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Sulfur removal from coal with supercritical fluid treatment

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Abstract−Conversion and sulfur removal of coal in sub- and supercritical water was studied in a micro reactor in the temperature range of 340-400 °C and water density 0-0.27 g/cm^3 for 0-90 min under N_2 atmosphere. The experiments were conducted to investigate the effect of reaction temperature, pressure, time and density of water on the sulfur removal in gaseous and liquid effluents, respectively. The results show that supercritical condition is more effective than sub-critical condition to remove the sulfur from coal. It is possible to reduce 57.42% of the original sulfur in coal for the reaction time of 90 min at 400 °C and 30 MPa. The main gas containing sulfur in the gaseous effluent is not SO_2 but H_2S, irrespective of operating condition. The sulfur removal in liquid effluents is much greater than that in gas effluents. Compared with temperature, the influence of water density and pressure is less significant.

Key words: Datong Coal, Supercritical Water, Sulfur Removal, Sub-critical Condition, Bituminous Coal

INTRODUCTION

Coal is still the major source of power for electrical generation worldwide and will continue to be used in the future. However, the severe pollution and hazardous emissions from combustion of the coal hinder its wide use as the main energy source in the future. Recently, many efforts have been devoted to develop so-called clean coal technology for removing trace elements as well as sulfur prior to burning the coal [1,2]. Desulphurization of coal involves the removal of both the inorganic and organic forms of sulfur. Several physical and a few chemical methods are available for the removal of inorganic sulfur. Removal of organic sulfur requires the use of chemical cleaning methods. Recently, supercritical water (SCW) processing of coal has been receiving increasing attention because the physicochemical properties of SCW can be easily controlled by the reaction temperature and pressure. Supercritical water (T_c= 374 °CK and P_c=22.1 MPa) is the dense fluid and thus can be made miscible with light gases such as H_2, CO and O_2. Above 350 °C, water becomes miscible with oils and aromatics, since the dielectric constant of supercritical water is reduced from 2 to 20, which is similar to that of polar organic solvents at room temperature. Reaction and sulfur removal processes of coal in SCW reported in the literature include hydrolysis and pyrolysis of coal in SCW [3-5], liquefaction of coal in SCW [6-8], extraction of coal with SCW and SCW mixtures [9-11], and desulfurization of coal with SCW [1,12-14].

This work presents the results of a sulfur removal technology using supercritical water. The objective of this study is to understand the transformations of sulfur in coal by supercritical treatment. A high rank coal (Datong) with total sulfur of 0.84 wt%, daf was extracted employing water under supercritical conditions with a micro reactor and molten salt bath. The experiments were conducted to investigate the effect of reaction temperature, time and dielectric constant of supercritical water on gas and liquid product, respectively.

EXPERIMENTAL

1. Material

The coal used in the experiments is Chinese Datong coal, which is bituminous coal. The entire coal sample used was pulverized powder of less than 200 mesh. Table 1 shows the proximate and ultimate analyses of this coal. Solvents used were tetrahydrofuran (THF, 99.9%, Aldrich,) and deionized water prepared by pure water fabricator (S. A. 67120, Millipore Co., U.S.A.).

2. Experimental Apparatus and Procedure

Fig. 1 shows the schematic diagram of the experimental apparatus and micro reactor. A micro reactor with I.D. 25.7 mm made of stainless steel (around 42.3 ml) was used as pressurized reactor, which was heated by a temperature-controlled molten salt bath. A pressure gauge and gas outlet port were connected with the reactor through stainless tube, T union and on-off valve. Temperature and pressure in the reactor were measured with a K-type thermocouple and a pressure gauge, respectively.

