

The Effect of DDS-Inhibitors on Suppressing the Spontaneous Ignition of Coal

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ABSTRACT

To identify an effective inhibitor to retard the self-heating and spontaneous ignition of coal, the effect of several retardants on bituminous coal has been investigated experimentally in a temperature-controlled oven. The activation energy of coal treated with retardants has been evaluated over the temperature range from 60 °C to 220 °C using the Frank-Kamenetskii model and the rate of temperature rise. One retardants was found to increase the activation energy by up to 20 ~ 57 kJ/mol for different particle sizes of the coal. Various factors influencing the inhibition effect are considered. On the basis of experimental results, a kinetic interpretation of the retardation mechanism is put forward involving both radical reaction and active centre theories. It has been observed that there are possibly two regimes for the oxidation of a bituminous coal in the temperature range studied, viz., a chemically controlled regime and a combination of pore-diffusionally and chemically controlled regime. Finally, the possibility of using DDS-series inhibitors in practical situations is discussed.

KEY WORDS: inhibitor, retardants, spontaneous ignition, self-heating, activation energy, coal, oxidation, Frank-Kamenetskii model, rate of temperature rise

NOMENCLATURE

A	pre-exponential factor	S	surface area per unit volume (1/m)
(C)	function of oxygen concentration	s	internal specific surface area(1/m)

(here assuming zero order reaction)	T_0	oven temperature (K)
c specific heat of coal (1.3J/kgK)	T_c	central temperature of coal sample (K)
E activation energy (kJ/mol)	T_k	critical self-ignition temperature (K)
h heat transfer coefficient (kJ/m ² h)	t	time (min)
Q combustion heat of coal (300kJ/molO ₂)	ρ	density of coal sample (kg/m ³)
R ideal gas constant (kJ/molK)	λ	thermal conductivity (0.116w/mK).
r characteristic dimension (mm), the half side of the cube	δ_c	critical F-K number(2.52 for cube)

1. INTRODUCTION

In many countries, in particular, China, the spontaneous ignition of coal poses serious problems in its mining, transportation, storage and treatment. The spontaneous ignition occurs because coal reacts with oxygen in air and the exothermic oxidation takes place even at initially ambient conditions. It is well known that if the heat released from the oxidation is not dissipated rapidly enough to the surroundings, the oxidation reaction will accelerate automatically. In these circumstances, an accumulation of coal may undergo a hazardous thermal runaway[1].

To prevent spontaneous ignition of coal, many inhibitors have been tested under different experimental conditions. Their inhibition effect can be determined in terms of the changes to the critical ignition temperature[2], the rate of temperature rise[3] or the activation energy of the self-ignition process of coal[1, 4-6].

Two basic theories may be used to help in the selection of agents for suppressing the self-heating of coal[5-6]. Firstly, the oxygen adsorption on the coal surface during the initiation period produces functional groups or initiates radical reactions; therefore, inhibitors are chosen to reduce the formation of functional groups or stop the radical reactions. These would be mainly organic compounds, but they are generally toxic and corrosive[2-3]. Secondly, there are active centers on the surface of coal at which the oxidation reaction occurs. Thus, agents may be selected to cover the active centers on the coal surface. Some known organic covering agents improve the inhibiting effect, but their effectiveness is limited and they cause environmental pollution.

It has been found that inhibitors containing a proprietary blend identified as DDS have a strong inhibiting effect on the self-heating of coal. There are also many factors, including water-retaining agent (glycerol), anti-oxidative agents, surfactants. How they contribute to the inhibition of the self-heating process is still uncertain. This experimental investigation was carried out to determine their effect on suppressing the self-heating.

It is well known that coal inhibition involves the kinetics of coal oxidation. Hence, the kinetic behaviour should be also considered.

There are two approaches which use the activation energy of the coal oxidation reaction to evaluate the effect of inhibitors on suppressing the self-heating of coal. Firstly, by means of F-K model, the effectiveness of existing inhibitors and DDS-4, DDS-5 has been evaluated through critical ignition temperature[5]. In comparison, the effectiveness of DDS-5, DDS-6 and DDS series of inhibitors without glycerol, is evaluated by means of rate of temperature increase measurements[6]. The inhibitor which increases activation energy by the greatest amount is likely to be the most effective. Finally, the effectiveness of this

inhibitor will be evaluated by considering the increased activation energy and the reduction in the rate of temperature increase.

