

**EFFECTS OF PARTICLE SIZE AND AIR FLOW RATES ON THE RUNAWAY
TEMPERATURE OF BITUMINOUS COAL AT 290K < T < 700K**

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INTRODUCTION

Spontaneous ignition and combustion of coal are major problems not only for actual mining of coal but also for its transportation and for industrial users. Most coals are prone to spontaneous combustion, but their susceptibility to ignition increases as the coal rank decreases (1). However, there are many anomalies to this straight rank order susceptibility. Chamberlain and Hall (1) have in fact, pointed out that some higher rank coals may be more susceptible to spontaneous ignition than lower rank coals.

The causes and mechanisms of spontaneous ignition are enigmatic because exceptions exist for every previously-suggested, single cause. Several models have been advanced to describe spontaneous heating (1-4), however. Among these are coal rank, electrostatic effects, geological factors, temperature, microbial ignition, the reduction in reactivity due to deterioration, air flow rates, particle size, pyrite content, porosity and water wetting of coal.

The purpose of this research was to examine the factors which may contribute to spontaneous ignition of ultrafine (particle size < 250 μm) bituminous coals and maceral enriched fractions under storage, air flow and/or dense phase pneumatic conditions and to understand physical interactions and chemical reactions pathways which may lead to spontaneous ignition of bituminous coals. We have initiated spontaneous ignition, FTIR, DSC, TGA and EPR measurements to accumulate data which can be used to propose mathematical models for spontaneous ignition of stored and pneumatically conveyed coals. In this report, we present our preliminary results on a high-volatile bituminous coal subjected to ignition temperature and FTIR measurements.

EXPERIMENTAL

To examine the effects of air flow temperature, particle size and air flow rates on the surface properties of coal, a high-volatile bituminous coal from Elkhorn #3 seam (Kentucky) was chosen. The coal samples were crushed and sieved and were divided into following particle size ranges : <44 μm , >63 μm <75 μm , >75 μm <106 μm , >106 μm <150 μm , >150 μm <250 μm , >250 μm <300 μm , >850 μm <900 μm .

The experimental arrangement used for determining the effects of air flow temperature and air flow rates on the coal's surface temperature is shown diagrammatically in Figure 1. The coal samples were packed in a quartz tube (10x120mm), and the sample tube

was inserted in the combustion tube assembly. The reaction zone was supplied with two thermocouples (T_1 and T_2) whose hot junctions were positioned along the axis of the sample bed. Thermocouple T_2 monitored the temperature of the fluid at the entrance of the sample tube; while thermocouples T_1 and T_3 monitored the temperature of the sample and exit gases, respectively. The sample tube's location in the tube (750mm length) was determined by the residence time required by the flowing gas to attain the required stable temperature at the entrance of the sample tube. The gas temperature was monitored for 1 hour before the sample tube was inserted in the combustion tube assembly. The compaction and packing of the sample in the tube plays an important role in determining whether exothermic reactions resulted or not. Therefore, every effort was made to ensure uniform compaction of the sample for each run.

Two grams of coal sample of various particle sizes were inserted in the sample tube and subjected to ignition experiments. Ignition was arbitrarily defined as the lowest air temperature which caused any part of the sample to exceed 150 K above the set temperature of the furnace. This value was chosen as an indication of a runaway reaction. Experience has shown that a rapid temperature rise, if one were to occur at all, would take place within a few minutes of the introduction of air, generally less than 20 minutes. If ignition did not occur, a fresh batch of the coal sample was used and the air temperature raised 10K higher than before air was introduced and the sequence was repeated. All FTIR spectra were obtained on an IBM IR-32 FTIR spectrometer equipped with an IBM 9000 computer. The alkali halide pellet technique was employed to record the spectra.

RESULTS AND DISCUSSION

Ignition Experiments:

Ignition experiments on high-volatile bituminous coals showed that the ignition temperature is strongly dependent on the mode of preheating the sample to the ignition temperature point, particle size, air flow rates, and sample compaction. When using air alone for preheating, it was found to be impossible to attain a uniform sample temperature just before ignition. Accordingly, a technique was evolved to first raise the temperature of the sample close to the ignition temperature by passing a stream of hot nitrogen or carbon dioxide through the sample. Once the constant temperature of the sample was obtained, the stream of gas was switched to air. A similar inert preheating procedure has been used by Hardman et.al. (5) to determine the spontaneous ignition temperature of activated carbons.

