

Production of low ash coal by thermal extraction with *N*-methyl-2-pyrrolidinone

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Abstract—Present study was conducted for the purpose of producing low ash coal from LRC (low rank coals) such as lignite and sub-bituminous coal through thermal extraction using polar solvent. Extraction from bituminous coal was also investigated for comparison. NMP as a polar solvent was used. The ratio of coal to solvent was adjusted as 1 : 10. Experimental conditions were established which include the extraction temperature of 200–430 °C, initial applied pressure of 1–20 bar and extraction time of 0.5–2 hr were used. Extraction yield and ash content of extracted and residual coal were measured. The extraction yield increased with the increase of extraction temperature, and the ash content of extracted coal decreased below 0.4% at 400 °C from the raw coal samples that have the ash contents of 4–6%. According to the analysis of experiments results, fixed carbon and calorific value increased, and H/C and O/C decreased.

Key words: LRC (Low Rank Coal), Solvent Extraction, Thermal Extraction, Clean Coal, Ash-free Coal

INTRODUCTION

Coal has long been used as an important energy source, and its exploitable deposit is three times larger than that of petroleum. With the development of human civilization, demand for coal has increased explosively but its utilization has confronted limitations due to excessive emission of air pollutants and carbon dioxide, one of the major global warming gases. Recently, however, with the crisis of exhaustion of petroleum and high oil price, there is increasing interest in purifying coal to utilize it as an alternative clean energy source.

Coal contains combustible hydrocarbons, but approximately 10% of inorganic components as well. Such inorganic components produces ash during combustion and it has created such problems as slagging and fouling on the boiler wall and tubes. Thus, a solution of address these problems has been sought to remove inorganic components from coal to make coal a clean fuel.

There are two methods for producing clean coal: leaching out inorganic components from coal by using alkali compounds, and extracting organic components from coal by using solvents as a catalyst. The former has been developed in USA and Australia and named as “UCC (ultra clean coal)” process; however, as its final product contains around 0.5% or more of inorganic components it is reported not usable directly to gas turbines or existing boilers successfully [1–3]. The latter has been developed in Japan and named the “Hypercoal” process. The research aims at developing ash-free coal with the content of inorganic component as low as 0.02% to enable direct use for gas turbines [4–8].

Particularly, the hypercoal process has been expected to be able to produce ash-free coal from low rank coal (LRC) such as lignite and sub-bituminous coal, which are as abundant as bituminous coal but have limited utilization because of their high moisture content

and low calorific value.

If organic solvent is used, only organic components in coal are extracted into the solvent. NMP (*N*-methyl-2-pyrrolidinone) is one of the most commonly used solvents for coal extraction. Iino et al. [9] reported that an extraction yield of over 60 wt% can be attained by mixing bituminous coal with the solvent mixture of NMP and CS₂ at a ratio of 1 : 1 at normal temperature. This report suggests that solvent loosens the bonding of organic matters in coal [9].

Okuyama et al. [5] and Yoshida et al. [7,10] reported that the use of non-polar solvent in bituminous coal can achieve an extraction yield of over 60%; however, the actual yield is below 60% in case of sub-bituminous coal. Miura et al. [11] reported that the use of non-polar solvent at around 350 °C can attain an extraction yield of 65–85%, whereas the use of polar solvent in sub-bituminous and lignite can attain an extraction yield of around 80%. Li et al. [8] reported that the polar solvent NMP increases the extraction yield in sub-bituminous coal compared to non-polar solvent 1-MN (1-methylnaphthalene). Okuyama et al. [12] reported that the Hypercoal process will be an effective way to upgrade the low rank coals. In their research for refining the quality of LRC by way of solvent extraction, in case of lignite, the ash content was maintained at 5% in residual coal from the raw coal that had an ash content of 2–3%, whereas calorific value increased from 4,700 kcal/kg to 7,300 kcal/kg.

In Korea, researches have been conducted to remove ash from coal by using alkali solutions. Lee et al. [13,14] examined the combustion characteristics of coal and changes in organic structure using domestic anthracite and imported bituminous coal treated by molten caustic leaching. According to the ultimate analysis of the results, IR (Infrared spectrometer) and NMR (Nuclear Magnetic Resonance), as the treated coals were carbonized, the ash content decreased and calorific value increased. However, treated domestic anthracite coal retained ash content around 4% and was unable to be processed into ash-free coal.

