On the Sorption of Water Vapour by Coal and its Spontaneous Heating

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1. Introduction

The effect of humidity on the rate of heat release due to oxidation of coal has been reported in an earlier communication(1). The results therein do not suggest that spontaneous heating in coal can occur due to oxidation reaction alone under normal ventilation practice. In the literature, however, frequent reference has been made by many investigators to the particularly humid conditions during heating incidents. Observations over a long period by Migdalski(2) and Wolowczyk(3) have revealed that in the Zwickau-Oelsnitz Coalfield in Germany the occurrence of spontaneous heatings coincided with the presence of high humidity in the mine atmosphere. According to Ashworth(4), humid air is "essential" for the starting of gob-fires. Mine fires have been reported starting at places where water issues in considerable quantity from the roof of the coal seam(3). The incipience of heating in stored coal especially after rainy weather is well known. According to Hoskin(5), fires in coal piles occur generally at the junction of wet and dry coals. Development of heating in the storage of coal-washery tailings has also been reported by Cabolet(6).

Earlier Winmill(7) and more recently Hodges and Hinsley(8) have reported that some dry coals catch fire when saturated oxygen is passed through them at 30°c, but the temperatures of the same coals rise only a little when dry oxygen is used. Subsequently, Hodges and Acherjee(9) have found that at a temperature of 30°c the heat release due to oxidation is very small in comparison with that due to sorption of water by the coal. Berkowitz and Schein(10) have commented that "the heat of wetting (or for that matter heat of condensation) may act as an important 'trigger'" in accelerating the oxidation of coal.

Although the above observations are useful in understanding the role of water vapour in the spontaneous heating of coal, the experimental conditions used in the tests fall far short of those generally found in practice. Extreme conditions of dryness and wetness of both coal and air (or oxygen) have been used in most cases. In practice, neither would the ventilation air in mines and the atmosphere in the vicinity of a coal pile necessarily remain saturated with water vapour, nor would the coal in question be dry all the time. Due to its hygroscopicity coal tends to remain in equilibrium with the surrounding atmosphere. If the humidity of the atmosphere increases, then the coal will take up some more moisture to achieve a new equilibrium. During the process of attaining equilibrium the coal undergoes certain chemical, physical and thermal changes. The present investigation is concerned with the estimation of thermal changes in various coals under such conditions. The coals equilibrated at a particular humidity have been subjected to air equilibrated at a higher humidity, and the heat release in coals has been estimated calorimetrically. Apart from the influence of humidity, the effects of some other variables on the process have also been studied.

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2. Experimental

The arrangement and operational procedure of the apparatus used in this investigation were similar to those described in an earlier paper(1). The additional feature was that after the whole system had attained stable thermal and hygrometric conditions, the flow of nitrogen was substituted by air of humidity higher than that with which the coal sample in the calorimeter had been brought to equilibrium. The experiments were carried out in an isothermal condition at 30°c, except on one occasion when the test was done at 35°c. The humidities at which these tests were performed were also the same as in the previous investigation. The data on the analysis of each of the eight coals used are given in Table 1. Generally, the coals were tested with samples of -72 mesh (B.S.S.), but to study the effect of particle size on the heating rate due to sorption of water vapour, four sized fractions of -25+36, -36+52, -52+72 and -72+200 mesh (B.S.S.) were prepared from the Coal F. Normal precautions using nitrogen were taken to avoid oxidation of the samples during their preparation and drying. In order to investigate the influence of weathering of coal on the process a few oxidised samples were prepared from the Coal H. A bulk sample of -72 mesh (B.S.S.) of this coal was oxidised at room temperature in dry condition by pure oxygen, and the sub-samples were subsequently withdrawn after 30, 50 and 70 days.

3. Results and Discussion

The progress of the experiments was registered by recording the output of the calorimeter, and the results were subsequently calculated from the thermograms. All the thermal data reported here are expressed on a dry coal basis, and the term "saturated" is used to state the equilibrium conditions of both coal and air at the particular relative humidity concerned. The Coals B, D, G and H were tested under several humid conditions using dry as well as moist samples. The rest of the experiments were done in one particular condition by passing air saturated with water vapour through dry coal at 30°c.

