Energy, Mines and Resources Canada
Énergie, Mines et Ressources Canada

CANMET
Canada Centre for Mineral and Energy Technology
Centre canadien de la technologie des minéraux et de l'énergie

INSTRUMENTAL ANTICIPATION OF DEFLUIDIZATION OF HEATED BEDS OF CAKING COALS

B.J.P. WHALLEY AND I. LAU
COAL RESOURCE AND PROCESSING LABORATORY

OCTOBER 1977

(Preprint - subject to revision before publication)

For Presentation to the 27th Canadian Chemical Engineering Conference, Calgary, Alberta, October 23-27, 1977.

ENERGY RESEARCH PROGRAM
ENERGY RESEARCH LABORATORIES
REPORT ERP/ERL 77-90 (OP)

INSTRUMENTAL ANTICIPATION OF DEFLUIDIZATION OF HEATED BEDS OF CAKING COALS

by

B.J.P. Whalley* and I. Lau**

ABSTRACT

In batch fluidized beds of caking coals, differential thermocouple (DT) probes are shown to detect initial defluidization appreciably sooner than pressure probes and with more definite response.

Different factors affecting the initial temperature of defluidization and the time between initial and total defluidization are discussed.

Fluidized beds incorporating probes would appear to have application to other materials and to characterization and control of fluidized bed operation.

---

*Research Scientist, and **Engineer, Coal Resource and Processing Laboratory, Energy Research Laboratories, CANMET, Department of Energy, Mines and Resources, Ottawa, Canada.

CONTENTS

INTRODUCTION

It is well known that in gas-solid (aggregatively) fluidized beds stickiness of the surface of the particles can cause defluidization that in an industrial process can be catastrophic. Defluidization problems were encountered in the early development of hydrogen reduction of powdered iron ores. They are also encountered in carbonization (thermal decomposition) of caking coals and in gasification of coals.

Caking coals, that is coals that become plastic upon heating at atmospheric pressure in an inert atmosphere (generally in the range of temperature from 350°-450°C(1), are especially troublesome. However, defluidization can also occur with non-caking coals when they are subjected to a variety of conditions including pressure and high concentrations of hydrogen.(2) The effect of the latter condition is of considerable current interest in connection with coal gasification.

The work of Gluckman et al(2) has thrown considerable light on the mechanism of defluidization and has shown that there is a direct relationship between thermal rheological properties of the materials (as measured by dilatation and sintering temperatures) and the temperatures of defluidization. Because defluidization ought not to be allowed to occur in a large pilot or industrial plant, reliable instrumental anticipation of total defluidization is a worthwhile objective.

Gas-solid fluidization is characterized by efficient mixing, and in a heated state only small temperature differences usually exist in the bulk of the bed except in the case of highly exothermic or endothermic reactions in inert beds. For example, in fluidized bed combustion of coal the bed comprises almost entirely coal ash and calcined limestone or dolomite, but individual particles of coal, as they burn, may reach temperatures as much as 200°C above the mean bed temperatures(3).

Because heat transfer in heated fluidized beds is dependent upon the intensity of particle circulation, any property of the system that interferes significantly with particle movement will, of course, cause temperature differences in bed. These temperature differences may be quite small, and use of pairs of electrically opposing thermocouples and an appropriate recorder is a convenient method of measuring such differences even at high temperatures (e.g. 1000°C). Opposing pairs of thermocouples may be considered as differential thermal (DT) probes. Their function resembles that of thermocouple pairs that are the essential feature of DTA (differential thermal analysis) cells used to detect thermally activated physical and chemical reactions(4). Other workers have used recording defluidization meters using pressure and force transducers(2)(5)(6).

This paper is part of an intended larger investigation designed to test the capability of DT probes to characterize and control the behaviour of heated fluidized beds. In particular it deals with results additional to preliminary observations made in this laboratory(7) on the ability of DT probes to anticipate defluidization* of heated beds of caking coals. At this stage, batch fluidized beds were used. Further work is planned to apply the technique to continuously-fed fluidized beds.

---

*By "anticipation of defluidization" is meant anticipation of total defluidization.

EXPERIMENTAL

Apparatus and Materials

The fluidized bed reactor used for most of the experiments was a batch-fed 10-cm diam electrically wall-heated unit of conventional design fitted with a fritted stainless steel distributor and supplied with the usual equipment for controlling the bed temperature and the flow of fluidizing gas. A schematic representation is shown in Fig. 1. Thermocouple entries were made through glands set in the column wall at different levels thus providing a variety of DT pair configurations as shown in Fig. 2. Although bare chromel-alumel thermocouple tips were used in early(7)(8) experiments, similar thermocouples with stainless steel shields were found to be sufficiently sensitive to give a satisfactory signal. Probes were used to continuously measure the pressure drop across the whole bed (ΔP_o) and across a fraction of the bed (ΔP_1) by inserting stainless steel tubing, as in Fig. 1, attached to voltage-producing transducers connected to a 2-channel recorder. The transducers were model 504-24 made by Viatran Corp., Grand Island, N.Y., U.S.A.

For bed material a high volatile A (hva) and a low volatile (lv) coal with a nominal size of minus 250 µm (-60 mesh, U.S.) were used. Their volatilities and plasticities and size analyses are shown in Table I and II. For rheologically inert material (hereinafter "inerts"), semi anthracite char (low temperature coke) at a nominal size of minus 250 µm was chosen. Its size analysis is shown in Table II. Unless otherwise stated, the minus 250 µm hva coal was used for all experiments. Bottled nitrogen with a reported O_2 content of <30 ppm was used as the fluidizing gas.

Procedure

To study defluidization, runs were made by subjecting the fluidized bed of caking coal to an approximately linearly rising temperature. The gas flow was calculated and adjusted manually to maintain a constant superficial space velocity (U_s) as the temperature was raised. DT probes were placed in various locations in pairs, and their differential temperature signals and that of the bed temperature from a single thermocouple were fed to recorders.

It seemed likely that the degree of anticipation, i.e. the interval between initial and total defluidization, would depend upon location of the thermocouples and variables such as rheological properties of the bed material (has it a sharp melting point or a wide, softening range?), its particle size distribution, the gas velocity and the heating rate. These latter variables were found by Gluckman et al(2) and Agarwal and Davis(5) to be important in determining defluidization temperatures.

Results

Location of Thermocouples

The first variable to be considered that would affect the extent of anticipation was the location and separation of the thermocouple (DT) pairs. In preliminary experiments in mild steel and in glass 10-cm diam columns(7), it was shown that for wall-heated units a radial separation of the thermocouple tips was the more effective and an axial separation for fluidizing-gas-heated (i.e. bottom-heated) units.

In following experiments for radial configurations, typically one thermocouple of the probe was located in the axis of the column and the other near (within 0.5 cm) the wall (Fig. 2). When a heated bed was thoroughly fluidized, a thermocouple pair inserted in the bed generally gave a practically zero base line as the temperature was raised. There were minor but rapid fluctuations (Fig. 3) of <±0.5°C probably caused by particles bombarding the near-wall thermocouple at temperatures above the mean bed temperature(9). The oscillations might also be explained by the action of gas bubbles because their frequency is of the same order as that reported by Gransden et al(6). Depending upon location and separation of the thermocouples and extreme operating conditions, some base lines drifted considerably.

