

## A STUDY ON SPONTANEOUS IGNITION OF BITUMINOUS COAL

by

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*The thermal properties of four bituminous coals were studied using isothermal and temperature-programmed calorimeters, such as a differential thermal analysis, a heat flux calorimeter C80 and an thermal activity monitor (TAM-III). The corresponding spontaneous ignition was measured in an adiabatic spontaneous ignition tester. It was found that there were weak exothermic activities in bituminous coal at 50-100 °C and meanwhile carbon monoxide and carbon dioxide was generated. These thermal behaviors are responsible for the self heating from 50 °C and spontaneous ignition at 80 °C.*

Key words: *self-heating, spontaneous ignition, bituminous coals*

### Introduction

It is well-known that coal has general tendency of self-heating. If the heat is ineffectively dissipated, a hot spot may develop within a stockpiled coal and lead eventually to spontaneous ignition. Extensive concerns and studies made efforts to understand this process. For dried coals one of the most important contributions comes from oxidation at the low temperature. Low temperature is used to denote the temperature range from room temperature to approximately 150 °C. This is significantly below the temperatures (300-450 °C) at which significant pyrolysis, combustion, and liquefaction chemistry occurs. The first concern is the heat source at the low temperature range. The mechanism by which these oxidation reactions occur remain poorly understood but previous studies [1-4] suggest that a three-step reaction sequence is common. Up to 70 °C the major feature is the formation of "coal-oxygen complexes" by reaction between oxygen and radical sites in the coal structure. Between 70-150 °C, these complexes decompose, and around 150 °C a new set of coal-oxygen complexes form exothermically. However, Gethner [5] pointed out that these steps merge to each other and actually multiple reactions occurs. The next concern is the consequence of these heat sources, that is, whether it may lead to self heating of coal and eventual ignition. The basis of the test for spontaneous ignition is that according to Frank-Kamenetskii (F-K) model of thermal ignition, critically in a 10 cm cube at 140 °C (413 K) is equivalent to criticality in a 3 m cube shipping stow at 50 °C (323 K), the highest temperature such a stow could attain purely by heat transfer from the outside [6, 7]. The contradiction of extrapolating the results from small scales to a huge one lies in that the oxidations at different temperatures exhibits multiple stage reactions and the Arrhenius kinetic at higher temperatures (such as 140 °C) is not descriptive of the oxidation chemistry at lower temperatures, and thus, the reaction measured at higher temperature in small scale tests could not be taken as representative of the reaction at lower temperatures when repre-

sented in the F-K theory formation and it may cause big excursion. In another word, it requires a direct measurement for self heating and ignition at low temperature range in laboratory.

The aim of the present study was to identify more clearly the chemistry responsible for self-heating of several bituminous coals by measuring their thermal properties, self-heating, gas evolution and ignition, and their correlation in particular at low temperature range. The chemical composition of coal varies widely. Very roughly, coal composes, by mass, about 80-90% carbon, 4-5% hydrogen, 3-11% oxygen, 1-3% nitrogen, 0.5-1% sulfur and much smaller quantities of other elements. Four bituminous coals, the percent of hydrogen and oxygen are at the high end [8]. Normally it is slight stable compared with those low rank coals, but the oxidations differed only by smaller amounts of the products formed. The effect of moisture was also examined by adding 20% water in the coals.

## **Experimental**

### ***Samples***

Four bituminous coals imported from Australia were used, which were labeled as A to D in this study.

### ***Thermal properties***

#### ***Simultaneous thermogravimetry / differential thermal analysis (TG-DTA)***

As a conventional thermal analyzer to examine the general thermal properties of the material in handiness and in a short time, a TG-DTA, Rigaku thermal plus TG 8120, was used to perform the preliminary screening measurements of heat release and weight loss from the sample, at a scanning rate of 2 K/min. Sample mass was 20 mg. An open aluminum sample cell was used as reference. The atmosphere was air supplied at a flow rate of 80 ml/min.

