

Gasification of ash-free coal prepared with microwave method

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Abstract—The production of ash-free coal as a clean fuel for high temperature fuel cell was investigated. The ash-free coal was made from a bituminous coal. It was prepared by solvent extraction using a microwave. The solvent-to-coal ratio and microwave irradiation time of raw coal were parameters for the extraction yield. The microwave method showed merits in terms of faster extraction and higher extraction yield than conventional heating methods. In addition, gasification behaviors of the ash-free coal were investigated by gas chromatography. Contrary to carbon, ash-free coal showed hydrogen as a dominant gas species in its gasification and did not require carbonate catalyst. The electrical conductivity of ash-free coal was found very low close to zero.

Keywords: Ash-free Coal, Solvent Extraction, Microwave, Molten Carbonate, Gasification

INTRODUCTION

Most fuel cells run with hydrogen fuel. In particular, molten carbonate fuel cells (MCFCs) and solid oxide fuel cells (SOFCs) have high operating temperatures, which allows reforming of methane inside the stack. Consequently, these systems are known as natural gas-based power systems. Generally, natural gas is not an economic energy source because of limited production and high cost for using. But it has very clean characteristics than other liquid and solid fuels. The high cost of natural gas is a hurdle for fuel cell commercialization. On this basis, recent focus has been on the direct carbon fuel cell (DCFC) as a power source.

Coal is a relatively abundant and economic energy source. However, a solid fuel has limited application because of difficulties in the transportation and ash treatment. For the clean use of coal, two processes for the ash-free coal (AFC) are under development: removing ash from the coal by acid or base treatment [1], and extracting organic compounds from the coal [2].

There are four steps in an AFC production by extraction: (1) mixing of coal with solvent to make slurry, (2) heating the slurry to extract organic materials from the coal, (3) separation of solid and liquid, and (4) solidification of the liquid to make AFC. Okuyama et al. reported that AFC is an economic source of energy regardless of these multi-process preparations, because it has a high calorific value and does not require ash treatment [3].

At the early stage, AFC was produced at room temperature. Iino et al. reported that they had ca. 60% of extraction yield (daf, dry-ash-free base) from a bituminous coal with a 1 : 1 ratio of N-methyl-2-pyrrolidinone (NMP) [4]. However, most cases reported that room temperature gave very low extraction yields [2]. Renganathan et al. reported that they had ca. 60% of extraction yield with NMP at the boiling point of 202 °C [5]. It was also reported that quinoline

at 1 MPa and 350 °C allowed ca. 80% of extraction yield [6]. Miura et al. used tetralin as an aprotic solvent and they had 65-80 wt% of extraction yield (daf) with their own continuous extraction equipment at 350 °C [7]. Li et al. compared two different polarity solvents, 1-Methylnaphthalene (1-MN) as an aprotic solvent and NMP as a polar one, by continuous extraction for 1 hr at 1 MPa and 360 °C, and they concluded that NMP had ca. 30-40% higher extraction yields than 1-MN [8]. Zhang et al. also compared solvent effect by using aprotic 1-MN and a mixture of 1-MN and protic indole (20 wt%) at 360 °C and 1 MPa [9]. They concluded that the mixture solvent had higher extraction yield by ca. 15% than 1-MN. Yoshiie et al. used 1-MN as a solvent and two different solvent-to-coal ratios at 360 °C [10]. They reported that a high solvent-to-coal ratio resulted in higher extraction yield. Li et al. also reported that acid pretreatment of coal with methoxyethoxy acetic acid (MEAA) raised extraction yield because acid removes metal ions of Mg²⁺ and Ca²⁺ and it relaxes cation cross linking in the coal [8].