Of configurations A-D, A-E, B-C, B-D, B-E, C-F, and E-F (Fig. 2) A-D was found under a variety of conditions to give the least drift (usually about 0.1°C of DT signal per 10°C of bed temperature) and clearest inflection at the initial defluidization temperature. B-D was almost as satisfactory. A-D was generally covered by about 4 cm of fluidized bed.

As shown in Fig. 3 at a certain temperature level, depending upon the nature of the coal and operating conditions, the DT signal curved away in a prominent manner from its straight base line. This change in DT signal had been previously identified by Whalley and Dykstra(8), with the onset of defluidization.

There was also a falling off of the total bed pressure, ΔPo, Fig. 4, corresponding to the DT initial defluidization signal, but this was invariably later, on an average of 1 min later. There was frequently a moderately distinct second inflection of the ΔP_o signal and this was of necessity arbitrarily (and conservatively) chosen as the occurrence of final defluidization. The peak of second pressure signal (ΔP_1) from a top fraction (typically 25%) of the bed was especially useful when the second inflection of ΔP_o was missing. It was taken as confirmation of the occurrence of total defluidization and corresponded closely with a distinct second inflection (where it occurred) in ΔP_o.

In Fig. 4 the large increase in the fractional pressure, ΔP_1, that usually occurred before final defluidization was evidently caused by evolution of volatiles that precede the softening of a caking coal. It is interesting to note that the onset of this effect was quite repeatable for identical conditions, but varied with the rank of coal and with gas velocity.

That ΔP_o did not increase like ΔP_1 is explained by the fact that ΔP_o is relatively unaffected by increases in gas velocity above the initial fluidization velocity, U_{mf}, since ΔP_o is practically equal to the bed weight. However, relatively large changes in weight occur (because of bed expansion) in (say) the top 25% of the bed that produces ΔP_1(10).

It will be noted from Fig. 3 that as defluidization was approached, the bed temperature became relatively constant despite increasing heat input evidently because of decreased solids circulation within the bed. Therefore, anticipation of defluidization was not measured directly in terms of a temperature range but in terms of elapsed time from initial to total defluidization.

The time between initial and total defluidization for the caking coals was considerably longer (minutes instead of seconds) than found by Gluckman et al for more closely sized and more sharply melting materials. However, Agarwal and Davis(5) and Gransden et al(6) have shown that defluidization can occur progressively over a long-time interval for widely sized iron ore. They also point out the importance of residence time upon the temperature of defluidization.

Effect of Fluidizing Gas Velocity

It is well known that for beds that have a tendency to stick, an increase in gas velocity will normally raise the defluidizing temperature, and this is shown in Figure 5(a), where initial defluidization temperature T_{di} is plotted against gas velocity. However, it is interesting that as fluidizing gas velocity increased, the extent of anticipation also increased as shown in Fig. 5(b).

Effect of Heating Rate

There was no appreciable effect of the heating rate within experimental error, upon T_{di} as will be seen from Fig. 6(a) or on the extent of defluidization as seen from Fig 6(b). This is surprising, and additional experiments using other coals will be required to prove these results in which considerable scatter occured.

Effect of Bed Depth

As can be seen from Fig. 7(a) and (b) the effect of increasing bed depth had little effect on T_{di} but caused an increase in the extent of anticipation.

Effect of Coal Rank and Particle Size Distribution

Both the hva and lv coal samples of nominally minus 250 μm (-60 mesh U.S.) were split in three fractions and reblended to produce sub-samples of different mean particle sizes. The size distributions of these sub-samples are shown in Table II.

It can be seen from Fig. 8(a) and (b) that the T_{di} for the lv coal increased with increasing size as would be the expected effect of coarser material and that the extent of anticipation decreased. For the hva coal there was little effect of size upon the T_{di} or the extent of anticipation and it was the reverse of that for the lv coal. The hva coal used was obviously an oxidized sample as indicated by its relatively low plasticity (500 ddm)*. A fresh unoxidized coal of this type would normally have a plasticity of about 20,000 ddm(12). This suggests that the finer sizes of hva coal were reacting as inerts and would therefore, with an increase in fines, tend to lower rather than raise the T_{di} and increase the anticipation of defluidization.

Effect of Additions of Inerts

The addition of inerts has been frequently used to inhibit sticking in fluidized beds(5). For these experiments char was mixed in different proportions with the hva coal. Both were nominally minus 250 μm. Char characterization data are shown in Table II.

The effect on the initial defluidization temperature T_{di} and the extent of anticipation are shown in Figure 9(a) and (b) respectively, from which it can be seen that the addition of char significantly increased T_{di} as expected, but the degree of anticipation decreased to a relatively constant level (within experimental error) with additions of 25% or more char.

Relationship of Initial Defluidization Temperature with Initial Plasticity Temperature

A mean of 18 values of T_{di} was 400°C (S:5.14)** compared closely with that of the initial Gieseler plasticity temperature (405°C) of the head sample of the hva coal. The mean of 4 values of T_{di} for the lv coal was 435°C (S:4.65); the initial plasticity temperature was 439°C. A similarly close relationship was shown by Gluckman et al(2) between the T_{di} and the initial temperature of dilatation.

---

*ddm: dial divisions per minute

**S: standard deviation

DISCUSSION

Evidence to date suggests that differential thermocouple probes can detect defluidizing conditions as significant temperature gradients within the bed. In a rising temperature regime, the bulk of a well fluidized bed will show virtually no thermal gradients. But where stickiness begins as the result of increasing temperature, circulation of the particles will be reduced. In a wall-heated column, an annulus can be imagined of particles of reduced circulation, thus impeding heat flow to the rest of the bed.

The ability of the DT probe to detect the onset of defluidizing conditions in advance of the total pressure signal ΔP_o can be explained by considering the difference in the conditions they detect. The initial ΔP_o inflection toward lower pressure was probably caused by part of the bed being loosely supported by the heated walls of the column, thus reducing the weight of the freely circulating particles. The ΔP_o signal might be expected then to occur after the more sensitive detection of impaired circulation by a DT probe. The second ΔP_o inflection can be accounted for by extensive channelling through a largely immobilized bed.

The pressure increase shown by ΔP_1 (Fig. 4) prior to initial defluidization can be explained by bed expansion caused by evolution of volatiles because its onset corresponded to that of the initial devolatilization temperature of the ranks of coals used. It was noted that the increase of pressure was less for the low volatile coal and for coal diluted with char.

The relatively long anticipation period for caking coal should allow application of the DT signal to trigger remedial measures such as increasing the gas velocity, adding of coarser material, lowering the temperature, adding inerts, or the combination of these measures.

More work will be required to characterize the behaviour of typical fluidized bed systems in the field between initial and total defluidization, especially with materials of high fluidities and in continuous (i.e. steady state) systems. In continuous fluidized beds, DT probes would be expected to react to temporary non-steady state conditions, especially increases in the proportion of fine particles, in the event of their causing incipient defluidization.

