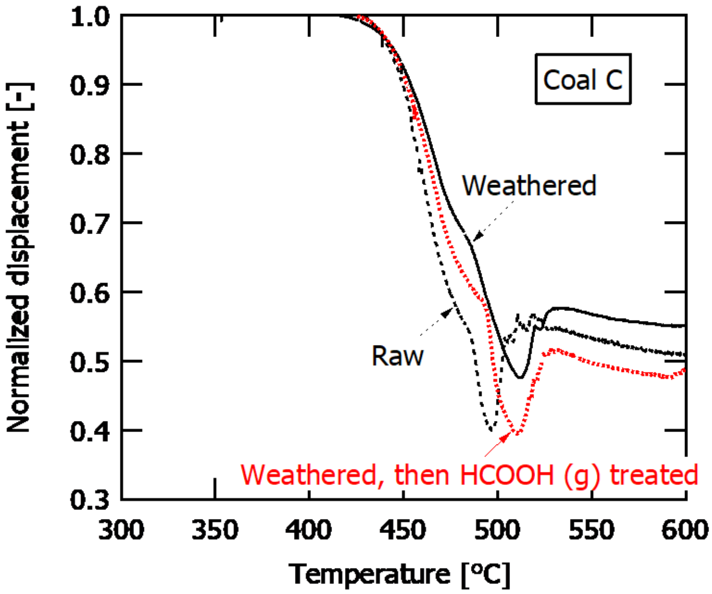


Figure 1.11. **TMA curves of the raw coal C, simulated weathered coal, and simulated weathered coal treated with formic acid vapor**

1. 4. Conclusions

As a method for reforming low-rank coal into a coke feedstock comparable to coking coal, a pretreatment method for reduction using formic acid under mild conditions of about 60 °C was first proposed, and the effectiveness was demonstrated. It was shown that the treatment by either aqueous formic acid or formic acid vapor significantly improved the thermoplastic performance of coal and enhanced the strength of the resulting coke. The consumption of the reductant formic acid was little enough to hardly change the elemental composition of the coals.

Formic acid as a reducing agent was capable of providing H radicals to coal under mild conditions and promoting the depolymerization of coal by stabilizing the inherent radicals in coal. The reduction reaction was found to proceed under mild conditions at 60 ^{o}C, 0.1 MPa when other coal depolymerization methods required higher temperature and higher pressure. When treated with gaseous formic acid, the reactant and the product, CO_2, were both gas, which is straightforward to separate. Thus, the proposed depolymerization treatment can be effectively applied as a pre-treatment process in coke production or other carbon materials production process to utilize low-rank coal more efficiently as raw materials, not as fuel.

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Chapter 2–Development of a novel mild depolymerization method of coal combining oxygen oxidation and formic acid reduction reaction

2. 1 Introduction

Coal has widely been applied as the raw material of value-added chemical products. Coke, carbon black, graphite electrodes, carbon fiber, aromatic chemicals, and other materials. can be produced by appropriate processing of coals.[1] Depolymerization of coal is the key to utilizing coal efficiently since the complete solubilization of coal in conventional solvents at ambient temperature is the ultimate target of coal utilization.[2] When low-molecular-weight compounds (LMWC) increase in coal, the thermoplasticity of coal would be enhanced, which is favorable for coke production, and the yield of tar and pitch would also increase, which means more value-added chemical products can be prepared from coal. Traditional methods for depolymerization of coals usually applied severe conditions such as high temperatures and high pressures, and also applied solvent which increased the separation process cost.[3-8]

In Chapter 1, the stabilizing of the inherent radicals of coals was focused on to prevent the cross-linking reactions between LMWC in coals. After the treatment, more LWMC can be reserved during the heat process so that the thermoplasticity and coking properties of coals would be enhanced. However, the inherent radicals in coals are countable, which would limit the effectiveness of the proposed pre-treatment method for increasing the LMWC of coals. Thus, in this chapter, the oxygen oxidation reaction was proposed for the cleavage of the coal structures combining the stabilization for the formed radicals by the H radicals provided by the co-existing formic acid (FA) vapor for the further effectiveness of depolymerization.

The mechanism of coal oxidation at low temperatures has been well studied, which is generally considered as two parallel reaction sequences; that is, the direct burn-off and sorption sequences. In the sorption sequence, firstly, the oxygen chemisorbs on surfaces of coal pores is inserted into C–H bonds of $–CH_2–$ or $–CH_3$ to form peroxides.[9] Thus, ethylene bridges and hydroaromatic compounds which are abundant in coal, are oxidizable.[10] Secondly, these peroxides are unstable and can immediately decompose to form H_2O, accompanied by C–C bond or C–O bond cleavage and radical formation.[9] Since the radicals formed are also unstable, they would reconnect with each other or oxygen and be polymerized again forming ether.[11] To suppress the polymerization, the H radical is needed to stabilize the coal radicals before the polymerization.

In this study, a method that combines oxidation reaction by molecular oxygen and radical stabilization reaction by FA was proposed to promote the depolymerization of coal under mild conditions. The reaction pathway is shown in Figure 2.1. Treatment with air containing FA vapor was performed, expecting oxygen oxidation to cleave C–C or C–O bonds in coal and FA to stabilize the radicals formed by oxygen oxidation immediately before the radicals reconnect to each other.

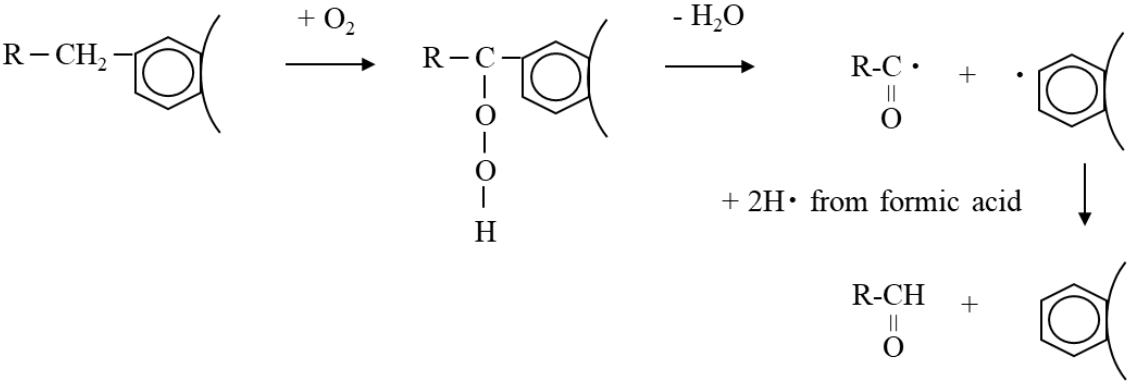


Figure 2.1. An example of the reaction pathways

2. 2 Experimental

2. 2. 1 Sample

An Australian bituminous coal was used in this study. The raw coal was mechanically sized into below 150 μm. The elemental compositions measured by CHN Corder (MT-6M, Yanaco) are given in Table 2.1.

Table 2.1. Elemental compositions of the raw coal used

Ultimate analysis [wt%, d.a.f.]				Atomic Ratio [–]		Ash
C	H	N	O (diff.)	H/C	O/C	(wt. %, d.b.)
86.9	4.5	0.8	7.8	0.62	0.067	4.7

d.a.f. :dry ash-free, d.b. : dry basis, diff. : differential

2. 2. 2 Experimental procedure of FA/air treatment

The coal was treated at 90 –150 °C for 90 minutes using the apparatus shown in Figure 2.2. Nitrogen was supplied at the flow rate of 130 cm^3/min while the temperature was raised at 10 °C/min and when the temperature reached the aimed value, the gas was switched to air at the same flow rate which was bubbled through 50 wt.% formic acid water solution. Treatment using nitrogen instead of air with the same bubbler was also carried out for comparison purposes. The gas at the exit of the quartz tube was collected in the gas bag.

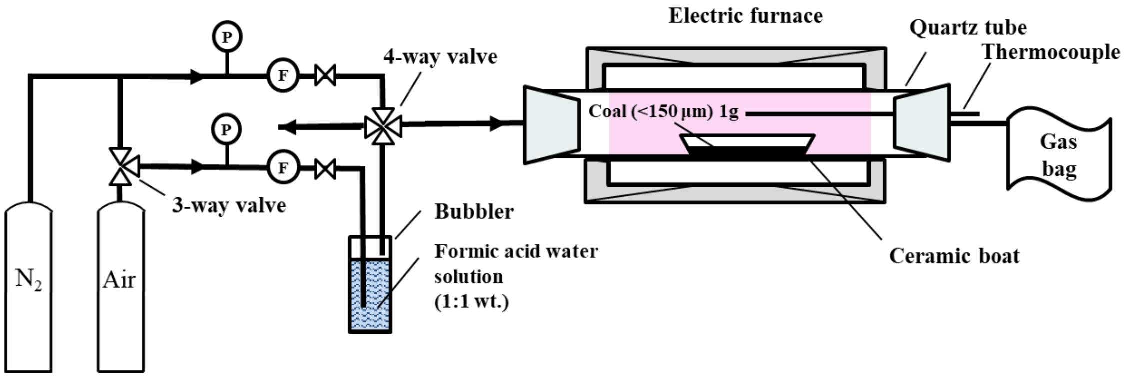


Figure 2.2. A schematic diagram of the apparatus adopted in this study

2. 2. 3 Analyses of the products

The gas collected in the gas bag was analyzed by gas chromatography (GC-12A, Shimadzu, Colume: Porapak Q, 200 °C, Detector: FID, 220 °C) to determine the amount of CO_2 formed during the treatment.

The coal treated under each condition was evaluated through various analyses. The thermomechanical analyzer (TMA-50/60, Shimadzu) was used to analyze the thermoplastic behaviors of the treated coals, the details can be found in the previous chapter. The TMA can be a convenient method to measure the degree of depolymerization of coals.[12] The solvent extraction method was applied to quantify the amount of LMWC of raw and treated coals, which was introduced in the previous chapter. Elemental analysis (CHN Corder MT-6M, Yanaco) was used to investigate the change in the elemental composition of the coal through the treatment. FT-IR spectroscopy (JIR-WINSPECT 50, JEOL) was employed to analyze the functional groups in the coal before and after the treatment. 2.5 mg samples were mixed with 500 mg KBr powders and then dried in a vacuum oven (Yamato, ADP-21) at 70 °C for 24 h. The dried mixture was made into a pellet under 60 MPa for 30 min and measured by FT-IR spectroscopy.

2. 3 Results and discussion

2. 3. 1 Product yield

The yields of the treated coals were shown in Figure 2.3. Whether the atmosphere was FA/air or FA/N_2, the treated coal yield stayed almost 100 % at 90–130 °C, which suggests that the proposed treatment method would not cause remarkable change to coal. The gas analyses showed that the gas formed in the treatment was mainly CO_2 and H_2O, since H_2O was also contained in a supplied gas, which was from formic acid water solution, it was difficult to measure the formed H_2O. Therefore, we focused on the CO_2 amount that evolved during the treatment.

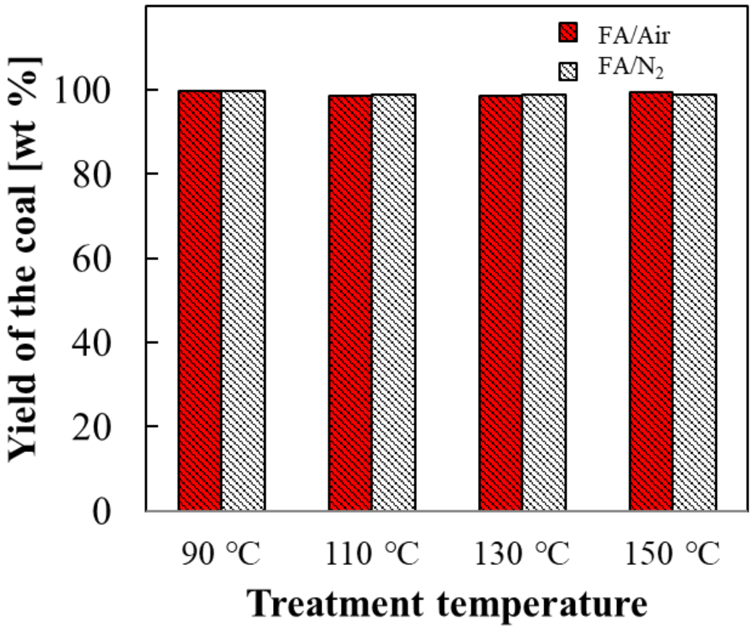


Figure 2.3. **The yield of coal under different treatment conditions**

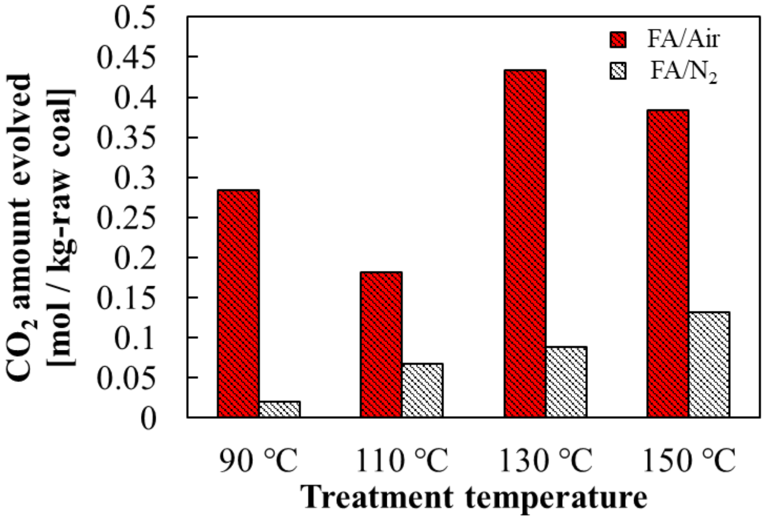


Figure 2.4. **CO_2 amount evolved under different treatment conditions**

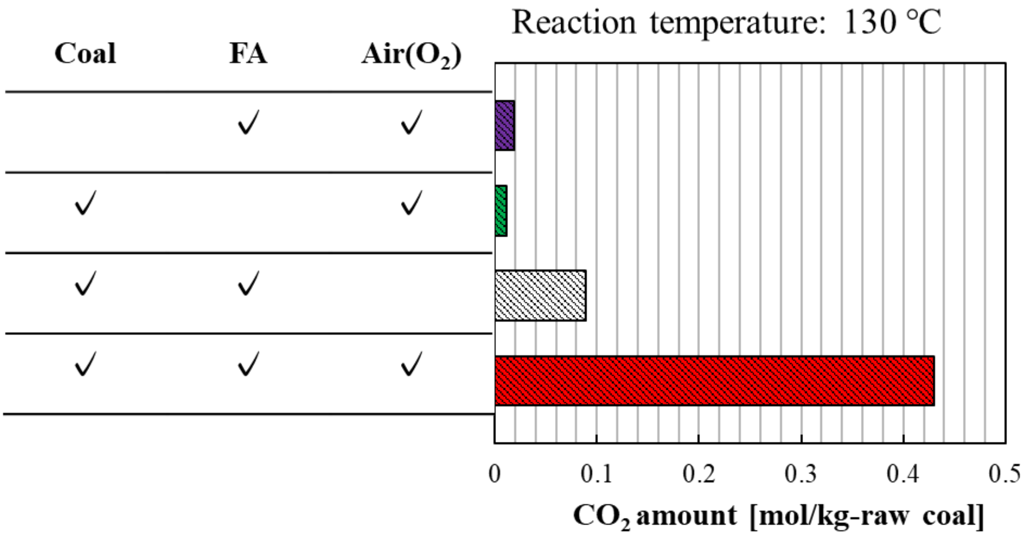
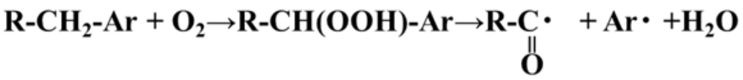


Figure 2.5. CO_2 amount evolved under each comparison experiment

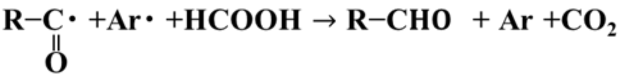
The CO_2 amount evolved in the treatment is shown in Figure 2.4. At each treatment temperature, the amount of CO_2 evolved under FA/air atmosphere was significantly more than that under FA/N_2, suggesting that the presence of O_2 promoted a reaction producing CO_2. The candidate reactions involving O_2 as a reactant and CO_2 as a product were listed below:

$$\mathbf{HCOOH + \frac{1}{2}O_2 \rightarrow H_2O + CO_2} \qquad \textbf{(A)}$$

$$\mathbf{C_{Coal} + O_2 \; - \;\; CO_2} \qquad \textbf{(B)}$$



$$\mathbf{R\text{-}CH_2\text{-}Ar + O_2 \rightarrow R\text{-}CH(OOH)\text{-}Ar \rightarrow R\text{-}\underset{\overset{\|}{O}}{C}\cdot \;\; + Ar\cdot \; + H_2O} \qquad \textbf{(C-1)}$$



$$\mathbf{R{-}\underset{\overset{\|}{O}}{C}\cdot \; + Ar\cdot \; + HCOOH \rightarrow R{-}CHO \;\; + Ar + CO_2} \qquad \textbf{(C-2)}$$

(C_{coal}, R, and Ar indicate a carbon in the coal, an alkyl group, and an aromatic group, respectively.)

