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LOW TEMPERATURE OXIDATION OF A HIGH VOLATILE BITUMINOUS TURKISH COAL

EFFECTS OF TEMPERATURE AND PARTICLE SIZE

Kemal Baris¹ and Vedat Didari¹

ABSTRACT: Low-temperature oxidation of a high volatile bituminous Turkish coal was studied using an isothermal flow reactor technique under different experimental conditions. Coal samples were ground and sieved to three different particle sizes namely -850 μm , -425 μm and -300 μm . The samples were oxidised at 40, 60 and 90°C with an oxygen flow rate of 45 mL/min. CO₂ and CO emissions were analysed using an HP 5897 Series II type gas chromatograph. Temperature was found to have a definite effect; as the temperature increased rates of formation of CO₂ and CO also increased significantly. Experimental results showed that the rates of formation of CO₂ and CO are independent of the particle size of the samples.

INTRODUCTION

Low-temperature oxidation of coal has been studied by a number of investigators since the reaction with oxygen may lead to self-heating and subsequent spontaneous combustion of coal (Polat and Harris, 1983; Kaji, Hishinuma and Yoichi, 1985; Itay, Hill and Glasser, 1989; Clemens, Matheson and Rogers, 1990; Krishnaswamy et al., 1996; Wang, Dlugogorski and Kennedy, 1999, 2002, 2003a, 2003b). Along with the safety problems the oxidation of coal also affects the molecular structure of coal and this causes negative effects on the mass and elemental composition of coal.

The spontaneous combustion of coal causes serious problems in the coal industry during mining, transportation, storage and treatment. It is reported that every year between 100 and 200 Mt of high quality coal is consumed by spontaneous combustion in China (http://www.itc.nl/~coalfire/problem/china_coalfire.html). Six spontaneous combustion events were reported in Karadon Colliery of Turkish Hardcoal Enterprise in the Zonguldak Basin between 1990 and 2000. Since has the potential to cause loss of property and life, special attention has been being paid to spontaneous combustion of coal.

Wang, Dlugogorski and Kennedy (2003a) stated that coal oxidation at low temperatures (i.e. below 100°C) is a complicated process and involves four phenomena: oxygen transport to the surfaces of coal particles, chemical interaction between coal and O₂, release of heat and emission of gaseous products. The diversity of chemical composition, physical properties (such as heat capacity and thermal conductivity) and porous structure of coal enhances the complexity of this phenomenon.

The reaction between coal and oxygen at low temperature depends on many factors including temperature, particle size, surface area, coal pore structure, moisture content, coal rank and the composition of air. This paper presents results of the effects of temperature and particle size on low-temperature oxidation of a high volatile Turkish bituminous coal by examining the characteristics of gaseous products, CO₂ and CO in particular, emitted during the oxidation process.

EXPERIMENTAL

A high volatile bituminous coal was obtained from Armutcuk Colliery operated by Turkish Hardcoal Enterprise, Zonguldak Basin, Turkey. Proximate, ultimate and petrographic analysis of the sample is presented in Table 1. Coal samples were crushed, ground in a sealed ball mill and then sieved to three different particle sizes of -850 μm , -425 μm and -300 μm (sieving was performed in a sealed glove box to minimise the contact of particles with air). Particle size distributions were determined using a Malvern Laser Beam Particle Sizer. Figure 1 shows the particle size distribution of the coal samples. d_{50} and d_{80} values are 0.389 and 0.512 mm for the -850 μm , 0.297 and 0.215 mm for the -425 μm and 0.112 and 0.179 mm for the -300 μm particle size, respectively. After comminution and

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sieving 125 g of sample from each size group were weighed and put in glass jars in a sealed glove box under nitrogen flow and then evacuated to be used in oxidation tests.

Table 1 - Proximate, ultimate and petrographic analysis of the coal sample

Proximate analysis (dry basis)		Ultimate analysis (dry ash free basis)			
Ash (%)	5.1	C (%)	81.7		
Volatile Matter (%)	37.3	H (%)	5.0		
Fixed Carbon (%)	57.6	N (%)	1.3		
Total Sulphur (%)	0.5	S (%)	0.93		
Calorific Value (kcal)	7606	O (%) by diff.	7.3		
Petrographic composition					Reflectance (R_m) (%)
Vitrinite (%)	Liptinite (%)	Semi-Inertinite (%)	Inertinite (%)	Mineral Matter (%)	0.768
52.2	8.4	15.8	23.0	0.6	