2. EXPERIMENTS AND RESULTS

2.1 Frank-Kamenetskii Model

2.1.1 Experimental Work. Freshly exposed bituminous coal was ground and sieved to the particle size between 1.70 mm and 2.00 mm, and sealed in nylon bags until required. Its analysis is 3.3% moisture, 35.8% volatile matter, 69.3% fixed carbon, 5.0% hydrogen, 1.0% sulphur and 8.5% ash.

The compositions (in mass percentage) of the five inhibitors and the loadings (ml/kg-coal) used in the preparation of the coal samples are listed in Table 1.

Five samples of coal were treated separately with the five inhibiting solutions by dipping in the solutions for 15 minutes, air-dried for 10 hours at 16°C and sealed in nylon bags until required. A sample of coal treated with tap water was prepared in the same way.

The critical self-ignition temperatures (T_k), of 4, 6, 8 and 10 cm cube of both inhibited and plain bituminous coal, were measured in a temperature-controlled oven under a temperature range from 60°C to 220°C. The samples were suspended centrally in the oven, with a thermocouple located at the center of the sample. The oven temperature was

monitored by the other thermocouple located 20 centimetres from top face of the cube. A chart-recorder was used to record the temperature changes at the centre of a cubical sample with time. In fact, the T_k is defined as the average of the highest measured sub-critical and the lowest measured super-critical self-ignition temperature[1]. The experimental data for the coal wetted with water and the coal treated with DDS-5 are listed in Table 2.

The temperature of the oven is controlled to $\pm 0.5^\circ\text{C}$. The errors of measured T_k are bracketed in $\pm 2.0^\circ\text{C}$. The errors in the activation energies are estimated to be within ± 2 kJ/mol.

TABLE 1. Compositions of inhibiting solutions (in mass percentage) and loadings of the solutions (particle size: between 2.00 mm and 1.70 mm)

Inhibitor group	1	2	3	4	5
Additives				DDS4	DDS5
Aniline	0.17	0.16	0.21	---	---
Phenol	0.17	0.17	---	---	---
Urea	---	0.33	0.33	0.67	0.67
Surfactants	0.32	0.32	0.31	0.28	0.28
Glycerol	0.67	0.67	0.67	0.67	0.67
Ammonium chloride	0.33	0.67	0.67	0.67	0.67
(NH ₄)H ₂ PO ₄	0.33	0.67	---	0.67	0.67
Sodium bicarbonate	---	---	0.33	---	---
Triethanolamine	0.10	---	---	---	---
Polyacrylamide	---	0.10	---	---	---
Inhibitor DDS	---	---	---	0.13	0.20
Loadings(ml/kgcoal)	139	145	136	142	156

2.1.2 F - K Model Results. By means of the well-known F - K model, the activation energies of both bituminous coal wetted with water and inhibited with inhibitors are evaluated using the correlation between sample size and the corresponding critical spontaneous ignition temperature[1]:

$$\ln\left(\frac{\delta_c T_k^2}{r^2}\right) = P - \frac{E}{RT_k} \tag{1}$$

$$P = \ln\left(\frac{EQA\rho}{R\lambda}\right) \tag{2}$$

Using data in Table 2, by plotting

$\ln\left(\frac{\delta_c T_k^2}{r^2}\right)$ against

$\frac{1}{T_k}$, the activation energy is evaluated

from the slope $-\frac{E}{R}$

of the straight line (least square fit to the data) as shown in Figure 1.