#### ***Heat flux calorimeters***

Two Calvet heat flux calorimeters, C80 and MS80 were used for precise determination of the thermal activities of coal at extensive temperature ranges. In the Calvet calorimeter, two experimental vessels are stayed in a calorimeter block which imposes the temperature of the experiment as fixed or variable. Two symmetrical thermal flux meters composed of thermocouples connected in series surround the experimental vessels and are thermally connected to the calorimeter block. This enables Calvet calorimeters to provide high quantification of measurements and excellent sensitivity. Under such conditions, a scanning throughout the whole temperature range was able to be conducted to clarify the reactions of the specimen at the full temperature range from the room temperature up to 300 °C in the C80 and to 200 °C in the MS80, respectively. In the C80, scanning rate was 0.1 K/min. In the measurement, 1.4 g coal was filled into the 12 ml stainless steel vessel. The same amount of alumina was put into the reference vessel. In addition of coal, coal with 20% water was also measured.

#### ***Isothermal measurements in TAM***

A thermal activity monitor, TAM 2277, Thermometric Co., Sweden, as one of the most sensitive thermometry, was used for isothermal measurement at 50 °C. The TAM thermostat is

stable to 0.1 m and a detect limit of 0.05 W/ml can be achieved. The sample and the reference,  $\text{Al}_2\text{O}_3$ , of about 1 g, were filled into their vessels of 4 ml. The measurements were conducted in air for coal and its mixture with 20% water.

### ***Gas evolution***

Coals with and without 20% water were stored in an 100 ml closed glass bottle for 10 days at the room temperature and 60 °C, respectively. The bottle was then merged into water upside down and gases released from the bottle were collected by a tetra bag and analyzed by gas chromatography.

### ***Spontaneous ignition measurements***

#### *Wire mesh cube test*

This test is described in the UN Test N.4 [6, 7, 9] to measure the ability of a substance undergoing oxidative self-heating in a volume by exposure of it to air at certain constant environmental temperatures. Cubic sample container, made of stainless steel net with a mesh opening of 0.05 mm, was 100 mm side with their top surface open. After the sample was filled, two chromel-alumel thermocouples of 0.3 mm diameter were inserted: one was placed at the centre of the sample and the other was between the sample container and the oven wall. In the measurements, temperatures of 90-190 °C, with 10 °C interval, were kept in a hot-air circulating oven. The temperature history was recorded. Measurements were undergone at least one week to see whether self-heating took place at a certain surrounding temperature and finally caused a spontaneous ignition.

#### *Spontaneous ignition tester*

To study the transition from self-heating to spontaneous ignition of coal, a more advanced detector is needed. The Shimadzu SIT-II, spontaneous ignition tester (SIT), was used for measuring materials susceptible to spontaneous ignition under an adiabatic condition, in which heat loss to the surrounding can be reduced to the minimum and any possible heat liberation from exothermal reaction can survive and be used for self-heating. The sample cell is made of quartz. The thermocouples and the heaters are set around the sample cell and the adiabatic condition can be kept by comparing the sample cell temperature between inside and outside. After an isothermal condition was obtained, whenever any heat release from the specimen is detected, the furnace is then switched to the adiabatic mode, which allows the specimen to self-heat by its heat of reaction. During the adiabatic heating period the temperature surrounding the specimen is so controlled that there is no temperature difference between the center and the surrounding of the specimen. The onset temperatures of measurements can be set in the range from 10 to 300 °C. In the furnace available at the SIT, about 1 g of sample was positioned in the tester and the specimen was then heated to a pre-selected temperature. The temperature of the specimen was recorded continuously until ignition occurred. During the SIT tests, air atmosphere of 5 ml per minute was replenished after the isothermal condition of the test system was established.

## Results and discussion

### Thermal properties

The value of heat of combustion of coal was 29 kJ/g. The four bituminous coals presented the common behaviors of TG-DTA, as seen in fig. 1. Table 1 lists the results of the TG-DTA. The adsorption of oxygen below 100 °C should cause weight increase and heat generation in coals, but these was unable to be observed due to water evaporation. On the TG curve, weight was lost at 100 °C by 2-5%, and it was not lost further up to 300 °C and contrarily increased a little. This implies that the adsorption of oxygen rather than significant decomposition happen below 300 °C. Correspondingly on the DTA curve, the onset temperature of heat release was about 110 °C, and it increased slowly until 300 °C. The significant weight loss and heat release happened at above 300 °C.