To elucidate the source of CO_2 evolved during the treatment, comparison experiments at 130 °C were carried out and the results are shown in Figure 2.5. When there is only

FA/air without coal or only coal/air without FA in the reactor, the amount of CO_2 was extremely little, which suggests that the reactions A and B hardly occurred under these conditions. When there were only Coal/FA without Air (O_2) in the reactor, the amount of CO_2 reached a higher level, 0.089 mol/kg-coal, than the former groups, 0.019 and 0.012 mol/kg-coal. It can be judged that the reaction C-2 had taken place for coal-inherent radicals. And when there were coal, FA, and air (O_2) all together in the reactor, the CO_2 amount became much higher than any other groups and reached 0.43 mol/kg-coal. These results suggest that the CO_2 is mainly generated from successive reactions of reaction C-1 followed by reaction C-2, where FA donated H radicals to coal radicals formed by the reactions with O_2 and FA turned to CO_2. It was thus suggested that the source of CO_2 in the proposed treatment method was not coal but mainly FA, and the reduction of coal by FA was promoted by the presence of O_2.

2. 3. 2 Thermoplastic behavior of the treated coal

The thermoplasticity of the treated coal can reflect the depolymerization degree of the coal as mentioned. In this study, the thermoplasticity of the treated coals obtained under different conditions was evaluated using thermomechanical analysis (TMA). The TMA curves of the treated coals and raw coal are shown in Figure 2.6. The displacement of the rod was normalized by the initial height of the coal sample bed. As the temperature increased, the coal began to soften and melt at around 400 °C and the displacement of the rod started to fall. The coal with the less value of minimum normalized displacement can be judged to have better thermoplasticity, which should result from the abundance of LMWC in the coal.

In FA/N_2 atmosphere, the TMA curves of the coals treated at 90 °C to 150 °C did not show significant change from that of the raw coal. However, when the atmosphere was FA/air and the treatment temperature was changed from 90 °C to 130 °C, the minimum normalized displacement dropped to a lower value than that for the raw coal. These results show that the treatments under FA/air atmosphere are effective in enhancing the thermoplasticity of coal, which is indicative of depolymerization of the coal.

Figure 2.7 shows the effect of the treatment temperature on the minimum normalized displacement value in TMA for the treated coals prepared under FA/air atmosphere and FA/N_2 atmosphere. When the treatment temperature for FA/air atmosphere was 150 °C, the minimum normalized displacement value of treated coal was greater than that of raw coal. However, for the treatment temperature in the range from 90 °C to 130 °C, the minimum normalized displacement value of the treated coal was less than that of raw coal and decreased with the decreasing of treatment temperature. It was suggested that there was a suitable temperature range for the proposed treatment method. When the treatment temperature was too high, polymerization would become dominant. This is presumably because the radical recombination reaction is faster than the reducing reaction by FA at high temperatures.

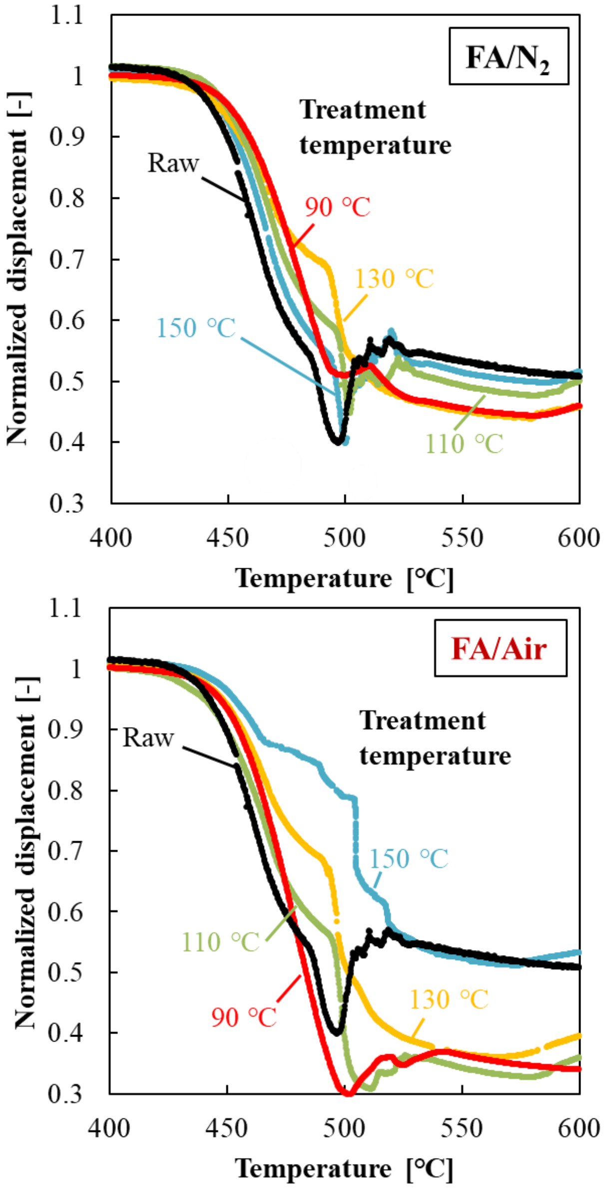


Figure 2.6. **TMA curves of the coals treated under different conditions**

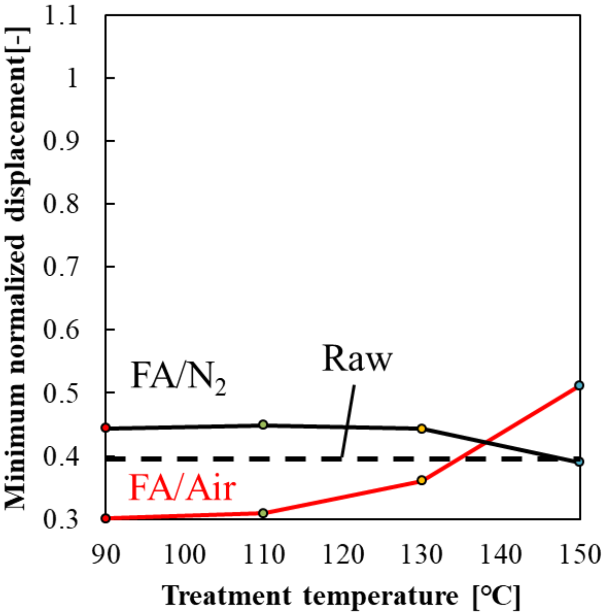


Figure 2.7. Comparison of minimum normalized displacement values in TMA

2. 3. 3 Necessity of coexistence of oxygen and formic acid in the treatment

To investigate the necessity of the coexistence of oxygen and formic acid in the proposed method, 1-step and 2-step experiments were carried out at 90 °C and 0.1 MPa. In the 1-step treatment, oxygen and formic acid coexisted while in the 2-step experiment, only air was supplied firstly for 90 minutes, and then formic acid vapor was supplied with nitrogen for 90 minutes. Figure 2.8 shows the TMA curves of the treated coal and the raw coal. In the 2-step treatment, the thermoplasticity of treated coal became even worse than raw coal whereas the thermoplastic behavior of treated coal became better in the 1-step treatment. These results suggest that when oxygen and formic acid were supplied separately in the 2-step treatment, the radicals formed by the oxygen oxidation reaction could not be terminated by H radicals but were immediately connected with each other, which resulted in polymerization. No radicals to be stabilized were left any longer when formic acid was supplied. Thus, it can be concluded that the coexistence of oxygen and formic acid is necessary for the proposed method.

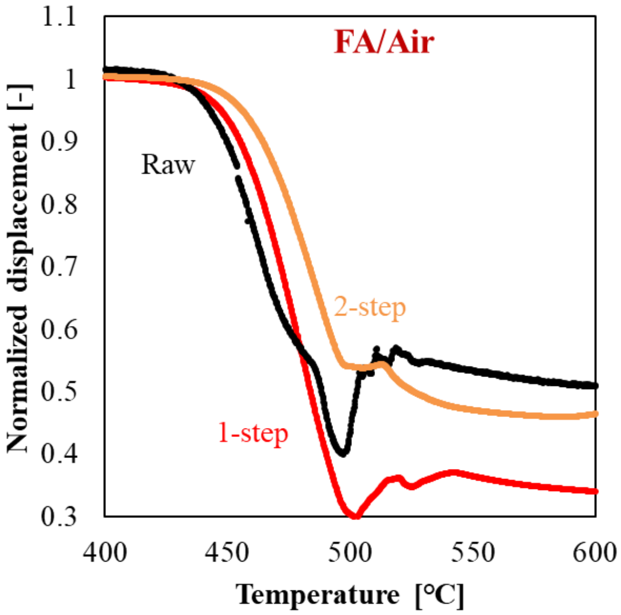


Figure 2.8. TMA curves of the coals obtained through 1-step and 2-step treatments. (90 °C, 0.1 MPa)

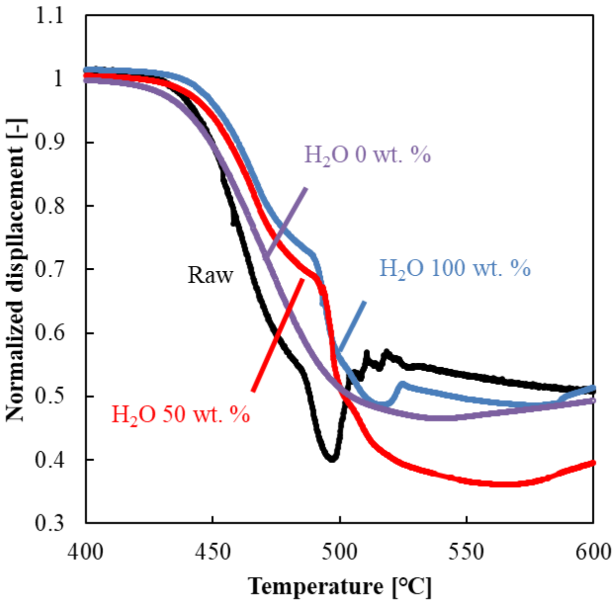


Figure 2.9. TMA curves of the treated coal under different H_2O fractions (130 °C, 0.1 MPa)

2. 3. 4 Effect of water vapor in the treatment

As FA was supplied as moist vapor, it is necessary to investigate the effect of water in the treatment. The experiments using a bubbler filled with FA solutions of different water fractions (0 wt. %, 50 wt. %, 100 wt. %) were carried out at 130 °C and 0.1 MPa for 90 minutes. Figure 2.9 shows the TMA curves of the treated coal and raw coal. The thermoplasticity of the coal treated with 0 wt. % H_2O or 100 wt. % H_2O was not enhanced compared to that of raw coal while the thermoplasticity of the coal treated with 50 wt. % H_2O was enhanced. It is suggested both water and FA are needed for the proposed treatment. This can be because water acts as a promoting agent during the interaction between coal and O_2 to accelerate the cleavage reaction in the treatment.[11]

2. 3. 5 Quantification of LMWC in the treated coal

The LMWC in the treated coal was quantified by the proposed solvent extraction method. Figure 2.10 shows the yield of each fraction for the raw coal and the coals treated at 90 °C and 110 °C under FA/air atmosphere. It was found that the yield of the total amount of deposit and soluble for both treated coals was higher than that of the raw coal. Especially for the coal treated at 90 °C which had the lowest minimum normalized displacement value in the TMA, the yield of the total deposit and soluble amount had increased by 10.1 % on dry raw coal basis, and by 29.0 % on total deposit and soluble amount basis of raw coal through the treatment. These results suggest that the treatment method proposed in this study can increase LMWC amount efficiently under mild conditions (>90 °C, 0.1 MPa).

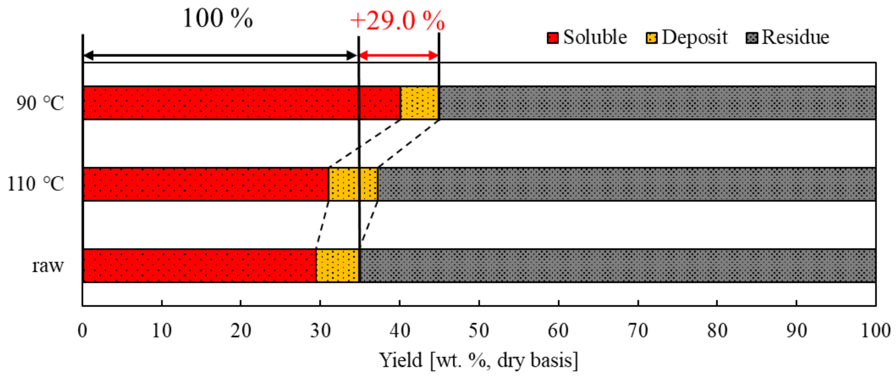


Figure 2.10. The yield of each fraction for the raw coal and treated coal under FA/air conditions

2. 3. 6 Elemental and functional group analyses of treated coal

To investigate the chemical change through the treatment, elemental analysis, and FT-IR analysis was conducted for the coal treated at 90 °C under FA/air atmosphere whose depolymerization degree was the most significant among the conditions employed in this study. Figure 2.11 shows the amount of each element in the treated coal and raw coal on raw coal basis. Carbon amount hardly changed through the treatment while oxygen and hydrogen amounts decreased by 0.29 and 0.66 mol/kg-raw coal, respectively. Even though molecular oxygen existed in the treatment, the oxygen content of the treated coal still decreased.