Bench-scale batch fluidized beds used in conjunction with DT probes should be useful tools in investigating the sintering properties of a number of materials, since initial defluidization is much more sensitive to sintering than is dilatation(2). Of special interest is coal fly ash since there appears to be a relationship between the sintering temperature of fly ash and boiler tube fouling(2).

CONCLUSIONS

Investigation of the ability of differential thermocouple pairs to anticipate total defluidization of high and low volatile caking coals, when subjected to rising temperatures in a batch fluidized bed, leads to the following conclusions applicable to coals:

1. Differential thermocouple (DT) probes can detect the onset and development of defluidization of caking coals under a variety of conditions and should have useful applicability in pilot and industrial scale fluidized bed units.
2. DT probes give a sharper and considerably earlier warning of total defluidization than do pressure-drop signals.

3. The effect of particle size upon the extent of anticipation is strongly dependent upon the rheological properties of the coal.
4. The extent of anticipation increases with the gas velocity and with increasing bed depth;
   - it is relatively independent of heating rate;
   - it decreases with increasing amounts of inerts.
5. The time interval between initial and total defluidization would appear for caking coals to be sufficient to prevent total defluidization by triggering remedial measures such as increasing the gas velocity, lowering the temperature, and/or adding inerts.
6. More work is required to determine its applicability to continuous (steady state) fluidized bed systems and for the improvement of signal response.
7. Bench-scale batch fluidized beds fitted with DT and pressure probes would appear potentially useful to supplement existing tools and techniques in the study of rheological properties of fine particles.

ACKNOWLEDGEMENT

The authors acknowledge with thanks Dr. J.F. Gransden, Energy Research Laboratories, for helpful discussions and suggestions, and Messrs. K.F. Hampel and G.H. Dicks for technical assistance.

REFERENCES

1. Loison, R., Peytavy, A., Boyer, A.F., Grillot, R., Chemistry of Coal Utilization, (H.H. Lowry, ed.), Supp. vol, p. 17, John Wiley and Sons Inc., New York, (1963).

2. Gluckman, M.J., Yerushalmi, J., Squires, A.M., Fluidization Technology, (D. Keairns, ed.), vol. II, p. 395, Proceedings International Fluidization Conf., Pacific Grove, Calif. Hemisphere Pub. Corp., Washington, (1975).

3. Skinner, D.G., The Fluidized Combustion of Coal, p. 46, Mills & Boon Limited, London, (1971).

4. Mackenzie, R.C., Differential Thermal Analysis, (R.C. Mackenzie, ed.), vol. I, p. 11, Academic Press, New York, (1970).

5. Agarwal, J.C., Davis, W.L., Chem. Eng. Prog. Symp., Ser. 62: 67, 101 (1966).

6. Gransden, J.F., Sheasby, Bergougnou, M.A., Chem. Eng. Prog. Symp., Ser. 66: 105, 208 (1970).

7. Whalley, B.J.P., Lau, I., unpublished work (1977).

8. Whalley, B.J.P., Dykstra, A. Proceedings, Inst. Briquetting and Agglomeration, vol. 13, 227 (1973).

9. Gelperin, N.I., Einstein, V.G., Fluidization, (J.F. Davidson and D. Harrison, eds.) p. 471, Academic Press, New York, (1971).

10. Pruden, B.B., Crosbie, D., Whalley, B.J.P., Fluidization Technology, (D. Kearns, ed.) Vol. II, p. 65, Proceedings, International Fluidization Conf., Pacific Grove, Calif., Hemisphere Pub. Corp., (1975).

11. Clendenin, J.D., The Year-Book of the Coke Oven Managers' Association, (E.T. Parry, ed.) p. 371, C.O.M.A. (Year Book) Ltd., Mexborough, Yorkshire, (1972).

TABLE I

Volatilities and Plasticities of Coals

Material	Volatile Matter (%)	Gieseler Plasticity Start Temp (^oC)	Gieseler Plasticity Max. Fluidity (ddm)
hva Coal	37.5	405	500
lv Coal	20.9	439	18

TABLE II

Size Distribution in Wt % of Coals and Char

Material	Sample No.	Size Range (mesh U.S.) +60	60-100	100-140	140-200	200-325	-325	dp (μm)
High Volatile Coal	1	4.7	27.1	5.4	4.5	29.9	28.5	70.2
	2	4.1	23.9	16.4	13.6	21.5	20.5	78.8
	3	8.0	46.6	9.2	7.7	14.6	13.9	99.4
	4	9.3	54.2	10.7	8.9	8.6	8.2	118.6
Low Volatile Coal	1	0.5	15.2	9.7	7.6	39.7	27.3	64.0
	2	0.7	22.8	14.6	11.4	29.9	20.6	73.5
	3	0.9	30.4	19.4	15.2	20.2	13.9	86.3
	4	1.9	63.8	9.7	7.6	10.1	7.0	119.5
Char	1	1.8	47.9	17.1	13.0	7.1	13.2	103.9

Where dp is the reciprocal mean particle diameter and is calculated from:

$$d_p = \sum \frac{Xi}{d_{pi}}$$

Xi = weight fraction of a size range i

d_{pi} = geometric mean diameter of the upper and lower limits of the corresponding size range