The ignition temperatures of three, high-volatile bituminous coals from Elkhorn #3, Ohio #5 and Pittsburgh seam are reported in Table 1. These three coals were chosen because of their large differences in their petrographic composition, especially in their vitrinite and exinite content. It has been suggested (1,2) that there is a close relationship between the coal maceral type and spontaneous oxidation potential. Chamberlain and Hall (1) demonstrated this kind of role when they found that exinites oxidized much more readily than vitrinites and inertinites. If such is the case then one will expect Ohio #5 coal to show the lowest ignition temperature. In fact, Ohio

#5 shows the highest ignition temperature among the three coals examined. Our preliminary results suggest that there may not be any correlation between the petrographic composition and ignition temperature. The sample bank, on which ignition experiments are conducted, needs to be expanded before arriving at definite conclusions.

TABLE 1
Ignition Temperatures of Three High-Volatile Bituminous Coals and Their Selected Petrographic Parameters.

	Elkhorn #3 Seam	Ohio #5 Seam	Pittsburgh Seam
Air Flow Rate (cm ³ /min)	900	900	900
Particle Size (µm)	<45	<45	<45
Ignition Temperature (K)	593±10	683±10	673±10
Reflectance (%)	0.93	0.74	0.79
Exinite (vol%)	9.10	26.20	3.90
Vitrinite (vol%)	75.20	55.30	84.20
Volatile Matter (wt%)	33.86	34.70	35.80
Fixed Carbon (wt%)	57.12	43.70	53.20
Moisture (wt%)	2.45	4.20	1.40
Ash (wt%)	6.57	17.40	9.60

Effects of Air Flow Temperature :

Surface reactions of coal under dense-phase pneumatic transport or under storage conditions play a crucial role in determining the initial heatup of coal. Consequently, it is of interest to determine the exothermic reaction pathways and the effects of the physical parameters on such reactions. The Elkhorn #3 seam coal was chosen to evaluate these effects since it showed the lowest ignition temperature. When coal samples of various particle size were inserted in the ignition tube assembly at temperatures lower than the ignition temperature, a typical 'particle temperature vs. time' plot is observed and is shown in Figure 2. Based on these profiles two parameters are defined:

$$\Delta T = \text{Runaway Temperature} = T_s' - T_g(t) \quad 1)$$

$$\Delta t = \text{Heatwidth} = \text{Time period for which } T_s(t) > T_g(t), \quad 2)$$

where T_s' is the maximum coal surface temperature, $T_s(t)$ is the coal surface temperature at time t , and $T_g(t)$ is the temperature of the flowing air at time t . Even though ΔT is arbitrarily defined, it represents the rise in coal surface temperature due to exothermic reactions under air flow conditions. In addition, ΔT and Δt measures the overall energy balance since they are related to the generation and dissipation of heat.

Figures 3 and 4 show the effect of air flow temperature (290 K < T_g < 700 K) on runaway temperature (ΔT) and heatwidth (Δt) values for Elkhorn #3 coal, respectively for three particle sizes. ΔT and Δt values were determined by using nitrogen preheat treatment before introducing air stream. The results indicate that there is a sudden jump in ΔT value at $T_g \approx 493$ K for particle size < 106 µm. As the particle size increases, the T_g value required to induce a sudden jump in ΔT value also increases. In fact, for particle size > 850 µm

no jump in ΔT value is observed at $290 \text{ K} < T < 700 \text{ K}$ with or without inert gas preheat treatment. This result suggests that there is a critical particle size below which Elkhorn #3 coal will be very susceptible to spontaneous ignition. This result is at variance with the recent numerical model proposed by Brooks and Glasser (3). From their numerical solution of the steady state equations, they suggested that the coal in the particle size range of (sub 1 mm) > (particle size) < (6 mm) is most susceptible to spontaneous combustion. Their prediction of the particle size effect on the spontaneous ignition is not consistent with our experimental results.

