

# AIR OXIDATION-INDUCED EFFECT ON THE PYROLYSIS BEHAVIOR OF A SUBBITUMINOUS COAL FROM SOUTHERN ALASKA

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## ABSTRACT

A subbituminous coal from Beluga coalfield, Alaska was oxidized in air at 120°C for about 8 days. The pyrolysis behavior of the raw coal and oxidized samples was determined using a Perkin-Elmer Series 4 thermogravimetric analyzer (TGA). The TGA pyrolysis behavior of partially demineralized raw and oxidized samples was also conducted to investigate any accompanying effect of demineralization. Results obtained indicate a decrease in the maximum decomposition rate and apparent reactivity and an increase in activation energy of devolatilization of the coal when it was air oxidized. The effect was found to be less significant in the demineralized coal.

## INTRODUCTION

The complex and heterogeneous nature of coal has made understanding of its structure very difficult. Oxidation is one of the methods of evaluating the physical and chemical structural properties of coal. Considerable emphasis has been placed on oxidation as a means of understanding coal chemistry[1]. Efforts have also been made to conduct studies in order to address some practical implications of oxidation on coking and agglomerating potentials[2] and ignition, and spontaneous combustion characteristics of coal[3-5].

Many studies have been conducted on coal oxidation, review of which has been given in the literature[6-8]. From these previous studies, impact of oxidation on the coal properties that are of practical significance to coal beneficiation and utilization has been established. For example, chemical changes that occur during coal oxidation affect flotation behavior of stockpiled run of mine coal and the coking potential of the stockpiled products[9].

In addition to the effect of atmospheric oxidation of coal on its properties, beneficiation, quality and utilization, coal oxidation in a stream of air has been used to enhance production of humic acids, which are used as fertilizers, from coal[3,10-13]. The materials produced during atmospheric coal oxidation depends on the rank, type, and nature of the coal and on the oxidation conditions (e.g. temperature and period of oxidation)[10,13]. While studies have been conducted on the production of humic acid from oxidized British coal[3], Spanish coals[10], European brown coals[12], and Alaskan coals[13], no study has been conducted to address the effect of atmosphere oxidation on the pyrolysis behavior of Alaskan coals. The effects of thermal upgrading on the performance of an interior Alaska low-rank coal during pyrolysis (an important stage of coal utilization processes) have only been recently studied[14]. About half of the U.S. coals are located in the state of Alaska[15]. Alaskan coals, which are estimated at about 5.5 trillion tons[15], are of Cretaceous and Tertiary age[16] and are mainly of low rank[17].

This paper discusses the results of a preliminary study on the effect of air oxidation and demineralization on the devolatilization behavior of Beluga subbituminous coal using thermogravimetric analysis (TGA) technique. Decomposition characteristics and reactivity of oxidized and unoxidized coal samples were obtained.

## EXPERIMENTAL

The coal sample used in this investigation was a subbituminous C coal from Beluga field, west of Anchorage, Alaska. Analytical characteristics of the coal are summarized in Table 1.

The bulk coal sample was collected in lump size from the mine and taken to the laboratory in plastic bag contained in steel metal container under nitrogen. The coal sample was crushed to pass through 60 mesh. The minus 325 mesh size fraction was sieved off. The 60 x 325 mesh fraction was split into 4. One split of the sample was partially demineralized, one split was oxidized while another split of each sample was used for the analytical characterization.

Prior to oxidation, one split of the sample was partially demineralized according to the method used by Estevez, et al.[10]. This was achieved by suspending the coal in 0.5N HCl (1:10 w/v) for one hour at ambient temperature with continuous mechanical stirring. The partial demineralization was done in order to evaluate the catalytic effect (if any) of the mineral matter on oxidation[10].