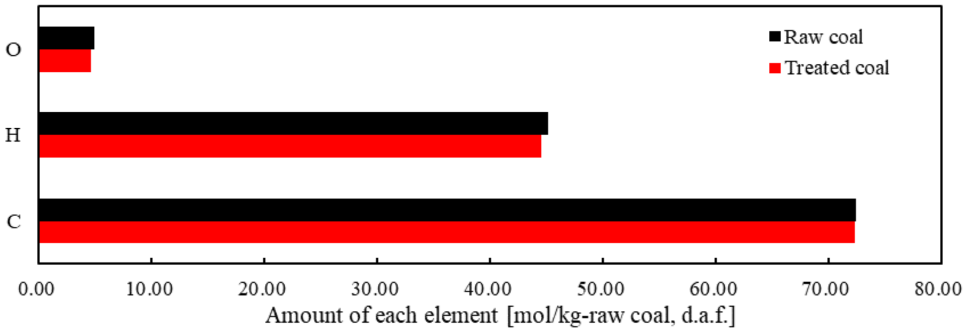


Figure 2.11. Amount of each element on raw coal basis in the raw coal and the coal treated at 90 °C in FA/air atmosphere

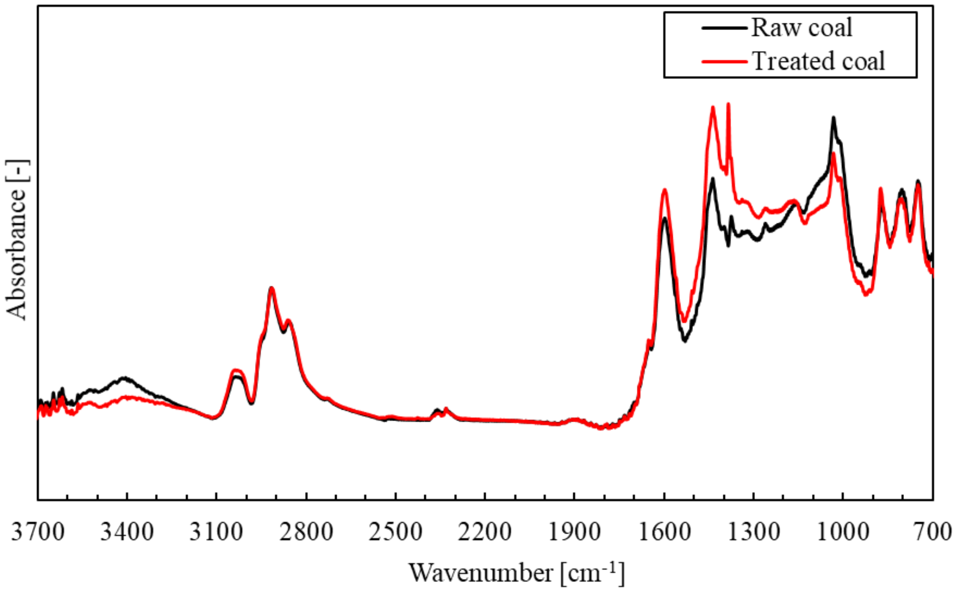


Figure 2.12. FT-IR spectra of the raw coal and the coal treated at 90 °C in FA/air atmosphere

Table 2.2 Reference FT-IR spectrum table[13]

Wavenumber (cm^{-1})	Functional Group	Compound Class
3700–2700	O–H stretching	alcohol
3100–3000	C–H stretching	alkene
3000–2840	C–H stretching	alkane
2830–2695	C–H stretching	aldehyde
2349	O=C=O	carbon dioxide
1720–1680	C=O stretching	carboxylic acid
1710–1680	C=O stretching	aldehyde
1685–1666	C=O stretching	ketone
1650–1566	C=C stretching	cyclic alkene
1440–1395	O–H bending	carboxylic acid
1390–1310	O–H bending	phenol
1275–1200	C–O stretching	alkyl aryl ether
1210–1163	C–O stretching	ester
1150–1085	C–O stretching	aliphatic ether
1205–1050	C–O stretching	alcohol

Figure 2.12 shows the FT-IR spectra of the raw coal and the coal treated at 90 °C under the FA/air atmosphere. The spectra were fitted with the baseline connected by the value in the wavenumber between 4100 cm^{-1}, 2500 cm^{-1} and 2500 cm^{-1}, 1700 cm^{-1} for a clearer comparison. The reference FT-IR spectrum table is shown in Table 2.2.

The intensity of the peaks attributed to O–H bending in carboxylic acid (1440–1395 cm^{-1}), phenol O–H bending (1390–1310 cm^{-1}), and aldehyde C–H bending (1390–1380 cm^{-1}) increased through the treatment while the intensity of the peak attributed to ether C–O stretching (1150–1085 cm^{-1}) decreased. One of the reasonable reaction paths in the proposed treatment was shown in Figure 2.13. The C–H bonds in the R–CH_2–O–Ar structure were oxidized by oxygen to form peroxide and then the ether link was cleaved in two ways as shown in the figure. H radicals from FA then stabilize the formed radicals to give aldehyde, phenol, and carboxylic acid. The path was also in good agreement with the elemental results that the carbon amount in the coal hardly changed through the treatment. Additionally, the decrease in peak intensity attributed to O–H stretching (3700–2700 cm^{-1}) was observed. Hydroxy groups which often form hydrogen bonds would become the cross-linking site and connect the molecules through a dehydration reaction upon heating, which would inhibit coal depolymerization. Thus, the elimination of hydroxy groups can also be considered an advantage of the proposed treatment although the reaction mechanism should be investigated in our future studies.

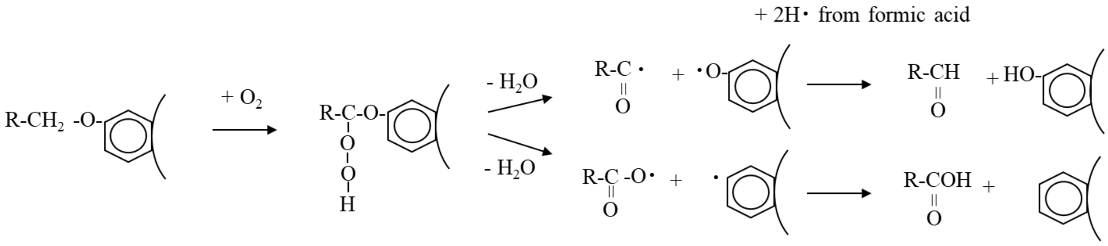


Figure 2.13. An example of reaction pathways occurring in the proposed treatment

2. 4 Conclusions

To depolymerize coal more efficiently, a novel coal treatment method combining oxygen oxidation reaction and formic acid reduction reaction has been proposed in this study. Oxygen oxidation reaction can cleave C–C bonds in coal at low temperatures. With simultaneous stabilization of the radicals formed, low-molecular-weight compounds in coal increased significantly as much as 29.0 % compared to the low-molecular-weight compounds of the raw coal at 90 °C and 0.1 MPa.

It was confirmed that oxygen and formic acid must coexist to depolymerize coal by the proposed method. Elemental and FT-IR analyses suggested that the proposed method cleaved the ether C–O groups in coal and stabilized the radicals formed for the depolymerization, and also, a part of the hydroxy groups which can inhibit depolymerization were removed as well. This depolymerization method is expected to contribute to the efficient utilization of coal such as increasing extracts and tar yield of coal in the extraction and pyrolysis process and upgrading coal to be more suitable for the raw materials of coke, carbon fiber, etc.

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Chapter 3–Depolymerization of coal under mild conditions with co-existing gaseous formic acid and hydrogen

3. 1 Introduction

In the previous chapters, several methods were proposed to depolymerize coals under mild conditions. The low-molecular-weight compounds (LMWC) of coals were successfully increased by the mild treatment at 60–110 °C and 0.1 MPa. In Chapter 1, the stabilization of inherent radicals in coals by the H radicals from gaseous and aqueous formic acid (FA) was applied to prevent the cross-linking reaction between LMWC so that more LMWC was reserved in the heat process; In Chapter 2, the oxidation reaction for the cleavage of coals structures and FA reduction reaction for the stabilization of the formed radicals were applied in the same time for the further depolymerization effectiveness of coals. However, since the H radicals source was from FA, the concentration of H radicals in the treatment has a limitation because of the limited FA partial pressure in the atmosphere. Also, the consumption of FA would produce CO_2 in the following formula:

$$HCOOH \rightarrow CO_2 + 2H^+ + 2e^- \quad (3.1)$$

To increase the effectiveness of the depolymerization as well as decrease the evolved amount of CO_2 in the treatment because of the high-recorded CO_2 emissions[1] in the world, a novel coal depolymerization method under mild conditions (<110 °C, 0.1 MPa) which uses gaseous formic acid (FA) and H_2 to treat one bituminous coal is proposed in this chapter, while the traditional depolymerization method applied severe conditions such as 250 °C–600 °C and 4 MPa–17MPa.[2-7] The co-existence of FA and H_2 enables high H radicals source concentration in the treatment which made it possible to cleave the C–C and C–O bonds in coals that connect LMWC of coals[8-9] without changing the coal structures by oxidation or pyrolysis. The co-existence of FA and H_2 also made it possible for FA to transport H radicals from H_2 to coal radicals and stabilize them. The considerable reaction pathway is shown in Figure 3.1. The gaseous FA is first attached to the coal and located near the inherent radicals of coal. Secondly, hydrogen provided H radicals and is transported by the FA attached to the coal. Finally, the radicals are stabilized by H radicals provided by H_2, and the FA is desorbed.

If the H radical source is H_2 in the proposed pathway, formic acid is not consumed in the treatment. Considering the H_2 price per mole (3.8–4.7 JPY/mol) is less expensive than formic acid(21.8–23.6 JPY/mol)[10,11] and does not produce CO_2, it is more desirable to use H_2 as the H radical source in treatment than FA. The validity of the proposed method was examined by evaluating the depolymerization degree of the treated coals.

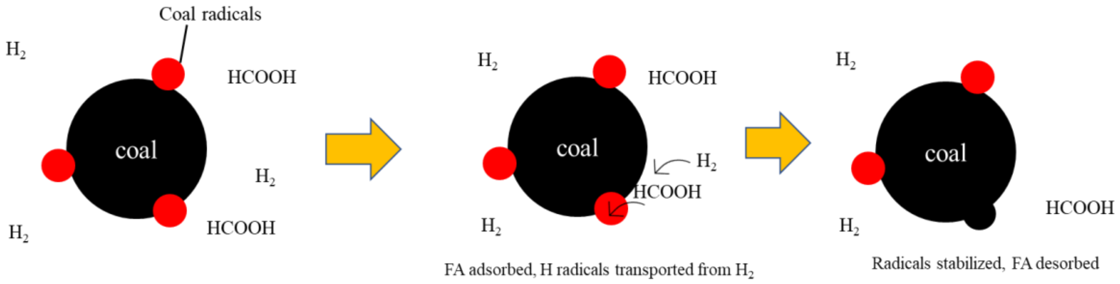

Figure 3.1. A schematic diagram of the considerable reaction pathway of the proposed treatment

3. 2 Experimental

3. 2. 1 Sample

An Australian bituminous coal, H5 coal, was used in this study. Elemental analysis results measured by CHN Corder (MT-6M, Yanaco) are shown in Table 3.1.

Table 3.1. Elemental compositions of the coal used in this study

Ultimate analysis [wt. %, d.a.f.]				Atomic ratio [–]		Ash
C	H	N	O [diff.]	H/C	O/C	(wt. % d.b.)
87.34	4.68	0.40	7.58	0.64	0.065	5.0

d.a.f. :dry ash-free, d.b. : dry basis, diff. : differential

3. 2. 2 Experimental procedure of FA/H_2 treatment

1 g sample was sized below 150 μm and set in the ceramic boat and put in the electric furnace shown in Figure 3.2. N_2 was supplied as the carrier gas firstly to purge the reactor at the flow rate of 100 cm^3/min and at room temperature for 30 minutes. After the purge, the electric furnace started to heat up at the heating rate of 10 ^{o}C/min under N_2 condition,

when reached the designed temperature, the carrier gas was changed to H_2 or kept as N_2 at the equal flow rate and continuously went through a bubbler containing FA (98 wt.%) and then went through the reactor. The bubbler was set in the water bath and the FA mole fraction was controlled by the temperature of the water bath. The coal placed in the reactor was treated for 90 minutes at the designed temperature and then the carrier gas was changed to N_2 to purge the reactor again. Treated coal was collected in a sample bottle for further analysis.

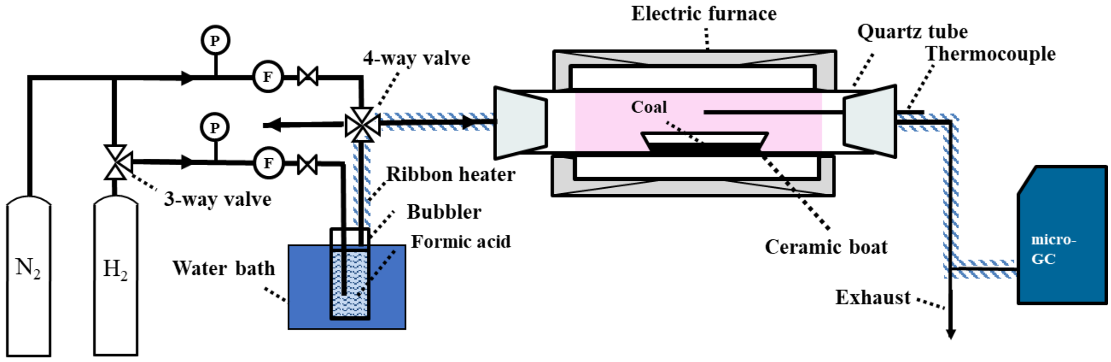

Figure 3.2. A schematic diagram of the apparatus adopted in this study

3. 2. 3 Analyses of the products

The gas evolved in the treatment was analyzed by micro-gas chromatography (CP-4900, Valian, Column: Porapak Q and Molsieve 5A, 180 °C, Detector: TCD). Coal samples were analyzed by different methods. The thermomechanical analyzer (TMA-60, Shimadzu) was used to analyze the thermoplastic behaviors of the treated coals during the heating up at a rate of 10 °C/min up to 900 °C in a nitrogen stream under the constant pressure of 0.098 N. The details about the thermomechanical analysis (TMA) procedure are available in the previous chapters. Elemental analysis (CHN Corder MT-6M, Yanaco) and FT-IR spectroscopy (JIR-WINSPECT 50, JEOL) were applied for the elemental and functional group change of the sample in the treatment.

The coal fractionation solvent extraction method was used to evaluate the depolymerization degree of coal in this study. The details about the solvent extraction method are available in the previous chapters.

3. 3 Results and discussion

3. 3. 1 Yields of products in the treatment

The yield of the coal treated under FA/H_2 (FA mole fraction = 7.5 %) conditions, 110 ^oC, 0.1 MPa was 100.3 wt. %, indicating that the treatment conditions would not bring too severe change to the samples. H_2O and CO_2 were the main gas products in the treatment, when the yield of H_2O was 1.36 mmol/kg-raw coal and CO_2 was 0.168 mmol/kg-raw coal.