The effects of air flow rates and coal particle size on runaway temperature and heatwidth of Elkhorn #3 seam were also examined. To determine these effects, the air flow temperature $T_g = 493 \text{ K}$ was chosen since a sudden jump in ΔT value was observed at this temperature. The samples were inserted into the ignition tube assembly under air stream. The results are shown in Figures 5 and 6 for particle size and air flow rates, respectively. The experimental data suggests a power relationship between the runaway temperature (ΔT) and the particle size of coal. The coal surface temperature (T_s) under air flow rate of $900 \text{ cm}^3/\text{min}$ suggests a relation:

$$T_s = T_g + 4726 (\text{Particle Size, } \mu\text{m})^{-0.84} \quad 3)$$

Schmidt and Elder (6) have suggested a correlation between the rate of oxidation and particle size.

$$\text{Rate of oxidation} = K^3 (\text{Specific Surface Area})^{0.5}, \quad 4)$$

where K is a constant dependent on both rank and temperature. It can be seen that our results cannot be explained by equation 4 even if it is assumed that particle shape is random. Our results suggest that Elkhorn #3 coal will be most susceptible to spontaneous ignition for particle size < $150 \mu\text{m}$. The runaway temperature shows a parabolic dependence on the air flow rates. The data shown in Figure 6 for $> 63 \mu\text{m}$ < $75 \mu\text{m}$ particle size was fitted to a 3rd order polynomial:

$$T_s = T_g - 3.80 + 0.12 (\text{Air Flow Rate}) + 8.3 \times 10^{-5} (\text{Air Flow Rate})^2 \quad 5)$$

These results indicate that the susceptibility of spontaneous ignition will increase as the coal particle size decreases. In addition, there may be a critical air flow rate range for which heat generated may exceed heat dissipated.

FTIR Measurements :

FTIR measurements were carried out on the Elkhorn #3 seam bituminous coal to determine the effect of air flow temperature (T_g) on the structure of coal. The samples used for the FTIR measurements were the same samples which were subjected to air flow temperature measurements (i.e., Figure 3, < $43 \mu\text{m}$). The samples were withdrawn from the ignition tube assembly after reacting with flowing air ($900 \text{ cm}^3/\text{min}$) at $290 \text{ K} < T < 700 \text{ K}$ for 10 hours. Figure 7 shows the effect of air flow temperature (T_g) on the FTIR spectrum of Elkhorn #3 coal. The details of the FTIR analysis of bituminous coal and the effects of low temperature (< 423 K) oxidation on its vibrational spectrum have been reported earlier in the literature (7-9). The assignment of the

observed vibrational bands was based on these published works. The FTIR spectrum of unprocessed Elkhorn #3 coal can be characterized by : (a) A very broad band with maximum near $\sim 3350 \text{ cm}^{-1}$ was observed and is attributed to hydroxyl (-OH) groups. However, it was not possible to discern whether this band was due to moisture in KBr pellets, moisture in coal or hydroxyl groups which are part of organic matrix. We believe that this band is due, in fact, to a combination of the three sources mentioned above. (b) A weak absorption band at 3030 cm^{-1} was assigned to aromatic CH stretch. (c) A shoulder at 2960 cm^{-1} and two main absorption peaks at 2920 and 2850 cm^{-1} were observed and are attributed to CH_3 groups and aliphatic CH_3 , CH_2 , and CH groups, respectively. (d) A weak shoulder at 1700 cm^{-1} was observed and is assigned to C=O stretch. (e) The aromatic C=C bonds produced a strong absorption at 1600 cm^{-1} , and it is believed that some oxygen containing functional groups also contribute to its intensity. (f) The medium intensity band at 1445 cm^{-1} is due mainly to CH_2 groups in coal. However, CH_3 bending mode and aromatic stretching vibrations may also contribute to the intensity of this band. The weak observed band at 1375 cm^{-1} has been assigned to CH_3 groups. (g) A weak absorption at 1261 cm^{-1} has been assigned to ethers of the types $\text{C}_6\text{H}_5\text{-O-CH}_3$ or $\text{-CH}_2\text{O-CH}_3$. In addition to 1261 cm^{-1} band, a broad weak band centered around $\sim 1160 \text{ cm}^{-1}$ was also observed and is assigned to aldehydes and/or ketones and/or ether groups in the Elkhorn coal. (h) Three absorption bands were observed in the aromatic region i.e., at 870 , 812 and 754 cm^{-1} . The band at 870 cm^{-1} has been assigned to substituted benzene rings and to aromatic HCC rocking. The band at 812 cm^{-1} has been attributed to substituted benzene rings with two neighboring H, while the band at 754 cm^{-1} is assigned to monosubstituted benzene rings and O-substituted benzene rings. Additional bands due to inorganic materials were also observed but will not be discussed in this paper.