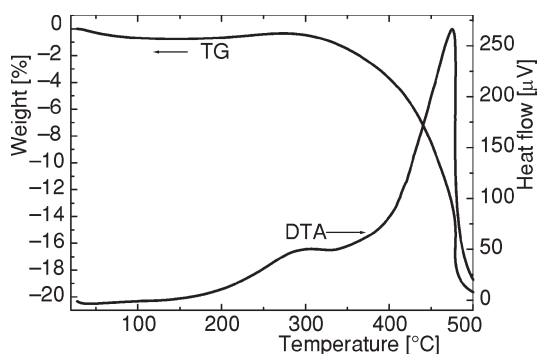


Figure 1. Typical curves of TG-DTA

Table 1. results of TG-DTA

Samples	DTA onset temperature, [°C]	TG mass loss at 100 °C, [%]
Coal A	117	4.91
Coal B	112	2.98
Coal C	106	2.81
Coal D	114	2.79

Typical curves of the four bituminous coals in the presence of water at the full temperature range in the C80 are given in fig. 2 since they had the common shapes. They are compared with two low rank coals subbituminous coal and lignite. The results of each coal are given in tab. 2. In contrast of the TG-DTA, weak thermal behavior is possibly observed in particular at

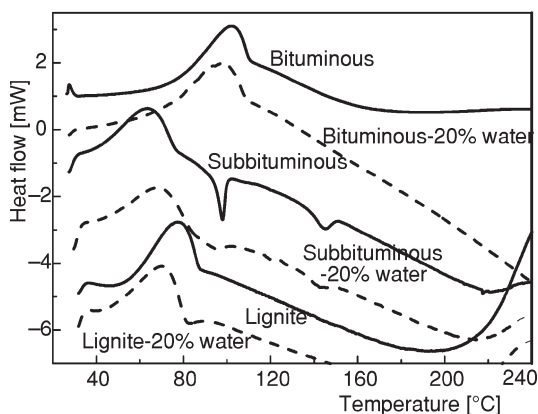


Figure 2. Typical curves of C80 for bituminous coal with comparison of low rank coals: subbituminous coal and lignite

low temperature regime due to the high sensitivity of the C80. There was a heat generation peak in bituminous coal which started from 50 to 60 °C. The onset temperature of low rank coals was lower than bituminous coal [3-5], for which subbituminous coal reached room temperature. At higher temperature, there was nearly no further heat generation up to 300 °C. The reason may lie in fact that in the closed cell of the C80, oxygen was depleted by the first reaction and no replenishment was continued to support the oxidation at higher temperature.

When coals were exposed to air or oxygen while being heating at a constant rate, this heating may have been obscuring some of the effects of low temperature oxidation.

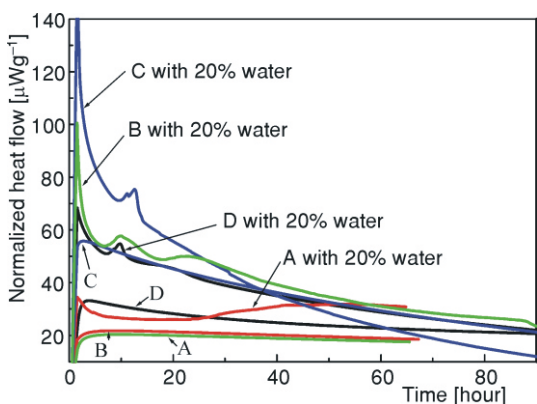
**Table 2. Results of bituminous coals and two low-rank coals in the C80**

Sample	Onset temperature [°C]	Accelerating temperature, [°C]	Peak temperature [°C]	Heat of reaction [J/g <sup>-1</sup> ]
Coal A	60 (54)	82 (73)	101 (100)	9.4 (14.6)
Coal B	56 (56)	81 (75)	102 (98)	10.2 (11.7)
Coal C	56 (52)	68 (66)	95 (94)	9.8 (10.1)
Coal D	52 (50)	71 (66)	97 (102)	13.2 (19.4)
Subbituminous coal	RT (RT)	46 (46)	60 (62)	13.6 (14.8)
Lignite	50 (42)	58 (46)	78 (72)	14.8 (15.2)