3. 3. 2 Thermoplasticity of the treated coal

The thermoplastic behavior of coal reflects its degree of depolymerization which resulted in the yields of the LMWC.[12] The TMA curves of raw coal and the coal treated at 110 °C, 0.1 MPa (FA mole fraction = 7.5 %) were shown in Figure 3.3. The TMA curve of treated coal obtained shows lower minimum normalized displacement than raw coal and started to fall at a lower temperature (lower around 20 ^oC), indicating that the FA/H_2 treatment was capable of improving the thermoplasticity of treated coal, and the degree of depolymerization was enhanced.

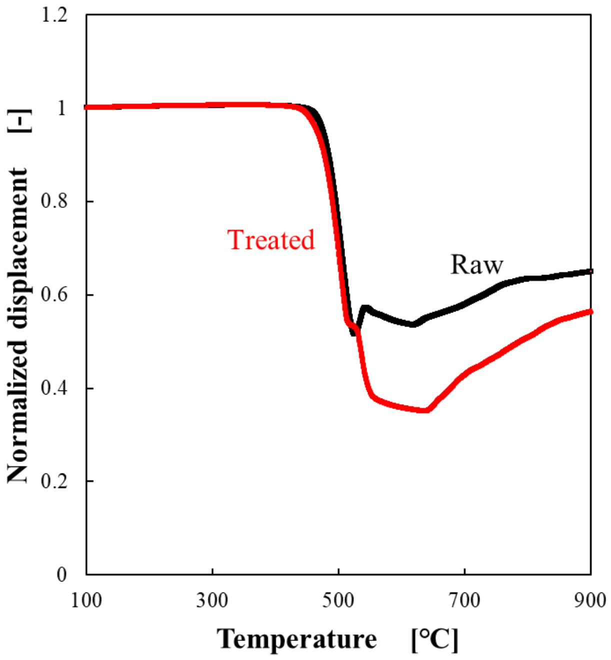

Figure 3.3. TMA curves of raw coal and coal treated under FA/H_2 condition (110 ^oC, 0.1 MPa)

3. 3. 3 Quantification of LMWC in the treated coal

The amount of LMWC (Deposit + Soluble) of raw coal and treated coal (110 °C, 0.1 MPa, FA/H_2 atmosphere) is shown in Figure 3.4. The amount of LMWC significantly increased by 15 % on raw coal base and 44 % on LMWC of raw coal basis which has a good agreement with TMA results. Over 50 wt % of the coal became extractable LMWC after the simple FA vapor treatment which demonstrated the effectiveness of the proposed treatment method.

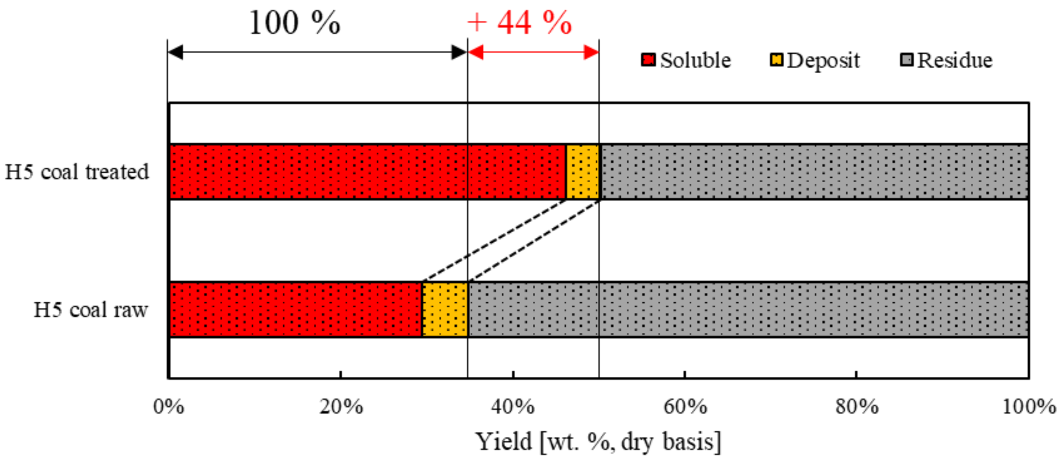

Figure 3.4. Yields of the extracts of raw coal and coal treated under FA/H_2 condition (110 °C, 0.1 MPa)

3. 3. 4 Elemental analysis of the treated coal

The elemental compositions of the raw coal and treated coal is shown in Table 3.2. The hydrogen content increases by about 0.04 wt. %. Meanwhile, about 1.91 wt. % oxygen decreased in the treatment. Since H_2O evolved in the treatment (about 2.4 wt. % of raw coal), the decreased oxygen may be removed by the H radicals to form H_2O in the treatment. Oxygen molecules in coals would become the cross-linking reaction active sites, thus, the removal of oxygen molecules can enhance the depolymerization of coal indirectly.

Table 3.2 Elemental composition of the raw coal and treated coal

Coal	Ultimate analysis [wt. %, d.a.f.]				Atomic ratio [–]	
	C	H	N	O [diff.]	H/C	O/C
Raw coal	87.34	4.68	0.40	7.58	0.64	0.065
Treated coal	88.98	4.72	0.63	5.67	0.64	0.048

3. 3. 4 FT-IR analysis of the treated coal

Figure 3.5 shows the FT-IR spectral of raw coal and the coal treated at 110 °C and 0.1 MPa, FA/H_2 condition (FA fraction = 7.5 %). The peak intensity of aliphatic ether C–O stretching (1150–1085 cm^{-1}) and alcohol C–O stretching (1205–1050 cm^{-1}) both decreased significantly, the peak intensity of O–H stretching (3700–2700 cm^{-1}) decreased slightly, which suggested that the ether, alcohol C–O bonds and O–H bonds of coal were cleaved in the treatment under mild conditions. Since the O–H bonds decreased in the treatment, the C–O bonds were probably cleaved to form O–H at first and then removed as H_2O by H radicals in the pathway as shown in Figure 3.6.

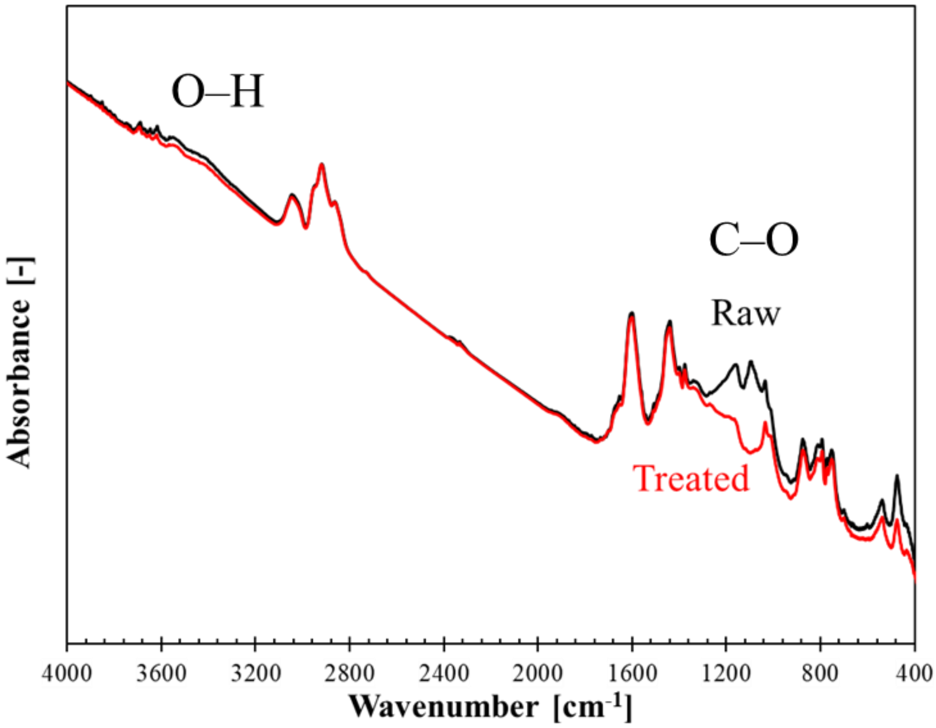

Figure 3.5. FT-IR analysis results of raw coal and coal treated at 110 °C, 0.1 MPa under FA/H_2 condition

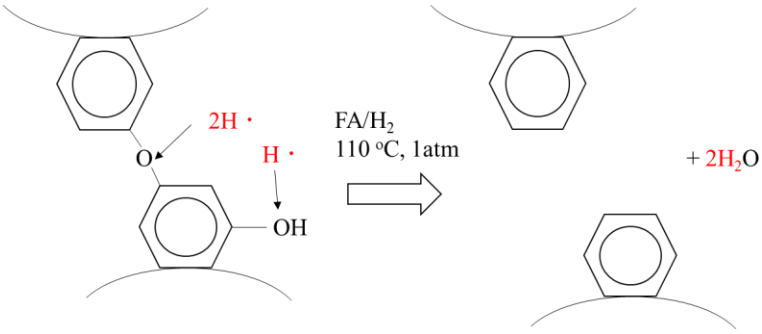

Figure 3.6. Considerable reaction pathway

3. 3. 5 The necessity of co-existing FA and H_2 in treatment

To elucidate the necessity of co-existing FA and H_2 in the treatment, comparison experiments were carried out at 90 °C and 0.1 MPa for 90 minutes, and the bubbler temperature was controlled at 40 °C when FA was supplied. The yields of each treated coal were close to 100 % as shown in Table 3.3, indicating that the treatment only caused a slight change to the treated coals. The elemental compositions of raw coal and treated coal under different conditions are shown in Table 3.4. The oxygen fraction of treated coal significantly decreased by 1.5 wt. % of the raw coal only when FA and H_2 coexisted. The O fraction of treated coal increased when under FA/N_2 atmosphere and hardly changed when under pure H_2 atmosphere. It suggested that both FA and H_2 are necessary for the deoxygenation of coal.

The TMA curves of raw coal and coal treated under different conditions are shown in Figure 3.7. The TMA curves of treated coal do not show lower minimum normalized displacement compared to raw coal under FA/N_2 or pure H_2 atmosphere, while under FA/H_2 atmosphere, the TMA curve of the treated coal showed significantly better thermoplastic behavior compared to raw coal and the other treated coals, which suggests that only when FA and H_2 co-existing, the thermoplasticity of coal would be enhanced. It is necessary to supply H_2 and FA at the same time in the proposed treatment method for depolymerizing coal.

Table 3.3. Yields of the coal treated under different conditions

Treatment atmosphere	Yield [wt. %, d.b.]
H_2	99.8
FA/N_2	102.1
FA/H_2	102.2

Table 3.4. Elemental composition of raw coal and treated coal under different conditions (90 °C, 0.1 MPa)

Conditions	Ultimate analysis [wt. %, d.a.f.]				Atomic ratio [–]	
	C	H	N	O [diff.]	H/C	O/C
Raw coal	87.64	4.67	0.85	6.83	0.64	0.058
H_2	87.99	4.19	1.18	6.63	0.57	0.056
FA/N_2	86.78	4.68	0.77	7.77	0.62	0.067
FA/H_2	88.68	4.69	0.92	5.33	0.64	0.048

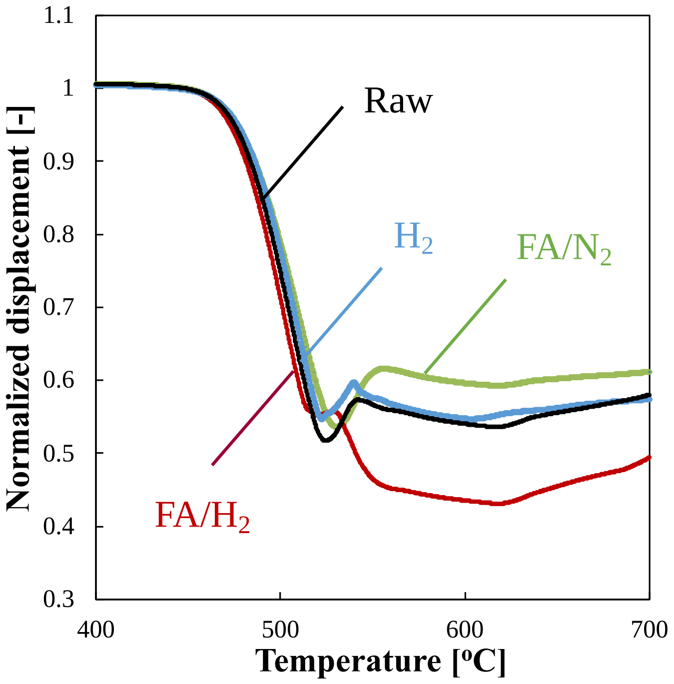

Figure 3.7. TMA curves of raw coal and coal treated under different conditions (90 °C, 0.1 MPa)

3. 3. 6 Source of H radicals in the treatment

As mentioned in the previous chapter, the enhancement of the thermoplasticity for treated coal needed H radicals to stabilize coal radicals. If the H radical supplied is from FA, CO_2 would evolve as the by-product from the following formula (3.2) and (3.3):

$$\mathrm{HCOOH} \rightarrow 2\mathrm{H}\bullet + \mathrm{CO_2} \quad (3.2)$$
$$\mathrm{H}\bullet + \mathrm{Coal}\bullet \rightarrow \mathrm{Coal{-}H} \quad (3.3)$$

The CO_2 evolved amount in the treatment of FA/H_2 and FA/N_2 is shown in Figure 3.8**.** The CO_2 amount evolved under the pure H_2 condition is negligible when CO_2 evolved amount under FA/N_2 and FA/H_2 conditions were rather little and almost equal (at around 0.191 mmol/g-coal), which suggests that the consumption of FA was so little from formula (3.2). From the TMA results, the coal treated under FA/N_2 did not obtain better thermoplasticity while the coal treated under FA/H_2 did, which suggests that more H radicals were supplied into coal for depolymerization when under FA/H_2 condition from formula (3.3). However, the CO_2 amount evolved under the FA/H_2 condition did not increase compared with FA/N_2, indicating that the additional H radicals source under FA/H_2 condition can not be FA from formula (3.2). Thus, the H radicals source under FA/H_2 treatment was probably the other H source, H_2, and FA worked as a shuttle to transport H radicals from H_2 to coal radicals. Since the cost of H_2 is much lower than FA, the proposed method which uses FA as a gaseous catalyst can reduce the cost further and also decrease the CO_2 emission from formula (3.2) during the treatment.

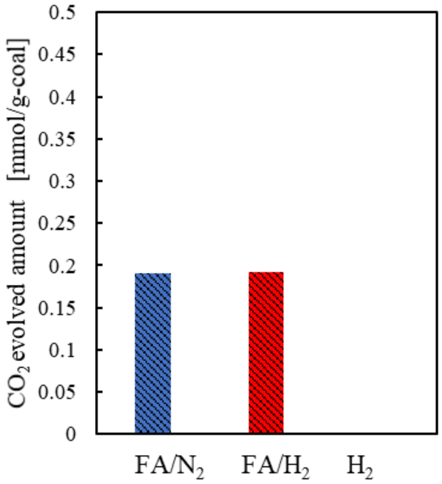

Figure 3.8. CO_2 evolved amount in the treatment (90 °C, 0.1 MPa)

3. 3. 7 The influence of the FA mole fraction in FA/H_2 treatment

Since the adsorption of FA occurred in the treatment, it is important to investigate the influence of FA mole fraction in the FA/H_2 treatment.

