

THERMAL STABILITY OF ACTIVATED CARBON IN AN ADSORBER BED

M. Hoyle<sup>a</sup>, G.R. Astbury<sup>b</sup>, and M.H. Chen<sup>c</sup>

<sup>a</sup>Zeneca Specialties, P.O. Box 42, Hexagon House, Blackley, Manchester, M9 8ZS

<sup>b</sup>Dept of Chemical Engineering, UMIST, P.O. Box 88, Manchester, M60 1QD

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Fires in activated carbon bed adsorbers are not uncommon. The investigation of a fire incident in an activated carbon adsorber unit, which had no solvent adsorbed on the carbon, showed the thermal stability of the activated carbon alone, in bulk, can be as low as the temperatures used to regenerate the bed. This paper discusses the incident fire and methods test methods used to determine its cause, and proposes an aerobic ramped adiabatic Dewar test method for use in determination of ignition temperature of activated carbons likely to be encountered under the operating conditions in an adsorber system.

Keywords: Carbon Bed Adsorbers, Thermal Stability, Activated Carbon, Ignition, Fire.

INTRODUCTION

Activated carbon bed adsorber systems are widely used in many industrial application for the removal / recovery of solvent from a laden air stream and adsorption of odorous or toxic material prior to discharge of waste streams to atmosphere. The use of carbon adsorber systems has increased dramatically due to greater environmental awareness due to release of material to atmosphere, and the financial benefit from recovery and recycle of materials.

The adsorbent properties of activated carbon has been known for many years, and after many fires in bulk storage so have the spontaneous ignition properties of the materials (1-4). Further to this, fires within carbon bed adsorbers are frequently reported in the literature (5-12). In many of the literature examples, the cause of an incident has been inconclusive, but many attribute the onset of a fire in the bed to the exothermic oxidation of the adsorbed solvent. Most fires seem to have a commonality in that they occurred on start-up after a prolonged system shut-down. It is the dormant state that allows reaction to occur in an essentially adiabatic environment within the bed, and under such conditions these reactions heat the localised environment creating a so called 'hot spot', albeit at an initially slow rate with the majority of solvents. On reintroduction of the process air stream there is an immediate supply of additional oxidant which can accelerate the rate of reaction and lead to ignition of the carbon. This tends to be seen as a propagating heat wave which passes through the entire bed if not dealt with immediately. The combustion of carbon can generate very high temperatures when there is a steady supply of air feeding the reaction. Furthermore, if flammable vapours come into contact with the bed once it is burning then there is a high risk of an explosion occurring within the system, as occurred in one reported incident (13).

INCIDENT DESCRIPTION

The mechanism by which a recent fire initiated within a carbon bed adsorber system could not be attributed to oxidation of the solvent being adsorbed as the carbon had just been renewed and no solvent laden air stream had been passed through the beds at the time of the fire.

The adsorber system was an end-of-line unit and adsorbed solvent from the vapour stream before venting to atmosphere. Under normal operation once a bed had completed adsorption duty it was regenerated to recover the solvent by application of a saturated steam purge under positive pressure, as this enabling the solvent to be condensed easily. The carbon bed was then cooled and dried by the passage of air before putting the bed back onto adsorption duty. The adsorber system had operated with a coal based activated carbon successfully and without incident since the system was commissioned. On deterioration of the adsorption performance over a six month period a change in grade of carbon was recommended by the carbon suppliers. The new carbon was a wood based activated carbon. This grade of carbon was used without incident for approximately 3 years. During a plant shut-down the carbon was renewed as its adsorption performance had deteriorated. The start-up sequence for the adsorber system required that each bed be pressure tested, along with testing the Programmable Logic Controller (PLC) and the valve positioners. After some delays, for repair of leaking valves and adjustment of valve positioners, the beds were ready for pressure testing prior to start-up. The bed on regeneration duty was the one to be pressure tested. The steam was isolated and air pressure applied at 2 barg. On starting the pressure test the temperature of the bed rose rapidly and then stabilised at 150°C before slowly rising a few more degrees over the next 2 hours. At this point the PLC cycle was stepped on manually to allow the pressure testing of the adjacent bed. This vented the previous bed and placed it on primary adsorption duty, so it now had a large flow of air passing through it. The temperature in the bed initially dropped on venting but shortly afterwards the temperature rose rapidly, exceeding 450°C in a short time. The maximum temperature in the vessel was not recorded as the thermocouple failed at 454°C, although it was estimated that the bed could have reached in excess of 1000°C.

