ADSORPTION OF Cr AND Fe IONS ON BEYPAZARI LIGNITE AND THEIR EFFECT ON DECARBOXYLATION

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Introduction

The presence of copper catalyzed decarboxylation reactions of lignites.[1,2] Starting at around 160°C, however, the catalytic effect of copper becomes significant and an increase of the order of 20% is observed in the higher heating value of the heat-treated lignite. Increasing the concentration of copper to values greater than 1% appears to have essentially no effect on its catalytic activity. The purpose of the present study is to investigate the effects of the transition metal ions Fe^{3+} and Cr^{3+} , loaded onto the lignite, on the decarboxylation of Beypazari lignite, in terms of energies of activation for the decarboxylation processes, the calorific values, the burning profile peak temperatures of the lignite samples obtained as a result of the decarboxylation process.

Experimental

Turkish Beypazari lignite (61.2% C) sample was ground to –65 mesh ASTM under nitrogen atmosphere, dried to constant weight at 110°C under vacuum and stored under nitrogen atmosphere. Pore volumes and average pore diameter greater than 20A o were determined by mercury porosimeter up to 2000 kg / cm 2 using a Carlo Erba model 200. The surface area of the coal sample was measured with a surface area apparatus (BET method). The lignite sample was demineralized with standart methods. Lignite samples about 5 g were stirred for 24 hours with solutions of chloride salts of Cr^{3+} and Fe^{3+} ions under the nitrogen atmosphere. Metal loading experiments were carried out for the wt% metal loadings of about 1, 2, 3, 4, 5% of the d.a.f. coal sample. The metal loaded lignite samples were decarboxylated at 100, 150, 200 and 230°C for a period of 30 minutes. For comparison purposes, blank samples of original and demineralized coal (i.e. containing no metal) subjected to exactly the same procedure, except that the initial slurry was made with distilled water. Calorific values of all lignite samples were determined. The sample which has the highest calorific value was determined in each lignite group. The selected coal samples (metalloaded), the blank original and demineralized coal samples were decarboxylated at 100, 150 and 200 °C for the periods of 10, 20, 30, 40, 50 and 60 minutes in the vacuum oven under nitrogen atmosphere. Then, by using the DSC device, coal samples obtained from the decarboxylation experiments were oxidized for 10 and 60 minutes starting from 35°C upto 500°C. Kinetics of the decarboxylation reactions was investigated for the blank original (no metal loading), the blank demineralized (no metal loading) and the selected samples that have optimum calorific value from each group. FTIR spectra of original (blank and metal loaded) and demineralized (blank and metal loaded) lignite samples were measured with a Mattson 1000 FTIR spectrometer.

Results and Discussion

The pore radii of Beypazari lignite were found to change between 10 and 40 nm. This indicates that the lignite contains mainly mesopores.

Decarboxylation process has been shown to increase the calorific value of low-rank coals. The calorific value of the original and demineralized Beypazari lignite was measured as 3663.4 J/g and 7435.7 J/g, respectively. In order to determine the experimental conditions for the most efficient results in terms of the highest calorific value of the lignite with plausible wt% metal loading and decarboxylation temperature after metal treatment, a set of experiments was carried out.

The decarboxylation experiments were carried out with the samples that have the wt% metal loading values between 1-5 % and decarboxylation temperature values of 100°C, 150°C, 200°C and 230°C. The duration of the decarboxylation experiments was kept constant at 30 minutes. To determine the optimum values of wt% metal loading and decarboxylation temperature for the best efficiency of metal catalyst, the calorific values of the samples were measured. The results obtained for the Fe^{3+} loaded original lignite show that; i) The variation of calorific value with wt% metal loading appears to pass through a maximum at 2% metal loading and then decrease with increasing wt% metal loading. ii) The variation of calorific value with decarboxylation temperature appears to pass through a maximum at 150°C and then decrease with increasing temperature. Also, it is apparent that the calorific values of the metal loaded original coal samples are greater than those of the blank original coal samples at all decarboxylation temperatures. The results obtained for the Cr^{3+} loaded original lignite show that; i) The variation of calorific value with wt% metal loading appears to pass through a maximum at 2% metal loading and then decrease with increasing wt% metal loading . ii) The variation of calorific value with decarboxylation temperature appears to pass through a maximum at 150°C and then decrease with increasing temperature. Also, it is apparent that the calorific values of the metal loaded original coal samples are greater than those of the blank original coal samples at all decarboxylation temperatures.

The results obtained for the Fe^{3+} loaded demineralized lignite show that; i) The variation of calorific value with wt% metal loading appears to pass through a maximum at 1% metal loading and then decrease with increasing wt% metal loading . ii) The variation of calorific value with decarboxylation temperature appears to pass through a maximum at 150°C and then decrease with increasing temperature. Also, it is apparent that the calorific values of the metal loaded demineralized coal samples are greater than those of the blank original coal samples at all decarboxylation temperatures.

The results obtained for the Cr^{3+} loaded demineralized lignite show that; i) The variation of calorific value with wt% metal loading appears to pass through a maximum at 1% metal loading and then decrease with increasing wt% metal loading .ii) The variation of calorific value with decarboxylation temperature appears to pass through a maximum at 150°C and then decrease with increasing temperature. Also, it is apparent that the calorific values of the metal loaded original coal samples are greater than those of the blank original coal samples at all decarboxylation temperatures.

After the determination of the calorific values, it is seen that the calorific values of the decarboxylated Beyapazari lignite samples with catalyst (that is metal loaded) are higher than those of the blank (no metal loading) lignite samples. As the decarboxylation temperature was increased calorific value of the lignite also increased reaching to a maximum value at 150°C and further increase in the temperature caused a decrease in the calorific value of the lignite. In all of the experiments the measured calorific values of the metal loaded and decarboxylated lignite samples were higher than those of the blank (no metal loading) and undecarboxylated lignite samples. The optimum wt% metal loading and reaction temperature in the decarboxylation experiments to obtain decarboxylated lignites with

the highest calorific value for each group of the metal loaded lignite samples are given below:

For original lignite samples:
Fe 2% – 150°C, Cr 2% – 150°C
For demineralized lignite samples:
Fe 1% – 150°C, Cr 1% – 150°C

Kinetics of The Decarboxylation Reaction. To evaluate the data, first order reaction kinetics were assumed for decarboxylation reactions of lignite samples. Metal ions acted as catalyst.

Table 1. The Activation Energies of the Decarboxylation Reactions of Metal Loaded Original and Demineralized Lignite Samples

Coal Sample	Activation Energy (kj/mol)
Original coal	69.9
Demineralized coal	60.7
Cr^{3+} loaded original coal	37.8
Fe^{3+} loaded original coal	39.8
Cr^{3+} loaded demineralized coal	39.6
Fe^{3+} loaded demineralized coal	41.9

After the computation of the energy of activation for the decarboxylation of each type of coal samples, it is apparent that the activation energy values for the metal loaded coal samples are lower than the energy of activation values for the decarboxylation of the blank (no metal loaded) original and demineralized coal samples. This results are consistent with the idea that the metal ions loaded on coal behave as a catalyst in coal processing, like the decarboxylation of coal.

References

(1) Stournas, S.; Papachristos, M.; Kyriacopoules, G.B.. *Fuel Processing Technology*, **1987**, *17*, 195.
(2) Özvatan, S.; and Yürüm, Y. *Energy Sources*, **2000**, in press.