The coals were treated under different FA mole fractions under 110 °C and 0.1 MPa for 90 minutes. The yield of each treated coal is shown in Table 3.5. It is noticed that the yields of treated coals were all almost 100 %, and little FA was adsorbed. The coal yield increased the least at the FA mole fraction of 7.5 %.

Table 3.5. Yields of treated coal under different FA mole fractions (110 °C, 0.1 MPa)

FA mole fraction [%]	Yield [wt. %, d.b.]
6.9	100.8
7.5	100.3
8.4	100.7
10.5	101.2

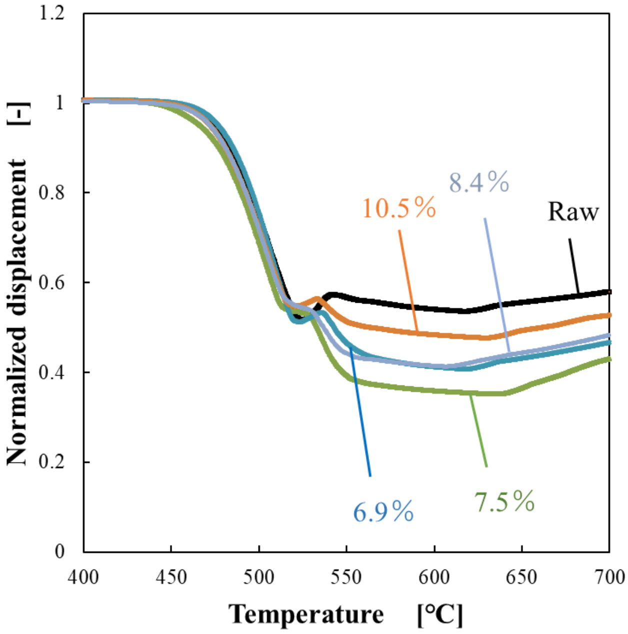

Figure 3.9. TMA curves of raw coal and coal treated under different FA mole fractions (110 °C, 0.1 MPa)

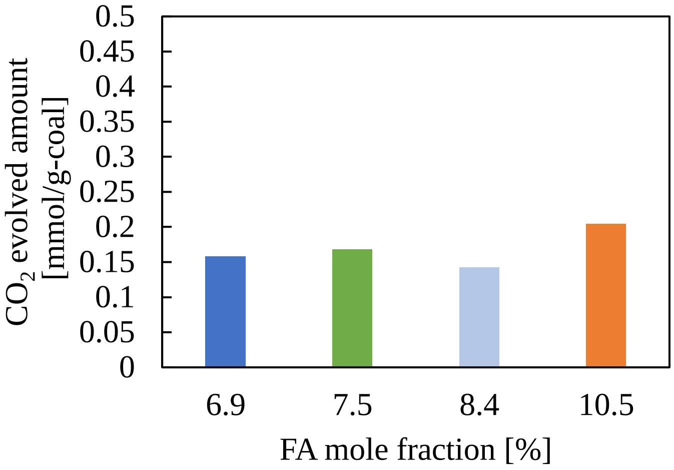

Figure 3.10. CO_2 evolved amount under different FA mole fractions (110 °C, 0.1 MPa)

Figure 3.9 shows the TMA curves of all the treated coals. From the FA mole fraction range of 6.9 % to 10.5 %, the thermoplasticity of all the treated coal was enhanced. When the FA mole fraction was 7.5 %, the treated coal obtained the best thermoplasticity, which can be relative to the FA adsorption amount in the treatment. It suggests that there is an optimal FA mole fraction condition for the proposed treatment.

The CO_2 amount that evolved in each treatment is shown in Figure 3.10. The CO_2 evolved amount at each condition was low, which suggests that FA was hardly consumed in the treatment under different FA mole fractions. Figure 3.11 shows the elemental analysis results of the coal before and after treatment at 110 °C under different FA mole fractions (6.9 –10.5 %) on dry raw coal basis. The H fraction of each treated coal all increased (when FA mole fraction = 8.4 %, the H fraction increased slightly), which suggests that H radicals have been added into coal for stabilizing coal radicals during the treatment. The oxygen fraction of each treated coal decreased, which was considered as oxygen molecules were also removed by H radicals by the FA/H_2 treatment, which is in good agreement with the previous FT-IR results that C–O bonds decreased. Thus, the H radicals provided into coal have two effects: stabilizing coal radicals and removing O from C–O groups, both of which can promote the depolymerization of coals. The slight increase in the C fraction was considered as the adsorption of FA. The possible reaction pathway of FA/H_2 treatment is shown in Figure 3.12. The H radicals were shuttled from H_2 to coal by gaseous FA, and stabilized the coal radicals as well as removed the oxygen-contained functional groups such as O–H and C–O.

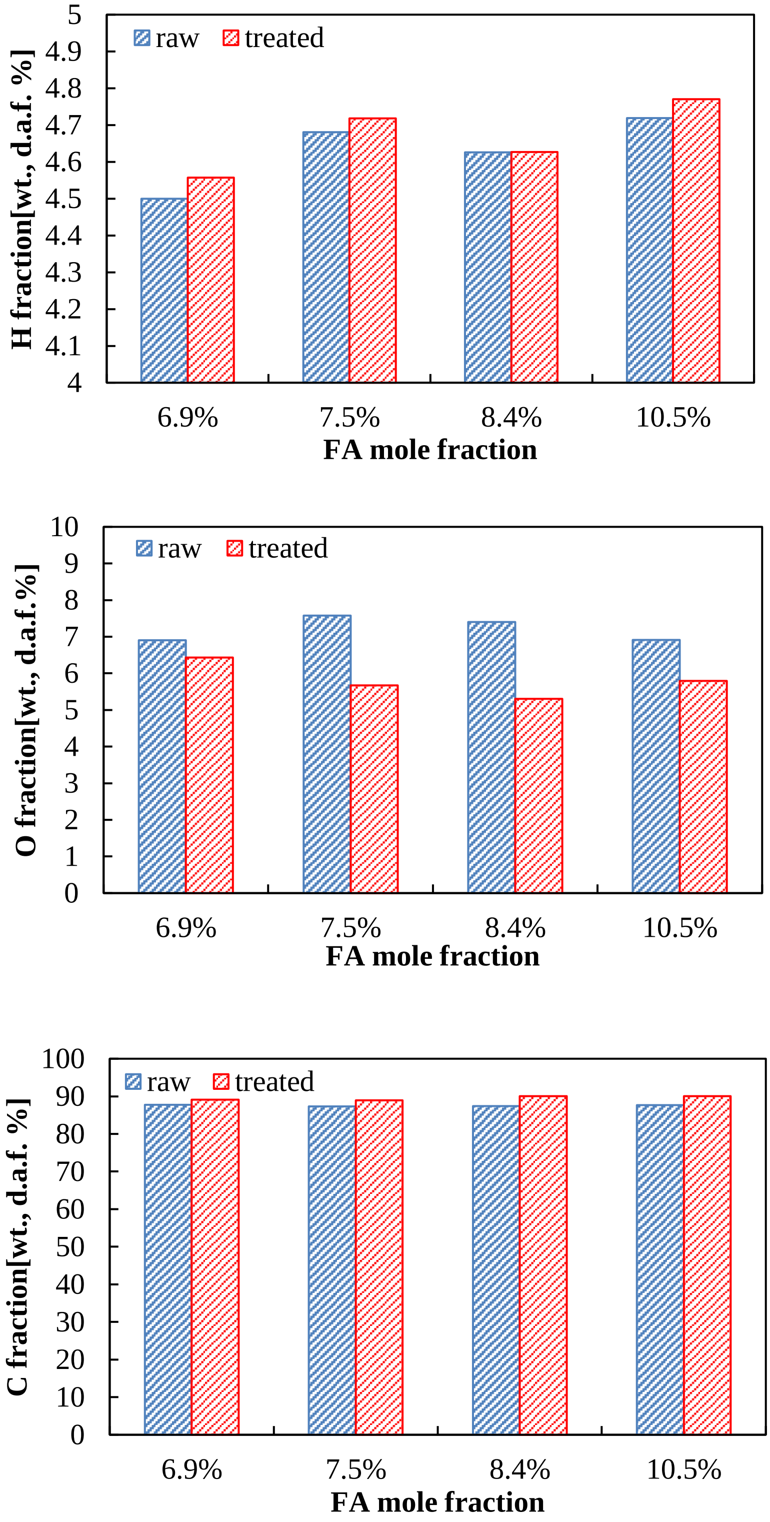

Figure 3.11. **Elemental analysis results of the coal treated under different FA mole fractions (110 ^{o}C, 0.1 MPa)**

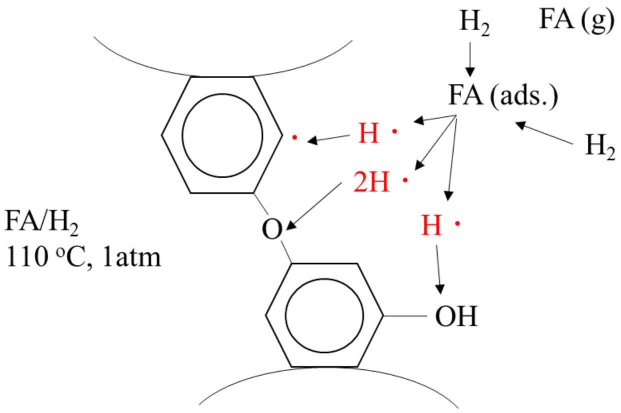

Figure 3.12. A schematic pathway of the FA/H_2 treatment

3. 4 Conclusions

In this chapter, a depolymerization method of coal using gaseous formic acid and hydrogen to treat a bituminous coal at 90–110 °C and atmospheric pressure was proposed. The co-existence of H_2 and formic acid allowed the high H radicals source concentration so that C–O bonds in coals could be cleaved without changing the coal structures. Also, formic acid (g) can transport H radicals from H_2 which is a cheaper H source to stabilize coal radicals in the proposed treatment. Formic acid worked as a catalyst in the treatment and was almost not consumed, which decreases both the cost and CO_2 emissions in the treatment so that the treatment method is environmental-friendly. The low-molecular-weight compounds of one bituminous coal significantly increased by 44 % on low-molecular-weight compounds basis of raw coal after the treatment under mild conditions, which increased more significantly than the treatment method proposed in Chapter 2 (29 %) under formic acid and air conditions.

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Chapter 4–The depolymerization of various carbonaceous resources using co-existing gaseous formic acid and hydrogen under mild conditions

4. 1 Introduction

With the depletion of bituminous coal[1], low-rank coal such as brown coal and lignite should be used as an alternative carbonaceous resource for carbon materials production because of their abundant recoverable reserve[2]. However, the high oxygen content and low thermoplasticity limit their further utilization. Lignin is the most abundant aromatic polymer in nature. The complex structure and low reactivity of lignin limit its further applications. Currently, most of the lignin is burned for generating energy[3]. Depolymerization is an important starting point for many lignin valorization strategies because it could generate valuable aromatic chemicals and/or provide a source of low-molecular-weight feedstocks suitable for downstream processing[4].

Compared to bituminous coals, brown coal and lignin have more oxygen content which connects the monocyclic aromatic hydrocarbons with ether C–O[5,6]. It is noticed if the ether C–O bonds can be cleaved, the low-molecular-weight compounds (LMWC) of these low-rank carbonaceous resources would increase, which can increase the tar and extracts yield to contribute to their further utilization. The traditional depolymerization method for coals and lignin applied severe conditions which are not suitable for commercial propose.[7-14]

The proposed depolymerization method using co-existing formic acid (FA) and H_2 which was described in Chapter 3 has succeeded in removing oxygen and cleaving C–O bonds of bituminous coal under mild conditions (<110 ^{o}C, 0.1 MPa), which suggests that the treatment method is also effective on brown coal and lignin for depolymerization.

In this chapter, the results of the proposed method to depolymerize three different coals (two kinds of bituminous coals and one brown coal) and one biomass (lignin) are compared. To increase the effectiveness of this treatment on low-rank carbonaceous resources, additional pre-treatment is applied, and the effectiveness of the method is demonstrated.

4. 2 Experimental

4. 2. 1 Samples

Three different kinds of coals (two bituminous coals H5 coal and DT coal, one brown coal LY coal) and one biomass (lignin) were used in this study. The elemental analysis results of the coals and the lignin (Dealkaline, Tokyo Chemical Industry Co., Ltd.) are listed in Table 4.1. Each sample was sized evenly below 150 μm.

Table 4.1. Elemental compositions of the samples used in this study

Coal and biomass	Ultimate analysis [wt. %, d.a.f.]				Atomic ratio [–]		Ash (wt.%, d.b.)	Moisture (wt. %, a.r.)
	C	H	N	O [diff.]	H/C	O/C		
H5	87.34	4.68	0.40	7.58	0.64	0.065	5.0	0.37
DT	79.92	5.68	1.08	13.32	0.85	0.13	11.8	1.8
LY	65.33	4.06	0.51	30.10	0.74	0.35	1.4	7.5
Lignin	61.35	4.82	0.09	33.73	0.94	0.41	13.4	10.07

d.a.f. : dry ash-free, d.b. : dry basis, a.r. : as received, diff. : differential

4. 2. 2 Experimental method

The samples were treated in an electric furnace, FA was supplied with a bubbler with H_2 at the flow rate of 100 cm^3/min. A detailed description can be found in the previous chapters. 0.3 g sample was treated under 110–250 °C, 0.1 MPa, and FA/H_2 conditions for 90–150 minutes. The mole fraction of FA was 7.5 %.

4. 2. 3 Analysis of the products

The gas evolved in the treatment was analyzed by micro-gas chromatography (CP-4900, Valian, Column: Porapak Q and Molsieve 5A, 180 ^{o}C, Detector: TCD) or by gas chromatography (GC-12A, Shimadzu, Colume: Porapak Q, 200 ^{o}C, Detector: FID, 220 ^{o}C). Coal samples were analyzed by different methods. The thermomechanical analyzer (TMA-60, Shimadzu) was used to analyze the thermoplastic behaviors of the treated coals. The details about the TMA procedure are available in previous chapters. Under the same heating condition, the weight decreasing curve of the sample was measured using the thermal gravimetric analysis (TGA-50, Shimadzu). Elemental analysis (CHN Corder MT-6M, Yanaco) and FT-IR spectroscopy (JIR-WINSPECT 50, JEOL) were applied for the ultimate analysis and functional group analysis of the sample.

4. 3 Results and discussion

4. 3. 1 Yield of the treated coal

The yield of three types of treated coal on raw coal basis were shown in Table 4.2. The yields of all coals were highly close to 100 % which suggests the treatment did not cause too severe change to all the coals.

Table 4.2. The yields of coals treated under FA/H_2 condition (110 ^{o}C, 0.1 MPa)

Coal	Yield [wt. % d.b.]
H5	100.4
DT	99.9
LY	99.9

4. 3. 2 CO_2 evolved amount in the treatment

The CO_2 involved amount is shown in Table 4.3. It is noticed that the LY coal had the CO_2 involved amount of 0.295 mmol/g-coal while H5 and DT coal had almost the same amount of 0.168 mmol/g-coal and 0.177 mmol/g-coal, which were all rather small amount.