The high temperature was noted by the operators, on seeing the outside of the lagging around the bed vessel glowing red hot. Realising that there was a bed fire, the operators, in conjunction with the Fire Service, opened the bed and slowly applied water to the top of the bed to quench the embers. Whilst the fire in this bed was being extinguished, it was realised that the adjacent bed was on fire, and the attention was subsequently switched to extinguishing it. The second bed caught fire due to the hot combustion products from the first bed passing through it, as arranged by the sequence of valves controlled by the PLC.

INVESTIGATIVE TEST WORK

The traditional method for determining thermal stability of bulk solid materials is to undertake a series of isothermal basket test at various temperatures. This is the Bowes-Cameron Cage test (6). The onset temperature is the lowest isothermal temperature at which ignition occurs in the sample. The test is repeated with different sizes of basket, and the logarithm of the volume to surface area ratio versus the reciprocal of absolute temperature is plotted to produce a Leuschke plot. This can be extrapolated to the volume to surface ratio of the full size bed to determine

the expected ignition temperature of the mass of carbon in the bed.

This test method was carried out for both the original coal based carbon used in the system and the wood based carbon which was involved in the incident. The results indicated that the coal based carbon originally used would have an ignition temperature of around 165°C for the size of bed operated. The wood based carbon involved in the incident showed that an ignition temperature of around 101°C would be expected in bed size operated. The Leuschke Graphs for both the coal and wood based carbons are shown in figure 1.

The standard ignition temperature of the two grades of carbon were quoted by the Supplier as 300-375°C for the wood based carbon, and 425-450°C for the coal based carbon previously used. These were obtained by ASTM D-3466 76 test method. This test method clearly states in its methodology that the test is only of comparative use, and the ignition temperature given should not be interpreted as the probable ignition temperature encountered in an application unless operating conditions are similar to those employed in the test method. Needless to say the conditions in the adsorber system did not equate to the test method conditions. Furthermore, the affect of the size and symmetry of the bed on the thermal stability of the carbons had not been taken into account.

It is well known that the assignment of an absolute thermal stability temperature to powders, or granular materials, is not possible due to the potential for non-uniform temperature distribution and the mechanism of heat transfer through the bulked material. The volume, and hence the potential for heat generation, increases as the cube of the linear dimension. However, the surface area, where cooling occurs, increases only as the square assuming geometric similarity is maintained on scale up. Hence, potential cooling is reduced as size increases. It then follows that a quoted ignition temperature for a self heating material cannot be meaningful unless it also refers to the size of the mass of material. At the centre of a large mass heat loss can be almost negligible and the conditions are essentially adiabatic. Hence, exothermic activity at this point could theoretically result in a runaway reaction. However, the extent to which oxidant, which is generally the oxygen in air, is available to support exothermic oxidation is of equal importance to the balance between heat generation and heat removal.

Taking the ignition temperatures predicted for the two grades of carbon in the adsorber bed size and comparing them with the operating temperature, i.e. the steam regeneration temperature, then it would suggest that ignition would be likely in the wood based carbon due to its ignition temperature being relatively low at 101°C. Therefore the adsorber system was operating under inherently unstable thermal conditions.

The mechanism by which ignition of a carbon bed ignites is a two stage process consisting of an initiation step whereby a hot spot(s) is formed followed by propagation as the carbon itself burns. The bed fire was likely to be initiated due to the application steam at a temperature above the exothermic onset temperature of the carbon itself. The bed was then pressurised with air whilst the carbon was hot and this could accelerate the oxidation reaction at the hot spot. However this pressurisation with air was insufficient to ignite the bed as the amount of oxygen present was limited. On venting the bed and applying the process air stream, which was devoid of

solvent at this point, there was thus a copious supply of oxygen, which accelerated the oxidation reaction, and the bed ignited. The second bed subsequently ignited as the hot combustion gases from the first bed fire passed to it heating the carbon to above its onset temperature.