Tests with glass wool under extreme conditions showed that the rate of heat release due to sorption of water vapour by the small amount of glass wool, mixed with the coal samples during experiments, had a negligible effect on the results obtained with the coals.

The variation of the rate of heat release with time for each of the coals studied at different humid conditions is shown in Figures 1 to 3. A few tests were carried out to isolate the heating effect of oxidation from that of water sorption. In some of these experiments nitrogen was used throughout as the moisture carrier, and in others the flow of moist air was changed to moist nitrogen or vice versa in the course of a particular experiment. It appears from the results that at temperatures of 30° and 35°c the rate of heat release due to oxidation is very small in comparison to that due to the sorption of water vapour by the coal. The absence of any recognisable effect of oxidation under such conditions has also been reported by other investigators(9 & 10). It is known that coal sorbs a comparatively larger amount of water than oxygen, and that the heat of oxidation is much less than the latent heat of condensation of water vapour. According to Sevenster(11), coal sorbs water vapour at a much faster rate than it consumes oxygen. Therefore, it is expected that in above conditions the heat release due to sorption of water vapour becomes the rate-determining factor.

Tests with Dry Coals

The results of this series of tests are shown in Figures 1 and 2. It is seen that excepting the curve for the anthracite (Coal A in Fig.1) all other rate curves have the common feature of a peak at the early stage of experiment. With the introduction of moist air (or nitrogen) into the dry coal there occurs a sharp rise in the rate of heat generation in the coal. After a short while it decreases for some time before rising again. It appears from Fig.2 that the height and shape of the initial peak are dependent on both the humidity of the moisture carrier and the type of coal. An attempt is made in a later section to explain the occurrence of this peak in the rate curves.

Scanning of the results reveals that the nature of the rate curve after the initial peak is related to the type of coal sorbing the water vapour. With the anthracite (Coal A in Fig.1) and high rank coal B (Fig.2) the rate of heat generation approaches the maximum value rapidly. However, it starts decreasing soon after at a faster rate, followed by a progressively slower rate. In the case of the medium and low rank coals (Coals C,D,E,F,G and H) not only does the rate reach the maximum gradually, but it also continues in that range for some time before decreasing slowly. This difference in the nature of the heating rate in various coals can be attributed to the difference in their hygroscopicity. From Fig.2 it is evident that with a particular coal the rate of heat generation increases with the increase in the saturation humidity of the atmosphere. This is discussed in detail in a later section.

Tests with Moist Coals

In this series the coals containing different amounts of moisture were subjected to moist air (or nitrogen) under conditions in which sorption of water vapour by the coals was ensured. The results, as plotted in Fig.3, show that the rate of heat release vs time curves do not have any initial peak as obtained in the previous series of tests. The curves for the tests with a particular coal, however, follow the general characteristics of those obtained after the initial peak during experiments with the same coal in dry condition. It is also evident that for each coal the rate of heat generation increases with the increase in the difference in the initial equilibrium humidities of the moisture carrier and the coal.

Influence of Various Factors on the Rate of Heat Release

The effects of several factors on the heating rate of coal due to the process under investigation have been studied on a common basis of comparison. The basis used is $Q_{t=20}$ cal/g of dry coal, the total heat produced in twenty hours of testing, and is termed the characteristic rate of heat release. In a few cases where the experiments have been terminated before twenty hours the $Q_{t=20}$ values are taken from the extrapolation of the respective graphs.

Influence of the Deficiency in the Equilibrium Humidity of Coal

The characteristic rates of heat release during various tests with each of the coals B, D, G and H are plotted against different values of e, representing the difference between the equilibrium humidities of the atmosphere and the coal, in Figure 4. In Fig.4(i) the results of the tests with dry coals are shown, and the $Q_{t=20}$ value at zero e for a particular coal is the characteristic rate of heat release during its dry oxidation(1). The results of the experiments with moist coals are illustrated in Fig.4(ii); and the corresponding $Q_{t=20}$ value at zero e for each coal is represented by the average of the $Q_{t=20}$ values obtained during oxidation of the coal in several moist conditions reported earlier(1).