In each run, the reactor was charged with 2 g Datong coal and

Table 1. Characteristics of coal sample

Proximate analysis (wt%)				
Moisture	Volatile matter	Ash	Fixed carbon	High heating value (kcal/kg)
10.62	27.74	7.95	53.69	7.020
Ultimate analysis (wt%, daf)				
C	H	N	S	O (difference)
75.0	4.48	1.03	0.84	18.65

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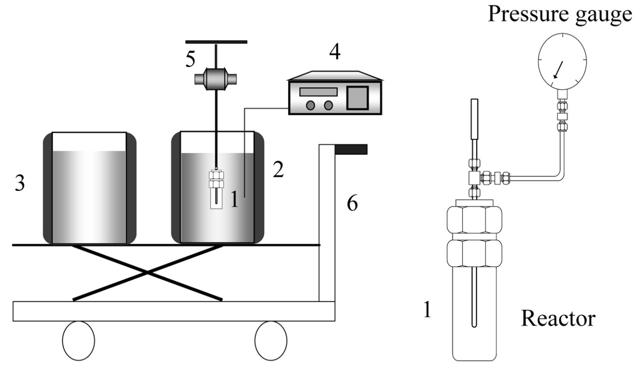

Fig. 1. Schematic diagram of experimental apparatus.
1. Micro reactor
2. Molten salt bath
3. Water bath
4. Temperature indicator
5. Shaker
6. Mover

2-30 g water which was calculated by water density under reaction temperature and pressure condition. Pressurized flushing with nitrogen was carried out to ensure the removal of oxygen and then the micro reactor was sealed. Though around 2 min is required to reach reaction temperature when a micro reactor put into molten salt bath, the reaction time is defined as the residence time in molten salt bath because a reaction can occur during the heating time. After reaction time, to terminate reaction, the micro reactor was taken out of the molten salt bath and suddenly cooled down to room temperature by placing it in water. Product gas was collected in a syringe and analyzed by the following procedure. The unreacted residue was collected from the reactor and filtered to separate the water. Then the residue after filtration and the product adhering to the inner wall of micro reactor and the connection tubes were washed out with tetrahydrofuran (THF). This final residue was separated from the slurry (mixture of THF solution and residue) by filtration through 1.2 μm glass filter. The solution separated by filtration is defined as THF solution.

3. Analyses

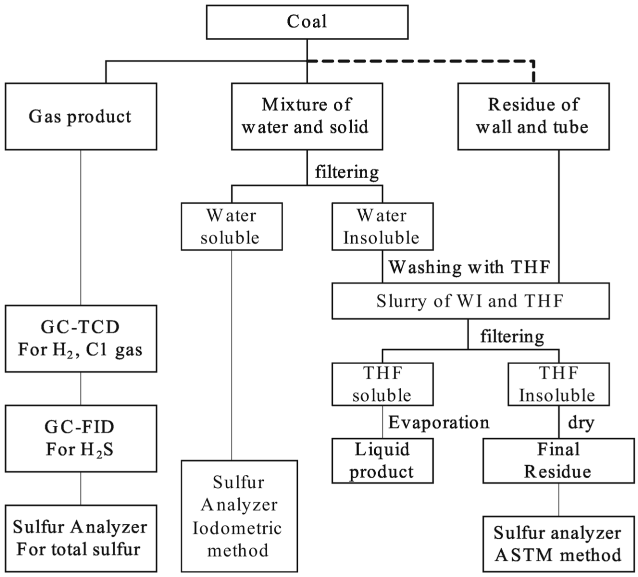

Fig. 2. The analysis procedure.

The procedure of analysis is shown in Fig. 2. Residue obtained after final filtration was dried in an oven at 60 °C, for 4 h and its weight was measured for conversion calculation. In calculating the conversion, it was assumed that all the ash in the coal was left inside the residue without reaction with SCW. Thus, weight of ash in the coal (Table 1) was subtracted from the weight of the residue prior to the conversion calculation. The conversion is given by Eq. (1). The sulfur contents in the coal and residual solids were determined by using LECO SC-432DR sulfur analyzer (SC-432DR, LECO Co., U.S.A.) in accordance with ASTM method D3176. The contents of the total sulfur removal were calculated by summarizing the contents of all the sulfur-containing species (the liquid and the gaseous effluents and the residue) detected in the samples.