The adsorber system had operated with the wood based activated carbon for some time though without incident. However, under normal operating conditions the carbon was exposed to steam temperature for only a short period before the main flow of cooling air was applied to cool the bed to the operating temperature. In the time period prior to the incident the bed was held at high temperature for a time well in excess of the normal period due to process problems. This prolonged hold at high temperature followed by pressurisation with air would have allowed an oxidation reaction to proceed to a significant degree whereby sufficient heat was produced to generate a hot spot and allow full propagation on applying the air stream. Furthermore, previous carbon renewals had been followed with direct adsorption of solvent. Hence, the bed being heated would have contained carbon containing adsorbed solvent. Any heat produced would tend to desorb solvent and hence adsorb latent heat conditions. Therefore the overall effect of adsorbed solvent tended to have an inerting effect on the carbon.

As a result of the investigation, the carbon has been replaced with the original coal based carbon, as this is thermally stable to a higher temperature, and the temperature and hold times are closely monitored especially when a new charge of carbon is made. Further experimental work is on going to evaluate the effect of ageing on carbon stability.

#### EXPERIMENTAL

##### The Aerobic Ramped Adiabatic Dewar Test

This test method was adopted to simulate the operation of an the actual carbon bed system. The Bowes Cameron Cage test method requires that small scale samples are exposed to high temperatures, as the ignition temperature of the material is inversely related to the volume of the sample. This can artificially desorb material from the surface of the carbon under investigation. The testing within an adiabatic environment should give a conservative ignition temperature for the carbon for an infinite bed size as there will be little volume dependency under these conditions. With the test being carried out at realistic plant temperatures this will give a better simulation of solvent activity on the carbon surface.

The carbon sample under investigation was charged to a stainless steel Dewar flask. The flask contained several thermocouples to monitor the temperature profile through the bed, and an air sparge tube which allowed air to be forced through the bed. The Dewar was mounted in an oven which could be controlled to ramp the air temperature at a steady rate. The air inlet to the flask was via a coil mounted in the oven, which allowed the air flow to be heated to the oven temperature before entering the bed. The air flow was monitored via a Rotameter mounted externally to the oven. The venting of air from the flask could be controlled by a pressure relief valve which thus allowed the bed to be operated under different pressures. The air pressure achieved in the system was monitored by a strain gauge pressure sensor. An automated solenoid cut out was linked to the air delivery system to stop the air flow through the Dewar on attaining a high temperature level in the bed, which would occur on igniting the carbon sample. This reduced the risk of destroying the equipment in the event of a full bed fire. The apparatus is

shown diagrammatically in figure 2.

The air flow distribution through the carbon sample within the Dewar is shown in more detail in figure 3.

#### Test Method

The oven was initially set to control isothermally at between 90 and 110°C for up to 4 hours. Air was introduced to the bed at the same superficial velocity as that encountered in the adsorber system. The isothermal hold period allowed the desorption from the carbon of any adsorbed moisture from the atmosphere. Once the sample had acquired a uniform temperature the oven was set to ramp slowly at a uniform rate of 0.5 K/min. This allowed the air temperature into the bed, which was monitored, to heat the bed uniformly by forced convection at the same rate as the oven ramp rate. Exothermic activity was detected by a deviation in temperature readings in the sample from the uniform air temp ramp rate. This was identified as the potential onset temperature of the carbon in a well insulated adsorber system. A typical trace is shown in figure 5.

The results of the thermal tests on the two grades of activated carbons are tabulated below:-

CARBON GRADE	Wood Based Carbon (involved in incident)	Coal Based Carbon (Origin Carbon used in bed)
Leuschke Plot predicted ignition temperature for the bed size	101°C	165°C
Adiabatic Dewar Exotherm Onset Temperature	117-120°C	190-195°C
ASTM D-3466 IGNITION TEMPERATURE*	350-400°C	425-475°C

\* The ASTM D-3466 Ignition Temperature is that quoted on the hazard data sheet for the activated carbon.