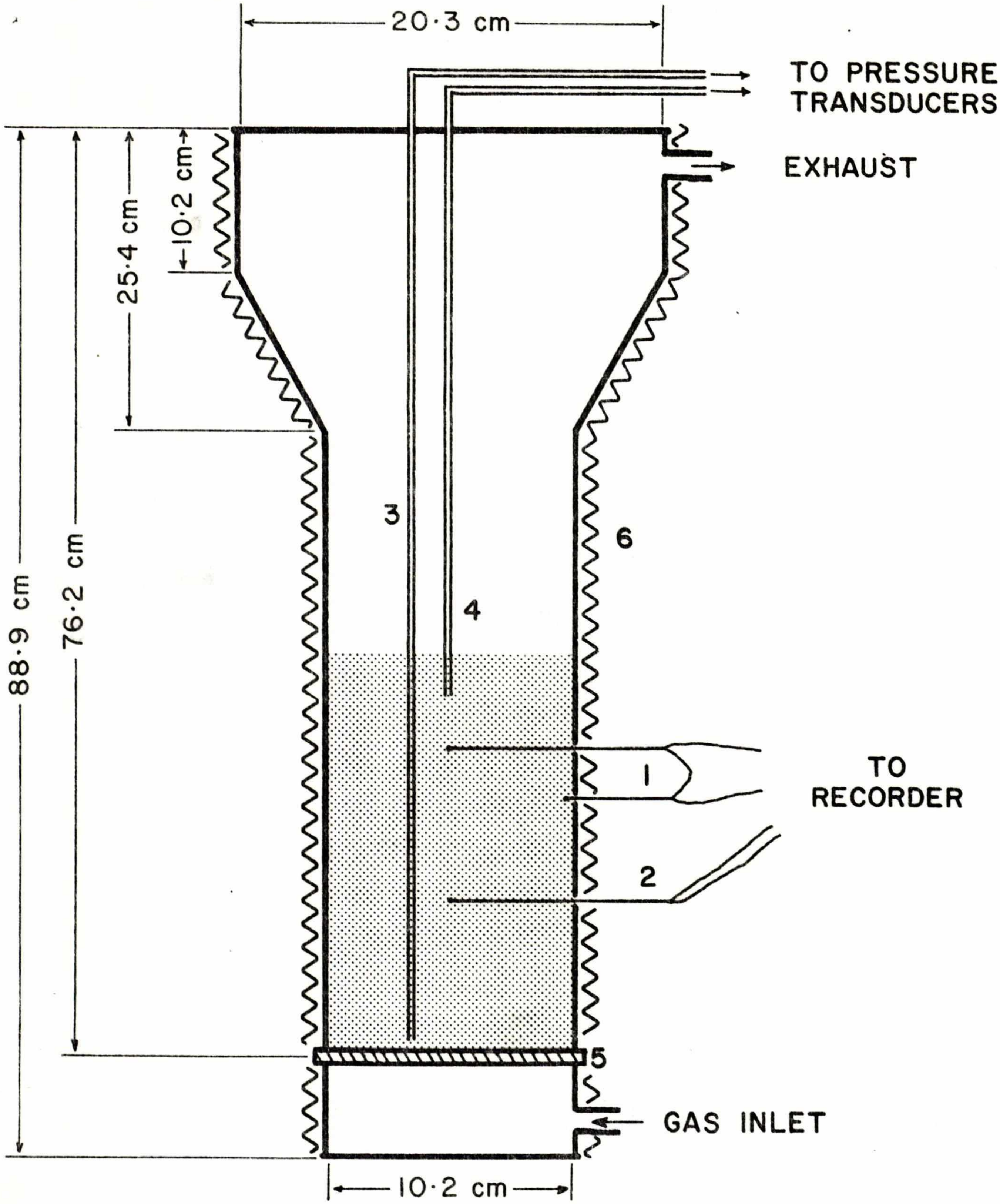

Figure 1. Schematic of Fluidized Bed Column

1.	*Differential Thermocouple Probe*	4.	*Fractional Bed Pressure Probe*
2.	*Bed Temperature Indicating Thermocouple*	5.	*Gas Distributor*
3.	*Total Bed Pressure Probe*	6.	*Heaters*