It is seen in Fig.4 that the characteristic rate of heat release for each coal increases with the increase in the equilibrium deficiency of the coal; the relationship, however, is not directly proportional. This is as expected because of the fact that the coal-water sorption isotherms, obtained from the equilibrium moisture values at various relative pressures of water vapour, are of sigmoid type. A comparison between the Figs.4(i) and 4(ii) show that in each case the rate of increase in $Q_{t=20}$ with e during the tests with dry coal is more than that obtained when the experiments were done with moist coal. To confirm this feature, however, it would be necessary to estimate the heat of sorption of water vapour by the coal during the process. The present experimental set-up precluded any such attempt.

Influence of the Rank of Coal

The general relationship between the characteristic rate of heat release due to sorption of water vapour and the rank of coal is illustrated in Figure 5. The $Q_{t=20}$ value for each coal in the above figure is taken from the result of the test with dry coal and air (or nitrogen) saturated at 100% R.H. at 30°c. The variations of the characteristic rate value with carbon and volatile matter contents of the coals are similar to those usually observed between the hygroscopic properties of coals and the parameters of coal rank. It appears, therefore, that the heat release due to sorption of water vapour in a coal is in general dependent on its hygroscopicity.

Influence of Coal Particle Size

Each of the four sized fractions of the coal F was tested under similar conditions. Dry samples of these fractions were subjected to air saturated at 100% R.H. at 30°c. The changes in the rate of heat release with time of sorption of water vapour by the sized fractions are shown in Figure 6. The curves are of similar nature, and there is a tendency for the rate to increase with the fineness of the coal particles. This feature is more prominent in Figure 7 where the characteristic rates are plotted against the average particle diameters. It is seen that while a decrease in particle diameter below about 358 microns has little effect on the characteristic rate, a significant decrease in the rate of heat release occurs when the particle sizes are increased from 358 to 511 microns.

The observed difference in heat release in various sized fractions of the same coal is due to the difference in the exposed external surface area of the samples. The common shape of the rate curves indicates that the mechanisms of the sorption of water vapour remain similar. The results also suggest that there may be a critical diameter of the coal particles below which any further sub-division has little effect on the rate of heat release. However, since only four tests were carried out it was not possible to find the point at which such distinct change takes place.

Influence of Weathering of Coal

For the purpose of investigating the effect of weathering on the heat generation in coal during sorption of water vapour, three oxidised samples of the coal H were tested under similar conditions. The rates of heat release in dry samples were measured when air saturated at 100% R.H. at 30°c was passed through them. The results are shown in Figure 8 together with those obtained during a similar test with the fresh sample of coal H. It is noticeable from the general feature of the curves that the mechanisms of heat release remain unaffected after weathering of the coal, although the rate of heat generation generally increases with the extent of weathering.

The equilibrium moisture contents of the above samples at the saturation vapour pressure at 30°c are shown in Table 2, together with the characteristic rates of heat release. Both the characteristic rate of heat release and the equilibrium moisture content increase with the period of weathering of the coal. The increased moisture retaining capacity of weathered samples is an established fact, and it is expected that there would be a corresponding increase in the total heat release at the end of the sorption process. The present data, however, show that with the extent of weathering there occurs an increase in the rate of heat release in the coal too, and this is of particular significance to the problem of spontaneous heating.

The Initial Peak in the Rate of Heat Release vs Time Curves for the Tests with Dry Coals

In absence of any quantitative data on the amount of water sorbed by the coals, it is only possible to put forward some qualitative explanations, on the basis of the present results and the existing knowledge on coal structure, for the appearance of the initial peak in the rate curves obtained from the tests with dry coals.

From the past work(2) it is apparent that this peak is not directly related to the rate of sorption of water in the early period of the process. The absence of any peak in the rate curve for the test with the anthracite (Coal A in Fig.1) seems to confirm this. A broad comparison of the heat release in the initial stage, until the rate curve starts rising again, in various coals tested under similar conditions, shows that this amount generally decreases with the maturity of the coal. It is also noticed that this quantity increases with decrease in the average particle diameter of the coal (Fig.6). The occurrence of similar peaks during the tests with moist nitrogen and also with the oxidised samples rules out the effect of oxidation. The close similarity in shape between the rate curves after the initial peak for the tests with dry coals and those obtained from the experiments with the respective moist coals indicates that the dry coal surface is probably responsible for the appearance of the initial peak.