The effects of air flow temperature (T_g) on the FTIR spectra of Elkhorn #3 coal in the frequency range $4000 - 1100 \text{ cm}^{-1}$ have been summarized in Table 2. The absorbance changes reported in this table were determined by subtracting the unprocessed coal spectrum from the processed ($290\text{K} < T_g < 700\text{K}$) coal spectrum. It was not possible to follow the changes in the organic bands of the processed coal at frequency $< 1100 \text{ cm}^{-1}$ due to strong overlapping inorganic bands. Attempts were made to remove the contribution of the inorganic bands by subtracting the spectrum of low temperature ash. However, this subtraction resulted in erroneous bands in the difference spectrum due to changes in the intensity and broadening of the inorganic bands at $T_g \geq 473\text{K}$. The effect of air flow temperature on the intensity of aromatic CH stretch at 3034 cm^{-1} and aliphatic CH stretch at 2917 cm^{-1} is shown in Figures 8 and 9, respectively. Figure 10 shows the absorbance changes in the accumulative oxygen functionalities of coal as a function of air flow temperature. The y-axis of this graph represents the sum of absorbance changes at 1835 , $1780 - 1700$, and 1560 cm^{-1} . At $T_g \geq 640\text{K}$, only inorganic bands were observed signifying that all the organic matter in coal has combusted. Thus the absorbance change points at $T_g \geq 640\text{K}$ in the graphs 8,9 and 10 represent a net loss of these functional groups i.e., all the organic matter is lost.

TABLE 2
The Effects of Air Flow Temperature on the Frequency of Principal Absorption Changes of Elkhorn #3 Bituminous Coal at 290K < T_g < 700K.

Air Flow Temp. (K)	Frequency ($\pm 4 \text{ cm}^{-1}$)
343	2913(+), 2845(+), 1700(+), 1445(+)
393	2917(-), 2851(-), 1835(+), 1770(+), 1700(+), 1445(-), 1375(-), 1021(-)
443	3034(-), 2917(-), 2851(-), 1770(+), 1700(+), 1560(+), 1445(-), 1375(-), 1109(+)
493	3034(-), 2917(-), 2851(-), 1835(+), 1770(+), 1725(+), 1560(+), 1445(-), 1219(+), 1136(+)
543	3034(-), 2917(-), 2851(-), 1835(+), 1770(+), 1721(+), 1555(+), 1445(-), 1267(+), 1211(+), 1100(+)
593	3034(-), 2917(-), 2851(-), 1835(+), 1770(+), 1725(+), 1560(+), 1451(-), *
643	3039(-), 2920(-), 2855(-), 1698(-), 1651(-), 1593(-), 1441(-), *, **
693	3048(-), 2918(-), 2857(-), 1692(-), 1598(-), 1445(-), *, **

+ Sign indicates that absorption increased or new bands appeared.
- Sign indicates that absorption decreased or bands disappeared.
* At frequency < 1200 cm^{-1} , it was difficult to follow the organic bands due to overlapping inorganic bands.
** Only inorganic bands were observed.

The increase in intensity of aliphatic vibrations (i.e., at 2917, 2851, and 1445 cm^{-1}) at T_g \leq 343K was most surprising. At these low temperatures a loss of some volatile matter is expected, and this loss should result in a decrease in the intensities of aliphatic vibrations. No intensity enhancement of these vibrations results if nitrogen or carbon dioxide is used under identical gas flow and temperature conditions. The intensity of the vibrational bands not only depends on the concentration of the functional groups in the sample but also on their dipole moment i.e., on the transition probability. We do not believe that the concentration of aliphatic groups has increased at T_g \leq 343K, but we conjecture that an oxygen attack on coal somehow alters the dipole moment of the aliphatic groups at this temperature. At T_g > 343K there is a steady decrease in the intensity of aliphatic bands at 2917, 2851 and 1445 cm^{-1} , with a major decrease located at 393K \leq T_g \leq 493K. As can be seen from Figure 9, there is no correlation between the absorbance change and the runaway temperature of this coal. Similar results were observed for aliphatic bands at 2851 and 1445 cm^{-1} . These results suggest that the loss of aliphatic groups from the coal matrix, in the form of volatile products, plays a little role in the magnitude of the runaway temperature. Under air flow conditions, the volatile products are expected to be swept away from the sample toward the exhaust of the combustion tube, thus drastically decreasing the residence time of volatile products around the sample. If the volatile combusts on the coal's surface as it leaves the coal, the combustion exothermic reactions should contribute to the runaway temperature. It is possible that these exothermic reactions contribute to the early profile of heatwidth, but it seems unlikely since no correlation exists between