The demineralized and undemineralized coal samples were oxidized at a temperature of 120°C for a period of about eight days in an air forced circulation oven. The pyrolysis behavior of the raw and oxidized coal samples was investigated using a Perkin-Elmer TGS-4 thermogravimetric analyzer. About 5 mg sample was scanned from 350°C to 950°C at a rate of 20°C/min. under nitrogen gas flowing at a rate of 80 cc/min. A series of runs was conducted before the actual runs to obtain the best conditions for excellent reproducibility. Reproducibility was best at the experimental conditions used. Sample was purged for about 15 minutes in nitrogen prior to run.

Thermograms and differential thermograms of the samples were obtained from which data, such as decomposition regions, pyrolysis rate, activation energy and thermal reactivity, were obtained and/or calculated.

## RESULTS AND DISCUSSION

Figure 1 shows the thermograms/differential thermograms (TG/DTG) for the raw Beluga coal used in this study. Two distinct weight loss regions, one at about 119°C and the other at about 343°C can be observed for the unoxidized coal. Corresponding TG/DTG curves were obtained for the oxidized demineralized (BDX8) sample and the oxidized undemineralized sample. Table 2 shows the rate of weight loss at the two regions and the temperature at which they occur for the feed and treated samples. The first weight loss region, which is attributed to loss of moisture, occurred at a slightly lower temperature for the oxidized coal than the raw coal. Partial demineralization appears to reduce the extent of decrease in the temperature at which the first region occurs as shown by the results on Table 2. The second weight loss region, which indicates onset of primary decomposition and entails primary devolatilization, occurred at 343°C for the raw coal and at 329°C and 331°C, respectively for the undemineralized oxidized and demineralized oxidized samples. Also, shown on Table 2 is the maximum devolatilization rate which occurred at the second region. It could be observed from the results on Table 2 that oxidation of the Beluga coal decreased its maximum decomposition rate from about 0.181 mg/hr/mg to about 0.156 mg/hr/mg. The maximum devolatilization rate of the coal was only decreased to 0.17 mg/hr/mg when the coal was demineralized prior to oxidation. Although the decomposition kinetics of coal are very complex [18-19], some useful kinetic information such as the activation energy was obtained. Apparent activation energies of decomposition over 475°C - 800°C temperature range were obtained for the raw and treated coal samples from the Arrhenius equation plotted in Figure 2, for the raw coal, oxidized coal, and oxidized demineralized coal, on the assumption that thermal decomposition was a first order that followed the relationship:

$$-dw/dt = kw \quad (1)$$

where  $dw/dt$  = instantaneous rate of weight loss,  $w$  = undecomposed decomposable matter, and  $k$  = specific reaction rate. The reaction rate was then related to the Arrhenius equation by

$$\ln k = \ln A - E_a/RT \quad (2)$$

where  $A$  = the frequency factor,  $R$  = the universal gas constant,  $E_a$  = activation energy and  $T$  = absolute temperature.

Values of  $k$  were obtained at various temperatures by using data from TG and DTG curves. The apparent activation energies for the raw coal and the oxidized undemineralized and oxidized demineralized samples were determined from plots of  $\ln k$  versus  $1/T$ , shown in Figures 2. The activation energy of the coal was increased by about 50% from 16.9 KJ/mol to about 26 KJ/mol when it was oxidized for eight days as depicted by the results on Table 2. Little or no change in activation energy was observed when the coal was demineralized prior to oxidation. Apparent activation energy of the raw coal in this study appears to be lower than those reported by others [19] for other coals of similar rank. However, activation energy of thermal decomposition of coal has been reported to be as low as 20 KJ/mol [20]. Maximum decomposition rate has been related to thermal reactivity of coal [19, 21-23]. From a kinetic view point the maximum decomposition rate is related to the reactivity  $R$  by

$$R = 1/w_i (dw/dt)_{\max} \quad (3)$$

where  $w_i$  = initial weight of coal (mg) and  $(dw/dt)_{\max}$  = maximum loss rate (mg/min).

Table 2 gives the value of reactivity for the raw coal and treated samples. A slight decrease in the reactivity of the coal could be observed when the coal was demineralized and oxidized for eight days. A more significant decrease in the reactivity occurred when the coal was not demineralized prior to oxidation as illustrated on Table 2.

