HYDROTHERMAL UPGRADING OF BROWN COAL WITHOUT WATER ADDITION

K. Laursen, M. Sakaguchi, H. Nakagawa, K. Miura

Department of Chemical Engineering
Kyoto University, Kyoto-Daigaku Katsura
Nishikyo, Kyoto 615-8510, JAPAN

Introduction

Low rank coals (brown coal and lignite) are very abundant in several regions throughout the world and they constitute a significant resource for both energy and fossil fuel derived products. However, in spite of their quantity and relatively low market price, these low-rank coals have not been utilized to nearly the same extent as higher rank coals. The lack of interest in low-rank coal is mainly due to the high water content (40-70 wt%)[1-2], which makes it economically unfeasible to transport the coal without some form of upgrading. Due to the problematic high water content most upgrading methods include removal of the moisture before any further treatment. The drying process is energy consuming, requiring up to 20% of the chemically bonded energy[1] and this significantly reduces the net energy output for low-rank coal. Methods used for water removal include: thermal evaporative, hydrothermal (i.e., non-evaporative) and mechanical dewatering processes as well as combinations of mechanical and thermal dewatering[3].

The work presented here focused on hydrothermal dewatering of a brown coal with very high moisture content. Hydrothermal treatment is commonly conducted by adding extra water to the coal prior to treatment and creating slurries with specific dry coal to water ratios ranging from 1:2 up to as high as 1:5[1-2, 3-6]. Because some brown coals should contain sufficient moisture to produce hydrothermal conditions without water addition, we wanted to explore this option for upgrading brown coal. The aim of this study was to evaluate the effects of the hydrothermal conditions on the chemistry and structure of the upgraded coal, with the objective of utilizing the upgraded coal for production of coke and coal-water-mixtures.

Experimental

Samples and experimental conditions. Hydrothermal treatment was conducted on Loy Yang coal from Latrobe Valley, Victoria, Australia. To reduce the particle size and homogenize the coal, a.r. Loy Yang was blended for 5 min and stored in airtight containers. For some experiments the blended coal was subjected directly to hydrothermal treatment (referred to as raw), whereas in other cases extra water was added to the blended coal to create a slurry with a coal:water ratio of 1:3. (referred to as slurry). The sample size for both raw coal samples and slurries was maintained at 5 g. Hydrothermal treatment was conducted in a 20 cm^3 stainless steel autoclave equipped with an in-situ thermocouple and connected to a pressure meter. The sealed autoclave was flushed with N_2 and inserted into a preheated fluidized sand bath and heated to the treatment temperature. In selected experiments the autoclave was pressurized with N_2 to 7 and 15 atm prior to heating. Hydrothermal treatment was conducted at 200, 250, 300 and 350°C for 30 and 180 min. Upon completion, the hot autoclave was cooled in water, and the sample was removed from the autoclave. The autoclave was carefully rinsed with distilled water and the total coal sample was filtrated on 0.45 μm filter.

Analytical methods. Proximate and ultimate compositions of a.r., blended and treated samples were determined using a CHN-corder (Yanaco, MT-6) and thermo gravimetry (Perkin Elmer, Pyris1). Moisture content was determined by drying to constant weight at 110°C in a vacuum oven. Organic carbon released to the waste water was analyzed by TOC (Shimadzu TOC 5000A). Changes in the coal structure were traced by use of in-situ FTIR (JEOL, Winspec 50) and XRD measurements (Shimadzu, XD-610).

Results and Discussion

Table 1 shows the results of proximate and ultimate analyses of "as-received" Loy Yang and a batch of blended coal. The a.r. coal has a moisture content of 58%, and mechanical blending of the coal led to a one percent decrease to 57%. The carbon content is in the upper range for lignite's[7], while the ash content is very low (1.6%) making the coal very suitable for upgrading. The change in proximate composition due to mechanical blending was insignificant, and probably mainly related to sample in-homogeneity. The high moisture content of a.r. Loy Yang leads to a coal:water ratio of approximately 1:1.2. Measured temperature vs. pressure relationship during the treatment of a.r. coal closely followed the vapor pressure cures (Figure 1) revealing that hydrothermal conditions are maintained throughout the experiments.