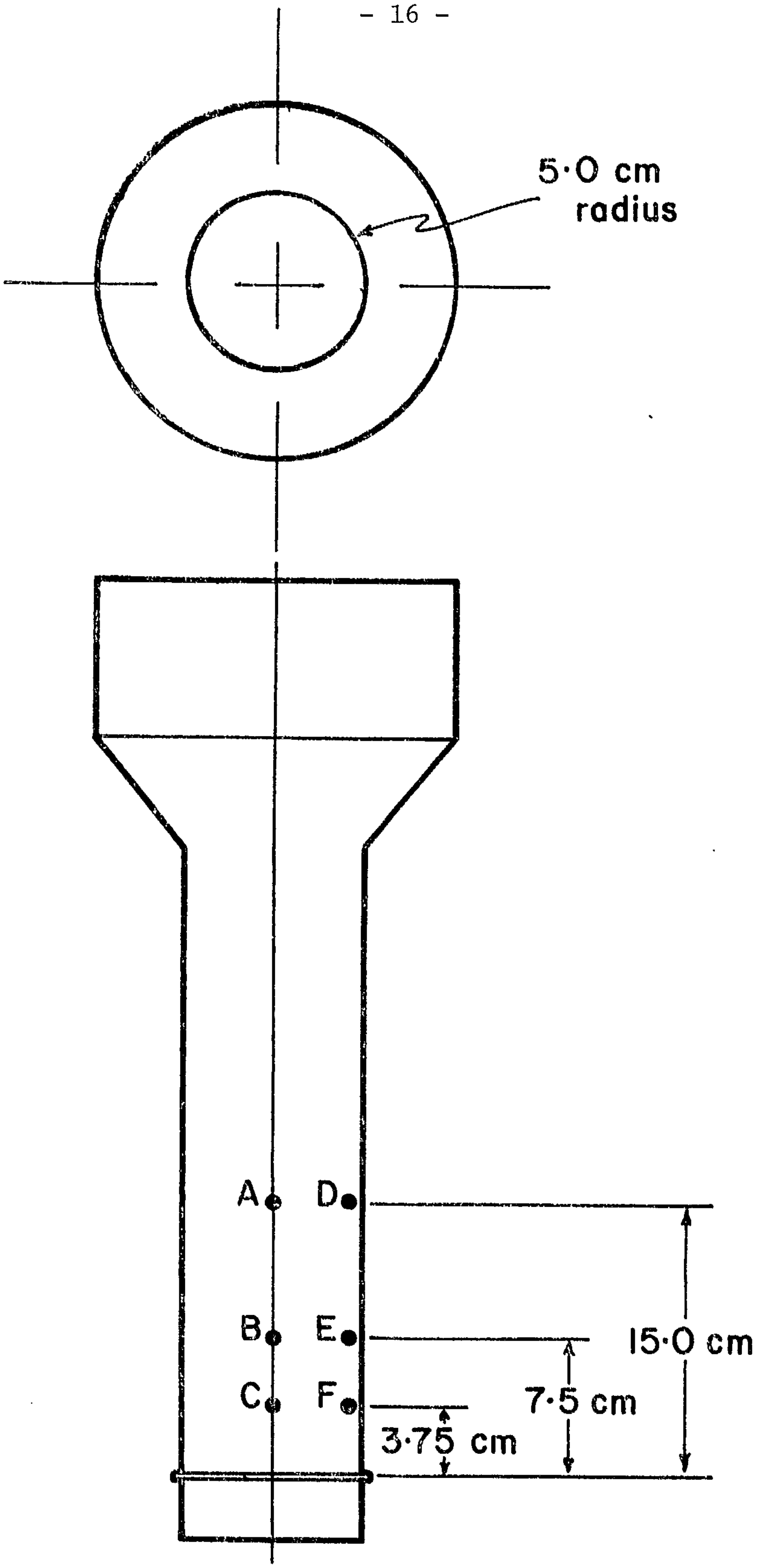

Figure 2. Differential Thermocouple Locations

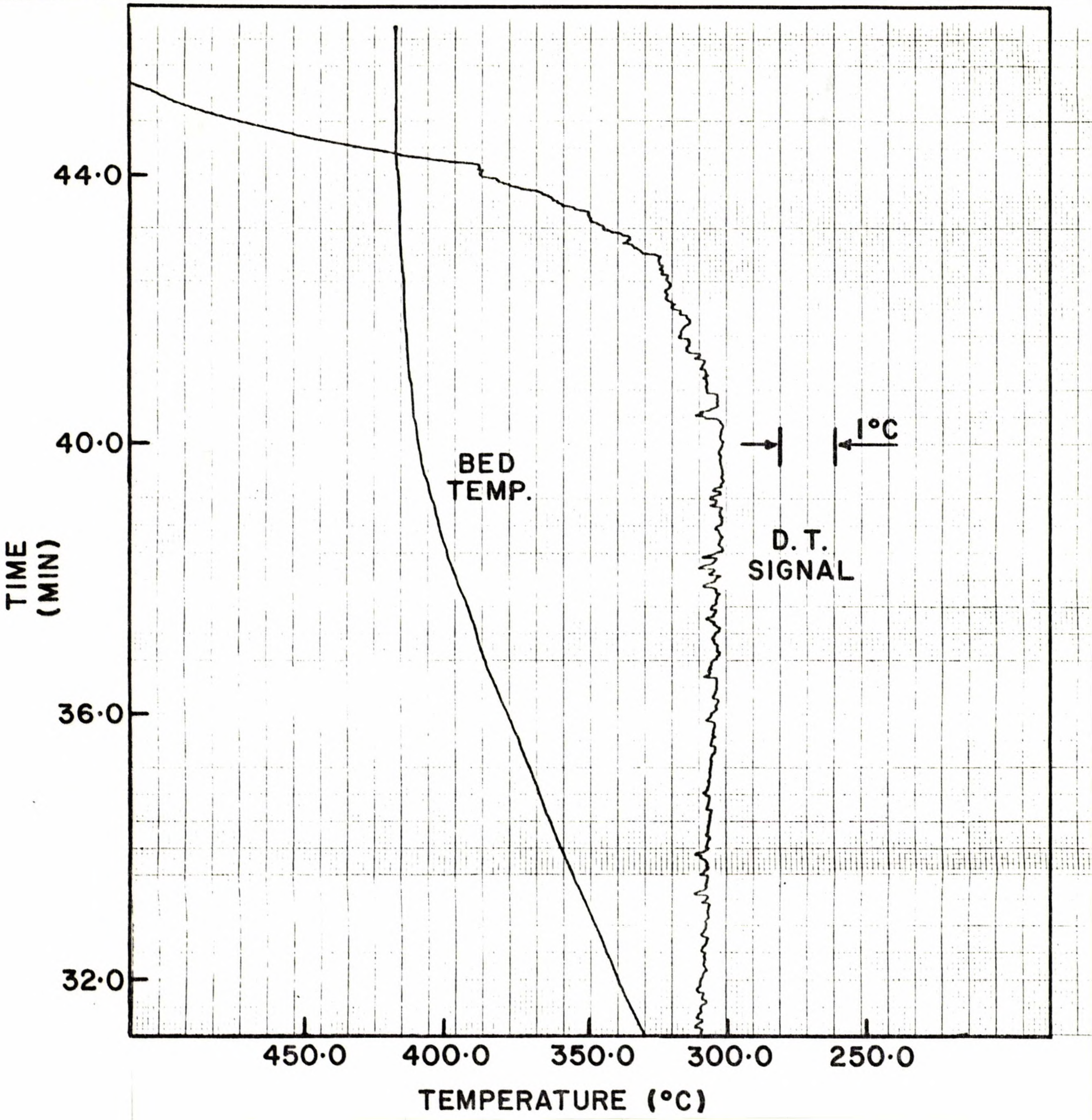

Figure 3. Typical Differential Thermocouple and Bed Temperature Trace

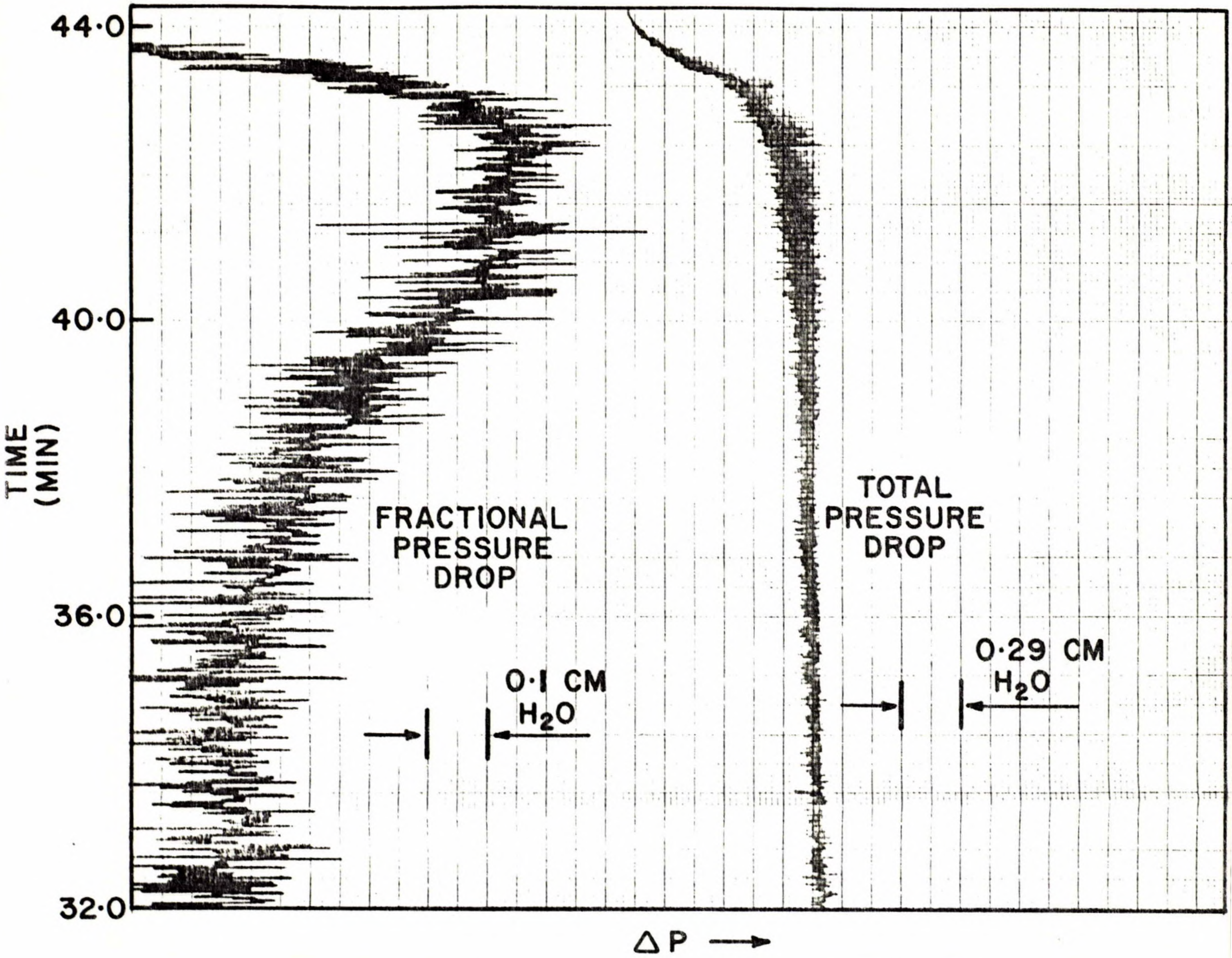