The activation energy for bituminous coal wetted with water is 45.6 kJ/mol while the activation energy for the coal retarded by inhibitor DDS-5 is 66.5 kJ/mol. The specific expression in the form of equation 1 for the coal wetted with water becomes,

TABLE 2. The critical self-ignition temperature of wet bituminous coal and the coal retarded by Inhibitor DDS-5 (particle size: between 2.00 mm and 1.70 mm)

Size of cube (2r, mm)	Critical self-ignition temperature (°C)		1000/T _k (K ⁻¹)		ln(δ _c T _k ² /r ²)	
	Water	Inhibited	Water	Inhibited	Water	Inhibited
40	164.0	180.0	2.287	2.206	7.094	7.165
60	140.0	162.0	2.420	2.298	6.170	6.273
80	114.2	145.0	2.581	2.391	5.465	5.618
100	102.0	133.5	2.665	2.459	4.955	5.116

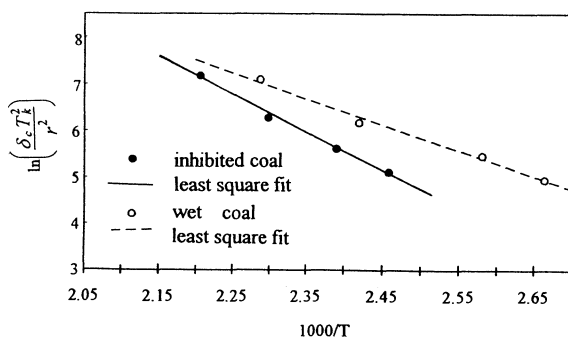


FIGURE 1. Evaluation of Activation Energy for the Wet Coal and the Coal Treated with DDS-5

$$\ln\left(\frac{\delta_c T_k^2}{r^2}\right) = 19.56 - \frac{5480}{T_k} \quad (3)$$

and for the coal retarded by Inhibitor DDS-5,

$$\ln\left(\frac{\delta_c T_k^2}{r^2}\right) = 24.76 - \frac{8000}{T_k} \quad (4)$$

2.1.3 Discussions on F-K Model Results. According to the increase of activation energy, the effect of the inhibiting solutions on suppressing the self-heating of bituminous coal is estimated to be in the order of group $5 > 4 > 3 > 2 \approx 1$ (see Table 1).

Inhibitor DDS-5 is the most effective of the five groups. The reasons may be explained qualitatively by applying the theories mentioned above. Firstly, Inhibitor DDS-5 contains ammonium chloride and dihydrogen orthophosphate that act as both electrolytes and agents to stop radical reaction. Secondly, adding anionic with non-ionic surfactant to the inhibitor leads to the nucleophilic centres on the coal surfaces being occupied by electron-donating agents. Thirdly, DDS in the Inhibitor DDS-5 that acts as adhesive and covering agent substantially reinforces the covering effect meanwhile it may improve the wettability of the retarding solution.

The activation energy derived from this model, which is an observed activation energy, is apparently enhanced by the contribution of these to the oxidation reaction of coal.

2.2 Rate of Temperature Rise

2.2.1 Experimental Work. Freshly exposed bituminous coal was ground and sieved to the particle size between 0.85 mm and 1.18 mm, and sealed in nylon bags until required.

Coal samples were treated separately with 0.1% and 0.2% DDS, 0.2% polyacrylamide, DDS-5 and DDS-6 solution by dipping in the solutions for 15 minutes, air-dried for 10 hours at 16°C and sealed in nylon bags until required. A sample of coal treated with tap water was prepared in the same way.

The compositions of inhibition solutions are listed in Table 3. The rates of temperature rise at the centre of 4 cm cube samples were recorded by a time-temperature chart recorder under a constant ambient

TABLE 3. Compositions of inhibitors (mass percentage)

Inhibitor Additives	0.1%	0.2%	0.2%	DDS	DDS
	DDS	DDS	PAA	-5	-6
Urea	---	---	---	0.67	0.67
Surfactants	---	---	---	0.28	0.28
Glycerol	---	---	---	0.67	---
Ammonium chloride	---	---	---	0.67	0.67
(NH ₄)H ₂ PO ₄	---	---	---	0.67	0.67
Polyacrylamide	---	---	0.20	---	---
DDS	0.10	0.20	---	0.20	0.20

Note: PAA stands for Polyacrylamide.

temperature in a temperature-controlled oven.