Young and Crowell(12) and Brunauer(13) have referred to the occurrence of similar initial peaks during sorption studies of some porous solids. They have explained it as the result of the heterogeneity of the sorbent surface which plays an important role, particularly at low sorbate pressures. Considering the heterogeneous nature of coal it seems reasonable that the above theory may also be applicable in general to the present observations. This theory, however, fails to explain not only the case of the anthracite, but also the observed initial peaks with the finer coal particles.

From the studies of coal constitution, it is known that the number of polar groups, such as -OH and =CO groups, in coal decreases with the maturity of the coal, and that these groups are almost absent in the anthracite(14). Evidence has also been put forward by a few investigators(15 & 16) suggesting that a part of the water in coal is held by forces other than physical. On the basis of these facts the present observations can be explained in the following manner.

During sorption of polar substances such as water there occurs immediate interaction between the water molecules and the active groups in coal, and thus more heat is liberated than that due to physical adsorption. As this preferential sorption proceeds and the most active sites become occupied, so the less active sites come into play resulting in lesser heat generation. With the progress of the process the rate of heat release starts increasing again as the phase changing of the water vapour takes place. Thus the observed difference in heat release during this early period of sorption of water in various types of coal is understandable. With the finer particles the active sites on the coal surface are more easily accessible to the water molecules and so an increased amount of heat release at the first stage is expected. More elaborate study is necessary for a complete picture of the phenomena involved.

4. Conclusions

It has been shown that under conditions where a coal is likely to sorb water vapour, the chance of heating is more. In a humid atmosphere when simultaneous sorption of water vapour and oxygen takes place, the rate of heat generation in coal due to the sorption of water vapour becomes the rate-determining factor. For a given coal, this rate of heating has been found to reach the maximum within a few hours of the start of the process, and to increase with the increase in the equilibrium deficiency of the coal.

The variations of the characteristic rate of heat release during sorption of water vapour with factors such as rank, particle size and weathering of coal are observed to be related to the hygroscopicity of coal. This indicates that the causes of self-heating in coal are in part associated with its fundamental nature; it also explains the greater susceptibility of low rank coals towards spontaneous heating. The method used in this work is found suitable for this kind of work, and the results obtained can serve as a basis for further work.

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References

1. Bhattacharyya, K.K., Hodges, D.J. and Hinsley, F.B.
The Mining Engineer, Feb. 1969, p 274

2. Migdalski, H.
Bergbau-Technik, 7, 1957, 1, p 3

3. Wolowczyk, P.
Bergakademie, 12, 1960, p 4

4. Ashworth, J.
Disc. on Trans. Inst. Min. Engrs., London, 51, 1915-16, p 545

5. Hoskin, A.J.
Purdue Univ. Expt. Sta. Bull., 30, 1928, p 61

6. Cabolet, P.
Gluckauf, 75, 1939, p 953

7. Winmill, T.F.
Trans. Inst. Min. Engrs., London, 48, 1914-15, p 535

8. Hodges, D.J. and Hinsley, F.B.
Trans. Inst. Min. Engrs., London, 123, 1963-64, p 211

9. Hodges, D.J. and Acherjee, B.
Trans. Inst. Min. Engrs., London, 126, 1966-67, p 121

10. Berkowitz, N. and Schein, H.G.
Fuel, 30, 1951, p 94

11. Sevenster, P.G.
Fuel, 38, 1959, p 405

12. Young, D.M. and Crowell, A.D.
Physical Adsorption of Gases, Butterworths, London, 1962, Ch. 7

13. Brunauer, S.
The Adsorption of Gases and Vapours, Vol.1, Oxford Univ. Press, 1945, Ch. 10

14. Lahiri, A. and Iyengar, M.S.
Jl. Sci. & Ind. Res., 17A, No.2, 1958, p 60

15. Mukherjee, P.N. and Lahiri, A.
Fuel, 36, 1957, p 176

16. Mukherjee, P.N., Nandi, S.P. and Lahiri, A.
Jl. Sci. & Ind. Res., 15B, No.11, 1956, p 638

TABLE 1

ANALYSIS OF COALS USED

(As supplied by the N.C.B. Coal Survey Laboratories)