Figure 4. Typical Pressure Drop across Total and Fractional Bed Depth

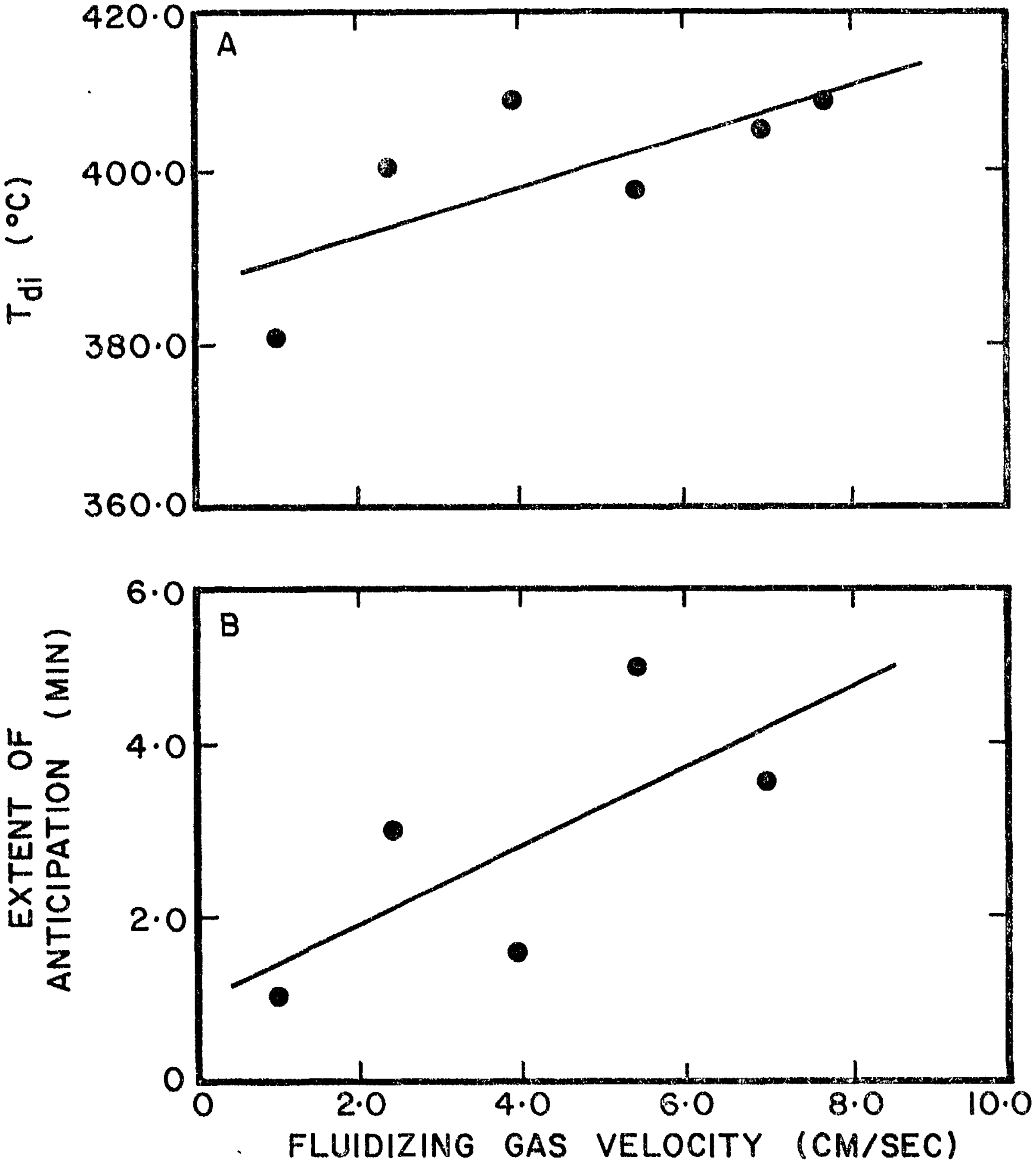

Figure 5. Effect of Fluidizing Gas Velocity on:
(A) Initial Defluidization Temperature (T_{di})
(B) Extent of Anticipation of Defluidization