Values in brackets are samples with 20% water; RT – room temperature

In order to more clearly identify the chemistry responsible for self-heating it is necessary to conduct experiments under isothermal conditions. Moreover, a more sensitive calorimeter is needed to figure out the weak exothermal behavior as much as possible. Figure 3 shows the curves of normalized heat flow vs. time for the coals with and without water in the TAM-III at 50 °C. Corresponding heat generations for all bituminous coals are listed in tab. 3. It was previously reported that the major feature of the isothermal traces is an immediate sharp exotherm when oxygen contacts the dried coal [3, 5]. This is also seen in some of weathered coals as in fig. 3. Coal C presented heat release at the very beginning and tapered off after several days, coal D presented a lower heat release, while the other two had no heat release. In the presence of water, a second exothermic peak appeared at about 10 hours (for coal A, it appeared later and broader) and the heat generation became larger. This was considered not being caused by the heat of oxygen adsorptions on coal as the first peak, but is assignable to the coal-oxygen complexes are produced and decompose to produce another series of coal-oxygen compounds and CO, CO<sub>2</sub>, and H<sub>2</sub>O. The second exotherm may result from such a decomposition. It is seen also that the presence of water significantly facilitates such a process in most bituminous coals.

Bhattacharyya [10] noted that for initially-dry coal, while adsorption of both oxygen and moisture are exothermic processes, heat generation due to moisture is the dominant effect.

**Figure 3. Curves at 50 °C in the TAM-III**

Matters are complicated because oxidation and moisture are coupled: initial oxidation tends to be inhibited unless there are at least traces of moisture present. There is an optimum level of moisture for maximum self-heating – for coal already holding a lot of water in the pore structure, increasing moisture correlates to a decreased oxidation rate due to flooding of the pore structure: pores which are water-filled cannot be oxidized. In one study, the optimum level was identified as 7%. The oxygen/moisture relationship is complex, because it has been determined that the major portion of the oxygen reacts with coal after first going into

**Table 3. Heat generation of bituminous coals in the TAM-III**

Heat of reaction [Jg <sup>-1</sup> ]	0-24 hours	24-72 hours	0-72 hours
Coal A	1.80 (2.31)	2.59* (4.38*)	4.39** (6.69**)
Coal B	1.66 (5.17)	2.68* (6.28)	4.34** (11.4)
Coal C	4.17 (6.46)	5.80 (5.35)	9.98 (11.8)
Coal D	2.49 (4.28)	4.16 (5.64)	6.65 (9.91)

Values in brackets are samples with 20% water; \* 24-64 hour; \*\* 0-64 hour

solution in the moisture present. The effect is further complicated since it appears to greatly depend on the coal type [11-13].

### Gas evolution

Table 4 shows the gas generation at two temperatures of bituminous coal D. It was not visible at 26 °C. Whereas small amounts of CO, CH<sub>4</sub>, and H<sub>2</sub> gave out at the elevated temperature of 60 °C. CO<sub>2</sub> was increased significantly at 60 °C, as 2.69 and 3.64% without and with water. Addition of water did not affect the results noticeably.

**Table 4. Gas generation from coal D after being stored 10 days**

Sample	CO	H <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>
26 °C	0.02% (10 ppm)	No (No)	0.13% (0.25%)	– (–)
60 °C	0.23% (No)	147 ppm (No)	2.69% (3.64%)	59 ppm (94 ppm)

Values in brackets are samples with 20% water

From the above results, it is considered that oxidation at the low temperatures occurred in bituminous coals. The results in the TAM can be correlated to gas evolution. This is a chemi-sorption process exothermically. Furthermore, with the fraction of oxygen that is chemically incorporated into the coal structure increasing, there may happen complex reactions between oxygen and radical sites (oxidation) that in turn contribute to heat generation of coal and cause at least two stages of exotherm [3]. The oxidation forms a certain amount of CO and CO<sub>2</sub>. The presence of water is another factor to contribute to the self-heating of coal, which is found only in the TAM-III, but it only slightly lead to more CO<sub>2</sub> generation.