#### Operation of the Test Under Positive Pressure: Comparison of Exotherm Onset of the Carbons

The test method employed was the same as that outlined previously, but a relief valve on the air vent line from the Dewar was adjusted to maintain a constant pressure in the system.

The results of the pressure tests are tabulated below and the results plotted in a graph, figure 4.

PRESSURE / $10^5 \text{ N m}^{-2}$	1.08	1.57	2.05	2.53	3.08
Wood Based Carbon Onset Temperature (°C)	117-120	114-117	107-112	102-105	98-102
Coal Based Carbon Onset Temperature (°C)	190-195		183-185	182-184	184-186

Comparison of Solvents : Effect of the Adsorbate on Exotherm Onset  
Temperature of Carbon

Several solvents were adsorbed onto the wood based carbon and the effect on thermal stability determined by following the same test method. It is acknowledged that a proportion of the adsorbed solvent is lost during the relatively high temperatures encountered, but it was the effect of any residual material that was of prime concern initially.

Solvents investigated included: water, solvent A<sup>1</sup>, monochlorobenzene, toluene, acetone, Tetrahydrofuran (THF), cyclohexane, diethyl ether, methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK).

The solvents were chosen as they are known to have been adsorbed in other plant systems and for their range of susceptibility to oxidation, ranging from easily oxidisable through to non-oxidisable. The list is not exhaustive and further work is planned to expand the solvents tested. The results of the tests are tabulated below.

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<sup>1</sup> Solvent A is a blend of recycled solvents used on the plant.

Adsorbed Solvent	Exotherm Onset / °C (solvent adsorbed on Wood Based Carbon)
Virgin Wood Based Carbon	≈117-120°C
Water	≈116
Solvent A	≈116
Monochlorobenzene (mCB)	≈114
Toluene	≈118
Acetone	≈105
Tetrahydrofuran (THF)	≈115
Cyclohexane	≈109
Diethyl Ether	≈108
Methyl Ethyl Ketone (MEK)	Onset at very low temperature (see fig 6)
Methyl Isobutyl Ketone (MIBK)	Onset at very low temperature (see fig 7)

#### DISCUSSION

The Bowes-Cameron Cage test allows free diffusion of air into the bulk sample which generally simulating storage conditions. However, within a typical carbon bed adsorber system solvent laden air stream is forced through the adsorbent mass. Under forced convection the heat transfer mechanism can be quite different. The exposure of smaller scale samples in the Bowes Cameron Cage test also require that they are exposed to unrealistically high temperatures as the ignition temperature is inversely proportional to the volume of the sample. These high temperature could desorb more material than would normally occur in an operational solvent recovery adsorber and this could give a false result. Thermal stability evaluations of materials should simulate the practical conditions that the material is likely to encounter during manufacture, transport, or end use. In an attempt to simulate these conditions the aerobic ramped adiabatic Dewar test was proposed. Furthermore it also allowed the investigation of the effect of varying air pressure on the onset temperature of the carbon mass and the adsorption/desorption effects under near plant conditions. The aerobic ramped adiabatic Dewar test was considered to be quick and simple test procedure.

Initial results from the new test would indicate that an onset temperature up to 30°C higher than predicted for the full size bed by the Leuschke plot of the Bowes Cameron Cage test result. That is, onset for the wood based carbon was around 117-120°C in the Dewar compared with an onset of 101°C predicted for the bed size, and coal based carbon onset was around 190-195°C in the Dewar compared with 165°C predicted for the bed size. Test work is still on going with the apparatus to evaluate the non-volume dependency of the results. Isothermal tests are to be carried out to determine a more accurate onset temperature and to compare these with the ramped test result.