If the exothermic oxidation reaction occurs on the surface of coal particles and the rate of the reaction is governed by the Arrhenius equation, the instantaneous rate of heat gain per unit volume of the coal particles is given by an equation of the following form:

$$\rho \cdot c \cdot \frac{dT_c}{dt} = s \cdot Q(C) \cdot A \cdot \exp\left(-\frac{E}{RT_c}\right) - h \cdot S \cdot (T_c - T_0) \quad (5)$$

When T_c , the temperature at the centre of coal sample, has increased from the initial temperature to the constant ambient oven temperature T_0 , there will be no heat loss from the coal sample to its surroundings, i.e.,

$$\frac{dT_c}{dt} = \frac{s \cdot Q(C) \cdot A}{\rho \cdot c} \cdot \exp\left(-\frac{E}{RT_c}\right) \quad (6)$$

Therefore, the activation energy and pre-exponential factor can be derived from the slope $\frac{dT_c}{dt}$ when T_c equals to T_0 . The effectiveness of inhibitor on suppressing the self-heating of coal is evaluated by the increase of activation energy compared to that of the coal wetted with water. The equation (6) can be changed into the following form,

$$\ln\left(\frac{dT_c}{dt}\right) = P - \frac{E}{RT_c} \quad (7)$$

where,

$$P = \ln\left(\frac{s \cdot Q(C) \cdot A}{\rho \cdot c}\right) \quad (8)$$

As shown in equation (8), P should be a constant. Plotting $\ln\left(\frac{dT_c}{dt}\right)$ against $\frac{1}{T_c}$ using the experimental results in Table 4, or by means of least square fit method using the same data, obtains a resultant line (see Figure 2, 4 and Table 5). The gradient

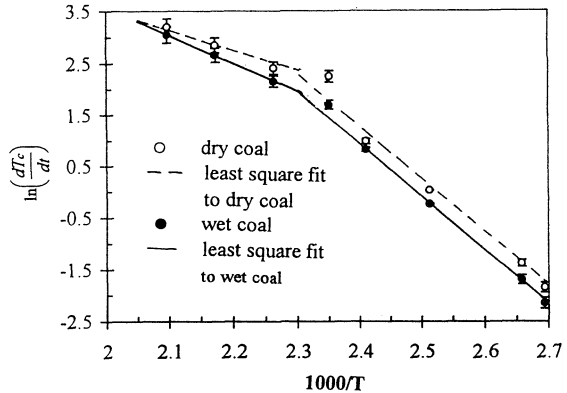


FIGURE 2. The Effect of Water

of the line is

$$-\frac{E}{R}$$

and the intercept of the line is P. Thus, the activation energy and the constant P that is based on the properties of coal, are derived.

Table 5 shows the different activation energies in the correspondent temperature ranges for the dry, wet and inhibited coal samples.

The oven temperature is controlled to within $\pm 0.5^\circ\text{C}$, and the errors for the measured rate of temperature rise is within $\pm 5\%$. The errors in the activation energies (see Table 5) are estimated to be ± 2.0 kJ/mol. It has been found that there are two

gradients ($-\frac{E}{R}$)

for all the cases over the range of experimental temperature. It also suggests that the mechanism of the oxidation reaction of coal should change over the range of temperature, as shown in Figure 2 to 4.

2.2.2 Results and Discussions. It can be derived, from the two gradients ($-\frac{E}{R}$)

of the resultant line obtained by the least square fit to the experimental results, that there are two controlled regimes for the oxidation of a bituminous coal over the range of experimental temperature, viz., a chemically controlled regime at low temperature (from 371 to 415 K),