absorbance changes at 2917, 2851, and 1445 cm^{-1} and heatwidth. Figure 8 shows that the aromatic CH stretch vibration at 3030 cm^{-1} remains unchanged at 290K $< T_r < 400\text{K}$. However, it is interesting to note that as the runaway temperature increases the intensity of CH stretch vibration decreases. This decrease is mirrored along with alterations in the aromatic region's vibrations i.e., at 900 - 700 cm^{-1} . At present it is not possible to calculate the absorbance changes in this region due to interference from inorganic bands. The dependence of aromatic stretch vibration on the runaway temperature strongly suggests that it is the oxidation of the aromatic groups that results in major contribution to the runaway temperature. As T_r increases from 293K, the C=O stretch vibration at 1700 cm^{-1} increases and shows maximum contribution at 443K. Mirrored with the increase in C=O stretch at 1700 cm^{-1} a very broad, weak band is observed in OH stretch, suggesting the formation of carboxylic acid groups largely of aliphatic type. It seems that the oxidation of aliphatic groups attached to the aromatic structure contributes very little to the runaway temperature. At 493K $\leq T_r \leq 593\text{K}$, strong absorbance bands at 1835, 1770, 1725, 1560, 1300 - 1100 cm^{-1} appear in the spectrum, indicating massive oxidation reactions in coal which leads to the formation of anhydrides, aldehydes, lactones, esters, ketones and ethers. Figure 10 shows the effect of air flow temperature on the accumulative absorbance changes in the oxygen functional groups at 1835, 1770, 1725, 1700, and 1560 cm^{-1} of Elkhorn #3 coal. These results clearly show that these oxidation reactions make major contribution to the heat generated i.e., to runaway temperature. It was surprising that at $T_r = 493\text{K}$, with the coal's surface temperature reaching 790K, complete combustion of the sample did not result. It appears that the oxygen functional groups generated on the surface of coal inhibit complete combustion reaction at $T_r \leq 593\text{K}$. Diffuse reflectance - and photoacoustic - FTIR studies are in progress on these samples to evaluate the effects of incomplete combustion reactions and runaway temperature.

ACKNOWLEDGEMENTS

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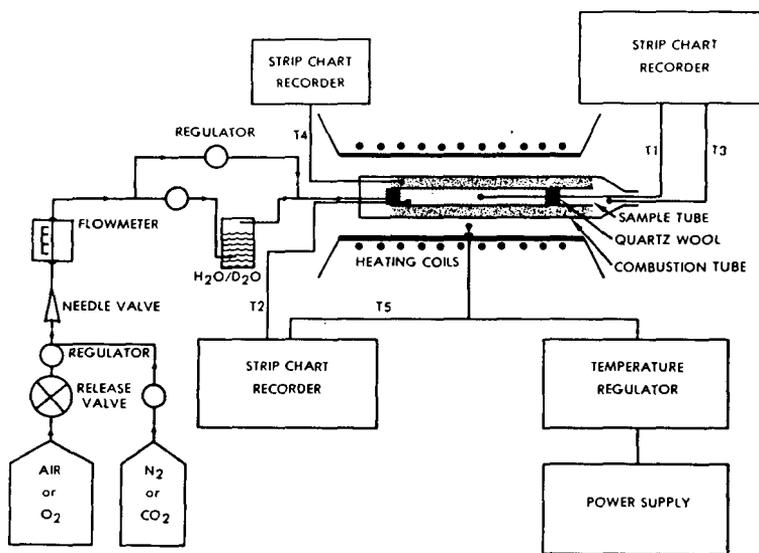


Fig. 1 Combustion tube assembly.

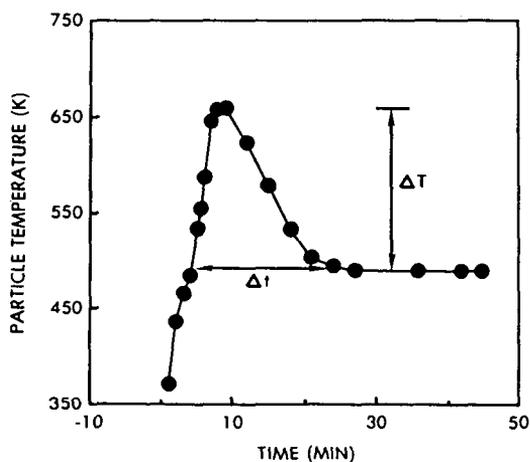


Fig. 2 Definition of runaway temperature (ΔT) and heatwidth (Δt).