Recently, Somnez et al. reported that microwave irradiation (MI) could be an effective heating method for the AFC production [11]. They used the polar solvents NMP and ethylenediamine (EDA) and the non-polar solvent tetralin. It was concluded that extraction yields with MI were comparable to those using the conventional heating method. Lei et al. also reported that an ionic liquid, 1-butyl-3-methyl-imidazolium chloride ([Bmim]Cl) is very effective for extracting Chinese lignite with the microwave method [12]. They compared lignite and sub-bituminous coals and concluded that the ionic liquid had about four times higher extraction yield for the lignite.

Lee et al. reported that carbon with carbonates was oxidized to carbon monoxide at over 700 °C and ca. 62 mol% of CO was produced [13]. The carbon chemically reacts with carbonate to produce carbon monoxide (Eq. (1)).



In this case, carbonates behave as a catalyst for the oxidation. It was also reported that carbon gasification with steam produced H₂

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as a dominant species [14].

Coal gasification is very similar to carbon gasification. In general, coal gasification has been carried out over 750 °C and carbonate has been used for the gasification catalyst. Steam has mostly been employed to produce H₂ during coal gasification.

However, the gasification behavior of AFC with molten carbonate has rarely been reported. In this work, AFC for the DCFC was produced from a bituminous coal using the MI method. Solvent-to-coal ratio and microwave irradiation time were parameters for the extraction yields. In addition, gasification behaviors of AFC were investigated in relation to temperature and AFC to carbonate combination.

EXPERIMENTAL

Berau bituminous coal was ground to be 70 mesh sizes. A certain ratio of coal powder and NMP was mixed in a rounded flask and placed in a microwave. The coal amounts used were 5 g, 10 g and 20 g, and the solvent amounts were 80 ml and 140 ml. The microwave was a commercial one made by LG Co. in Korea with up to 1 kW output power. The upside of the flask was connected to a water cooling condenser, as shown in Fig. 1. The microwave reached 202 °C during 30 min preheating and the temperature was held for 5, 10, and 30 min.

The microwave-treated slurry was filtered with a glass filter to separate solid and liquid phases. The liquid contained extracted coal and solvent, while the solid was residual coal. The extracted coal was dried in a vacuum oven for 40 hrs at 160 °C and became AFC. The extraction yield of AFC was determined as follows:

$$\begin{aligned} \text{Extraction yield (wt\%, daf)} \\ = \frac{\text{feed coal (daf)} - \text{residue coal (daf)}}{\text{feed coal (daf)}} \times 100 \end{aligned} \quad (2)$$

Industrial analyses of coal, such as water, volatile material and fixed carbon content, were carried out with a TGA-701 (LECO). Elemental analyses of C, H, O, N were conducted using an analyzer (Thermo, EA1108). Organic bonds in the coal were analyzed by Fourier transform infrared spectroscopy (FT-IR, Nicolet 6700). Thermo-gravimetric analysis (TGA, MettlerToledo 851) was also

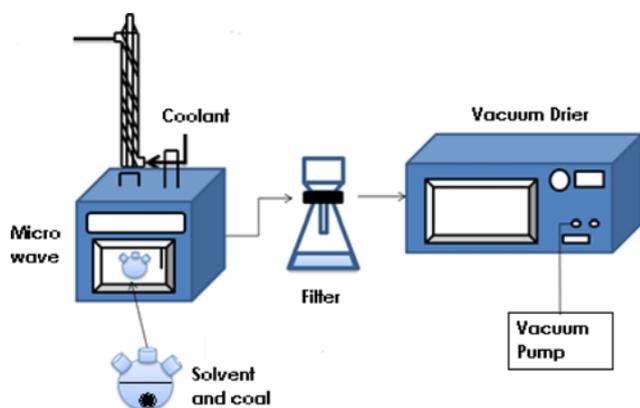


Fig. 1. Atmospheric microwave irradiation system for the solvent extraction from raw coal.

used to investigate thermal behavior with 10 °C/min rate and 0.1 L/min N₂ flow. The structure of coal was analyzed with an XRD (Rigaku, D/MAX2500H). The electrical conductivity of AFC was also measured with a resistivity meter (MCP-T370, Mitsubishi Chemical Analytech).

