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REMOVAL OF CALCIUM BY DISSOLVED CO_2 AND THE EFFECTS ON COAL LIQUEFACTION

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ABSTRACT

Calcium was removed from Tunçbilek and Soma-Merkez subbituminous coals and Seyitömer, Muğla-Yatağan and Bolu-Göynük lignites with dissolved CO_2 technique. The effect of pretreatment on the liquefaction yield was investigated. With this technique 82.4 % removal of the ion exchangeable and 45.1 % removal of the nonexchangeable calcium were reached. Pretreating the coals with dissolved CO_2 had an adverse effect on Bolu-Göynük lignite and resulted in decreased liquid product yield while for the rest of the samples tested 8.9- 27.7 % increase were observed in tetraline soluble fractions.

INTRODUCTION

Bituminous coals contain inorganic matters, such as calcite, illite, and pyrite, in dispersed forms. For the lower ranking coals, however, mineral matters are mostly fused to the organic structure while some may still present in the dispersed form[1]. On the other hand lower ranking coals contain oxygen in higher proportions compared to the bituminous ones and most of the organic oxygen structured in carboxylic acid groups. Exchangeable cations, forming the structurally connected mineral matter are mostly alkali and alkaline earth metals interfused with the carboxylic groups which too present in larger amounts in lignites[1,2]. A considerable amount of research have shown that removal of calcium and magnesium increases the reactivity in pyrolysis, gasification, and liquefaction processes of coals[1,3,4,5,6]. Calcium binds two carboxylate ions and increases the cross-linking in the coal structure. Therefore, solvent diffusion to the pores and back diffusion of liquefied products become restricted. This assumption suggests that liquefaction yield should increase with the removal of cross-linked calcium. On the other hand, pyrite, sulphur, clays, metals, and earth metals present in the molecular structure produce a catalytic effect for the liquefaction process[7,8,9,10], and removal of these would decrease the yield.

Minerals connected to the organic structure, can not be removed by simple physical operations. Acid washing, on the other hand, is effective in removing both the dispersed and structurally fused minerals but alters the coal structure[3]. In this study, effect of mild removal of calcium on liquefaction yield was focused thus acid washing was not adopted.

Hayashi et. al. reported that both the dispersed and structurally connected mineral matters could be isolated by dissolved CO_2 method without altering the coal structure[11]. They liquefied so treated coals and obtained higher yields of oil and asphaltenes compared to the original, untreated coals. However, cation removal can not be stated as the only factor for enhanced liquefaction since a pre-heating was applied prior to treating with dissolved CO_2. In this present communication calcium removal by dissolved CO_2 method and its effects on liquefaction yields for the two subbituminous coals and three lignite samples are reported.

EXPERIMENTAL

Materials

Soma-Merkez and Tunçbilek subbituminous coals and Muğla-Yatağan, Seyitömer, and Bolu-Göynük lignites were tested in this study. Solvents (tetraline, hexane, toluene, and tetrahydrofurane) were acquired from Merck AG and used without further purification. Coal samples were ground to -50 mesh (300 μm) and stored in dark coloured, air tight bottles. Table 1 presents the proximate and elemental analysis data for the samples tested in this study.

Ca^{2+} analysis

Ash content of coal samples were determined according to the ASTM-D 3174 standard[12] and the calcium in the ash was determined by atomic absorption according to the ASTM-D3682-78[13] standards. The product of calcium percent in the ash and the ash percent of the coal sample yielded the calcium percent of the coal. Calcium contents of samples are presented in Table 2.

Ca removal by CO_2 dissolved in water

3.0 g of coal sample and 30.0 g of water were introduced into a stainless steel bomb reactor of 250 ml in size. The pressure in the reactor was raised to 600 kPa using CO_2 gas at room temperature and the suspension was mechanically stirred for 2 hours at 1500 rpm. After the pressure was released, the solid phase was filtered off, and dried to constant weight at ambient conditions to carry out calcium analysis.

Table 1. Proximate and Elemental Analyses of Coals

	Bolu-Göynük	Seyitömer	Muğla-Yatağan	Tunçbilek	Soma-Merkez
Proximate analyses (w %)					
Volatile matter	28.39	28.82	41.39	33.82	36.01
Fixed carbon	29.61	20.38	33.21	43.78	47.59
Ash	35.00	41.00	13.00	15.00	7.00
Moisture	7.00	9.80	12.40	7.40	9.40
Ultimate analyses (w % daf)					
C	60.97	61.45	65.31	71.90	72.63
H	5.57	5.72	5.10	5.37	5.24
N	1.69	2.36	1.47	2.60	1.05
S	3.34	2.66	5.47	1.41	0.82
O[a]	28.43	27.81	22.65	18.72	20.26
H/C[b]	1.08	1.10	0.93	0.89	0.86