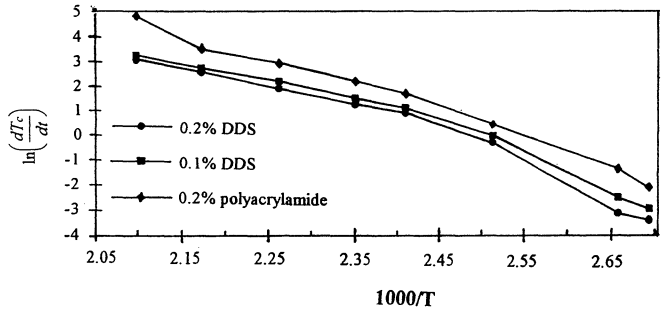


FIGURE 3. The Effect of Covering Agents

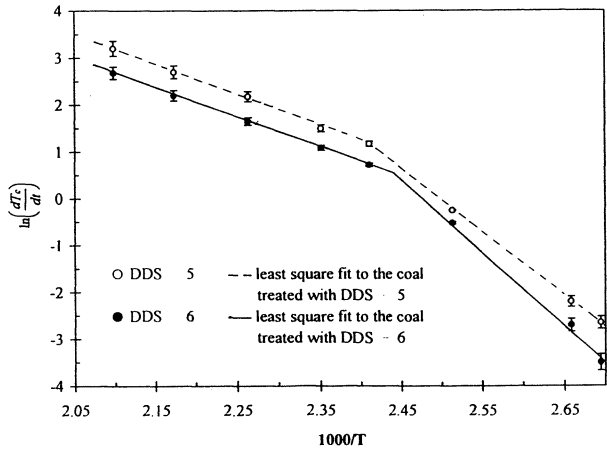


FIGURE 4. Effect of Water-retaining Agent (Glycerol)

and a combination of pore-diffusionally and chemically controlled regime at higher temperature (from 415 to 478 K). This occurs because at lower temperature the intrinsic chemical reaction is much slower than gas diffusion, while at higher temperature the pore diffusion resistance contributes more to the total reaction processes of coal oxidation. The change of activation energy in the two regimes is significant, which shows a change in the mechanism of coal oxidation.

TABLE 4. The rate of temperature rise at the correspondent oven temperature (4 cm cube, particle size: between 0.85 mm and 1.18 mm)

T(K)	$\frac{dT_c}{dt}$ (K.min ⁻¹)						
	dry	water	0.1% DDS	0.2% DDS	DDS -5	DDS -6	0.2% PAA
476.6	24.53	21.12	25.79	22.20	24.53	14.58	127.74
460.2	17.29	14.30	14.88	13.20	14.88	9.02	33.12
441.9	11.13	8.58	9.02	6.69	8.85	5.21	20.49
425.4	9.49	5.47	4.48	3.53	4.48	2.94	10.48
414.9	2.67	2.27	3.00	2.53	3.22	2.05	6.36
397.9	1.02	0.787	0.980	0.741	0.779	0.594	2.12
376.2	0.252	0.183	0.082	0.044	0.111	0.067	0.286
371.2	0.157	0.116	0.052	0.030	0.071	0.030	0.134

The Effect of Water In comparison with dry coal (cf. Fig. 2), the coal wetted with water has a little difference in activation energy, and the reduced dT_c/dt is limited especially at the chemically controlled regime. Thus, it may be deduced that the coal wetted with water leads to an increase in the pore diffusion resistance, which causes an increase in the observed activation energy.

The Effect of Covering Agents. The covering agents tested here are DDS and polyacrylamide.

Their inhibiting effects are estimated through the amount of the activation energy increased by the agents and through the absolute rate of temperature rise of the coal treated with the agents, in comparison with that of water. As shown in Figure 3 and Table 5, DDS increases the amount of activation energy much higher than polyacrylamide solution does at lower temperature. Contrarily, DDS has a lower absolute rate of temperature rise. Although 0.2% polyacrylamide solution increases

TABLE 5. Derived activation energy (kJ/mol) (4 cm cube, particle size: between 0.85 mm and 1.18 mm)