Table 4. 3. CO evolved ${}_2$ amount in the treatment (110 ^{o}C, 0.1 MPa)

Coal	CO_2 evolved amount [mmol/g-raw coal, d.b.]
H5	0.168
DT	0.177
LY	0.295

4. 3. 3 Thermomechanical and thermogravimetric analysis results of different treated coals

The thermomechanical analysis (TMA) curves and thermogravimetric (TG) curves of different raw coals and treated coals after the treatment under FA/H_2, 110 ^{o}C conditions are shown in Figure 4.1. The solid lines represent TMA curves and the broken lines represent TG curves.

When focused on the TMA curves, it is noticed that H5 coal and DT coal could soften and melt while LY coal could not. After the FA/H_2 treatment, H5 coal and DT coal both gained better thermoplastic behavior while LY coal did not show significant change.

When focused on the TG curves, the H5 coal almost had the same pyrolysis property before and after the treatment, indicating that the change in TMA curves of H5 coal is not due to the weight decrease caused by the decomposition but the improvement in thermoplasticity. The treated DT coal had more weight loss than raw DT coal before it started to melt at around 400 ^{o}C, which suggested that the volatile matter in DT coal increased after the treatment. The treated LY coal also had more weight loss than raw LY coal, which was a similar change to the TMA curve, indicating the volatile matter in LY coal increased after the treatment and released under TMA, which resulted in the change of the TMA curves.

From these results, it is suggested that the FA/H_2 treatment under mild conditions (110 ^{o}C, 0.1 MPa) successfully increased the degree of depolymerization of the three coals, but for LY coal, the depolymerization was not so significant.

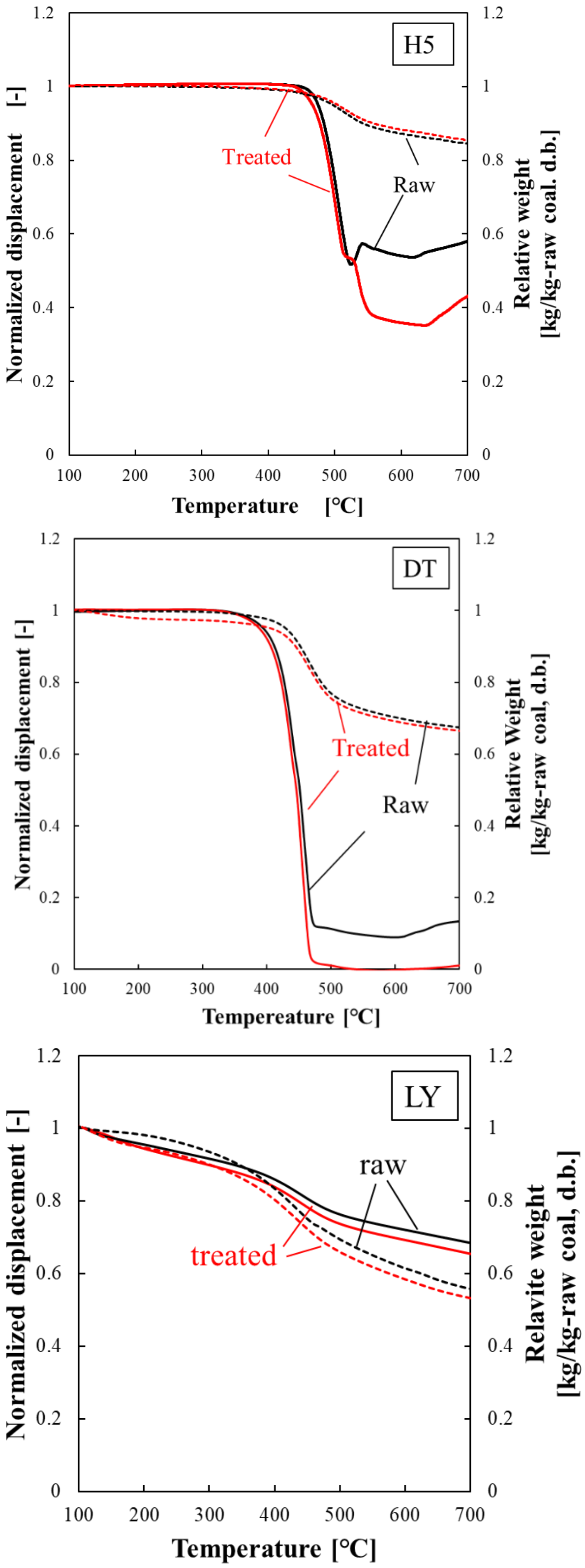


Figure 4.1. TMA (solid line) and TG curves (broken line) of different raw and treated coal (110 °C, 0.1 MPa)

4. 3. 4 Elemental amount changes of different coals in the treatment

The elemental amount changes in the treatment of the coals on raw coal weight basis are shown in Figure 4.2. For H5 coal, the H and C amount increased slightly by 0.4 mol/kg-raw coal and 1.2 mol/kg-raw coal, respectively. The increase of C can be considered as the adsorption of FA in the treatment. Meanwhile, the O amount decreased by 1.2 mol/kg-raw coal, which can be removed in the treatment.

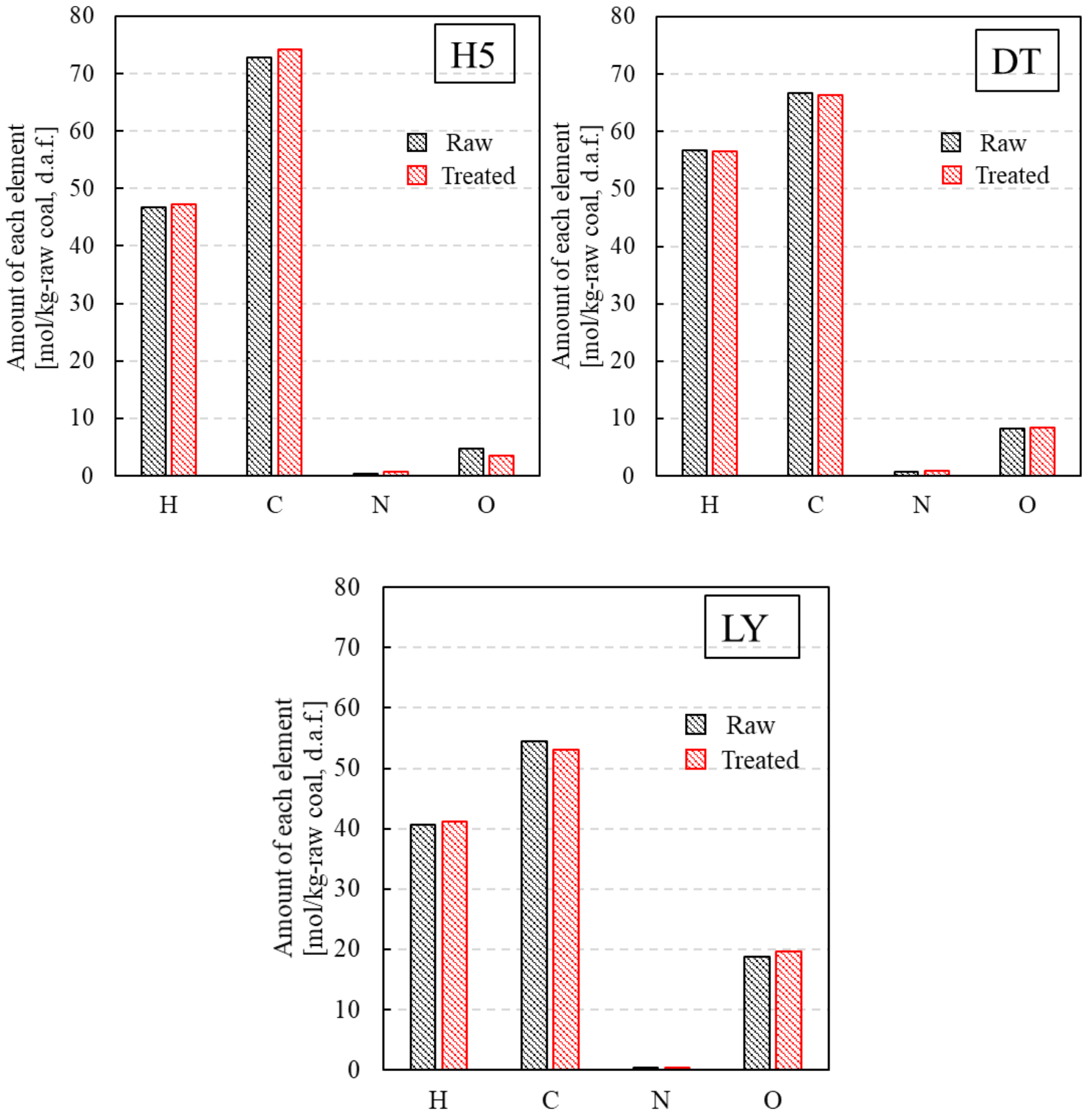


Figure 4.2. Amount of elemental composition changes after the treatment in different coal (110 ^{o}C, 0.1 MPa)

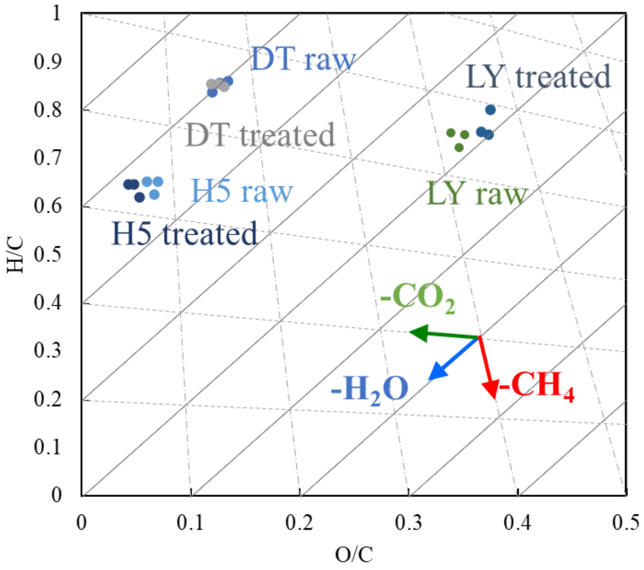


Figure 4.3. Elemental compositions of raw and treated coals on H/C vs. O/C plot

For DT coal, all the elemental compositions hardly changed in the treatment.

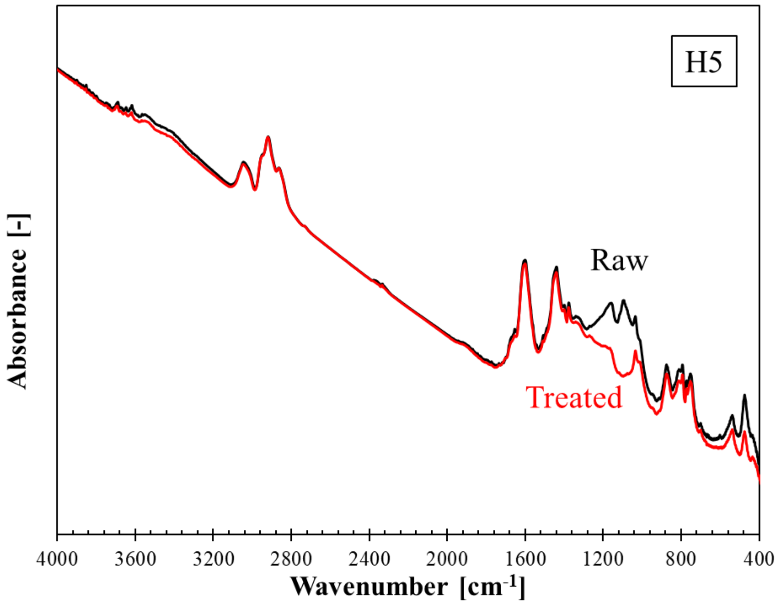
For LY coal, the C amount decreased by 1.3 mol/kg-raw coal which was the most among the three coals. This was considered as the carbon in LY coal was easier to be released as CO_2 in the treatment compared to the other two coals since the most CO_2 evolved amount was detected in the treatment of LY coal from Table 4.3. The oxygen amount increased from 0.9 mol/kg-raw coal could be considered as the adsorption of FA in the treatment. The H amount increased from 0.4 mol/kg-raw coal.

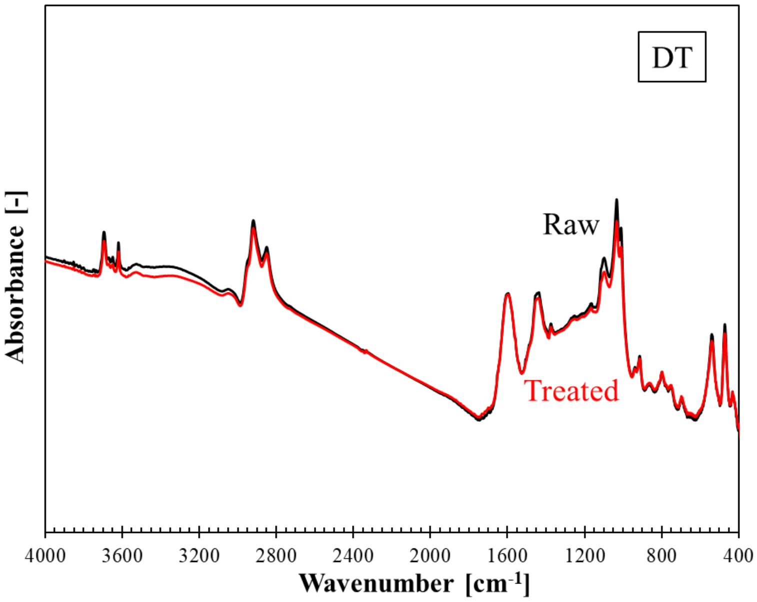
Figure 4.3 shows the elemental composition changes of the treated coal and the raw coal on H/C vs. O/C plot on dry basis. It is noticed that H5 coal has a lower O/C ratio and almost an equal H/C ratio after the treatment. DT coal does not show a significant change in O/C and H/C ratios after the treatment. LY coal has a higher O/C ratio after the treatment. From these results, the proposed treatment method seems to have different effect on the element compositions depending on the average rational formula of coals: a deoxidation effect on bituminous coal of which the average rational formula is $CH_{0.64}O_{0.065}$, with almost no effect on the element compositions of coal of which the average rational formula is $CH_{0.85}O_{0.13}$, and would increase the O/C ratio for the brown coal of which average rational formula is $CH_{0.74}O_{0.34}$.

4. 3. 5 FT-IR results of the different treated coal

FT-IR spectra of each coal before and after the treatment are shown in Figure 4.4. For H5 coal, after the treatment, the peak intensity of aliphatic ether C–O stretching (1150–1085 cm^{-1}) and alcohol C–O stretching (1205–1050 cm^{-1}) decreased compared to raw coal, which suggests the C–O functional groups of H5 coal were cleaved during the treatment, and the peak intensity of O–H stretching also decreased slightly as well. These results are in good agreement with the elemental analysis results that the O ratio of H5 coal decreased. For DT coal, the peak intensity of ether C–O stretching, alcohol C–O stretching, and O–H stretching also decreased slightly which is similar to H5 coal after the treatment. The slight change in the functional groups did not reflect on the elemental results. LY coal also showed a similar change with the decreasing of O–H stretching.