SAMPLE DETAILS			*ANALYSIS, PER CENT*							
			Air-dried					*dmmf* *		
Index	*Colliery*	*Seam*	*Moisture*	*Ash*	*V.M.*	*F.C.*	*Total S*	*V.M.*	*C.*	*H.*
A	Cynhaidre	Pumpquart	1.6	1.3	4.8	92.3	1.2	4.8	94.2	2.8
B	+	+	1.9	5.0	29.7	63.4	0.7	30.6	88.5	5.2
C	Easington	High Main	1.6	5.1	32.1	61.2	1.6	33.9	86.6	5.4
D	Thoresby	Top Hard	7.5	4.9	30.2	57.4	0.8	33.5	83.7	4.9
E	Bentinck	Yard	5.8	7.4	31.6	55.2	1.4	35.4	83.9	5.6
F	Whitewell	High Hazles	8.4	2.7	33.3	55.6	1.3	36.9	82.8	5.4
G	Denby Drury Lowe	Belpar-Lawn	4.6	7.5	34.2	53.7	1.9	39.9	81.5	5.8
H	Measham	Stockings	5.3	6.0	36.7	52.0	1.6	42.1	80.7	5.2

* Dry, mineral-matter free

\+ Supplied by Cardiff Coal Survey Laboratory, Sample No. CSL 2708

Table 2

Effect of weathering of coal on the equilibrium moisture content and the characteristic rate of heat release due to sorption of water vapour

Days of oxidation	0	30	50	70
Equilibrium moisture, % (w/w)	19.22	20.83	21.80	23.44
$Q_{t=20}$, cal/g (dry coal)	56.70	62.28	63.07	69.12

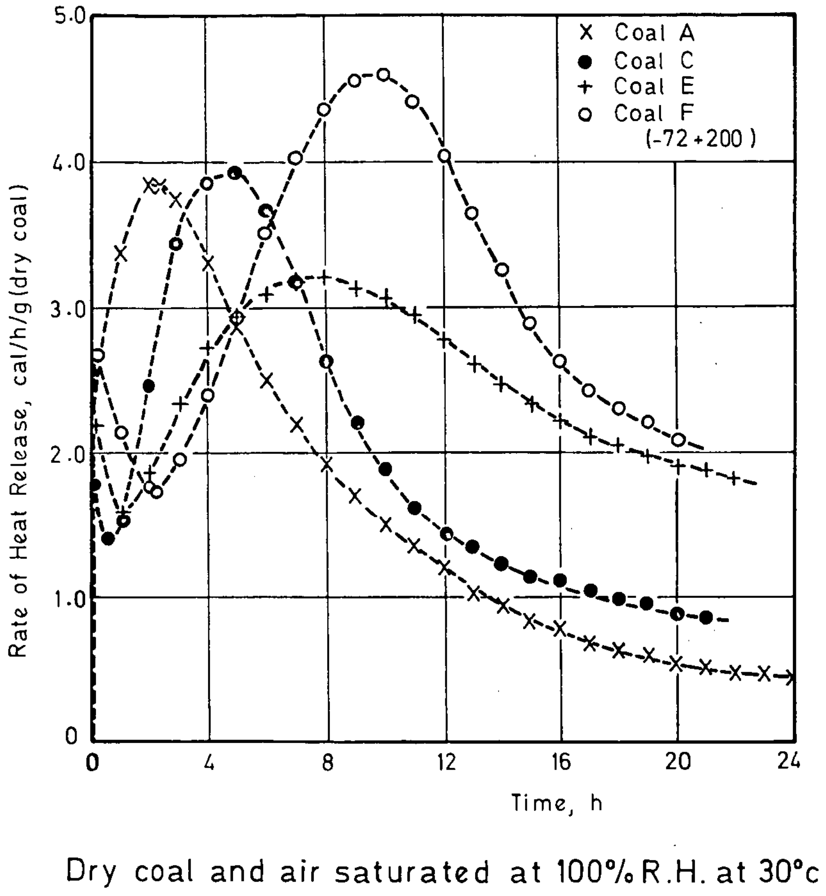


Figure 1. Variation in the rate of heat release with time during oxidation and sorption of water vapour by dry coals.