$$\text{Conversion (\%)} = 100 - \left(\frac{\text{wt of residue} - \text{wt of ash}}{\text{wt of coal, daf}}\right) \times 100 \tag{1}$$

Gas product was collected in a syringe and analyzed by GC-TCD (Acme 6000, YoungLin, Korea). Helium was used as a reference gas, and a packed column of carbosphere (80/100) was employed for gas separation. In addition, the total sulfur of gas product was analyzed by using sulfur analyzer (9000NS, ANTEK, U.S.A.) and H_2S in gas product was analyzed with GC-FID (6890GC, Agilent Co., U.S.A.) with GS-GasPro column. The weight of gas product was calculated from the average molecular weight and the volume of gas at standard temperature and pressure. The yield of gas product and the sulfur removal of original coal were defined as Eq. (2) and Eq. (3), respectively.

$$\text{Yield (wt.\%daf)} = \left(\frac{\text{wt of gas product}}{\text{wt of coal, daf}}\right) \times 100 \tag{2}$$

$$\text{Sulfur removal in gas (wt.\%daf)} = \left(\frac{\text{wt of sulfur in gas product}}{\text{wt of sulfur in coal, daf}}\right) \times 100 \tag{3}$$

The water product in the reactor was separated from the residue by filtration. The sulfur contained in liquid effluents was titrated idiometrically using auto-titrator (670 Titroprocessor, Metrohm Ltd., Swiss). Similarly, the sulfur removal in liquid effluents was obtained by using sulfur weight in water through Eq. (4).

$$\text{Sulfur removal in liquid (wt.\%daf)} = \left(\frac{\text{wt of sulfur in liquid effluent}}{\text{wt of sulfur in coal, daf}}\right) \times 100 \tag{4}$$

RESULTS AND DISCUSSIONS

As technological advances are made and low-sulfur coal supplies diminish, higher-sulfur coals will become mined more frequently and in larger quantities. In addition, the recognition of limitation of petroleum resources has led to investment increases in new and renewable energy and clean coal technology. In the past, precombustion technologies have received little attention relative to post combustion technologies. However, as trace elements such as HAPs and sulfur become more widely recognized in emissions and publicized as potential health threats, it becomes necessary to find methods of controlling them. When air pollutants from coal combustion are considered, sulfur is commonly the first element that comes to mind. In this work, precombustion treatment of these hazardous

Table 2. Balance of sulfur (P: 30 MPa, T: 400 °C)

	Amount	Content of total sulfur	Amount of total sulfur	Totals
Coal sample	2.00 g	0.84 wt%	16.80 mg	
Sulfur in gas effluent	50 ml	5.50 mg/*l*	0.275 mg	
Sulfur in liquid	15.6 ml	0.60 g/*l*	9.371 mg	
Sulfur in solid residue	1.7037 g	0.44 wt%	7.47 mg	
Before reaction				16.8 mg
After reaction				17.11 mg
Error				1.8%

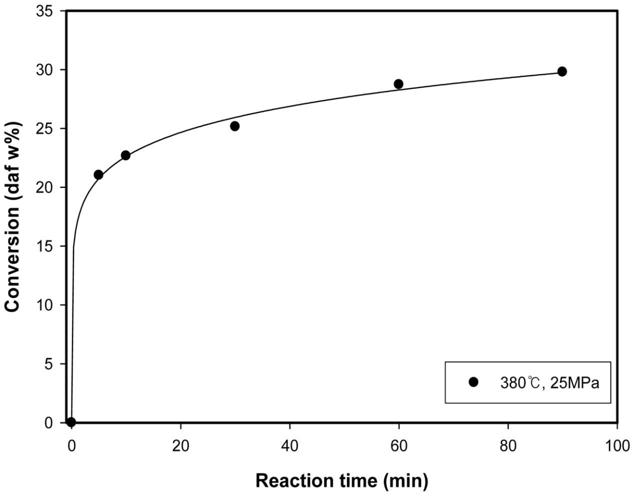

Fig. 3. Effect of reaction time on conversion of coal at 380 °C and 25 MPa.