Considering the situation of Korea with little energy resources

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Table 1. Analytical results for the sample coals

| Coal brand | Proximate analysis (wt%) | | | | Ultimate analysis (wt%) | | | | | H/C | O/C | Calorific value (kcal/kg) |
|------------|--------------------------|-------|------|-------|-------------------------|------|------|-------|------|------|------|---------------------------|
| | M | VM | Ash | FC | C | H | N | O | S | | | |
| Kideko | 7.37 | 33.61 | 6.05 | 52.97 | 75.60 | 5.03 | 0.76 | 12.19 | 0.37 | 0.80 | 0.12 | 6,720 |
| Roto south | 25.58 | 36.89 | 3.44 | 34.09 | 68.76 | 5.36 | 0.65 | 21.73 | 0.06 | 0.94 | 0.24 | 5,980 |
| Sunhwa | 12.51 | 30.58 | 5.15 | 51.76 | 76.45 | 4.89 | 0.32 | 12.91 | 0.28 | 0.78 | 0.13 | 6,730 |

*M: Moisture, VM: Volatile matter, FC: Fixed carbon, C: Carbon, H: Hydrogen, N: Nitrogen, O: Oxygen, S: Sulfur

available, refining and utilization of LRC can contribute to stable energy supply, and the use of clean coal in power plants or large industrial boilers can reduce the emission of CO₂, one of major causes of the global green house effect [15].

In this study, the whole process of extracting organic components from coal using the NMP (N-methyl-2-pyrrolidinone) to eventually produce low ash coal was investigated. As the extraction of organic components from coal can be affected by those conditions of extraction temperature, pressure and time, the effect of these variables on the characteristics of both extracted and residual coal was also examined.

EXPERIMENTAL

Three kinds of coal samples, i.e. Indonesian Kideko, Roto South and Chinese Sunhwa coal, were used. Roto South and Kideko coals are sub-bituminous coal, whereas Sunhwa coal is bituminous coal. Coal was crushed and separated by using a 200 mesh (<75 μm) standard sieve. Table 1 shows proximate and ultimate analysis results and calorific values of raw coal samples. The ash content was 6.05% in Kideko coal, 3.44% in the Roto South coal, and 5.15% in

Sunhwa coal, respectively. NMP (N-methyl-2-pyrrolidone, C₅H₉NO) was used as a solvent. NMP is a 5-member ring, which has a boiling point of 202 °C and is water soluble.

The experiment used an autoclave of 0.5 L. Fig. 1 shows a schematic diagram of the apparatus used in this experiment. It is largely composed of extractor, filter and dryer. The first is the slurry-making by mixing a specific amount of coal and solvent. Then, the slurry was put into the autoclave and nitrogen was purged up to adjust the initial pressure inside the vessel. After that, the coal slurry was heated to a certain temperature level while agitating with a magnetic agitator. A ceramic heater was used for heating. After reaching a certain target temperature, the temperature was maintained for a fixed amount of time. When the extraction process was finished, there were both solution extracted into the solvent and non-extracted solid matter [hereinafter referred to as “residual coal”] inside the reactor. The valve was open and the solution was separated from the solid matter by filtering. Either glass filters or metal sintered filters were used for filtering. The solution and residual coal remaining after filtering were dried in a vacuum oven at 160 °C for 24 hours. After the remaining solvent in the solution evaporated all, only solid material was left, which is called extracted coal. The yield of extracted coal, which was in a dry ash-free state, was calculated as follows.

$$\text{Extraction yield (\%)} = \frac{(\text{Weight of feed coal} - \text{Weight of residual coal})}{\text{Weight of feed coal}} \times 100$$

20 g of coal and 200 g of solvent were used. Extraction temperature ranged from 200 °C to 430 °C. In most experiments, initial applied pressure was changed from 1 bar to 20 bar, but the pressure changed with increasing temperature. Extraction time ranged from 0.5 hour to 2 hours, and was generally one hour in average. The pore size of glass filters used in filtering was 0.7 μm and that of sintered metal filters was 0.5 μm.