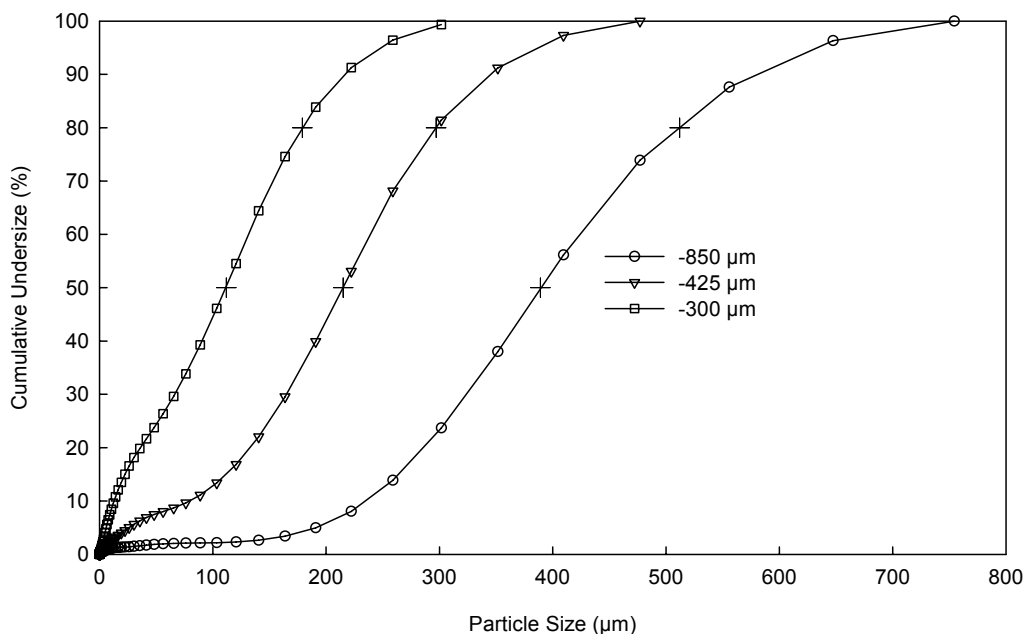


Figure 1 - Particle size distribution of coal samples

An isothermal flow reactor technique was used for the oxidation tests. Figure 2 shows the detail of the setup used in the experiments. Before starting an experiment, 125 g of sample was placed into the reactor in a sealed glove box and dried by purging ultra-high-purity nitrogen under 65°C for 15 hours. After drying the oven was set to the desired temperature. As soon as the temperature of the coal sample in the reactor and the temperature of the oven equilibrated a gas stream of oxygen (99.6 % purity) was introduced to the system at a flow rate of 45 ± 0.5 mL/min. In order to monitor gas emissions (CO_2 , CO and hydrocarbons) an HP 5897 Series II type gas chromatograph equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) was used. For each oxidation test 15 consecutive analyses were performed by using GC. Total oxidation period was 337.5 minutes. The variation of oxygen concentration was monitored by a Rapidox 3100 oxygen analyser.

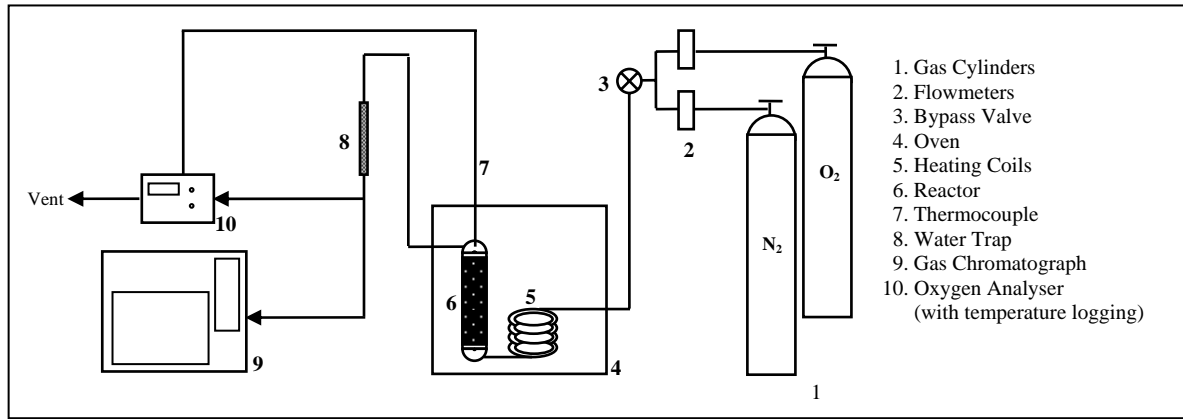


Figure 2 - Experimental setup used for oxidation tests

The oxidation tests were repeated for each size by modifying the heating temperature to investigate this effect on oxidation of coal at low temperatures. The temperature of coal samples was monitored for each oxidation test. Table 2 shows the experimental conditions for each size.