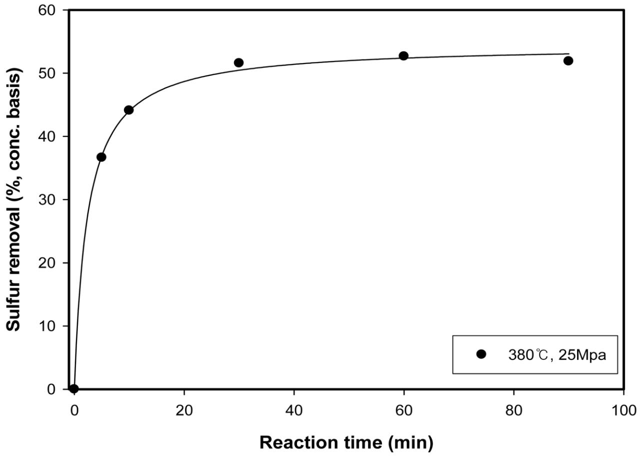

Fig. 4. Effect of reaction time on sulfur removal at 380 °C and 25 MPa.

elements using supercritical water was studied to determine the effectiveness of water on their removal from coal.

In general, coal converts into residue, liquid and gas by the supercritical water treatment [13,15,16]. The sulfur distributions in the above phase were analyzed. Table 2 shows typical results of the sulfur distributions in gas, liquid and residue. The sulfur of the original coal was removed mainly through liquid phase while the amount of sulfur in the gaseous effluent was relatively less than that in liquid. This balance of sulfur was made for each run to test the reliability of the experiments and analysis. The low level error of the sulfur balance indicated that the experimental procedure and the analysis methods were convincing to obtain credible results.

Fig. 3 and Fig. 4 show total conversion and total sulfur removal at 380 °C and 25 MPa according to various reaction times, respectively. As shown in Fig. 3 and Fig. 4, the total conversion of coal was increased as increasing reaction time, while the sulfur removal increased with the increase of reaction time up to 30 min and reached a constant value (ca. 52%) over 30 min. Namely, the sulfur removal versus time curve can be classified into two portions: a sharply increasing part and an almost constant part. In the first part the total sulfur removal increased sharply from 0% to 51.6% within 30 min. The fact that the sulfur removal can occur within short reaction time assumes that there is sufficient energy to promote phase separation and bond breaking from the complex coal matrix through supercritical treatment. It indicates that the higher diffusivity and lower viscosity of water at supercritical conditions enhance contact with normally hydrophobic organic material, implying intimate contact between water and coal, which promotes energy transfer and inorganic salvation [17]. In addition, it is possible that bonds in the coal were cleaved both by solvent attack and thermal reaction with lower activation energies due to solvation [18]. In the second part, longer reaction time did not change the sulfur removal significantly; therefore it seemed that the reaction reached a steady state within about 30 min at 380 °C and 25 MPa. In this work, reaction time is fixed at 90 min to obtain high conversion though the sulfur removal reached a steady state.

The change of total conversion with increasing temperature and pressure is shown in Fig. 5. The conversion of coal increased as increasing reaction pressure and temperature. At all cases, the conversion of coal in supercritical condition is higher than that of subcritical condition. It is seen that the supercritical condition was favorable to the desulfurization of coal. In the sub-critical region the total conversion did not exceed more than 23% while in the supercritical region the total conversion reached maximum (34.6%) when the pressure was 30 MPa at the condition of 400 °C. In addition, as shown Fig. 5, it is known that the total conversion jumped up dramatically in the region of SCW. Namely, the conversion increased considerably when the state of water converted from sub-critical to supercritical state.