The proximate analyzer (TGA-701, LECO Co., U.S.A.) and elemental analyzer (CHN-2000, LECO Co., U.S.A.) were used to analyze chemical properties of coal samples. Calorific value was measured by calorimeter (Parr 1261, PARA Co., U.S.A.).

RESULTS AND DISCUSSION

1. Extraction Yield

Coal is classified by rank into lignite, sub-bituminous and bituminous coal according to characteristic properties such as moisture, volatile matter and fixed carbon. Because chemical structure was different according to the rank, the results of extraction with solvent were also different. Bituminous coal has a softening point of temperature at around 350–400 °C, when thermal relaxation hap-

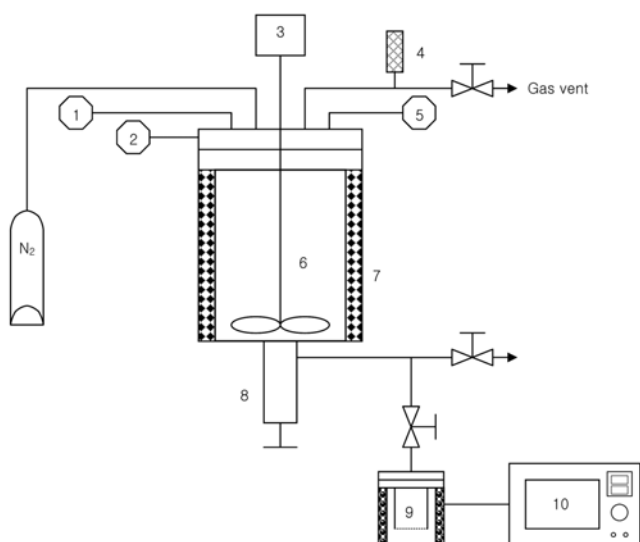


Fig. 1. Schematic diagram of experimental apparatus for thermal extraction.

- | | |
|----------------------|--------------------------|
| 1. Pressure gauge | 6. Extractor (Autoclave) |
| 2. Thermocouple | 7. Ceramic heater |
| 3. Magnetic agitator | 8. Pressure bottom valve |
| 4. Relief valve | 9. Filter |
| 5. Slurry feeding | 10. Vacuum oven |

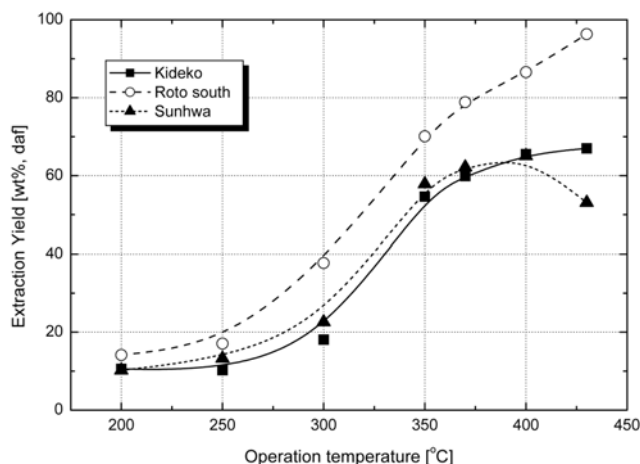


Fig. 2. Variation of extraction yield with extraction temperature.

pened in coal structure. Okuyama et al. [5] reported that, for bituminous coal, the yield of solvent extraction is highest at the softening temperature and decreases at higher temperature. Yoshida et al. [10] reported that, in bituminous coal, the extraction yield has close correlation with softening temperature showing a correlation index of 0.84. It was reported, however, that LRC hardly has softening temperature, so extraction yield continues to increase with the increase of the extraction temperature.