### Spontaneous ignition

Figures 4-7 show the behaviors of self heating and spontaneous ignition of bituminous coal D in the SIT. Self heating occurred to make the temperature rise to 100 from 60 °C and to 63 from 50 °C after 1500 minutes, respectively. Spontaneous ignition occurred at 80 °C, which is consistent with observed by Muratani [14] and Kuwabara [15].

Table 5 lists the results of the spontaneous ignition in the wire mesh cube and the SIT. The wire mesh cube can not capture the weak heat source because of its significant heat loss. By contrast, the adiabatic condition of the SIT can avoid these factors. More important, air is re-

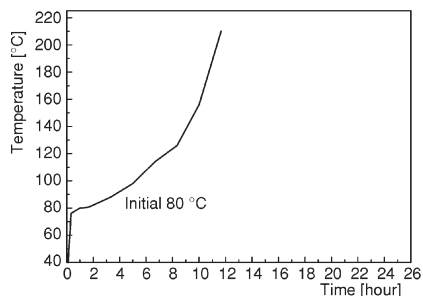


Figure 4. Bituminous coal at 80 °C in the SIT

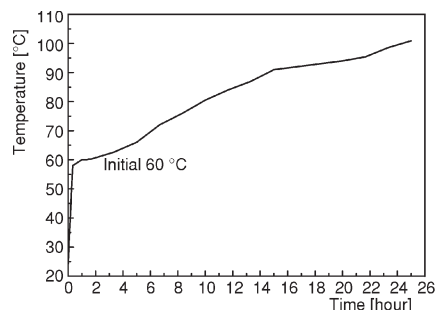


Figure 5. Bituminous coal at 60 °C in the SIT

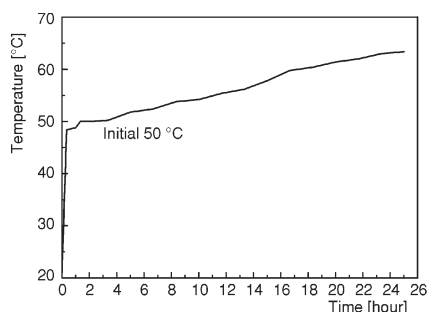


Figure 6. Bituminous coal at 50 °C in the SIT

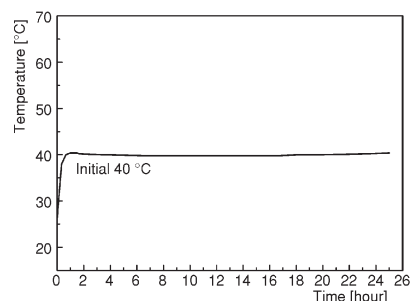


Figure 7. Bituminous coal at 40 °C in the SIT

plenished during the measurement, and thus the oxidation if exists can be maintained. The ignition temperature of coal was 130 °C in the wire mesh cube, whereas it was 80 °C in the SIT. It implies that by conventional testing method, like the wire mesh cube, the ignition by such weak heat sources is not found. But the potential hazard exists and should not be neglected.

Table 5. Spontaneous ignition temperature in the wire mesh cube (UN test) and SIT

Sample	SIT		Wire mesh cube	
	Ignition temperature [°C]	Induction temperature, [min.]	Ignition temperature [°C]	Induction time [min.]
Coal D	80	477.2	130	540

## Conclusions

In this study thermal properties of bituminous coals were examined by thermal calorimeters such as TG-DTA and more sensitive C80 and TAM-III at temperature ramp and isothermal conditions. It was found that the heat release started at 50 °C in C80. At this temperature in the TAM, the major feature of the isothermal traces is an immediate sharp exotherm. In the presence of water, a second exothermic peak appeared and the heat generation became larger. This was considered not to be caused by the heat of oxygen adsorptions on coal as the first peak, but is assignable to the coal-oxygen complexes are produced and decompose to produce another series

of coal-oxygen compounds and CO, CO<sub>2</sub>, and H<sub>2</sub>O. The second exotherm may result from such a decomposition. This process may relate to forming a certain amount of CO and CO<sub>2</sub>, as measured by gas chromatograph. CO<sub>2</sub> attained 3% at 60 °C. It is seen also that the presence of water significantly facilitates such a process in most bituminous coals. The corresponding spontaneous ignition of one bituminous coal was measured in an adiabatic SIT at 80 °C.

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