[a] By difference

[b] Atomic ratio

Table 2. Calcium Content of Coals

	Bolu-Göynük	Seyitömer	Muğla-Yatağan	Tunçbilek	Soma-Merkez
% CaO in ash	4.50	3.21	20.00	1.39	6.60
mg Ca /g coal	11.25	9.40	18.57	1.49	3.30
Ca (w %)	1.12	0.94	1.86	0.15	0.33

Exchangeable calcium content

Exchangeable calcium content of the coal samples were determined by extracting with ammonium acetate according to the method proposed by Morgan and Jenkins[6]. 150 g of sample were continuously stirred with 1 L of 1 M ammonium acetate solution for 3 hours under nitrogen atmosphere. The solid phase was filtered off, mixed with fresh solution of 1 M ammonium acetate, and stirred for 3 hours again under inert atmosphere. This procedure was repeated for five times. At the end, the sample was washed twice with 200 ml distilled water, and dried to constant weight. Calcium content of this sample corresponds to non-exchangeable calcium and when subtracted from that of the untreated coal gives the amount of the exchangeable calcium content.

Liquefaction

1.0 g of coal sample and 3.0 g of tetraline were introduced into the bomb reactor and the pressure was raised to 500 kPa with N_2 gas. The reactor was heated to 300 °C in 2 hours, while the pressure increased to 1400 kPa. The reaction was allowed to continue under these conditions for 10 more minutes and the reactor was cooled down to room temperature. The reactor contents were filtered off and the solid residue was soxhlet extracted with THF. The extract and the filtrate was combined together. THF and tetraline were removed from the filtrate by a rotary evaporator, and the residue was set aside for overnight after mixing with 100 ml of hexane. Asphaltenes (AS) and preasphaltenes (PAS) remained in the solid residue while the oil was extracted to the hexane phase. Solid mixture was treated with 100 ml of toluene and AS were allowed to dissolve. Filtering off the mixture resulted a toluene phase containing AS and a solid phase composed of PAS.

RESULTS AND DISCUSSION

Table 3. presents the calcium content of coals removed by dissolved CO_2 method.

Table 3. Amount of Calcium and Ash Removed by Dissolved CO_2

Removal	Bolu-Göynük	Seyitömer	Muğla-Yatağan	Tunçbilek	Soma-Merkez
% Ash	4.00	11.95	3.00	11.33	16.86
mg Ca / g coal	0.69	1.23	1.10	1.00	0.72
% Ca	6.16	13.05	5.92	66.83	21.90

As seen from Table 3 the amount of calcium removed by dissolved CO_2 method ranged in 0.69-1.23 mg per gram of coal. Original Ca content of Muğla-Yatağan lignite was 18.57 mg per gram of coal and 1.10 mg of this amount were removed. Interestingly, Tunçbilek coal contained 1.49 mg Ca per gram of coal and 1.00 mg of this amount were also removed. One should definitely expect higher removal of Ca from coals containing higher amounts of calcium. However, amounts of calcium removed remained almost the same for the samples containing disparate amounts of calcium. In the dissolved CO_2 method carbonic acid (H_2CO_3) is in equilibrium with the CO_2 in the solution.

H^+ ions in the medium form according to the following reactions,

$$H_2O + CO_2 \leftrightarrows H_2CO_3$$

$$H_2CO_3 \leftrightarrows H^+ + HCO_3^-$$

and $CaCO_3$ dissolves in water by

$$CaCO_3 + H^+ \leftrightarrows Ca^{2+} + HCO_3^-$$

The possible reason for the removal of similar amounts of Ca from different type of coals can be the insufficiency in H^+ . Accordingly, Hayashi et al. studied the calcium removal from two subbituminous coals and a lignite sample by dissolved CO_2 technique at various pH levels, coal by water ratios and at different reaction times[11]. Their study also showed that increasing pH values resulted in lower removal yields.

Cations, connected to the carboxyl groups in the coal structure are named as ion exchangeable cations. Ammonium acetate extraction removed ion exchangeable calcium from coal and the non-exchangeable ones remained in the structure. The amounts of non-exchangeable calcium determined by atomic absorption are shown in Table 4. The balance represented the ion exchangeable calcium and presented in Table 5 for the coals studied.