Fig. 2 shows variations of extraction yield by the extraction temperature. For all extraction conditions, extraction time was set at 1 hour. The extraction yield did not change much until the temperature reached at 250 °C but increased rapidly from 300 °C and reached 60% at 350 °C. Particularly in the case of Roto South coal, the extraction yield reached 70% at 350 °C. If extraction temperature had increased up to 400 °C and over, the extraction yield would have shown different depending on the coal rank as mentioned earlier. The extraction yield of Roto South coal reached a peak of over 85% at over 400 °C, showing a higher increase rate than Kideko coal. In case of Kideko coal, the extraction yield increased slowly with the increase of extraction temperature, reaching 67% at 430 °C. In case of Sunhwa coal, however, the extraction yield reached a peak of 65% at an extraction temperature of 400 °C, and at a higher temperature it rather decreased and showed 53% at 430 °C. These results are consistent with the report that in sub-bituminous coal the extraction yield increases with the increase of temperature, but in bituminous coal it reaches a peak when the extraction temperature reached at a certain level and then decreases at a higher temperature [11]. In addition, Roto South coal, which is sub-bituminous coal, showed higher extraction yield than Sunhwa coal, which is bituminous coal.

It has been reported that NMP, a polar solvent, is more effective in the extraction of LRC such as lignite and sub-bituminous coal than in the extraction of high rank coals such as bituminous coal [8]. In general, bituminous coal has a softening point at which its structure becomes relaxed, and beyond the softening point the coal is restructured by cross-linking, which results in a decrease of extraction yield. Thus, the extraction could be proceeded more easily at around the softening point regardless of the polarity of the solvent. In case of LRC, however, there is no softening temperature at which the structure becomes relaxed, so it was needed to destroy

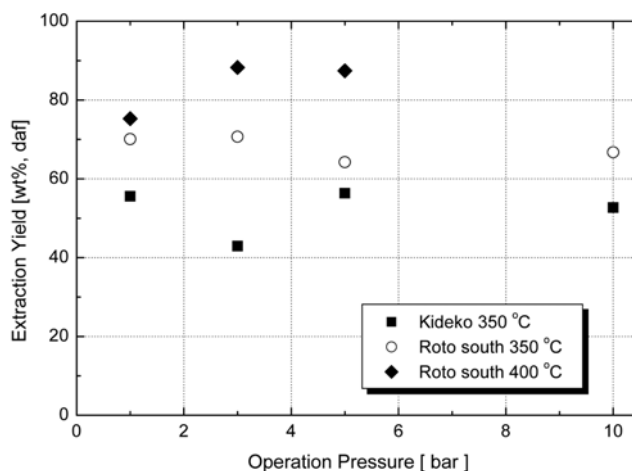


Fig. 3. Variation of extraction yield with initial applied pressure.

the structure using polar solvent in order to increase the extraction yield.

Fig. 3 shows the effect of pressure on the extraction yield of Kideko and Roto South coal. Pressure rise of the extractor was quite different from the change of the initial applied pressure. When the initial applied pressure was 1 bar, the highest pressure inside the vessel increased up to 10–15 bar, and at 5 bar and 10 bar, the inside pressure climbed up to 30–50 bar and over 50 bar, respectively. Despite the rise of initial applied pressure, however, the extraction yield was below 60% in Kideko coal and around 70% in Roto South coal, showing no significant change. However, when extraction temperature was 400 °C, the extraction yield at initial applied pressure of 1 bar was around 75% but if the initial applied pressure was increased to 3 bar, the yield increased by up to 90%. These results suggest that the initial applied pressure does not have a significant effect on the extraction yield, and extraction yield can be enhanced more by increasing extraction temperature rather than initial applied pressure.

Fig. 4 shows a variation of the extraction yield associated with extraction time in Kideko coal. When extraction temperature was maintained constantly at 350 °C, the extraction yield increased from

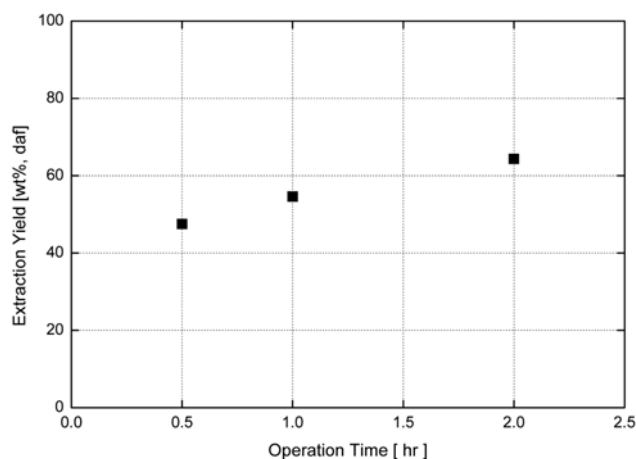


Fig. 4. Variation of extraction yield with extraction time for the Kideko coal (350 °C, 1 bar).