Table 1. Ultimate and proximate analyses of Loy Yang coal.

Sample	Ultimate comp. (wt%) (d.a.f.)				Proximate comp. (wt%) (d.b.)			Moisture
	C	H	N	O	Fixed C	Volatiles	Ash	(a.r.)(wt%)
as-rec.	67.3	4.9	0.9	26.9	47.0	51.5	1.6	58
blend	67.3	4.3	0.4	28.2	47.2	51.3	1.5	57

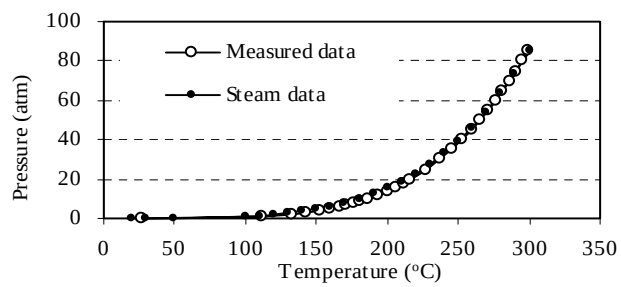

Figure 1. Temperature and pressure relationship measured during treatment of a.r. Loy Yang coal and vapor pressure curve.

The moisture content of raw coal samples treated for 30 min decreased with increasing temperature from 60% in a blank sample (i.e. sample rinsed with water and filtrated) to 26% in samples treated at 350°C (Table 2). Increasing the treatment time to 180 min led to no further moisture content reductions at any of the tested temperatures.

Table 2. Effects of treatment temperature and time.

Temperature (°C)	time (min)	Moisture (wt%)	Carbon d.a.f (wt%)	Ash (wt%)	Yield (% d.b)	TOC (mg/ g coal)
20*		62	65.2	1.26	95	0.0736
200	30	56	67.3	0.92	94	0.2640
250	30	40	67.8	1.12	96	0.6930
300	30	22	71.7	1.09	94	1.1910
350	30	26	79.0	1.00	84	1.6890
200	180	54	69.8	1.05	97	0.3610
250	180	40	70.0	1.09	87	0.9980
300	180	23	73.4	0.98	79	2.2840
350	180	26	83.0	1.18	69	2.8980

* washed and filtrated under the same conditions as used for treated samples

As expected, the carbon content increased with treatment temperature, and at higher temperatures (i.e., 300 and 350°C) the carbon content of the solid also increased with treatment time (Table 2). Dissolved C increased with temperature, and also with time; a significant increase was seen for the 300 and 350°C samples treated

for 180 min. High solid yield was achieved at 200 to 300°C for 30 min treatment, but a decrease was seen when the temperature was increase to 350°C. For long-term treatment the yield decreased significantly with increasing temperature. The hydrothermal treatment led to a slight decrease in ash content (10-15%), but there was no systematic changes with temperature. Because the composition of the ash in many cases is more important than the actual amount, especially for low ash content coals, work is currently being undertaken to identify the changes in the ash composition.

As shown above, a combination of increasing temperature and pressure leads to a chemical upgrading of the coal. To determine the relative effect of the two independently, the reactor was pressurized prior to heating with 7 and 15 atm N_2 (Table 3). Increasing the pressure "artificially" above the steam pressure with N_2 did not lead to any significant or systematic changes in the composition of the treated coal. This would indicate that the temperature is the more controlling factor during hydrothermal treatment.

Table 3. Effects of treatment pressure.