The increase in air pressure applied to the carbon samples showed that the onset temperature decreased with increase in pressure, almost linearly, for the wood based carbon (Figure 4, appended). However, the coal based carbon showed an initial decrease in onset temperature, by about 10°C, but no further decrease with increase in pressure (Figure 4, appended). This result helps to further explain the occurrence of the fire when the wood based carbon was used. The application of 2 bar gauge air pressure to the system could lead to a further reduced onset of around 90°C (extrapolation of the curve in Figure 4). The resulting decrease in the exothermic activity onset temperature when the bed is operated under a positive pressure is not that surprising as the partial pressure of oxygen present in the gas phase is increased and therefore the oxidative reactions are likely to proceed at an increased rate. What was surprising was that this trend was noted for the wood based carbon but not to the same extent with the coal based carbon. Although an initial drop in onset temperature was noted with the coal based carbon, the downward trend of onset temperature did not continue with the increase in pressure. A possible explanation for this may come from the origin of the carbons is that coal has a higher initial carbon content than wood of approximately 70-80% compared with approximately 30-40%. In the coking process of the wood based material there could be a higher proportion of contamination, be it e.g. high boiling fractions, metal oxides, etc, and this may account for the increased surface activity. Wood also has a higher voidage and this may allow easier passage of oxygen to reactive sites in the activated carbon making it more reactive.

#### Effect of Adsorbed Solvent on Activated Carbon Stability

Complex chemical and physical processes are involved in adsorption systems and these are not well understood. The nature of the adsorbed material on the carbon has been implicated with the onset of exothermic activity, and ultimately fires, within carbon beds on more than one occasion. The surface activity of activated carbons is difficult to predict, but it is suspected that some reaction catalysis may occur at the surface. Aldehydes and ketones are the most common solvents implicated with fires in carbon beds. As mentioned in the introduction to this paper these seem to have a commonality in that the adsorber beds have been left dormant for a length of time and then when they are put back into active duty a fire within them follows. This suggested that the oxidation of solvent occurs slowly on the surface of activated carbon under ambient conditions and since the beds are essentially under adiabatic conditions the heat of such reaction is not dissipated and the reactions could accelerate. However, under shut-down conditions the reactions will be limited by the amount of oxygen present, but this could still produce significant 'hot spots' in the bed. Once the air flow is applied the 'hot spots' are fed with copious amounts of oxygen and this propagates the fire through the mass of the carbon bed. This was noted in experiments carried out with methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK) shown in figure 6 and 7. Attempts to heat the bed to a uniform temperature in these tests resulted in ignition of the carbon over a period of less than 90 minutes with MEK and the time period would have been similar for MIBK. However, with MIBK the air flow was interrupted at several times during the experiment and this stopped the exothermic activity. Substitution of nitrogen for the air also stopped the exothermic activity. However, reintroduction of air gave rapid reaction and ignitions after only a matter of minutes.



Acetone, diethyl ether and cyclohexane lowered the onset temperature recorded in the aerobic ramped adiabatic Dewar test, whereas the other solvents tested had little effect. The solvents more susceptible to oxidation can be concluded to show some reaction activity on the carbon surface. This supports the conclusion that solvents amenable to partial oxidation lower the onset temperature of carbons. The investigation of solvent activity on the onset of bed fires is an on going project.

#### CONCLUSIONS

The prime cause of the fire incident in the carbon bed adsorber was that the grade of carbon used was thermally unstable at the temperatures involved in the steam regeneration of the system.

In general, the chemical reactions and system dynamics occurring in activated carbon adsorber systems are not well understood generally.

Investigation of the factors which can affect the thermal stability of the carbon itself needs to be ascertained before such systems can be operated free from fire and explosion hazards.

The ignition temperature of the carbon under similar operating conditions to the bed needs to be determined before a bed is put into service.

The effect of the solvent being adsorbed also needs to be investigated with respect to the potential oxidation reactions occurring on the surface of the carbon.

The aerobic adiabatic Dewar test allows quick assessment of the exothermic onset of carbons under plant conditions of any airflow, pressure, isothermal hold period and adiabatic conditions.

The test also allows some estimation of the heat of adsorption, allows desorption to be carried out, and can simulate the effect of solvent retention at desorption temperatures.

To date, the test method has given slightly higher onset temperatures than those predicted by the Bowes Cameron Cage Test. However, this was somewhat expected due to the different conditions being simulated.