Fig. 6 presents the effect of temperature on composition of gas products at 30 MPa. The results shown in this figure are the average of two or more runs. With the increase of temperature, the total amount of product gas increases from 2.99 ml to 49.83 ml and the

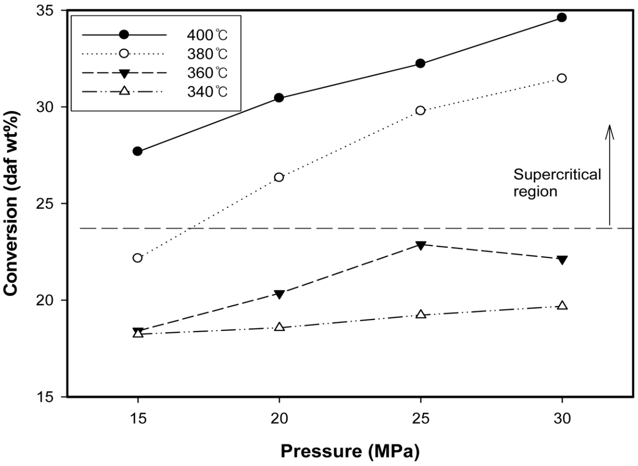

Fig. 5. The relations between total conversion and pressure at different temperatures.

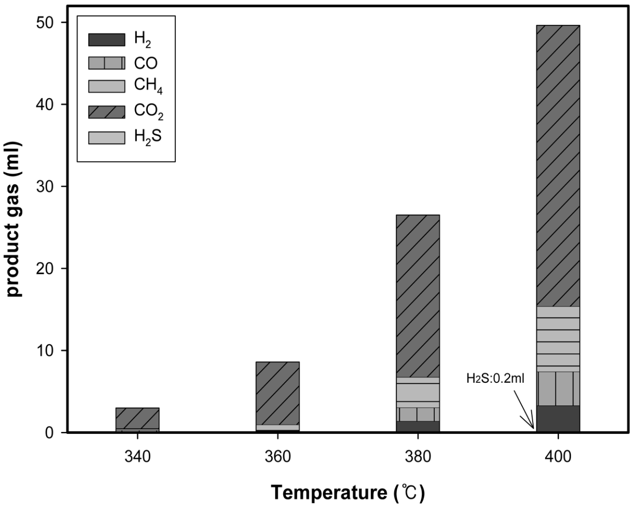

Fig. 6. Effect of temperature on composition for gas products (30 MPa).

contents of CH_4, CO, CO_2, H_2 and H_2S also tend to increase. In all conditions, CO_2 is the major component and H_2S is a trace element. An interesting observation is that H_2 is formed not in the subcritical region but in the supercritical region, indicating that SCW has a strong ability to extract hydrogen. In addition, it is thought that CO_2 is mainly produced from carboxyl decomposing. At high temperature, nearly all the carboxyl in the coal matrix has decomposed into CO_2 and as the temperature increases, coal fragmentation is enhanced in gas phase and more H_2 and CH_4 are produced. The effect of pressure on composition of gas products at 400 °C is summarized in Table 3. In contrast to the effect of temperature, it seemed that the reaction reached a steady state over 25 MPa. Therefore the effect of temperature at 30 MPa is more dominant than that of pressure at 400 °C in the light of the amount of product gas. In addition, it is known that the sulfur component in gaseous effluents is H_2S mainly and that the sulfur removal portion in the form of gas is less than 0.275 mg at 400 °C and 30 MPa.

Table 3. Effect of pressure on composition of gas products at 400 °C

Component	15 MPa	20 MPa	25 MPa	30 MPa
H_2 (%)	-	-	-	6.603
CO (%)	16.1662	9.4239	9.2316	8.231
CH_4 (%)	16.1547	16.907	16.615	15.94
CO_2 (%)	67.6789	73.668	74.153	68.50
H_2S (%)	0.147	0.319	0.381	0.385
Total gas (ml)	14	29	47	50