The gases released from AFC with increasing temperature were analyzed by gas chromatography (HP 5890II). The AFC 3 g only or a mixture of AFC 3 g and 3 g of molten carbonates (62 mol% Li₂CO₃+38 mol% K₂CO₃) was put in an alumina tube 1.5 cm in diameter and 10 cm in length (Fig. 2). Both ends were plugged with Ni foam to prevent leakage of coal powder, so that gas could come out of the alumina tube. This small alumina tube was inserted in a larger alumina tube (3 cm ID, 25 cm length and open at one end). The alumina tube was set in a furnace which had a hole to insert the tube. The open end of the tube was plugged with glass wool. A 1.5 mm diameter alumina tube was installed to sample the gas inside.

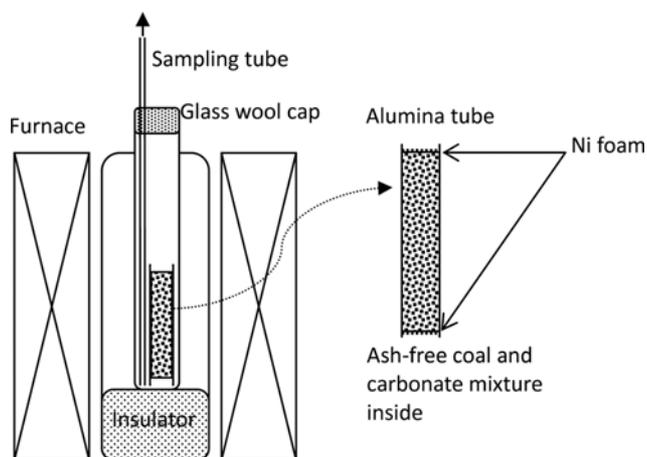


Fig. 2. Gas sampling system from AFC and carbonate mixture.

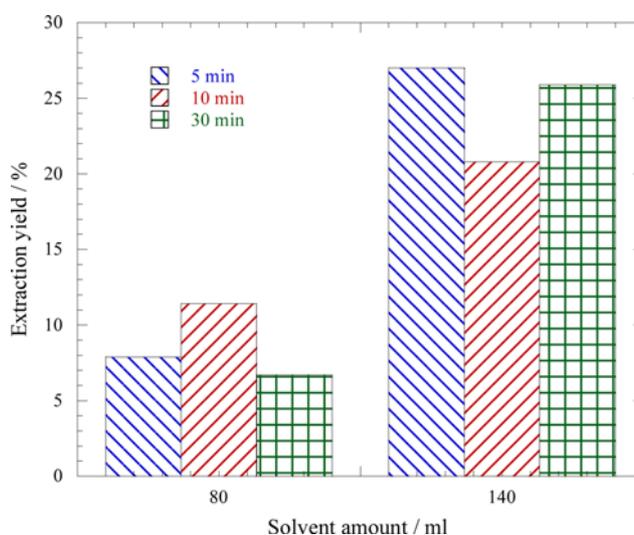


Fig. 3. Comparison of extraction yields in terms of solvent amounts with a fixed 5 g of raw coal at 202 °C. The bars indicate three times of repeated experiments for 5, 10, and 30 min holding, respectively.

Temperature started at 100 °C and was increased to 900 °C in 100 °C increments with 10 °C/min rate. At each step a gas sample was collected and analyzed.

RESULTS AND DISCUSSION

Fig. 3 compares the solvent-to-coal (S/C) ratio with the extraction yields. In this case, 5 g of coal was used. The results show that high S/C ratio definitely gives high yield. About twice the solvent amount results in almost triple the yield. This behavior can be explained by the microwave absorption by the polar solvent. A polar solvent has higher microwave absorbance than a non-polar one [11]. Thus, a larger amount of solvent effectively interacts with coal and extracts organic materials. As shown in Fig. 3, the radiation time cannot be a dominant factor for the extraction. According to Somnez et al. [11], over 10 min of irradiation results in negligible differences in the extraction yield. In this work, over 5 min of holding time for irradiation resulted in insignificant differences in the extraction yields. This is acceptable because there is 30 min of preheating to 202 °C, which is enough time to extract AFC sufficiently.