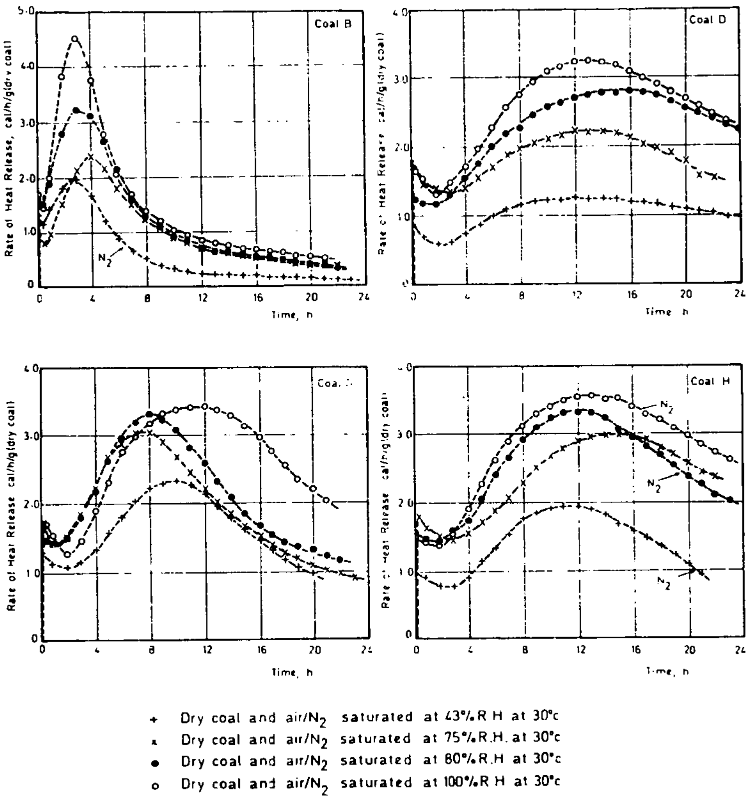


Figure 2. Variation in the rate of heat release with time during oxidation and/or sorption of water vapour by dry coals.

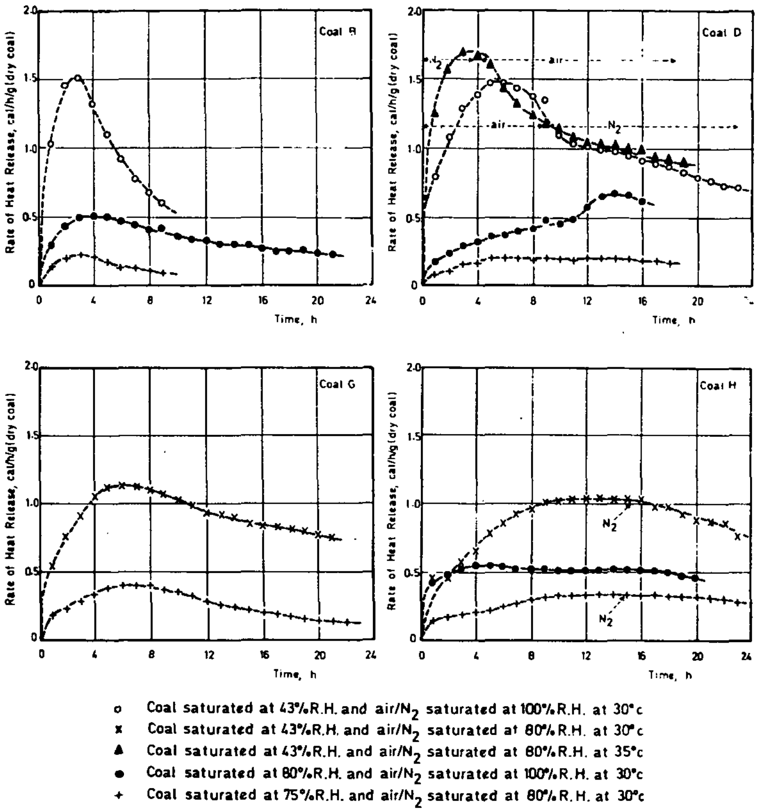


Figure 3. Variation in the rate of heat release with time during oxidation and/or sorption of water vapour by moist coals.