Avg. Particle Size: 118 μm
Fixed Bed Hgt: 15 cm
Heating Rate: 9°C/min

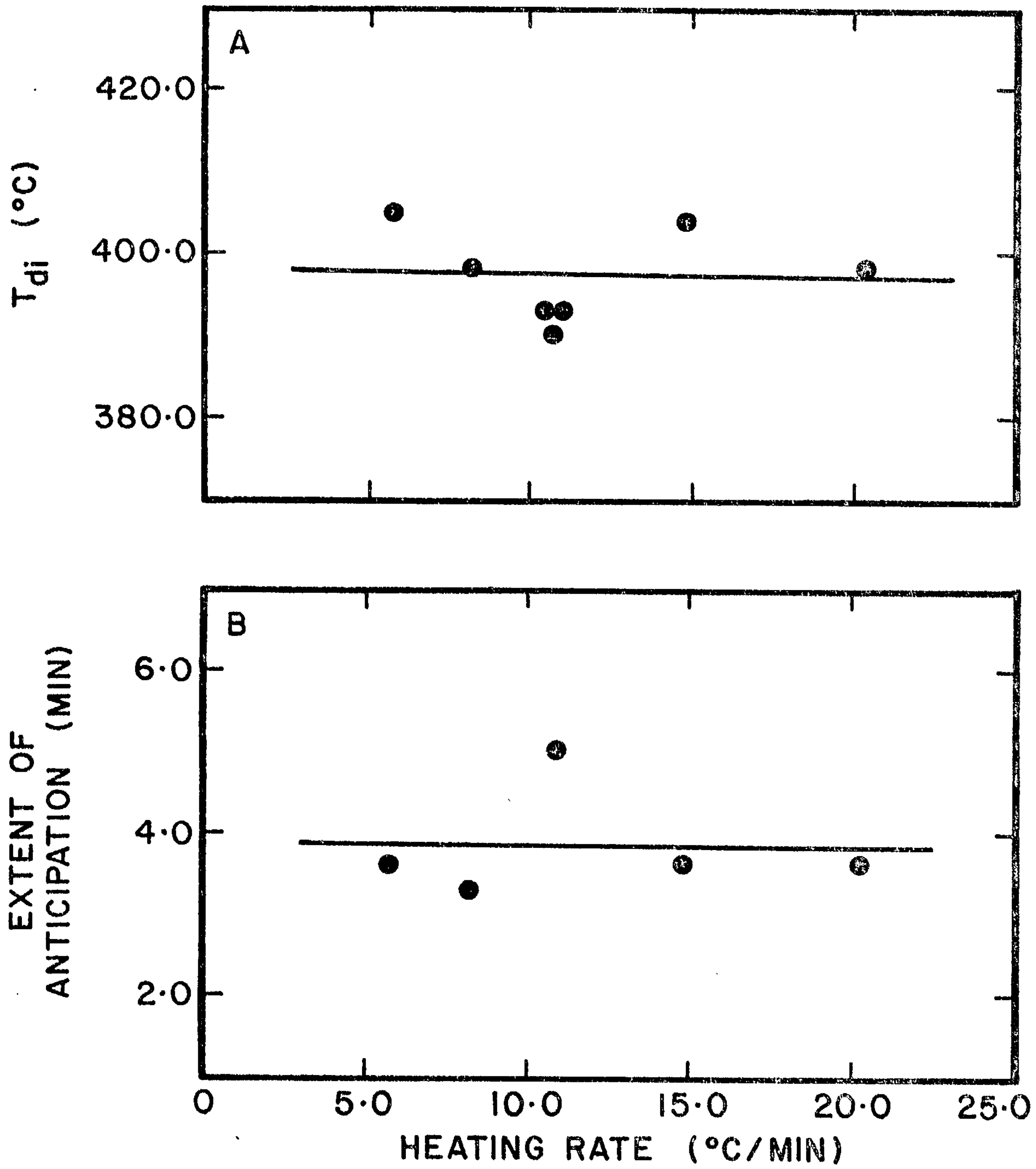

Figure 6. Effect of Heating Rate on:
(A) Initial Defluidization Temperature (T_{di})
(B) Extent of Anticipation of Defluidization

Avg. Particle Size: 118 μm
Fixed Bed Hgt: 15 cm
Fluidizing Gas Velocity: 4.4 cm/sec

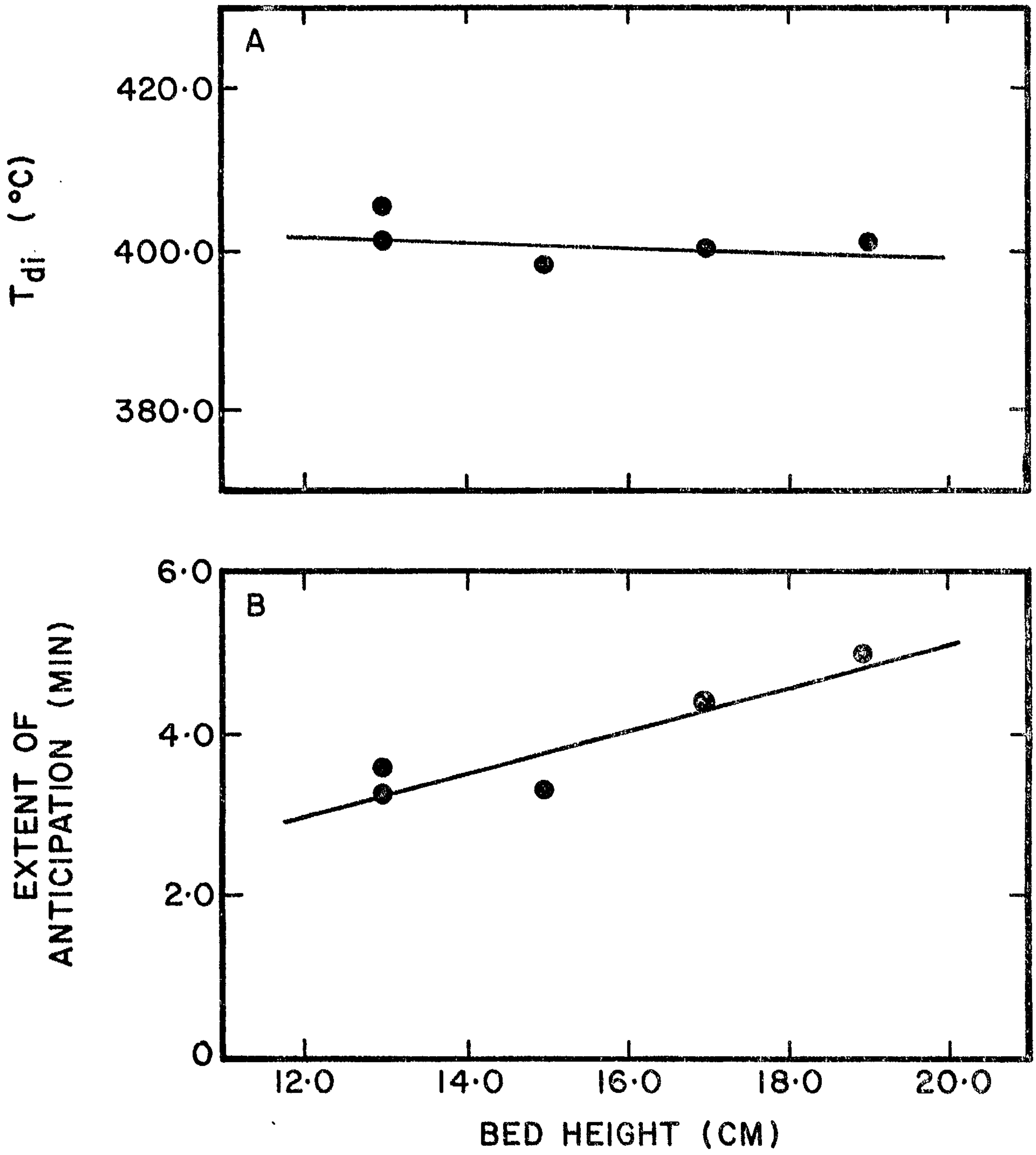

Figure 7. Effect of Bed Height on:
(A) Initial Defluidization Temperature (T_{di})
(B) Extent of Anticipation of Defluidization

Avg. Particle Size: 118 μm
Fluidizing Gas Velocity: 4.4 cm/sec
Heating Rate: 8°C/min