Table 4. Ash and Calcium Contents of Coals Treated with Ammonium Acetate

w %	Bolu-Göynük	Seyitömer	Muğla-Yatağan	Tunçbilek	Soma-Merkez
Ash	21.090	28.310	5.830	13.120	3.010
CaO in ash	1.870	1.700	8.800	0.680	4.700
Ca	0.281	0.344	0.366	0.064	0.101

Table 5. Ion Exchangeable and Non-exchangeable Calcium Fraction of Coals

	Bolu-Göynük	Seyitömer	Muğla-Yatağan	Tunçbilek	Soma-Merkez
mg Ca^a/g coal	2.81	3.44	3.66	0.64	1.01
mg Ca^b/g coal	8.44	5.96	14.91	0.85	2.29
% Ca^b	75.00	63.45	80.27	57.25	69.39

[a]Nonexchangeable
[b]Exchangeable

Morgan et al. investigated the effect of ammonium acetate on dolomite, calcite, gypsum, illite, kaolinite, montmorrinolite, and quartz, and reported that only gypsum dissolved in ammonium acetate and the solubility of the rest were negligible[14]. Gypsum can effect the amount of the exchangeable calcium, however the coals tested in this study were assumed to be free of gypsum and calcium content calculated represented the calcium connected to the carboxyl groups.

Coals treated with dissolved CO_2 were also subjected to ammonium acetate extraction to determine the removal of exchangeable calcium amounts. As seen from Table 6 dissolved CO_2 method removes both the exchangeable and non-exchangeable calcium.

Table 6. Amount of Ion Exchangeable and Non-exchangeable Calcium Removed by Dissolved CO_2

Removal	Bolu-Göynük	Seyitömer	Muğla-Yatağan	Tunçbilek	Soma-Merkez
mg Ca^a/g coal	0.27	0.49	0.20	0.29	0.02
% Ca^a	9.73	14.14	5.57	45.05	1.98
mg Ca^b/g coal	0.42	0.74	0.89	0.70	0.70
% Ca^b	4.93	12.47	6.01	82.42	30.56

[a]Nonexchangeable
[b]Exchangeable

The results show that treatments applied in this study are not adequate to remove all the calcium from the structure. Removal may be enhanced by higher CO_2 pressures since carbonic acid and consequently H^+ concentration will then increase.

Effects of exchangeable cations on liquefaction

Liquefaction yields of original and CO_2 treated coals are presented in Table 7.

Table 7. Liquefaction Yields of Raw and CO_2 Treated Coals

W % in daf coal	Bolu-Göynük	Seyitömer	Muğla-Yatağan	Tunçbilek	Soma-Merkez
Untreated Coals					
Oil	18.50	35.90	9.50	13.40	20.10
Asph.	20.80	5.70	8.30	4.90	4.50
Preasph.	9.90	1.90	7.10	2.40	8.90
Total	49.20	43.50	24.90	20.70	33.50
CO_2 Treated Coals					
Oil	17.00	31.20	16.50	9.60	16.50
Asph.	3.40	10.40	8.20	8.40	12.90
Preasph.	1.70	6.90	7.10	8.40	7.10
Total	22.10	48.50	31.80	26.40	36.50

As can be deduced from Table 7, both the total yield and the oil yields decreased with increasing H/C ratio for the original samples. However, yields start to increase for coals having H/C ratios greater than 0.9. This observation is also consistent with the previously published reports[15].

As seen from Table 7 liquid product yields increased by 8.9 % and 27.5 % for Soma- Merkez and Tunçbilek subbituminous coals and by 11.5 % and 27.7 % for Seyitömer and Muğla-Yatağan lignites, respectively. CO_2 pretreatment had an adverse effect on Bolu-Göynük lignite and resulted in 55.1% reduction in yield. The breakage of ionic bonds between the calcium and carboxyl groups became more effective than the catalytic effect of calcium.

Kershaw et al studied the supercritical gas extraction on two acid washed lignite samples and reported that total conversion increased for one lignite and decreased for the other[16]. Mesci subjected the acid washed coal samples to swelling test and claimed that Ca^{2+} removal increased the swelling ratio[3]. Joseph and Forrai treated the coal samples with ammonium acetate and reported an increased yield while re-treating these samples with calcium acetate decreased the yield back. Some tests were performed for Na^+ and K^+ and effect of calcium was found to be more severe[1]. For the Bolu-Göynük lignite, on the other hand, only 4.93 % and 9.73 % of respectively exchangeable and non-exchangeable calcium were removed. Therefore, one were to expect only a slight change in the yield. However, substantial decrease in liquid product yield was observed for this lignite. This might be due to the absence of catalytic effect of non-exchangeable calcium and other cations removed together with calcium.

CONCLUSION

Treating coal samples with CO_2 dissolved in water at pressures of 600 kPa is not adequate to remove all the calcium present in the coal structure and washing with 1 M HCl[3] is more effective than CO_2 treatment. Dissolved CO_2 method resulted in increased liquid product yield for four of the coals tested while a decreased yield was observed for one type of the coal samples. Oil fractions of the samples, except Muğla-Yatağan lignite, decreased when treated with CO_2. However the amount of the oil fraction is the quality factor for the liquid products and needs to be increased.

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