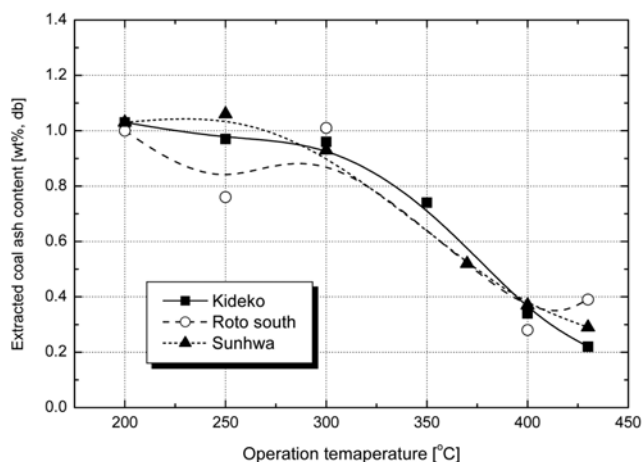


Fig. 5. Variation of ash content of extracted coal with extraction temperature.

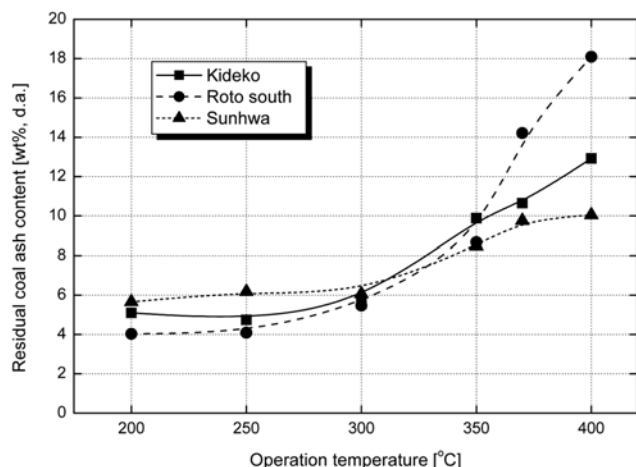


Fig. 6. Variation of ash content of residual coal with extraction temperature.

50% to 65% with the extension of reaction time to 0.5 hour, 1 hour and 2 hours gradually.

2. Ash Content

Figs. 5 and 6 show variation of the ash content in extracted coal and residual coal associated with the extraction temperature. As in Fig. 5, it was common in all kinds of coal samples that the ash content in extracted coal decreased with the increase of extraction temperature. Up to 300 °C, the ash content maintained between 0.9% and 1% but began to decrease rapidly from 350 °C and to reach 0.2–0.4% level at 400 °C. Fig. 6 shows variation of ash content in residual coal with the extraction temperature. Up to 300 °C, ash content in residual coal was not much different from the raw coal; however, the ash content in residual coal increased sharply with the increase of extraction temperature beyond 300 °C.

Figs. 7 and 8 show the changes of the ash content in extracted coal and residual coal with initial applied pressure for the Kideko and Roto South coal samples. As in Fig. 7, no particular change caused by the increase of initial applied pressure was observed with the extraction temperature. Just when extraction temperature was increased to 400 °C, ash content was below 0.3%. Accordingly, as

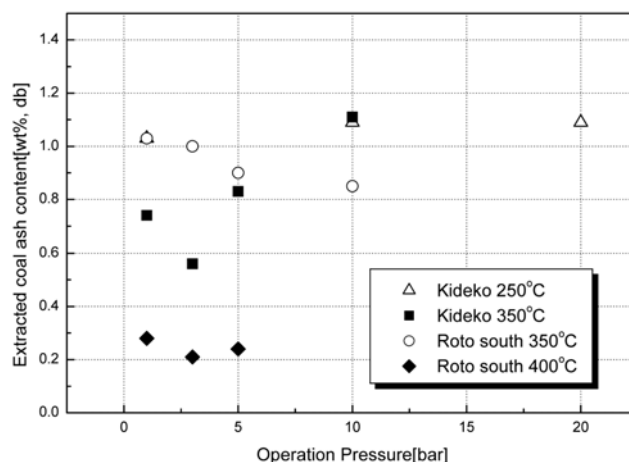


Fig. 7. Variation of ash content of extracted coal with initial applied pressure.