Comparing the spectra of the three coals, it is noticed that LY coal has the most abundant O–H functional groups. Because the depolymerization of LY coal was not so effective compared to the other coals, the abundant O–H functional groups may be the reason to inhibit the depolymerization of LY coal in the treatment because the hydrogen bonds between the O–H functional groups of FA and LY coal may inhibit the transport of H radicals from H_2 to coal via FA in the treatment.





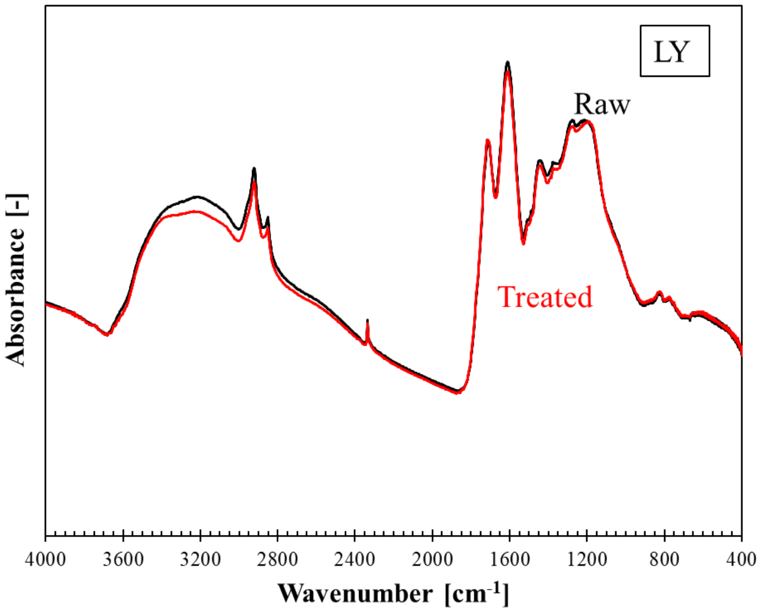


Figure 4.4. **FT-IR spectral of different coals after the treatment (110 ºC, 0.1 MPa)**

4. 3. 6 Attempt to increase the depolymerization effectiveness of FA/H_2 treatment on LY coal

To elucidate whether the O–H functional groups in LY coal inhibit the depolymerization of FA/H_2 treatment or not, additional pre-treatment for removing O–H functional groups in LY coal was applied before the FA/H_2 treatment.

A 2-step treatment was designed to depolymerize LY coal more effectively. 0.3g LY coal was heated up to 350 °C and was kept for 90 minutes in nitrogen gas flow at the flow rate of 100 cm^3/min for removing the O–H groups in LY coal. And then, the pre-treated LY coal was treated under FA/H_2 at 110 °C following the same procedure as mentioned before. The properties of the LY coal treated in the 2-step treatment were compared with that in the 1-step treatment which was treated under FA/H_2 at 110 °C directly.

The FT-IR spectra of LY coal treated under different conditions are shown in Figure 4.5. The peak intensity of O–H groups in LY coal significantly decreased by the pre-treatment in N_2 at 350 °C compared to raw coal, which indicates the purpose of the pre-treatment to remove O–H groups was achieved. The decrease in the peak intensity of C–O groups of LY coal treated by FA/H_2 at 110 °C after the nitrogen pre-treatment was first observed. It suggests that with the removal of O–H groups, C–O groups of LY coal can be cleaved in the following FA/H_2 treatment at 110 °C, which is beneficial for depolymerization.

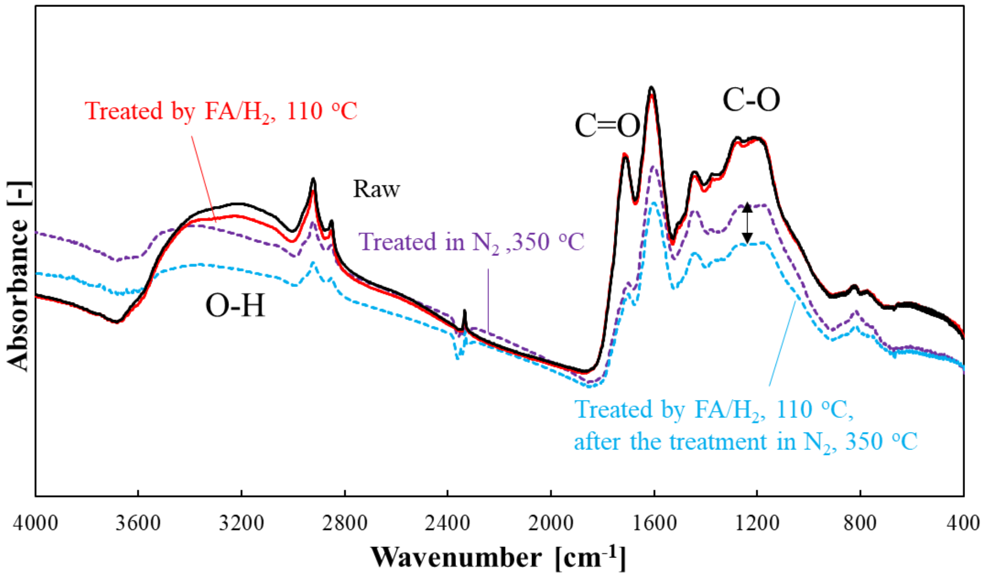


Figure 4.5. FT-IR spectra of LY coal treated under different conditions

Table 4.4 Yield of LY coal treated after each step

Treatment step	Yield [wt. %, d.b.]
1st step	78.5
2nd step	73.2

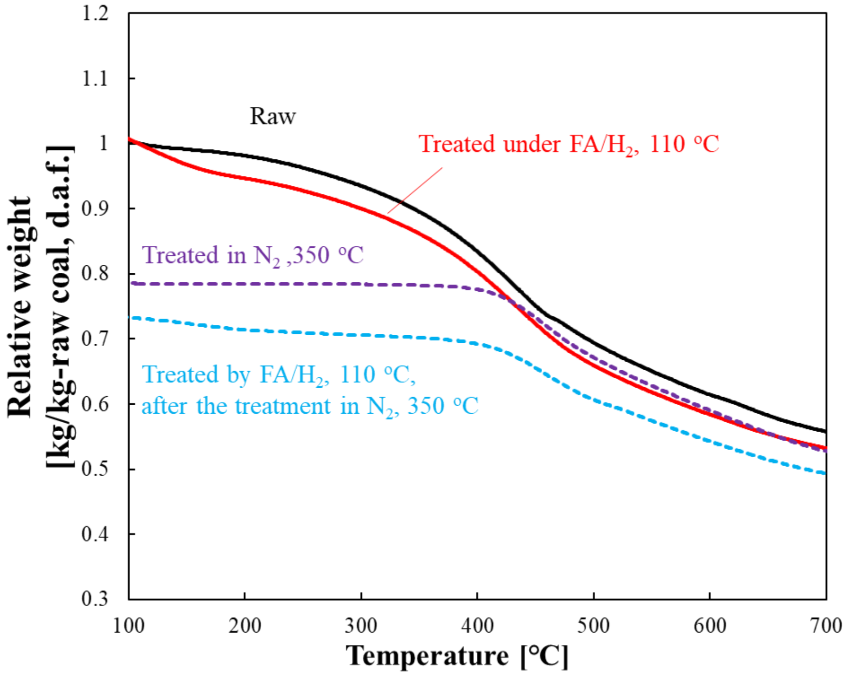


Figure 4.6. TGA curves of LY coal treated under different conditions

The yield of LY coal treated after each step is shown in Table 4.4. After the 1st step treated in nitrogen at 350 °C, the yield of LY coal was 78.48 % on dry raw coal basis. And after the 2nd step treated FA/H_2 at 110 °C, the yield of treated coal decreased to 73.15 % on dry raw coal basis (Yield is 93.2 % for the 2nd step treatment). When treated by FA/H_2 at 110 °C directly, the yield of LY was 99.9 wt. %, which suggests more LMWC was released in the 2nd step treatment. Since the CO_2 evolved amount in 2nd step was only 24.7 wt. % on the total weight loss basis in the 2nd step treatment and no other inorganic gas was detected, it suggested that most of the LMWC released in the 2nd step treatment were organic gas or tar.

The TGA curves of LY coal treated under different conditions are shown in Figure 4.6. It is noticed that after the treatment under N_2 and 350 °C condition, LY coal hardly showed weight decrease at 400 °C in TG analysis, but when treated the coal again under FA/H_2, 110 °C conditions, the coal started to lose weight in, which suggests that the LMWC in LY coal was increased by the FA/H_2 treatment at 110 °C. Considering the yield of LY coal also decreased by 7.8 wt. % in the following FA/H_2 treatment after the N_2 pre-treatment. Thus, the proposed treated method of depolymerization of coal would be more effective for the removal of O–H groups in LY coal.

4. 3. 7 The effectiveness of the FA/H_2 treatment on biomass (lignin)

The effect of the proposed method on biomass was demonstrated. 0.15 g lignin was sized below 150 μm and treated at 250 °C and 0.1 MPa for 150 minutes in the electric furnace in the atmosphere of FA/H_2, FA/N_2, and N_2. The FA mole fraction was controlled at 7.5 % when FA was supplied.

Table 4.5 shows the yield of the treated lignin under different conditions. The yield of treated lignin reached the lowest at 80.5 % when under FA/H_2 atmosphere when under N_2 was the highest at 84.8 % and under FA/N_2 was 82.7 %, indicating during the treatment under FA/H_2 atmosphere the most LMWC was released.

The TG curves of treated lignin under different conditions are shown in Figure 4.7. Lignin treated under FA/H_2 had the most weight decrease in the TG analysis compared to the other two conditions and raw lignin under 700 °C, which suggested the lignin treated under FA/H_2 increased the most LMWC than the other two conditions.

Table 4.5. Yields of lignin treated under different atmospheres (250 °C, 0.1 MPa)

Treatment atmospheres	Yield [wt. %, d.b.]
N_2	84.8
FA/N_2	82.7
FA/H_2	80.5

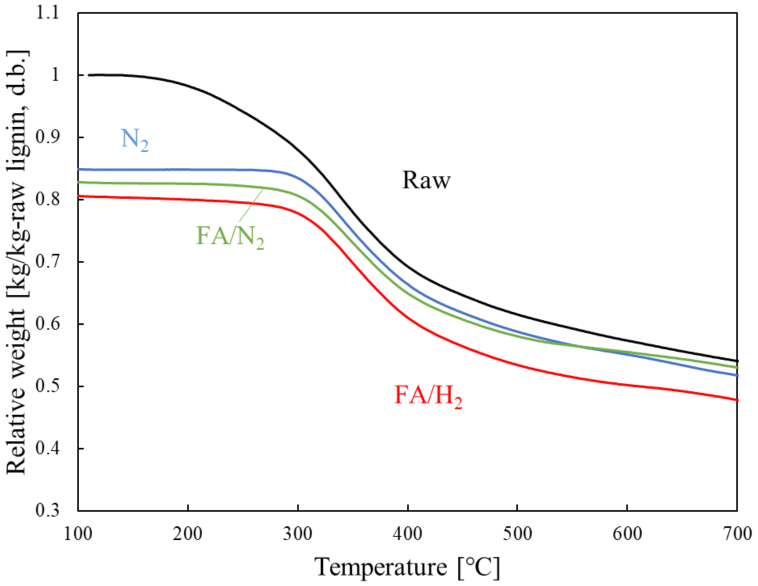


Figure 4.7. TG curves of lignin treated under different conditions (250 °C, 0.1 MPa)

Figure 4.8 shows the FT-IR spectra of each treated lignin and the raw lignin. The peak intensity of C–O stretching (1040–1310 cm^{-1}) significantly decreased by FA/H_2 treatment compared to the other treatment conditions. The peak intensity of O–H stretching (3200–3550 cm^{-1}) decreased in each treated lignin and decreased the most under FA/H_2 and N_2 conditions. The peak intensity of C=O stretching (1650–1818 cm^{-1}), C=C stretching (1600–1670 cm^{-1}), and C–H bending (1380–1465 cm^{-1}) decreased in each treated lignin compared to raw lignin when C=O groups decreased the most under FA/H_2 and FA/N_2 conditions. It is noticed that the FA/H_2 treatment was capable of effectively removing the C–O functional groups in the treatment, as well as other O-containing functional groups like C=O and O–H groups.

Figure 4.9 shows the element amount of all the treated lignins and raw lignin on dry ash-free basis. The oxygen decreased in each condition compared to raw lignin, and the lignin treated under the FA/H_2 condition had the lowest oxygen amount compared to other treatment conditions which is in good agreement with the FT-IR results. It is suggested that the FA/H_2 treatment effectively enhanced the deoxygenation of lignin, which contributed to the depolymerization of lignin. The decrease in H amount is considered due to the decrease of O–H groups in FA/H_2 and N_2 treatment from the FT-IR results.

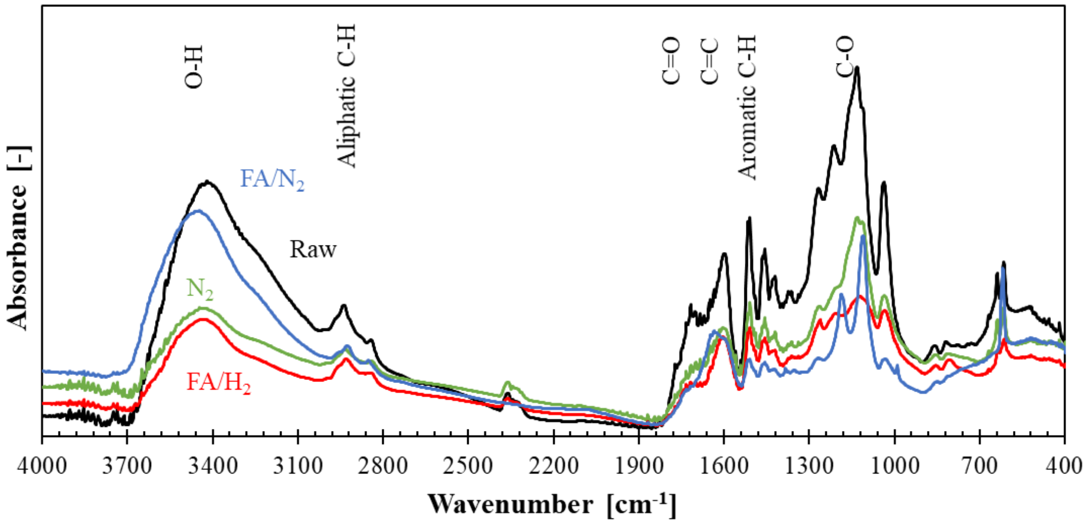


Figure 4.8. FT-IR spectral of the lignin treated under different conditions (250 °C, 0.1 MPa)