Fig. 4 shows the effect of coal amount at a fixed solvent amount of 140 ml. Increasing the amount of coal reduces the S/C ratio and yields. As mentioned, high yield can be obtained at a high S/C ratio. In addition, the effect of holding time is found not to be a domi-

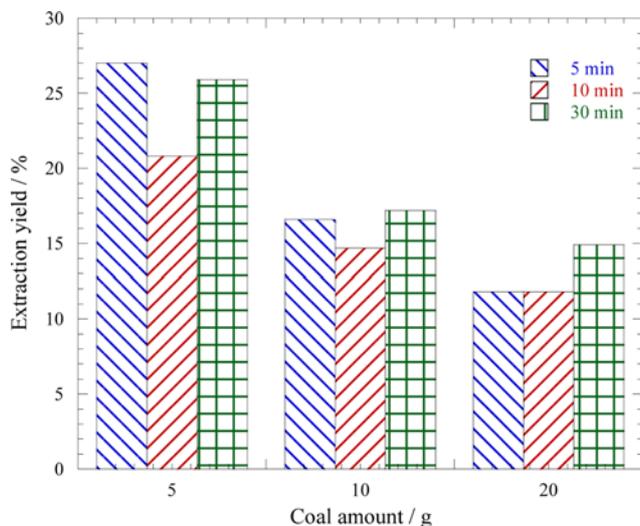


Fig. 4. Comparison of extraction yields in terms of coal amounts with a fixed 140 ml of solvent at 202 °C. The bars indicate three times of repeated experiments for 5, 10, and 30 min holding, respectively.

Table 1. Proximate analysis of raw coal and AFCs from conventional thermal extraction and microwave irradiation method

	Raw coal	Thermal extraction	Microwave irradiation
Moisture (wt%)	15.74	2.35	2.14
Volatile (wt%)	41.06	52.74	51.34
Ash (wt%)	7.78	1.61	1.37
Fixed carbon (wt%)	35.42	43.29	45.15

nant parameter at the S/C ratios as shown in Fig. 3.

Table 1 compares proximate analysis of the raw coal and AFC with microwave irradiation (MI) and the conventional heat method. The results of the heat method and MI show similarity among the parameters. Water and ash components are drastically decreased in the AFC compared with raw coal. Since the solvent dissolves organic components from the coal and then dried, the AFC has very low amount of ash and water. However, the ash content of AFC with MI is 1.37 wt%. This is 13,700 ppm of ash, which is a much larger amount than 200 ppm as a general limit for the AFC. The reason is related to the point that a polar solvent has high interaction with coal, so that the polar solvent of NMP has larger ash content (0.51-1.25 wt%) than non-polar one of 1-MN and LCO (0.02-0.14 wt%) at the same temperature of 370 °C [15,16]. From a previous work [16], the components of ash in Berau coal are Fe₂O₃ (32.7 wt%), SiO₂ (29.7 wt%), Al₂O₃ (19.3 wt%), CaO (10.1 wt%), and other minor species of MgO (2.9 wt%) and K₂O (1.6 wt%).

Table 2 shows the ultimate analysis of raw and AFCs. Components of N, H, and O are increased by the MI treatment. Since NMP has N, H, O elements, their increases can be accepted.

Fig. 5 shows XRD data for raw coal and AFC. The raw coal shows very broad peaks, which indicates a typical amorphous structure. Very similar pattern for the AFC also represents its amorphous structure.