Temperature range(K)	371-415	415-478	Activation Energy	
			371-415	415-478
dry coal	28.120-11134/T _c	11.253-3861/T _c	92.57	31.2
wet coal	27.112-10861/T _c	14.323-5372/T _c	90.3	44.7
0.1% DDS	36.780-14744/T _c	17.222-6891/T _c	122.6	57.3
0.2% DDS	39.816-16074/T _c	17.936-7075/T _c	133.6	58.8
0.2% PPA	33.375-13122/T _c	24.113-9333/T _c	109.1	77.6
DDS-5	33.624-13472/T _c	16.978-6564/T _c	112.0	54.6
DDS-6	36.308-14716/T _c	15.864-6285/T _c	122.3	52.2

the activation energy by the greatest amount at higher temperature, the absolute rate of temperature rise is also the highest over the range of the experimental temperature. Thus, polyacryl-amide can not be used as a covering agent for the inhibition of coal because it is itself subject to oxidation at the temperature. The activation energy of the oxidation of coal treated with 0.2% DDS is increased by 43.3 kJ/mol (about 48%) compared to that of coal wetted with water. It is also found that when the concentration of DDS solution increases 0.1%, the activation energy is raised by around 9%. Therefore, DDS has a strong effect on suppressing the self-heating of coal. This result is in accordance with the theory of active centres to select covering agents mentioned earlier in the introduction section of this paper. One conclusion can be derived from the analyses above that as to selecting an effective inhibitor or covering agent, it should cover the surface and adhere well, but not be oxidized.

The Effect of Water-retaining Agent (Glycerol). Considering the absolute rate of temperature rise and the increased activation energy of the retarded coal (cf. Figure 4 and Table 4, 5), the effectiveness of DDS-6 (DDS-5 without glycerol) is greater than DDS-5 because glycerol in DDS-5 is subject to being oxidized. Thus, water-retaining agent in inhibitors, such as glycerol, can not be used as a fire-proofing agent of coal.

The Effect of Anti-oxidants. As shown in Table 4, the rate of temperature rise of the coal treated with DDS-6 (containing 0.2% DDS) is lower than that of coal treated with 0.2% DDS over the range of experimental temperature. This shows that anti-oxidants in DDS-6, to some degree, improve the inhibiting effect. It seems to be true in this experiment that DDS as a covering agent contributes more than anti-oxidants to the effect on the suppressing the self-heating of coal.

3. CONCLUSIONS

3.1 F-K model Results

- 1) According to the increase of activation energy, the effect of the inhibiting solutions to suppress the self-heating of bituminous coal, is in the order of group $5 > 4 > 3 > 2 \approx 1$ (see Table 1).
- 2) The activation energy for bituminous coal treated by Inhibitor DDS-5 is 66.5 kJ/mol, 46 percent higher than that for the coal wetted with water. Namely,

for the plain bituminous coal,
$$\ln\left(\frac{\delta_c T_k^2}{r^2}\right) = 19.56 - \frac{5480}{T_k};$$

for the coal retarded by Inhibitor DDS-5,
$$\ln\left(\frac{\delta_c T_k^2}{r^2}\right) = 24.76 - \frac{8000}{T_k}.$$

3.2 Results through the Rate of Temperature Rise

- 1) There are probably two controlled regimes for the oxidation of a bituminous coal, viz., chemically controlled regime from 371 to 415 K, and the combination of pore-diffusionally

and chemically controlled regime from 415 to 478 K.

2) The activation energy of coal retarded by 0.2% DDS increased by 43.3 kJ/mol (about 48%) compared to that of the coal wetted with water. Although 0.2% polyacrylamide increases the activation energy by the greatest amount at higher temperature, it can not be used as an inhibitor because polyacrylamide itself is subject to oxidation at the temperature. An effective inhibitor or covering agents, should cover the surface of coal and adhere well, but not be oxidized.

3) The inhibiting effect of DDS-6 is better than DDS-5 because glycerol in DDS-5 as a water-retaining agent is subject to being oxidized. On the basis of activation energy increase and absolute value of the rate of temperature rise, the most effective inhibitor having been tested is DDS-6.

4. APPLICATION

Apparently, DDS-6 and 0.2% DDS solutions have a strong effect on suppressing the self-heating of a bituminous coal. It is expected that they will have even stronger effect for lumped coal of low-rank in practice, as the lumped coal has a lower specific surface area. In comparison with the existing inhibitors, DDS-6 and inhibition solutions of DDS series cost less, are non-toxic and non-corrosive. They are safer in the practical application as an inhibiting agent for low-rank coals during storage, transportation, treatment and mining.

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