Further testing is to be undertaken to compare the exotherm onset temperatures from the ramped test with those obtained from isothermal tests in the same equipment.

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Leuschke Plot of the Wood and Coal Based Carbon Grades Investigated

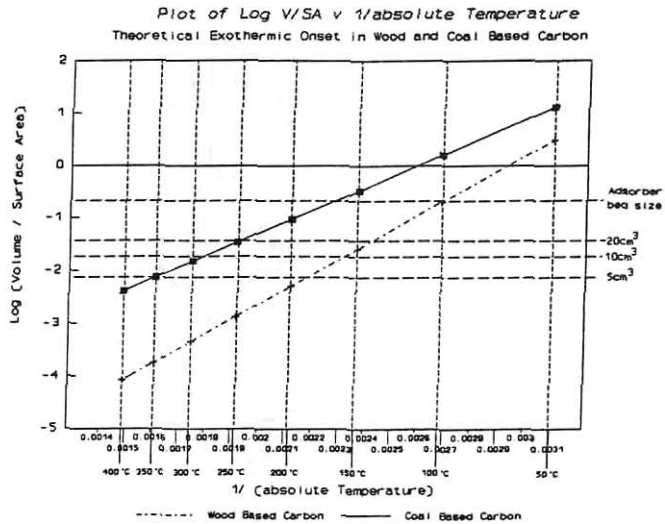


Figure 2

Outline Diagram of the Aerobic Adiabatic Dewar Apparatus

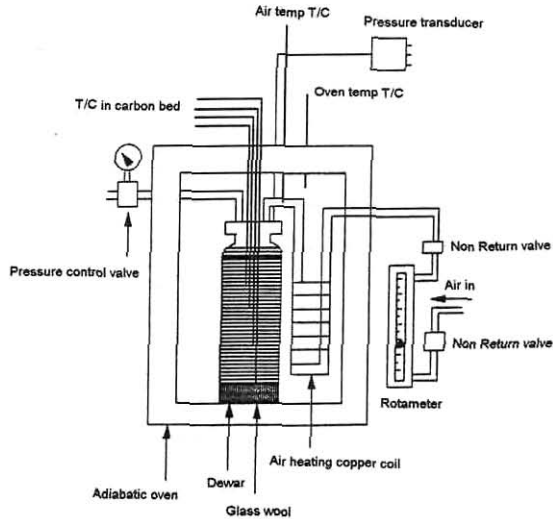


Figure 3

Outline of the Airflow Distribution through the Dewar

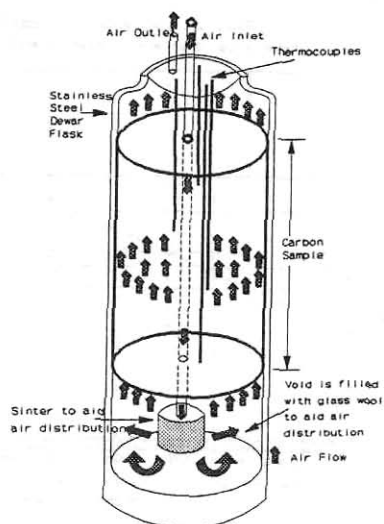


Figure 3

Pressure Effect on Exotherm Onset Temperature of Carbons Tested

Exothermic Activity Onset of Activated Carbon  
At Varying Pressure (Pressure measured at the air outlet from the bed)

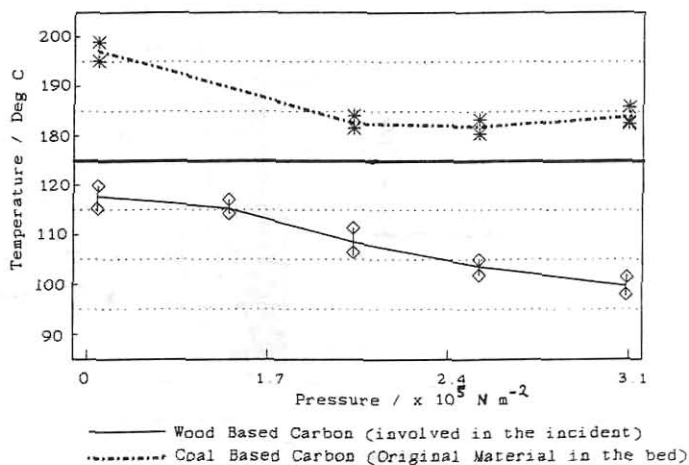


Figure 4

Typical Aerobic ramped Adiabatic Dewar Test  
 Coal Based Carbon (Isothermal Hold at 110°C then ramp at 0.5 k/min)