Fig. 6 compares TGA behaviors of raw coal and AFC. The steep decrease for the raw coal up to 100 °C is probably due to water evap-

Table 2. Elemental analysis of raw coal and AFC with microwave method

	Raw coal	AFC
N (wt%)	1.32	2.90
C (wt%)	72.46	72.23
H (wt%)	4.08	5.24
O (wt%)	14.16	18.26
Ash (wt%)	7.78	1.37

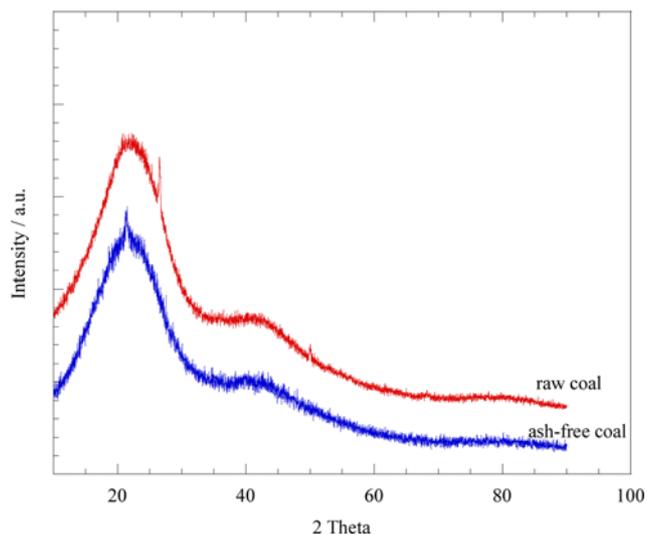


Fig. 5. XRD patterns of raw coal and AFC.

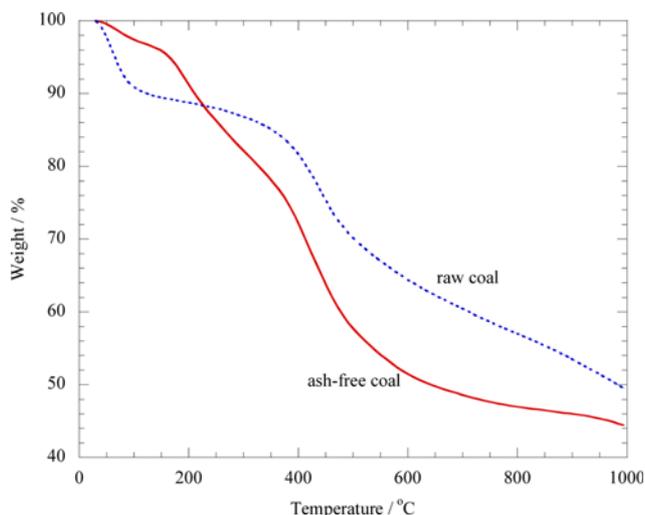


Fig. 6. TGA results of raw coal and AFC with 10 °C/min under 0.1 L/min N₂ environment.

oration because the Berau coal was used as received. Then another rapid decomposition is observed over 400 °C for the raw coal. Organic species should be responsible for this weight loss. On the other hand, the AFC shows a mild decrease up to 190 °C because it was vacuum dried. The decomposition is responsible for the very volatile materials. Over 200 °C a steeper decrease in the weight is observed until 400 °C. Then further rapid decomposition is obtained above 400 °C. Finally, the decomposition diminishes and arrives at ca. 45% at 1,000 °C. The TGA was carried out under N₂ condition, and most organic materials decompose above 300 °C, so the remains at 1,000 °C would be carbon species. Considering ca. 8 wt% of ash content in the raw coal, the weight difference between the raw coal and AFC at 1,000 °C can be acceptable. Therefore, about 50% of organic materials are decomposed up to 1,000 °C.