Table 2 - Experimental conditions for each size fraction tested.

Size (μm)	Flow rate (ml/min)	Temperature ($^{\circ}\text{C}$)
-850	45	40
		60
		90
-425	45	40
		60
		90
-300	45	40
		60
		90

The rates of formation of CO_2 and CO were calculated using Equations (1) and (2):

$$R_{\text{CO}_2} = \frac{C_{\text{CO}_2,0}}{W} V_{\text{gas}} \quad (1)$$

$$R_{\text{CO}} = \frac{C_{\text{CO},0}}{W} V_{\text{gas}} \quad (2)$$

where $C_{\text{CO}_2,0}$ and $C_{\text{CO},0}$ are concentrations of CO_2 and CO at the reactor exit, V_{gas} denotes the flow rate of the gas stream and W represents the dry mass of coal sample. W was measured after each experiment and it was observed that the increase in the mass of coal sample is almost negligible.

RESULTS AND DISCUSSION

Typical experimental results showing the time-dependent rates of CO_2 and CO formation are presented in Figure 3. Note that the first experimental data were removed from the graphs since it is considered that dilution of nitrogen remaining in the reactor could mask any trends in the formation of carbon oxides.

It is observed that the rate of formation of CO_2 decreases gradually with time. Rate of production of CO also exhibits a similar behaviour. It is known that the reason for the decay in formation rate of CO and CO_2 is because of the gradual accumulation of stable complexes at the surface of coal pores

during coal oxidation as stated in the literature (Carpenter and Giddings, 1964). In their studies Wang, Dlugogorski and Kennedy (2002) also argued that especially in the first few hours of experiments, rapid decrease in formation rates may be due to distinct reaction pathways for the liberation of these products. Although the observed decrease in the production rates of CO_2 and CO are not so sharp a substantial decrease shown in Figure 3 supports this argument.

Temperature has a significant effect on the production rates of CO_2 and CO . As the temperature increases the level of emission of CO_2 and CO also increases. Figure 4 shows the effect of temperature on low-temperature oxidation of the coal sample. Although the formation rate of carbon oxides increase with time for a few experimental results the rates in general exhibit a decreasing trend for most of the experimental results. Even if the formation trend is increasing with time oxidation tests performed at higher temperatures always result in higher level of emissions of CO_2 and CO . This result is in agreement with other experimental findings (Carpenter and Giddings, 1964; Kaji, Hishinuma and Yoichi, 1985; Wang, Dlugogorski and Kennedy, 2003b).

Since the heating temperatures were rather low the temperature of coal samples showed rather a quick increase at the beginning of each test due to the rapid oxidation, then temperature rise had almost a constant rate.

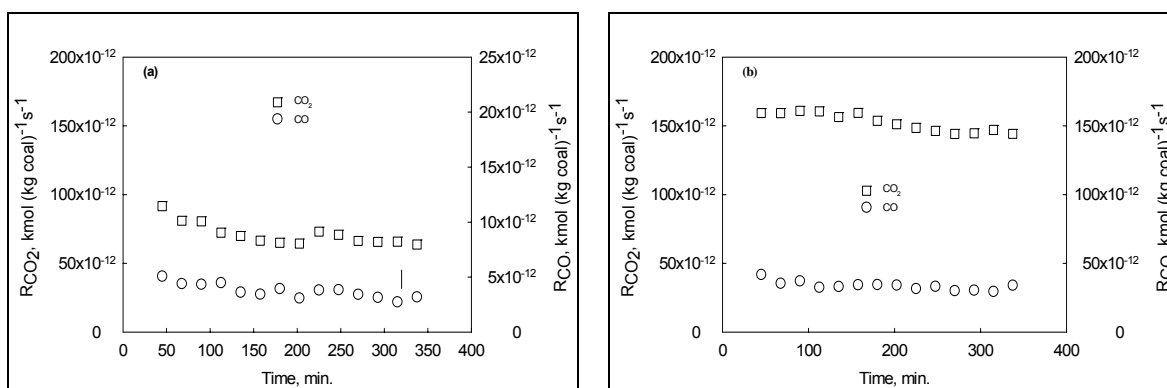


Figure 3 - Variation in the rates of production of CO_2 and CO (a) with a particle size of $-300 \mu\text{m}$ at 60°C (b) with a particle size of $-425 \mu\text{m}$ at 90°C