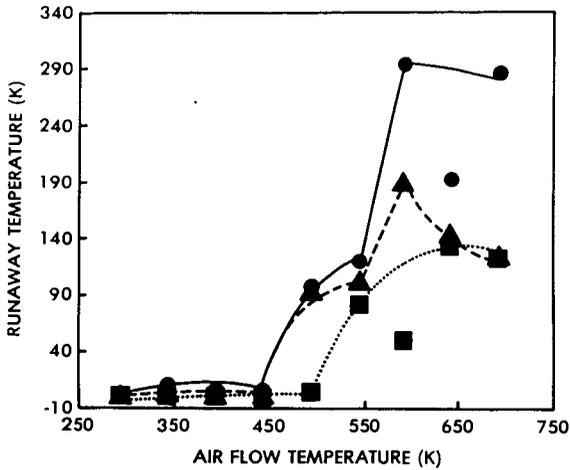


Fig. 3 Effect of air flow temperature on the runaway temperature of Elkhorn Coal. Air flow rate = 900 cc/min., ● <45 μm, ▲ 75 > <105 μm, ■ 150 > <250 μm.

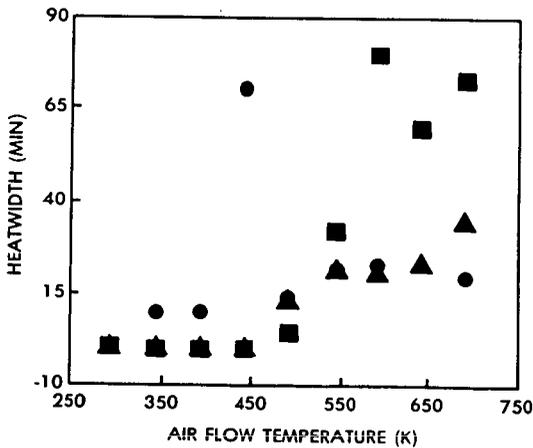


Fig. 4 Effect of air flow temperature on the heatwidth of Elkhorn coal. Air flow rate = 900 cc/min., ● <45 μm, ▲ 75 > <105 μm, ■ 150 > <250 μm.

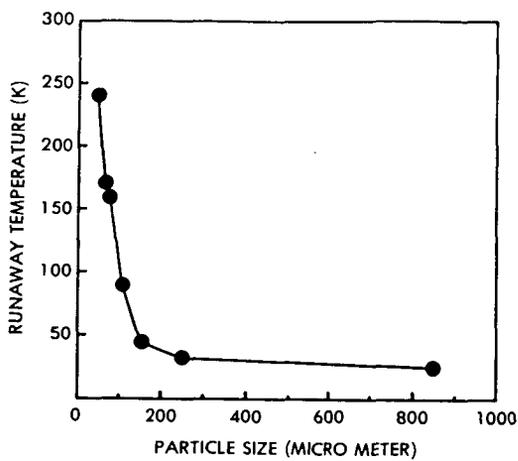


Fig. 5 Effect of particle size on the runaway temperature. $T_g = 493K$, air flow rate = 900 cc/min.

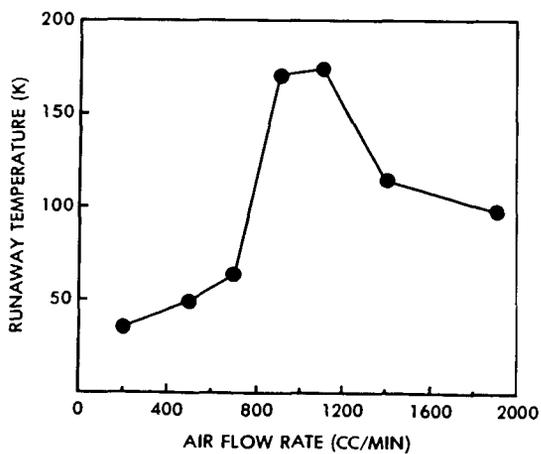


Fig. 6 Effect of air flow rate on the runaway temperature. $T_g = 493K$, particle size = $<45 \mu m$.