Temperature (°C)	Preheating N_2 pressure (atm)	Treatment pressure (atm)	Moisture (wt%)	Carbon d.a.f (wt%)	TOC mg/ g coal
200	0	16	56	67.3	0.2640
250	0	41	40	67.8	0.6930
300	0	98	22	71.7	1.1910
200	7	28	50	66.3	0.2066
250	7	47	47	67.3	0.4780
300	7	102	23	70.1	1.8917
200	15	32	53	63.0	0.1690
250	15	61	40	68.8	0.3186
300	15	113	33	72.4	1.6150

A series of experiments were conducted to evaluate the differences in the products from raw coal treated samples and slurries (Table 2 and Table 4). The slurries were prepared by pouring the coal and the water into the autoclave. The sample were either heated with no further blending or blended for 1 min in the autoclave with an ultrasonic irradiation prior to heating. Comparisons between the raw hydrothermally treated samples (Table 2) with a coal:water ratio of 1:1.2 and the slurries reveal that a lower final moisture content can be reached if no extra water is added to the coal prior to treatment. The C content of the treated coal seems to be unaffected by the coal:water ratio.

Table 4. Effects of coal water ratio.

Temperature (°C)	Coal : water	Mixing	Moisture (wt%)	Carbon d.a.f (wt%)	TOC (mg/ g coal)
200	1:3	no	62	65.4	0.2002
250	1:3	no	57	67.1	1.7574
300	1:3	no	45	72.0	2.1450
200	1:3	yes	63	66.7	0.9519
250	1:3	yes	62	67.7	0.9510
300	1:3	yes	53	71.8	1.7886

The low ash content of Loy Yang makes it very suitable for both XRD and FTIR analysis of the organic structure because no interfering and dominating inorganic peaks are seen. Two broad diffraction peaks around 20° and 26° 2-theta representing alkyl and aromatic structures, respectively, are present in coal, and the relative intensity of the two peaks reflects the rank of the coal[8]. Preliminary XRD results of dried raw coal and 3 samples treated for 180 min at 200, 250 and 300°C, respectively, are shown in Figure 2. These preliminary XRD analyses show that treatment at 200 and 250°C does not chance the structure, but treatment at 300°C leads to an upgrading of the coal towards a higher rank coal structure. Work is currently being undertaken to quantify these observed changes.

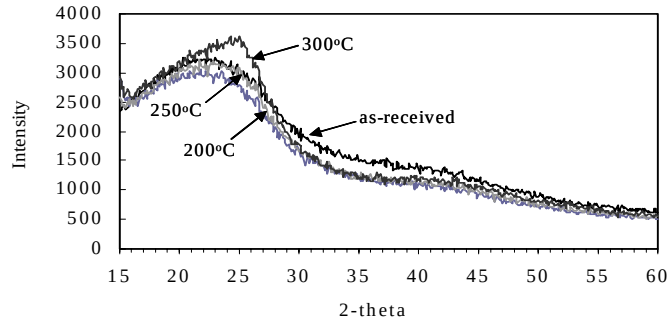

Figure 2. X-ray diffractograms of as-received and hydrothermal treated Loy Yang coal.

In-situ FTIR is powerful tool for tracking coal structure changes during heatup[9-10]. FTIR spectra of a.r. and a sample treated at 300°C for 30 min shows a significant decrease in the peak representing carboxyl groups around 1700 cm^{-1} in the treated sample (Figure 3). Significant peak reduction is also seen for the peaks in the region 2800-3800 cm^{-1} representing OH-groups[9-10]. Further work is currently being done to quantify these changes in carboxyl and OH-groups.

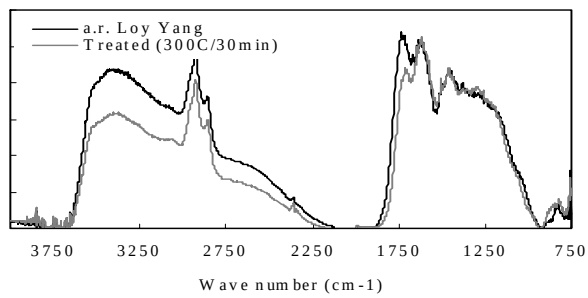

Figure 3. FTIR spectra of a.r. Loy Yang and treated coal.

Conclusions

Hydrothermal experiments conducted in an autoclave on a high-moisture-content coal (Loy Yang) revealed that hydrothermal conditions can be maintained in the autoclave with out addition of water. The drying process is more efficient when no further water is added and high-yield carbon-rich solids can be produced. FTIR and XRD analyses confirm that the upgrading process involves loss of carboxyl and OH groups.

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