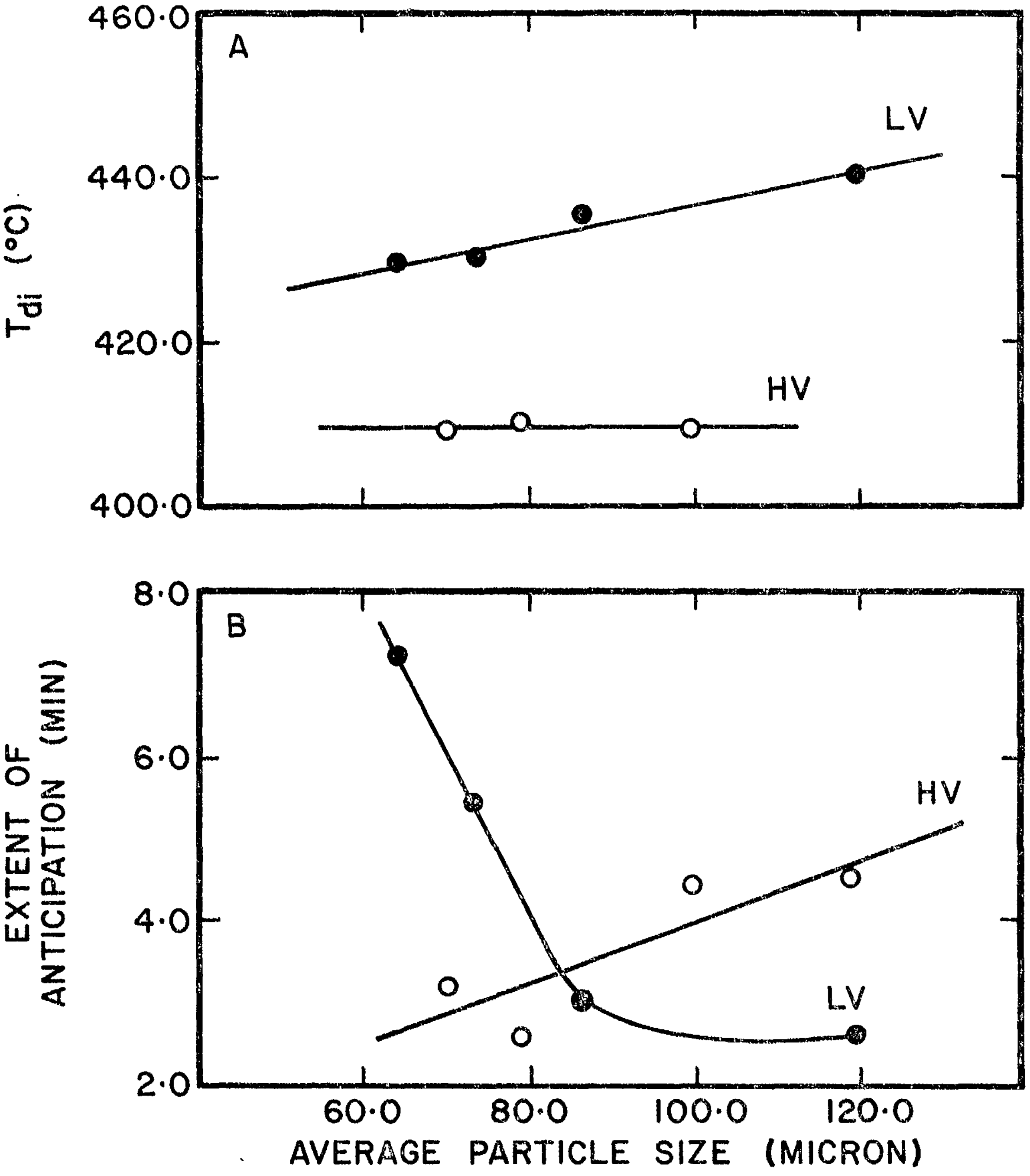

Figure 8. Effect of Particle Size and Coal Rank on:
(A) Initial Defluidization Temperature (T_{di})
(B) Extent of Anticipation of Defluidization
● Low Vol. Coal; ○ High Vol. Coal

Fixed Bed Hgt: 15 cm
Fluidizing Gas Velocity: 4.4 cm/sec
Heating Rate: 9.5°C/min

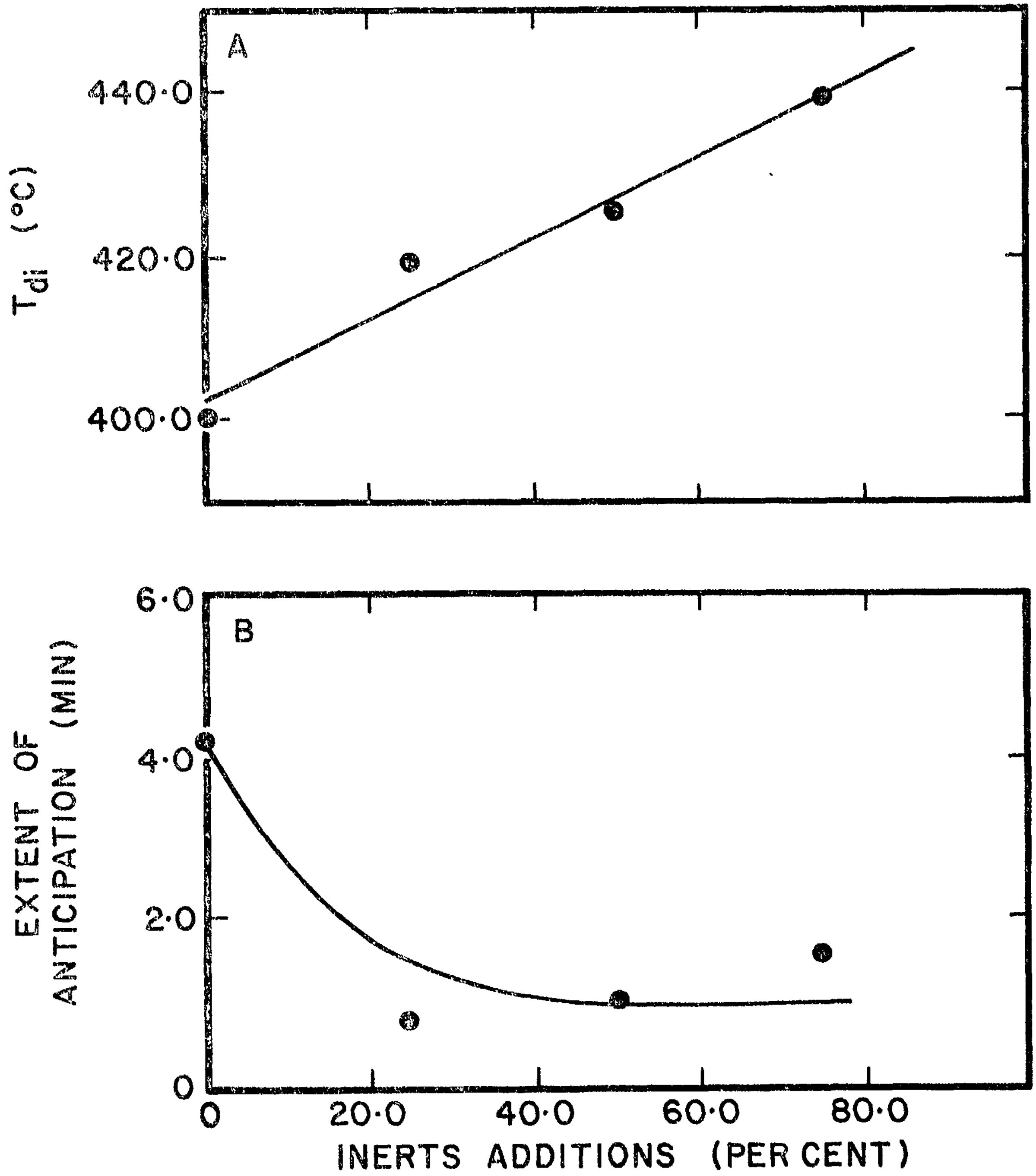

Figure 9. Effect of Inerts Addition on:
(A) Initial Defluidization Temperature (T_{di})
(B) Extent of Anticipation of Defluidization

Fixed Bed Hgt: 15 cm
Fluidizing Gas Velocity: 4.4 cm/sec
Heating Rate: 10°C/min