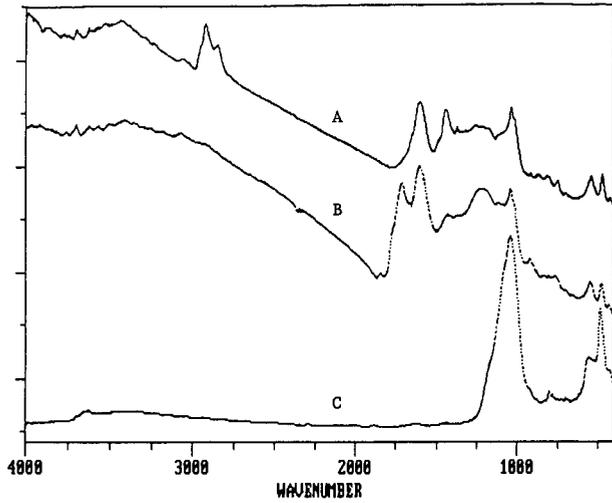


Fig. 7 FTIR spectrum of Elkhorn coal subjected to air flow experiments. (A) 293K, (B) 493K, and (C) 693K.

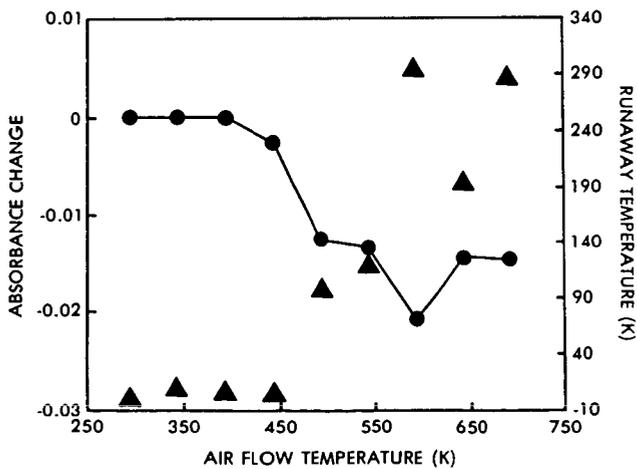


Fig. 8 Effect of air flow temperature on the absorbance of 3034 cm^{-1} band (●) and runaway temperature (▲).

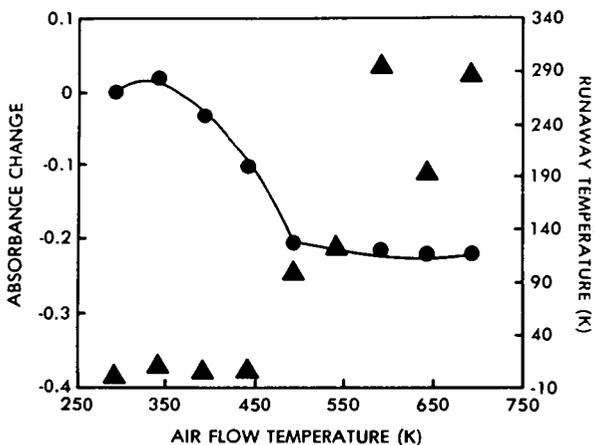


Fig. 9 Effect of air flow temperature on absorbance of 2917 cm^{-1} band (●) and runaway temperature (▲).

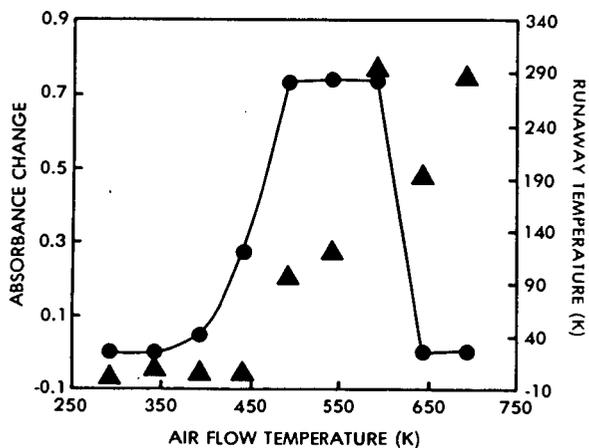


Fig. 10 Effect of air flow temperature on the accumulative absorbance of 1835, 1770, 1725, 1700 and 1560 cm^{-1} bands (●) and runaway temperature (▲).