Fig. 7 shows FT-IR spectra of raw coal with solvent (ml)-to-coal

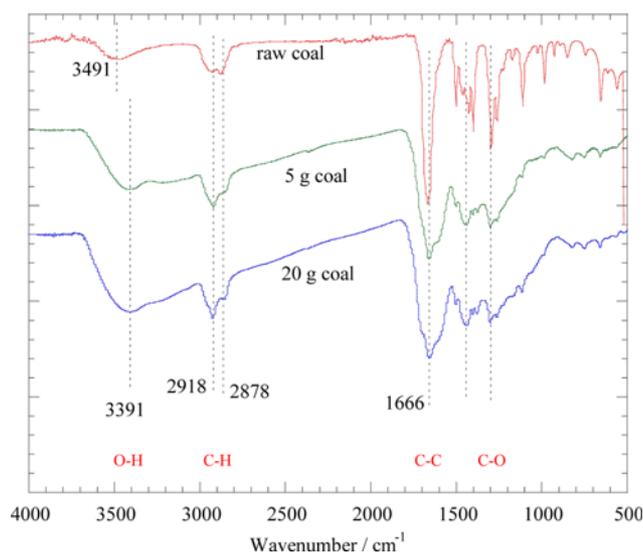


Fig. 7. FTIR patterns of raw coal and AFCs from 5 g (S/C=28/1) and 20 g (S/C=7/1) raw coals to 140 ml solvent.

(g) (S/C) ratios of 28/1 and 7/1. As 140 ml of solvent were used in all cases, coal amounts were 5 g and 20 g, respectively. At 3,492 cm⁻¹, small absorption is observed for the raw coal, while AFC has a much larger peak at 3,391 cm⁻¹. Those two peaks could be attributed to the O-H bond. Lei et al. reported that reduction of O amount in the AFC reduced the peak height of 3,420 cm⁻¹ [12]. The AFC in this work had a larger amount of O species than the raw coal. Thus, the increased O amounts in the AFC enlarged the peak height. The two peaks at 2,918 and 2,878 cm⁻¹ are due to C-H bonds, and the height ratio between them is reversed in the AFC. The peak at 1,666 cm⁻¹ is mainly due to the C=C bond in the aromatic ring, and the peak at 1,300 cm⁻¹ is mostly due to the C-O bond. Therefore, the AFC has various chemical bonds among C, H, and O.

The electrical conductivity of AFC was close to zero and found to be non-conductive material. Since the solvent dissolves the organic species from the coal and then it is dried to be a solid, the AFC becomes an organic solid material and its non-conductivity can be accepted.

For the coal gasification, air or oxygen is introduced to the reactor to maintain the temperature by burning coal. Thus the outlet gas composition is determined by the inlet gas species. An air inlet makes a nitrogen gas mixture for the outlet gas, while oxygen only produces C, H, and O mixed compounds.

Molten carbonate based DCFC generally uses carbon and carbonate mixture for the anode fuel. The carbonate behaves as a catalyst for the carbon oxidation to the carbon monoxide. Since the DCFC has difficulty in the gas sealing inside, inert gas is introduced into the anode chamber to increase the gas pressure inside and to prevent oxygen diffusion from outside. In a previous work, humidified nitrogen and air flow produced H₂ as a main gas component in the carbon and carbonate mixture at 800 °C [14]. It indicates that steam reforming of AFC is possible in the DCFC.

To investigate the oxidation process of AFC in a DCFC, we measured gas composition without flowing any gas species into the anode. Fig. 8 shows gas composition changes with only 3 g of AFC according to the temperature rising. The temperature was increased incrementally up to 900 °C, and at each temperature gas analysis was carried out with three times using a gas chromatography. At 100 °C,