Early investigators reported that CO is the main product of coal oxidation at low temperatures (i.e. below 70°C). However, present results do not support these observations. It is clear that the formation rate of CO_2 is always much higher than that of CO in all experimental conditions even at 40°C . It seems that CO_2 is the major product of oxidation at low temperatures. This argument is supported by a number of researchers (Carpenter and Giddings, 1964; Kaji, Hishinuma and Yoichi, 1985, Wang, Dlugogorski and Kennedy, 2002)

The experimental results show that the production rates of CO_2 and CO exhibits no dependence on the coal particle size although a few experimental results seems to show a dependence on the coal particle size. Figure 5 illustrates a typical trend for the effect of particle size on low temperature oxidation of the coal sample. As seen in Figure 5, the rate of formation of CO_2 does not seem to have a dependence on the particle size at 60 and 90°C although there seems particle size dependence at 40°C with some scatter in the experimental data. However, there is no obvious dependence on particle size for the rate of formation of CO in all experimental conditions. These results may indicate that the production of carbon oxides is not controlled by mass transport of these species in coal pores but it is controlled by chemical reactions as confirmed by several researchers (Kaji, Hishinuma and Yoichi, 1985; Wang, Dlugogorski and Kennedy, 2002).

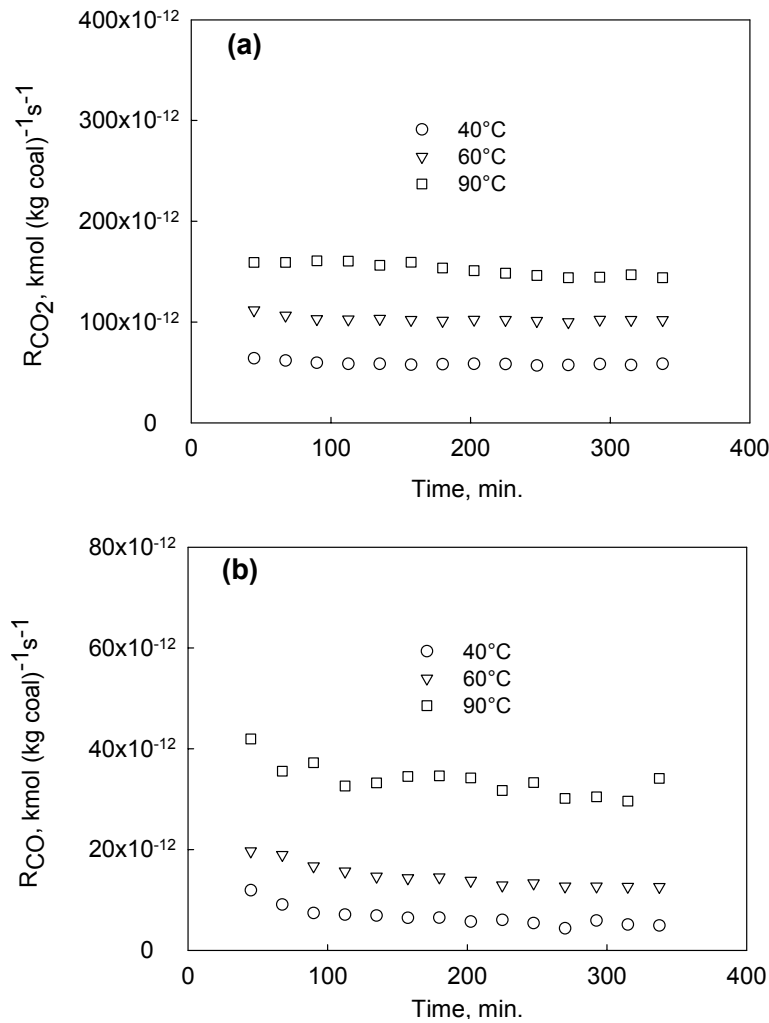


Figure 4 - The effect of temperature on the formation rate of (a) CO₂ and (b) CO with a particle size of -425 μm