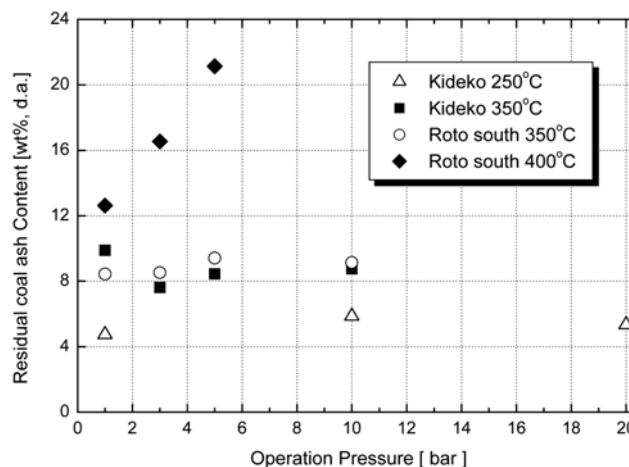


Fig. 8. Variation of ash content of residual coal with initial applied pressure.

mentioned earlier, it is considered desirable to raise extraction temperature rather than to raise initial applied pressure in order to achieve lower ash content in extracted coal. Fig. 8 shows the change of ash content in residual coal associated with the change of the initial applied pressure. Despite the increase of initial applied pressure, the ash content in residual coal showed no significant difference as long as extraction temperature remained the same. However, the ash content in residual coal increased slowly with the rise of extraction temperature.

Fig. 9 shows the changes of the ash content in extracted and residual coal for the Kideko coal along with the change of extraction time. The ash content in extracted coal was 1.1% when reaction time was 0.5 hour, and it decreased slowly to 0.9% after 1.0 hour and 0.6% after 2 hours. This is, as explained above, because the amount of organic components dissolved into the solvent increases over extraction time. Fig. 9 also shows the change of the ash content in residual coal with extraction time. Contrary to the case of extracted coal, the ash content in residual coal increased with the increase of extraction time.

3. Changes in the Characteristics of Coal

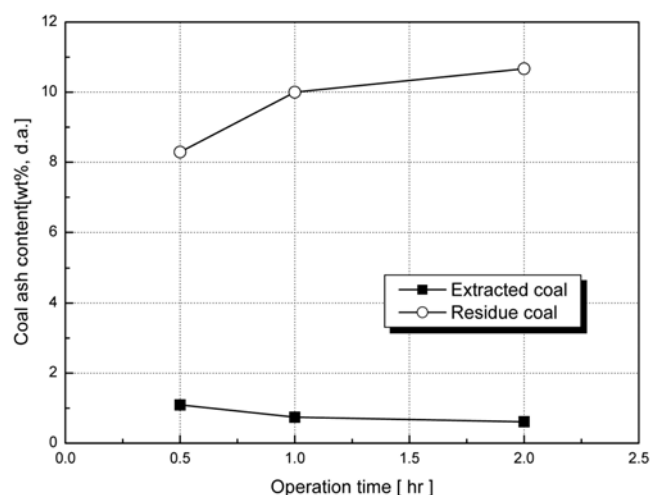


Fig. 9. Variation of ash content of extracted and residual coal for the kideko coal samples with extraction time.

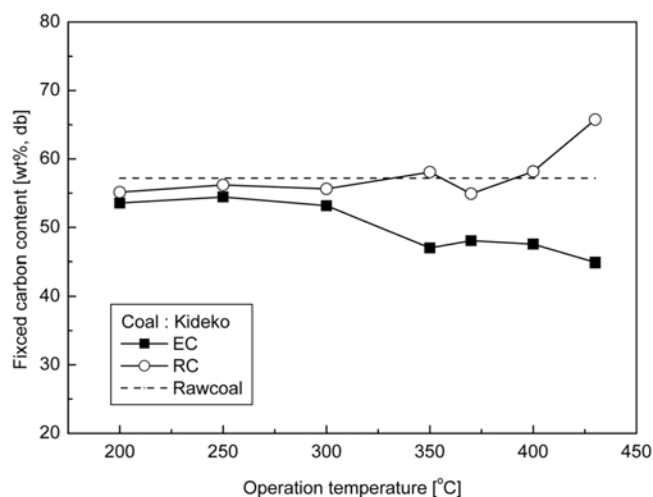


Fig. 11. Variation of fixed carbon contents with extraction temperature.