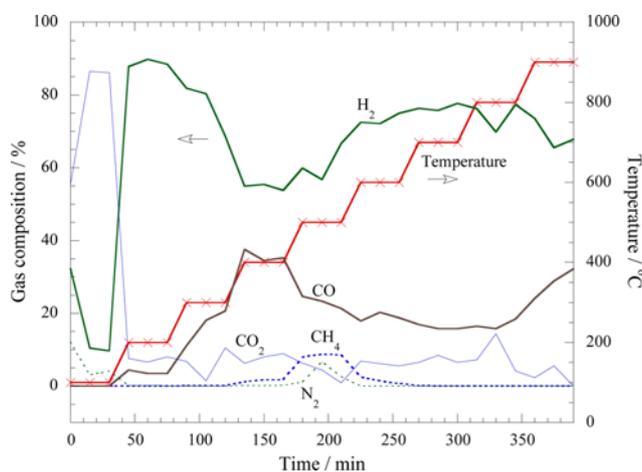


Fig. 8. Gas compositions from only 3 g of AFC during step like temperature rising from 100 °C to 900 °C.

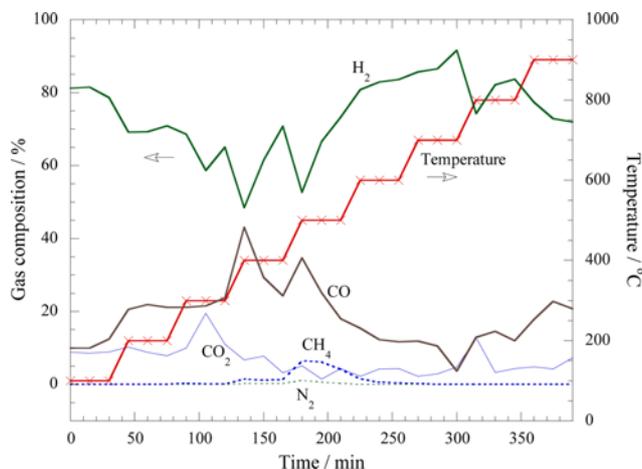


Fig. 9. Gas compositions from 3 g of AFC and 3 g of Li-K carbonates during step like temperature rising from 100 °C to 900 °C.

a significant amount of CO_2 was observed at the bottom of the AFC container. In general, carbon cannot be burnt at this temperature. The reason is as yet unclear, but it is plausible that CO_2 -containing compounds would be decomposed. At 200 °C, over 80% of H_2 was observed. Contrary to the carbon gasification, AFC produces a sufficient amount of H_2 even at 200 °C. From 300 °C, CO generation is observed. It is maximized at 400 °C, and CO composition is reduced above this temperature. The species of CH_4 and N_2 are observed at 500 °C, and these components are liberated from the AFC. Above 600 °C, the gas compositions are invariable up to 900 °C.

Fig. 9 shows gas generation of 3 g AFC and 3 g of carbonate mixture. At 100 °C, a very large amount of H_2 and low amount of CO_2 are observed. Except for the behavior, the composition change with temperature is very similar to those of Fig. 8. Even with the molten condition of carbonate over 500 °C, the gas compositions are comparable to those in Fig. 8. The similarity of gas composition with temperature between Figs. 8 and 9 indicates that carbonate may not behave as a catalyst for the gasification of AFC. Unlike carbon, AFC contains various compounds and their gasification progresses without the need for a catalyst.

CONCLUSION

AFC production from a bituminous coal has been conducted by using a solvent extraction method with a microwave. The microwave irradiation method has very fast extraction time compared with the conventional heating method; ca. 30 min was sufficient to extract AFC, while the conventional heating method took ca. 24 hrs. The AFC yield was significantly dependent on the solvent-to-coal (S/C) ratio; high S/C ratio gave high yield. The structure of AFC

was amorphous and very similar to the original coal according to XRD measurement. The chemical bonding of AFC was very similar to that of the original coal except for a stronger O-H bond in the AFC. The gasification of AFC with and without carbonate from 100 °C up to 900 °C was very similar; H_2 was the dominant gas species for all temperature ranges and CO was the second largest species. The species of CO_2 , CH_4 and N_2 had minor compositions. The results indicate that the gasification of AFC did not require a carbonate catalyst.

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