## CONCLUSIONS

The thermal reactivity and apparent activation energy of the Alaskan subbituminous C coal have been found to be affected by oxidation in air at a temperature of 120°C. A decrease in reactivity and a corresponding increase in apparent activation energy have been observed when the coal was oxidized for eight days. Demineralizing the coal prior to oxidation was found to reduce the effect of oxidation on both thermal reactivity and apparent activation energy.

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TABLE 1. Characteristics of Beluga coal

<u>Beluga Coal</u>	
Proximate analysis: (wt%, ASTM equilibrium moisture basis)	
Moisture	24.40
Ash	7.71
Volatile matter	33.72
Fixed carbon	34.18
Ultimate analysis: (wt%, ASTM equilibrium moisture basis)	
Carbon	46.73
Hydrogen	6.88
Nitrogen	0.71
Sulfur	0.18
Oxygen	37.79
Heating Value (MJ/kg)	18.84

TABLE 2. Summary of Results

	Raw Coal BxO	Oxidized Coal for 8 days, Bx8	Oxidized demineralized coal for 8 days, Bdx8
Peak Temperature of Region 1, (°C)	119	110	113
Peak Temperature of Region 2, (°C)	343	329	331
Weight Loss Rate at Region 1, (Mg/Min)	0.028	0.022	0.019
Weight Loss Rate at Region 2, (Mg/Min)	0.181	0.156	0.170
Maximum Decomposition Rate, (Mg/Min)	0.181	0.156	0.170
Temperature of max. dw/dt, (°C)	343	329	331
Apparent Reactivity, daf, (Mg/hr/mg)	2.43	1.98	2.06
Activation Energy, (KJ/mol *k)	16.90	25.98	16.7

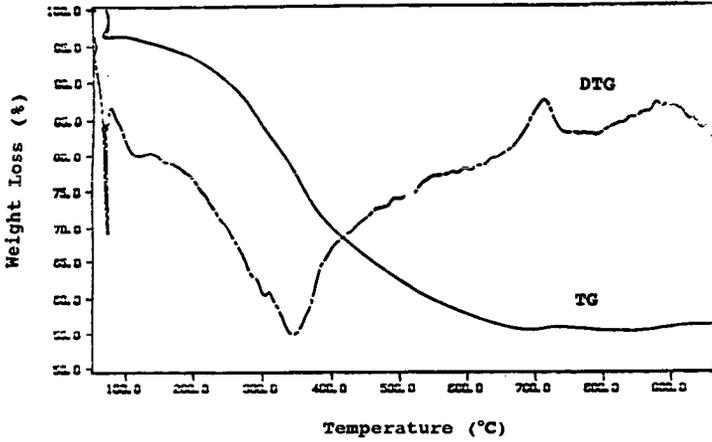


Figure 1. Thermograph of Raw Coal

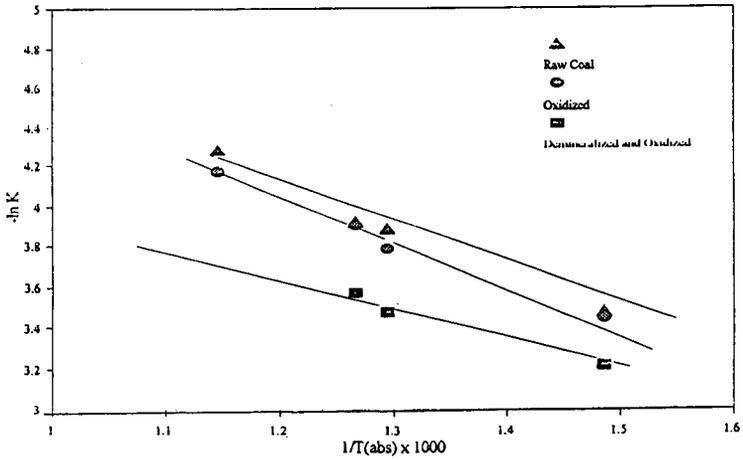


Figure 2.  $-\ln K$  versus  $1/T$  (abs. x 1000)