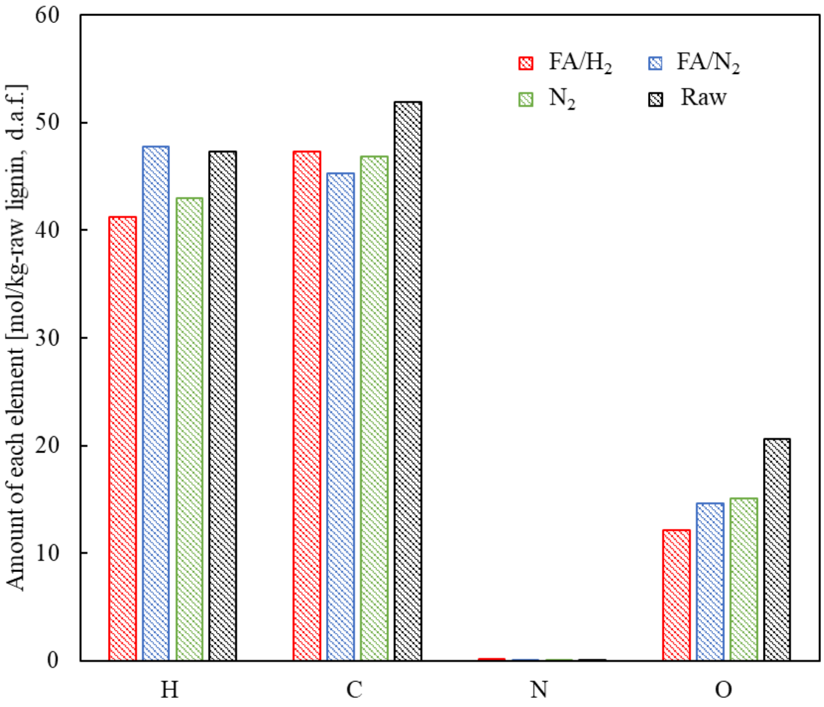


Figure 4.9. Amount of elemental composition in lignin treated under different conditions (250 °C, 0.1 MPa)

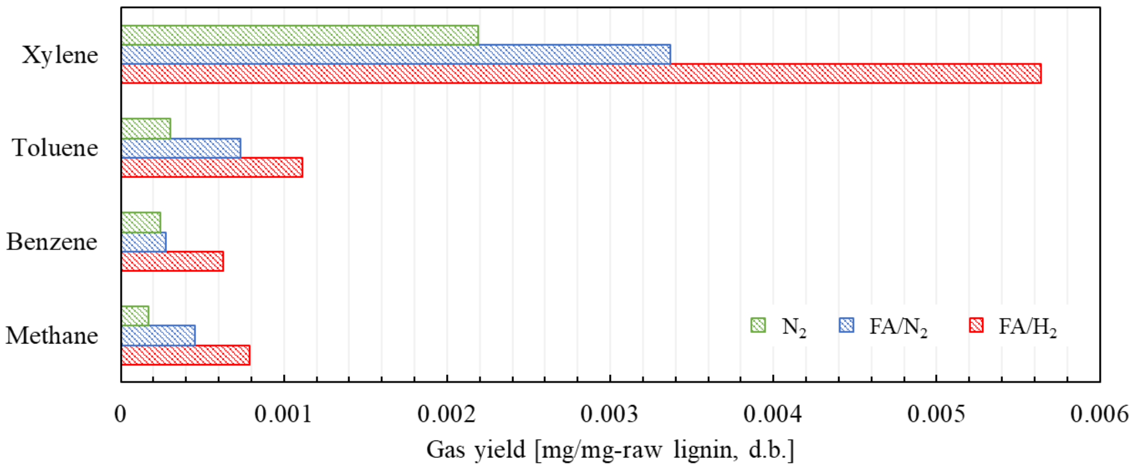


Figure 4.10. **Yields of the gas evolved from lignin treated under different conditions (250 ºC, 0.1 MPa)**

The exhaust gas collected in the gas bag in the treatment under each condition was analyzed. The yields of the gas evolved from lignin in different treatments are shown in Figure 4.10. It is noticed that in each condition, methane, benzene, toluene, and xylene evolved, which was because these hydrocarbon molecules were released after the C–O connections were cleaved, and when under FA/H_2 condition, the yields of all gases reached the highest amount. The results are in good agreement with FT-IR and elemental results that the C–O bonds and aromatic C–H bonds decreased in the treatment. The considerable reaction pathway in the treatment is shown in Figure 4.11. It suggested that the co-existing of FA and H_2 can promote the cleavage of C–O bonds in lignin and enhance the degree of depolymerization.

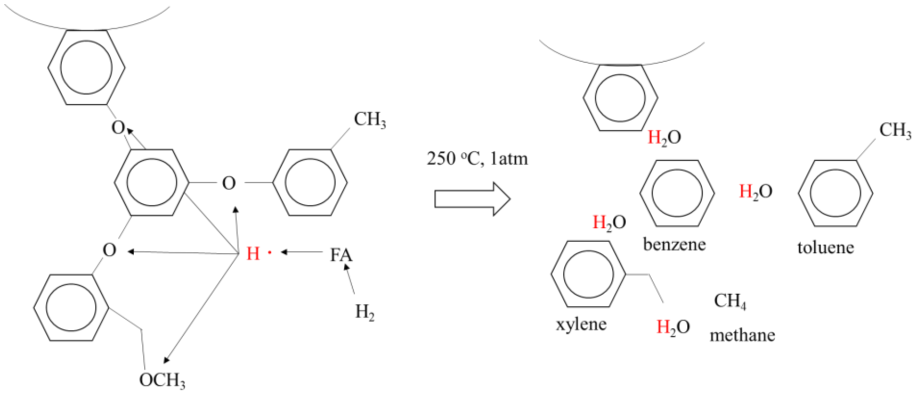


Figure 4.11. **Considerable reaction pathways occur in the proposed treatment for lignin**

4. 4 Conclusions

The versatility of the method proposed in Chapter 3 was tested for 4 types of coals and biomass, including two bituminous coals, one brown coal, and lignin.

The proposed treatment method showed good results in depolymerization under mild conditions at 110 ^{o}C and 0.1 MPa for the two bituminous coals, which can be found in the improvement in thermoplasticity and the decrease in oxygen fraction. For brown coal, the proposed treatment at 110 ^{o}C showed a better effect on depolymerization after the removal of O–H groups, which can be found in the decrease of C–O bonds, more weight decrease in the treatment and TGA curves. For lignin, when treated under 250 ^{o}C, 0.1 MPa, the treated lignin had less oxygen content, a higher gasification rate, and more valuable hydrocarbon compounds like BTX and methane evolved in the treatment.

Thus, the proposed method showed the possibility to depolymerize various carbonaceous resources by cleaving the C–O groups or stabilizing the inherent radicals under mild conditions to increase their low-molecular-weight compounds, which can be a hint to solve the depletion of high-rank carbonaceous resources and the CO_2 emission problems by upgrading low-rank carbonaceous resources at a low cost.

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Conclusions

This study has been aiming to develop a method to increase the value of the carbonaceous resources by increasing their low-molecular-weight compounds under mild conditions as at 60 °C–250 °C and 0.1 MPa when other traditional depolymerization methods for carbonaceous resources required high temperatures and high pressure such as at 110–600 °C and 4–17 MPa. The proposed treatment method can enhance the thermoplasticity of coal, which makes it more suitable for coke preparation, increase the yield of valuable extracts with low energy consumption when combined with the fractionation solvent extraction method, and also increase the yields of the valuable chemical materials like BTX and methane of lignin. Thus, the proposed treatment method can contribute to the more efficient 'non-fuel' use of carbonaceous resources and decrease CO_2 emissions.

In Chapter 1, compared to the traditional methods which applied severe conditions to cleave the structures of coal for depolymerization, this study has focused on the stabilization of coal inherent radicals under mild conditions to inhibit the cross-linking reaction between radicals of low-molecular-weight compounds. Formic acid, which is found to be able to provide H radicals itself under mild conditions was first proposed in the study. Low-rank coal and weathered coking coal were treated under mild conditions at 60 °C and 0.1 MPa by reduction using formic acid to stabilize the inherent radicals of coals. It was shown that the treatment by either aqueous formic acid or formic acid vapor significantly improved the thermoplastic performance of low-rank coal and weathered coal, and the strength of the resulting coke was also enhanced. The consumption of the reductant formic acid was small enough to hardly change the elemental composition of the coals. The proposed depolymerization treatment can be effectively applied as a pre-treatment process in coke production or other carbon materials production process to utilize low-rank coal more efficiently as raw materials, not as fuel.

The inherent radicals of coals are limited, thus, the proposed treatment method in Chapter 1 has a limitation. For the further depolymerization effect, in Chapter 2, a novel coal treatment method that combined oxygen oxidation reaction and gaseous formic acid reduction reaction to treat a bituminous coal under mild conditions (<90 °C, 0.1 MPa) was proposed. The C-O bonds in coal were first cleaved by the oxidation reaction, and the formed radicals were stabilized by H radicals provided by formic acid immediately.

It was found that the coal treated under formic acid and air atmosphere has better thermoplasticity than under formic acid and N_2 atmosphere which was the method proposed in Chapter 1. Low-molecular-weight compounds of the treated coal under formic acid and air atmosphere successfully increased by as much as 29.0 % as compared to the low-molecular-weight compounds of the raw coal under mild conditions at 90 °C, 0.1 MPa measured by the solvent fractionation extraction method. The possible reaction pathway was proposed.

If the H radicals source is only gaseous formic acid which was proposed in Chapters 1 and 2, the H radicals concentration would have a limitation for the limited formic acid partial pressure. To solve the problem, in Chapter 3, another coal treatment method was proposed by using co-existing gaseous formic acid and hydrogen to treat coal, and the effectiveness was demonstrated. The H radicals concentration was much higher when H_2 was the carrier gas so that the treatment can cleave C–O bonds easily in coals under mild conditions without changing the structures of coal such as using oxidation and pyrolysis. Additionally, the co-existence of formic acid and H_2 allowed formic acid (g) to transport H radicals from H_2 which is a cheaper H source. Formic acid worked as a catalyst in this case and was almost not consumed, which can decrease the CO_2 emissions in the treatment and is environmental-friendly. The low-molecular-weight compounds of one bituminous coal significantly increased by 44 % on low-molecular-weight compounds basis of raw coal after the treatment under mild conditions, which increased more significantly than the treatment method proposed in Chapter 2 (29 %) under formic acid and air conditions for the same coal. The possible reaction pathway was proposed.

In Chapter 4, the versatility of the proposed method in Chapter 3 was demonstrated by testing 4 types of coals and biomass, including two bituminous coals, one brown coal, and lignin. The proposed treatment method showed good effects on depolymerization under mild conditions for the two bituminous coals. For brown coal, with the removal of O–H groups with an additional pre-treatment, the proposed treatment showed a better effect on depolymerization than treating directly which can be found in the decrease of C–O bonds, more weight decrease in the treatment and TGA curves. For lignin, the proposed method decreased the oxygen content and increased the gasification rate, more valuable hydrocarbon compounds like BTX and methane were also evolved in the proposed treatment which could be another benefit of the proposed treatment.

Thus, the proposed method shows the possibility to depolymerize various carbonaceous resources by stabilizing the inherent and formed radicals or cleaving the C–O groups under mild conditions to increase their low-molecular-weight compounds, which can be a hint to solve the depletion of high-rank carbonaceous resources and the CO_2 emission problems by upgrading the low-rank carbonaceous resources at a low cost.

Acknowledgments

It is the greatest challenge I have ever had to finish this doctoral dissertation. Without the patient help and guidance of the following people, this dissertation can not be completed. I would like to thank them with my greatest sincerity.

I would like to express my deepest appreciation to my supervisor, Prof. Motoaki Kawase, a professor of the Department of Chemical Engineering, Kyoto University. Prof. Kawase is full of wisdom and kindness. Although my research topics are not fit with his specialized field, he always gave me very useful advice from other aspects which made my mind expand. Also, he taught me a lot of Japanese as well as academic English, which benefited me very much. What's more, his cheerful character brought me a very comfortable 5-years academic life.

I would also like to appreciate lecturer Ashida sincerely, who was the main advisor for this dissertation. lecturer Ashida is unbelievably kind and clever. He was always so willing and patient to answer my unripe questions in the daily discussions despite he was so busy. He has also encouraged me to think independently in experiments and writing, increasing my confidence and ability to contribute more to science. Besides research, he has also given me very useful advice in life. I doubt I will ever be able to repay his kindness.

My sincere thanks also go to my doctoral dissertation committee: Prof. Masahiro Ohshima and Prof. Noriaki Sano not only for their meaningful comments and advice, but also for the questions from various perspectives which expand my mind for the research.

I also extended my gratitude to Dr. Noriyuki Okuyama and Dr. Koji Sakai from KOBELCO who helped me a lot with the dissertation. I also gratefully appreciate the financial support by JST SPRING (Grant number JPMJSP2110).

I also thank all the members of Reaction Engineering Lab, Kyoto University, especially Mrs. Miho Kageyama and Mrs. Ayano Kimura, the researcher in the lab. Mrs. Kageyama has always arranged excellent and convenient life in the lab for all of us, and Mrs. Kimura, who has worked in the similar specialized field with me, helped me a lot in the experimental and gave me much inspiration through daily discussions. Not forget to thank Mrs. Yuko Enomoto, the secretary of the lab, who is always kind to assist with all-related academic issues.

I also appreciate my friends Yulei Ma and Yafei Li, who fully support my work, study, and life. Special thanks to my girlfriend, Xinke Yang, who always support me during my good and bad times. Always be grateful to Kyoto University, the most beautiful university I have ever met and supporting my master's and doctoral life.

Last but not least, I would like to express y sincere gratitude to my family. My beloved parents Yihua Ren and Xuping Feng, always trust me and let me study in Japan, and support me all the time.

List of publications

Journal papers

1. Ryuichi Ashida, Ko Takahashi, Jie Ren, Motoaki Kawase, Koji Sakai, Noriyuki Okuyama. Improvement of Coking Property of Low-Grade Coals by Mild Reduction Treatment. Submitted to ISIJ International, under review. (Chapter 1)

2. Jie Ren, Ryuichi Ashida, Motoaki Kawase, Koji Sakai, Noriyuki Okuyama. Development of a novel mild depolymerization method of coal combining oxygen oxidation and formic acid reduction reaction. ACS Omega, 2023 8(2), 2531-2537. (Chapter 2)

3. Jie Ren, Ryuichi Ashida, Motoaki Kawase, Koji Sakai, Noriyuki Okuyama. Depolymerization of coal under mild conditions with co-existing gaseous formic acid and hydrogen treatment. In preparation. (Chapter 3)

4. Jie Ren, Ryuichi Ashida, Motoaki Kawase, Koji Sakai, Noriyuki Okuyama. The depolymerization of various carbonaceous resources using co-existing gaseous formic acid and hydrogen under mild conditions. In preparation. (Chapter 4)

International conference proceeding related to the dissertation

1. Jie Ren, Ryuichi Ashida, Motoaki Kawase, Koji Sakai, Noriyuki Okuyama, Depolymerization of coal under mild conditions via redox reaction by oxygen and formic acid. *2022 International Pittsburgh Coal Conference*, 106, Online, September 19–22, 2022. (Chapter 2)

Other International conference proceedings

1. Jie Ren, Yumiko Segawa, Ryuichi Ashida, Motoaki Kawase, Kinetic Study on Weathering of Coking Coal, *The 18th Asian Pacific Confederation of Chemical Engineering (APCChE 2019)*, E306, Sapporo, Japan, September 2019.
2. Jie Ren, Yumiko Segawa, Ryuichi Ashida, Motoaki Kawase, Rate Analysis of Weathering of Coking Coal, *The 32nd International Symposium on Chemical Engineering (ISChE 2019)*, OB03, Deajeon, Korea, December 2019.