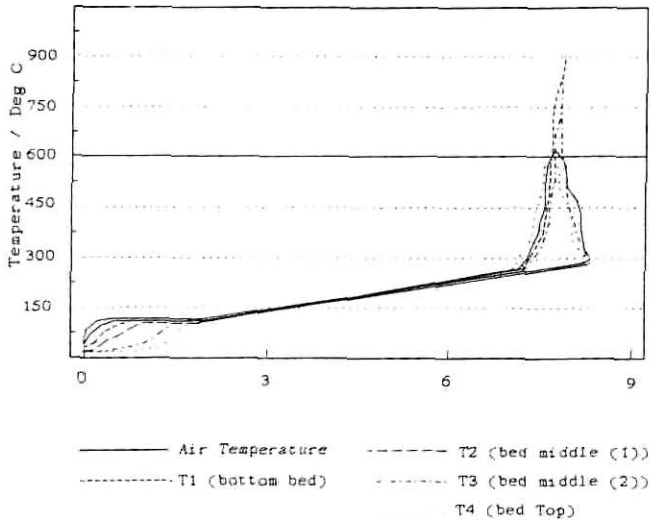


Figure 5

Wood Based Carbon with Methyl Ethyl Ketone Adsorbed  
 Isothermal hold at 90 deg C (air temperature)

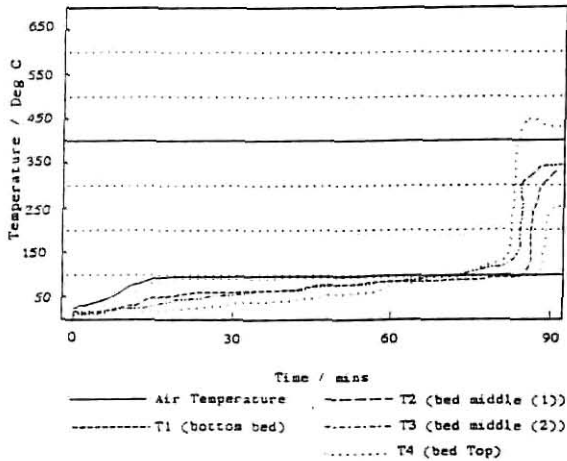


Figure 6

Wood Based Carbon with Methyl Isobutyl Ketone Adsorbed

Isothermal hold at 90 deg C (air temperature)

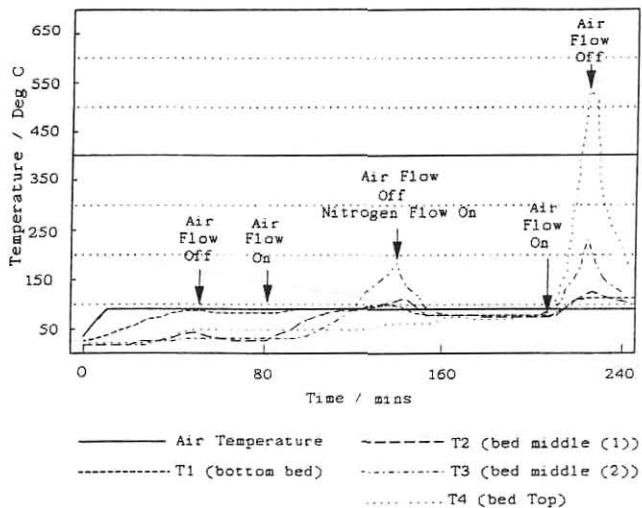


Figure 7