CONCLUSIONS

The effects of temperature and particle size on the low-temperature oxidation of a high-volatile Turkish bituminous coal were examined at 40, 60 and 90°C and for the particle sizes of -850, -425 and -300 μm by measuring CO and CO₂ formation rates. It is observed that CO₂ is the major product of oxidation at low temperatures rather than CO. The formation rate of CO₂ is always much higher than that of CO in all experimental conditions. The formation rates of CO₂ and CO decrease with time though there was some scatter evident the experimental data. This may be attributed to deactivation of active sites in coal structure. Temperature has a pronounced effect on the rates of formation of CO₂ and CO. When the temperature is increased the production rate of carbon oxides also increases. Furthermore, the formation rate of CO₂ and CO is independent of particle size which may indicate that the production of CO₂ and CO is controlled by chemical reaction rather than mass transport in coal pores.

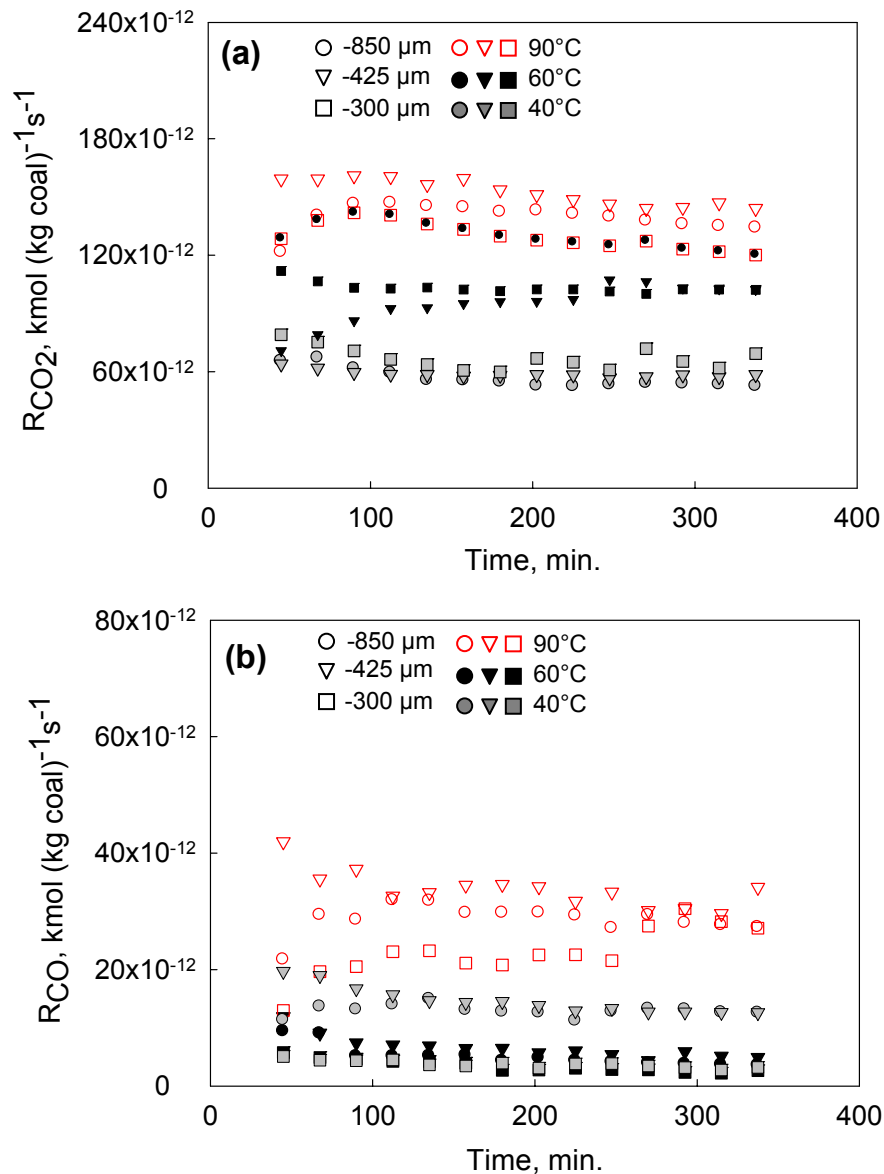


Figure 5 - The effect of particle size on the production rates of (a) CO₂ and (b) CO at 40, 60 and 90°C

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