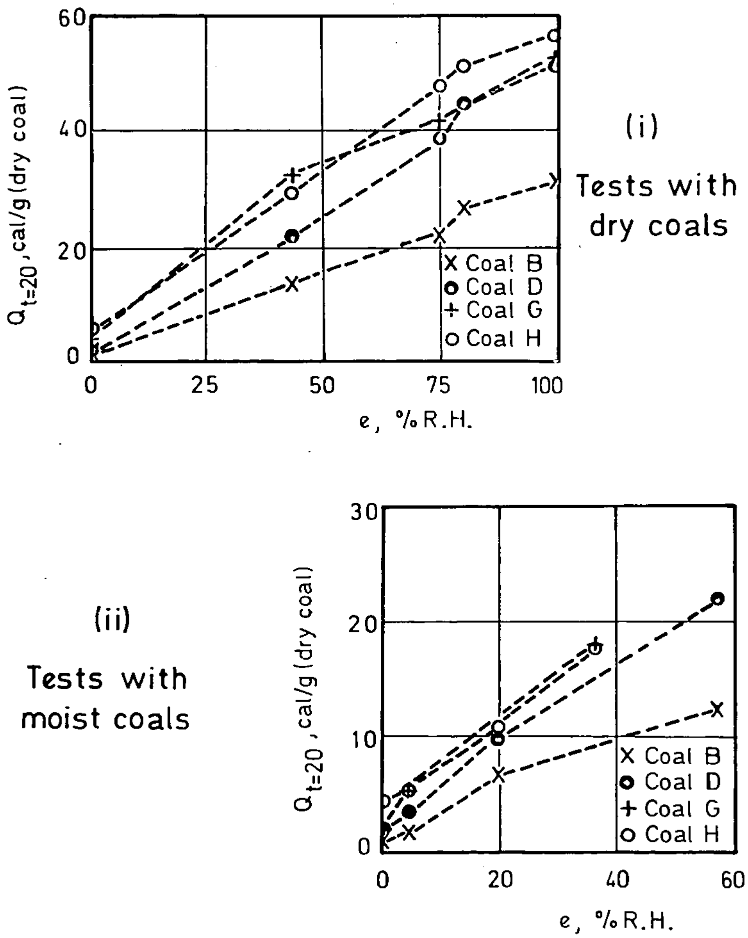


Figure 4. **Variation in the characteristic rate of heat release with the equilibrium deficiency of the coals.**