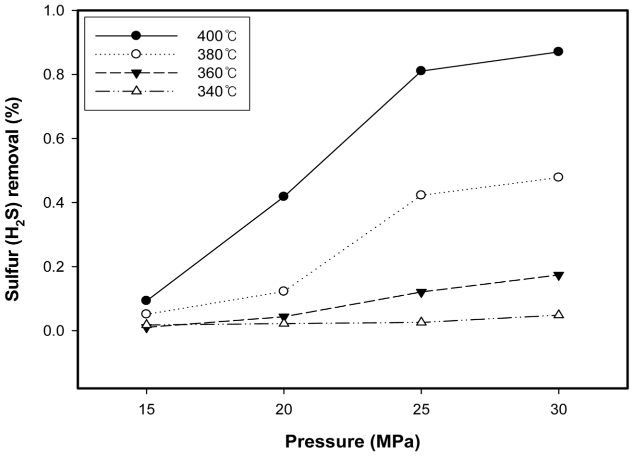

Fig. 7. Sulfur removal in the gas effluent at various temperatures and pressures.

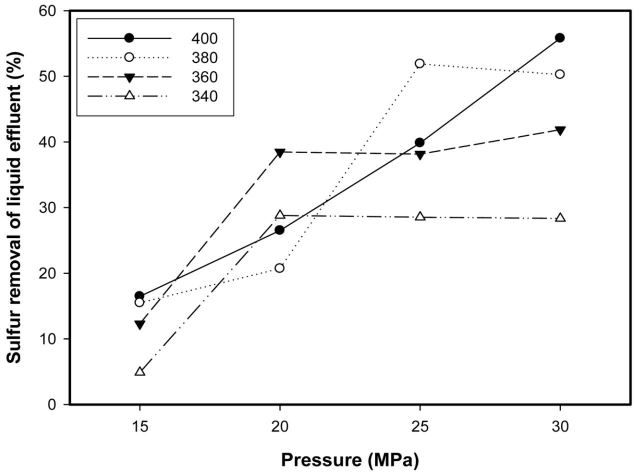

Fig. 8. Sulfur removal in the liquid effluent at various temperatures and pressures.

Fig. 7 is the dependence of total sulfur content in the gas effluent on the reaction temperature and pressure. It is observed that the total sulfur increased as increasing the reaction temperature and pressure. This indicated that more amount of sulfur was released from the coal at higher reaction temperature due to the faster SCWO reactions at higher temperature. As shown in Fig. 7, it is known that the effect of pressure in supercritical region is more dominant than that in sub-critical region. Fig. 8 shows the effect of temperature and pressure on the sulfur removal under same conditions. In the case of gas effluents, the sulfur removal is dependent on reaction

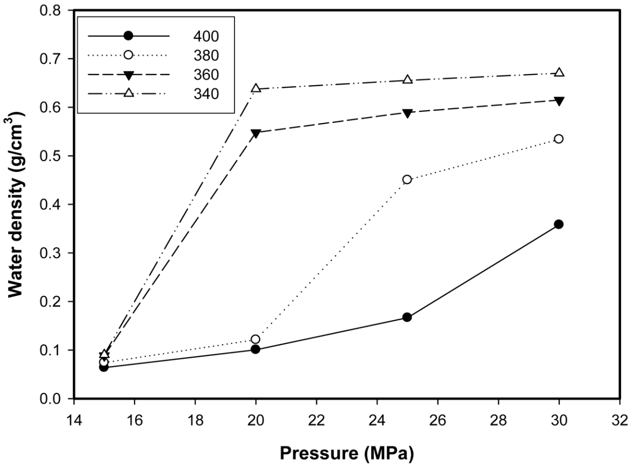

Fig. 9. Density change according to reaction temperature and pressure.

temperature, while the sulfur removal in liquid effluents is irrelevant to reaction temperature. The sulfur removal in liquid effluents increased with increasing pressure in supercritical condition. On the contrary, in sub-critical condition, the sulfur removal increased up to 20 MPa and reached a constant value. These results are thought to be related with the solvent power of a supercritical solvent. The solvent power of a supercritical solvent depends on its density, which at a given temperature is most affected by pressure. In the region of 20-30 MPa at 340 and 360 °C, as the density of the water was held almost constant, the effect of pressure was considerably reduced. These results coincide with the report of Sunggyu [19]. Fig. 9 shows the density change of water according to reaction conditions. Though the sulfur removal in liquid effluents has low value in sub-critical condition, in the comparison of Fig. 7 and Fig. 8; it is noticeable that the sulfur removal in liquid effluents increases by approximately 60 times that in gas effluents.