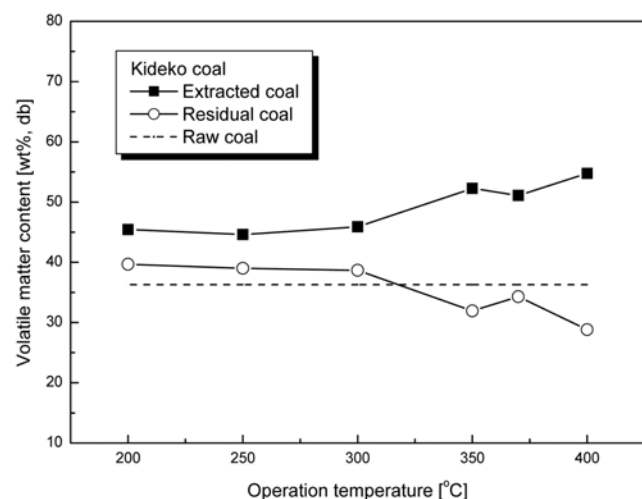


Fig. 10. Variation of volatile matter contents with extraction temperature.

Fig. 10 shows a variation of volatile matter content with the extraction temperature for extracted coal and residual coal for the Kideko coal samples. In the extracted coal, volatile matter increased because the quantity of organic components which were separated from the raw coal and dissolved into the solvent, increased with the hike of extraction temperature. In residual coal, on the contrary, volatile components decreased with the increase of extraction temperature.

Fig. 11 shows variation of fixed carbon with the extraction temperature for extracted coal and residual coal for the Kideko coal samples. Fixed carbon was less in extracted coal than in raw coal, and it decreased with the rise of extraction temperature. It was larger in residual coal than in extracted coal and increased slightly with the rise of extraction temperature.

Table 2 shows the results of proximate, ultimate analysis and calorific values of extracted coal and residual coal. According to the results of ultimate analysis, the total carbon content in extracted coal increased up to 81-84%. The total carbon content in residual coal

Table 2. Analytical results for the extracted and residual coal

| Coal | | Temp. (°C) | Pre. (bar) | Yield | Proximate analysis | | | | Ultimate analysis(wt%, db) | | | | | H/C | O/C | Calorific value (kcal/kg) |
|-----------------------|----|---------------|---------------|-------|--------------------|-------|-------|-------|----------------------------|------|------|------|------|------|------|------------------------------|
| | | | | | M | VM | Ash | FC | C | H | N | O | S | | | |
| Roto south coal | EC | 370 | 1 | 78.95 | 0.37 | 53.82 | 1.25 | 44.56 | 81.25 | 6.20 | 5.97 | 5.26 | 0.07 | 0.92 | 0.05 | 7,870 |
| | RC | 370 | 1 | 78.83 | 1.44 | 36.34 | 14.01 | 48.21 | 69.00 | 4.50 | 4.31 | 8.11 | 0.07 | 0.78 | 0.09 | 6,280 |
| | EC | 400 | 1 | 87.97 | 0.72 | 46.50 | 0.28 | 52.20 | 83.00 | 6.09 | 7.47 | 3.14 | 0.02 | 0.88 | 0.03 | 8,030 |
| | RC | 400 | 1 | 86.56 | 0.76 | 31.41 | 17.95 | 49.88 | 68.76 | 4.21 | 4.28 | 4.63 | 0.17 | 0.73 | 0.05 | 6,200 |
| Kideko coal | EC | 370 | 1 | 60.93 | 1.45 | 50.35 | 0.85 | 47.35 | 81.05 | 6.13 | 5.81 | 6.10 | 0.06 | 0.91 | 0.06 | 7,790 |
| | RC | 370 | 1 | 59.86 | 1.41 | 33.81 | 10.65 | 54.13 | 73.35 | 4.21 | 4.19 | 7.19 | 0.41 | 0.69 | 0.07 | 6,510 |
| | EC | 400 | 1 | 66.59 | 0.92 | 54.26 | 0.33 | 44.48 | 83.90 | 6.04 | 6.70 | 2.93 | 0.05 | 0.86 | 0.03 | 8,070 |
| | RC | 400 | 1 | 65.53 | 0.91 | 28.55 | 12.92 | 57.63 | 75.17 | 4.16 | 3.67 | 3.77 | 0.31 | 0.66 | 0.04 | 6,750 |
| Sunhwa coal | EC | 370 | 1 | 52.34 | 0.67 | 48.81 | 0.51 | 50.01 | 82.80 | 6.22 | 6.08 | 4.33 | 0.06 | 0.90 | 0.04 | 7,980 |
| | RC | 370 | 1 | 62.17 | 0.80 | 30.93 | 9.69 | 58.59 | 76.95 | 4.38 | 3.98 | 4.75 | 0.25 | 0.68 | 0.05 | 6,950 |
| | EC | 430 | 1 | 49.22 | 0.57 | 41.30 | 0.28 | 57.84 | 84.15 | 5.83 | 9.86 | 0.14 | 0.02 | 0.83 | 0.00 | 8,080 |
| | RC | 430 | 1 | 53.07 | 0.57 | 30.84 | 7.15 | 61.44 | 80.00 | 4.60 | 5.79 | 2.24 | 0.22 | 0.69 | 0.02 | 7,270 |