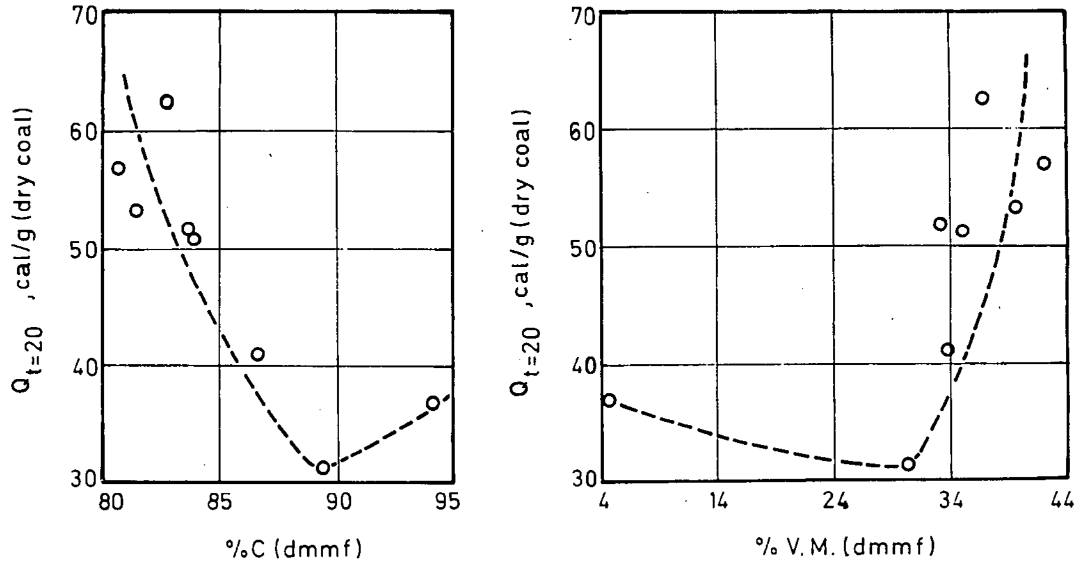


Figure 5. Variation in the characteristic rate of heat release with the rank of coal.

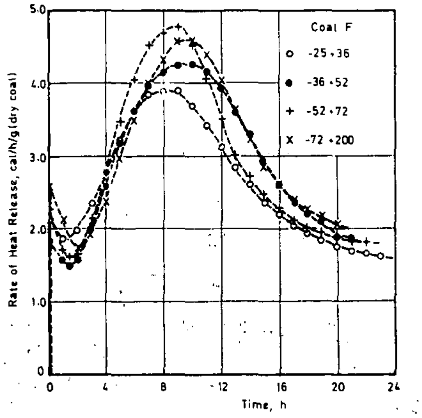


Figure 6. Effect of coal particle size on the variation in the rate of heat release with time during oxidation and sorption of water vapour by dry coal.

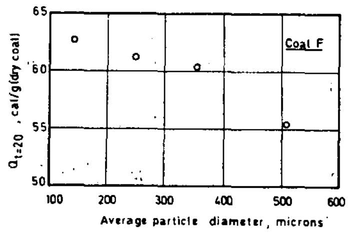
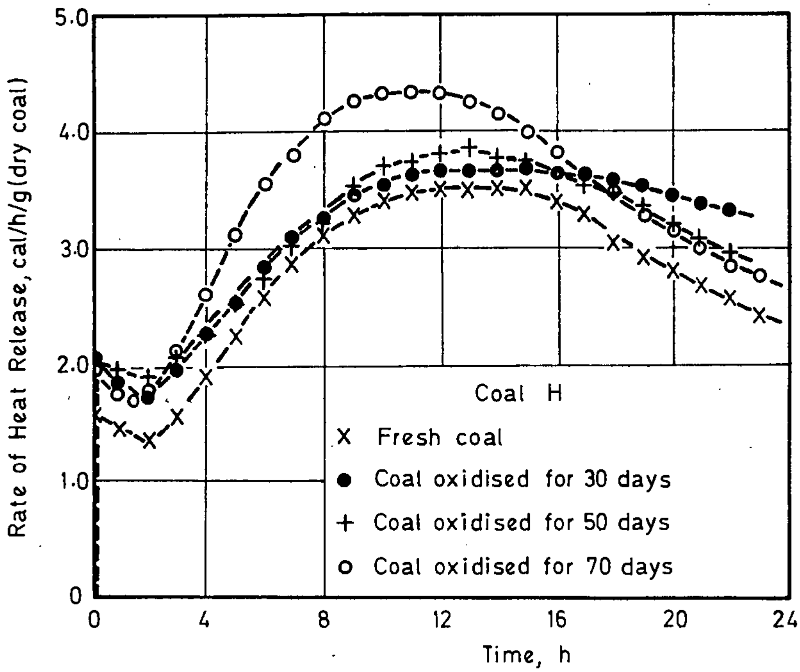


Figure 7. Effect of average coal particle diameter on the characteristic rate of heat release.



Dry coal and air saturated at 100% R.H. at 30°c

Figure 8. Effect of weathering on the variation in the rate of heat release with time during oxidation and sorption of water vapour by dry coal.