CONCLUSIONS

The role of SCW and the effects of operating variables such as reaction temperature, pressure, and water density on the treatment of Datong coal are investigated in a batch type micro reactor. Compared with sub-critical condition, the treatment of coal in supercritical condition promotes the extraction of sulfur in coal, resulting in higher sulfur removal. It is also found that reaction temperature is the most important factor that affects the sulfur removal. With the increase of temperature, the coal sulfur releases into the liquid and gas effluents. However, the sulfur removal in liquid effluents is much greater than that in gas effluents. The sulfur removal of original coal reaches a maximum 57.42% in the reaction time of 90 min at 400 °C and 30 MPa. Reaction time has little effect over 30 min because the sulfur removal reaches a steady state within 30 min. Water density influences the solvent power of a supercritical water and the sulfur removal in liquid effluent tends to decrease with increasing water density.

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NOMENCLATURE

T : reaction temperature [°C]
T_c : critical temperature [°C]
P : reaction pressure [MPa]
P_c : critical pressure [MPa]
t : reaction time [min]
wt : the weight of the sample [g]
I.D. : inner diameter [mm]
daf : dry ash free [-]

REFERENCES

1. M. Abdollahy, A. Z. Moghaddam and K. Rami, *Fuel*, **85**, 1117 (2006).
2. Y. W. Nam and K. S. Park, *Korean J. Chem. Eng.*, **21**, 370 (2004).
3. L. Cheng, R. Zhang and J. Bi, *Fuel Process. Technol.*, **85**, 921 (2004).
4. X. Liu, B. Li and K. Miura, *Fuel Process. Technol.*, **69**, 1 (2001).
5. T. Sakaki, M. Shibata, Y. Adachi and H. Hirosue, *Fuel*, **73**, 515 (1994).
6. S. Sangon, S. Ratanavaraha, S. Ngamprasertsith and P. Prasassarakich, *Fuel Process Technol.*, **87**, 201 (2006).
7. Y. Matsumura, H. Nonaka, H. Yokura, A. Tsutsumi and K. Yoshida, *Fuel*, **78**, 1049 (1999).
8. L. A. Amestica and E. E. Wolf, *Fuel*, **65**, 1226 (1986).
9. F. Czechowski, M. Stolarski and B. R. T. Simoneit, *Fuel*, **81**, 1933 (2002).
10. R. Garcia, A. Arenillas, F. Rubiera and S. R. Moinelo, *Fuel Process. Technol.*, **86**, 205 (2004).
11. T. M. Aida, T. Sato, G. Sekiguchi, T. Adschiri and K. Arai, *Fuel*, **81**, 1453 (2002).
12. K. Charutawai, S. Ngamprasertsith and P. Prasassarakich, *Fuel Process. Technol.*, **84**, 207 (2003).
13. R. C. Timpe, M. D. Mann, J. H. Pavlish and P. K. K. Louie, *Fuel Process. Technol.*, **73**, 127 (2001).
14. P. K. K. Louie, R. C. Timpe, S. B. Hawthorne and D. J. Miller, *Fuel*, **73**, 1173 (1994).
15. J. R. Kershaw, *Fuel Process. Technol.*, **13**, 111 (1986).
16. G. V. Deshpande, G. D. Holder, A. A. Bishop, J. Gopal and I. Wender, *Fuel*, **63**, 956 (1984).
17. J. W. Tester and J. A. Cline, *Corrosion*, **55**, 1088 (1999).
18. Y. Yueruem and A. Tugluhan, *Fuel Sci. Technol. Int.*, **8**, 221 (1990).
19. S. Lee, S. K. Kesavan, A. Ghosh and K. L. Fullerton, *Fuel*, **68**, 1210 (1989).