was similar to that in raw coal, or slightly higher in case of Sunhwa coal. The sulfur content showed considerable decrease in the extracted coal compared to that in raw coal. In case of Roto South coal, no significant change was observed since the sulfur content in the raw coal was low. However, in Kideko and Sunhwa coal, the sulfur content decreased by around 80% compared to that of the raw coal. The inorganic sulfur in extracted coal by solvent extraction is completely removed, and only some organic sulfur remained. Therefore, the sulfur content in extracted coal decreased comparing with that in raw coal decreased. In residual coal, the sulfur content was similar to or slightly higher than that in the raw coal.

As shown in Table 2, extracted coal has a calorific value of about 7,870-8,080 kcal/kg, around 20-30% higher than that of the raw coal. In case of Roto South coal, Hydrogen/Carbon atomic ratio decreased compared to the raw coal. However, in Kideko and Sunhwa coal, H/C increased slightly. In both extracted coal and residual coal, Oxygen/Carbon atomic ratio decreased significantly compared to that in raw coal.

The increases of total hydrocarbon and calorific value and the decreases of H/C and O/C in extracted coal showed a significant change of raw coal. This trend showed that the extracted and residual coal could change both physically and chemically through thermal extraction.

CONCLUSIONS

The present study conducted experiments to produce low ash coal from three kinds of coal samples by means of thermal extraction process using NMP (N-methyl-2-pyrrolidinone) as a solvent. In the experiments, the variables such as extraction temperature, initial pressure applied, extraction time were changed and the extraction yield, ash content and other properties of extracted coal and residual coal were examined. The results are summarized as follows.

In all kinds of coal samples used in the experiment, the extraction yield increased with the increase of extraction temperature. In case of Roto South coal, which is sub-bituminous coal, the extraction yield was over 70% at a temperature of 350 °C and beyond. In addition, Sunhwa coal, which is bituminous coal, showed the highest extraction yield at 400 °C and then the yield decreased at a higher temperature, whereas Roto South and Kideko coals showed continuous increase of extraction yield with the increase of temperature. The extraction yield was higher in sub-bituminous coal than in bituminous coal because of the polar solvent used.

In extracted coal produced through thermal extraction process, the ash content decreased with the increase of extraction tempera-

ture, down to 0.21% at around 400 °C. This is because high extraction temperature makes coal structure loose through the thermal extraction by solvent, and as a result organic components can be extracted easily. Initial applied pressure appeared to have little effect on the extraction yield and the ash content. The increases of total hydrocarbon and calorific value and the decreases of H/C and O/C in the extracted coal showed significant physical and chemical changes from the raw coal.

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