



# Assessment of Activated Carbon Stability toward Adsorbed Organics

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Activated carbon adsorption technology is an important industrial process used in solvent recovery and air pollution abatement systems. The safe use of activated carbon requires an understanding of the conditions that might promote carbon bed exotherms. A test method has been developed which evaluates the relative oxidative activity characteristics of carbons containing organic molecules and their relative potentials for resulting in carbon bed exotherms. Results indicate that the degree of oxidizability of adsorbed organic molecule plays an important role. However, various carbons exhibited different levels of oxidative behavior toward adsorbed oxidizable organic solvents. The solvent reaction initiation temperature for methyl ethyl ketone oxidation on the carbons investigated ranged from 329 to 383 K. Observed reaction enthalpies indicated a difference of more than a factor of 5 between the least reactive and most reactive carbons. This test method predicts trends in carbon and solvent reactivities similar to those determined from column studies reported in the literature.

## Introduction

Activated carbon technology is widely employed in solvent recovery and air pollution abatement systems. Activated carbon beds containing organic molecules sometimes come into contact with air or oxygen, in some cases, as a consequence of their normal operations. A number of investigators (Miller et al., 1987; Chapman and Field, 1979) have reported exothermic runaway reactions under these conditions. In almost all cases, oxidizable organic solvents such as ketones, aldehydes, and the like were present, to some extent, during the thermal runaway processes (Naujokas, 1979, 1985). Concern for carbon bed combustion has led to numerous studies reported in the literature. These investigators (Miller et al., 1987; Chapman and Field, 1979; Naujokas, 1979, 1985; Takeuchi et al., 1990; Mathewes, 1986; Wildman, 1988; Cameron and MacDowall, 1972; Bowes and Cameron, 1971; Johnson and Woods, 1971; Boiston, 1968; Hardman and Street, 1980; Hardman et al., 1980) have studied the problems associated with carbon bed exotherm, employing various conditions conducive to simulation of this process. However, the test procedures employed in most of the cited studies generally require elaborate equipment and/or long durations.

This study reports the development of a comparatively simple and rapid test procedure for assessment of the relative oxidative activity characteristics of activated carbons containing organic solvents. It also compares observed results to those of literature reports on column studies (Naujokas, 1979, 1985).

## Experimental Section

**System Description and Calibration.** All experiments were performed on a Du Pont Model 1090 thermal analysis system fitted with Model 910 DSC and Model 951 TGA accessory modules. The DSC (differential scanning calorimeter) measures heat flow into or out of a sample, while the TGA (thermogravimetric analyzer) measures sample weight changes. The DSC cell was calibrated using an indium standard. Indium samples of 15-18 mg were typically used. The fusion endotherm was recorded usually after one initial "conditioning" heat-cooled cycle through the transition (up to 533 K) which allowed for good thermal contact between the pan and the indium sample. Adipic acid was also employed as a DSC calibration standard. Fusion temperatures ( $T_f$ ) and heat of fusion ( $\Delta H_f$ ) were calculated using a Du Pont DSC interactive analysis program. The DSC system amplifier and recorder were wired so that exothermic peaks are displayed upward and endothermic peaks displayed downward. The TGA system was calibrated using high-purity tin, zinc, or silver wires (depending on temperature range of interest) and calcium oxalate. All calibration experiments were conducted in a nitrogen atmosphere. Nitrogen flow rates and heating rates for calibration experiments were the same as listed in Table I.

**Table I. DSC and TGA Experimental Parameters**

Gas type	N <sub>2</sub> , O <sub>2</sub> , or air
Gas flow rate	100 mL/min
Initial temperature	293 K
Heating rate	17 K/min

Final temperature	723 K
Hold temperature	none
Sample size <sup>a</sup>	7-15 mg
Sample particle size	50 x 200 mesh (0.297 x 0.074 mm)
Sample organic loading	30 wt % (mass ratio)

<sup>a</sup>7 mg for DSC (based on solvent-free carbon; 10-15 mg for TGA).

**Materials.** The characteristics of activated carbons investigated are listed in Table II. The solvents (>99% purity) investigated were employed with no further pretreatment. Also, oxygen (99.6%), nitrogen (99.99%), and air (zero grade) were used as received from the supplier with no further treatment.

**Sample Preparation and Test Procedure.** All activated carbons were crushed, sized to 50 x 200 mesh, and dried overnight (approximately 18 h) at 378 K. Enough of the dried carbon (usually 1g) was loaded with 30 wt % (mass ratio) of organic solvent of interest, by thoroughly mixing the carbon and the solvent in a tightly capped vial and allowing to equilibrate overnight (about 18 h) before evaluation. (Although solvent laden samples were allowed to equilibrate overnight for this study, 2-3 h is usually sufficient). Samples were weighed after equilibration to determine equilibrium loading. Minimum exposure of solvent-loaded carbons to ambient conditions was adopted to avoid excessive devolatilization of the solvent prior to reactivity tests, since the carbons were loaded to, or close to saturation. All reactivity tests on any particular carbon were completed in less than 36 h from time of solvent adsorption. The DSC and TGA experimental parameters employed to evaluate reactivity are listed in Table I. For DSC experiments, samples on both the reference and the sample sides were counterbalanced, compensating for the weight of solvent on carbon. Where organic loading was less than 30 wt % (mass ratio) due to low carbon adsorption capacity, DSC sample sizes were adjusted to maintain the same amount of adsorbate as in the case of 30 wt % loading. This typically amounted to 2.1 mg of adsorbed solvent per DSC sample. However, in studying the effects of solvent concentration levels and size of solvent-laden carbon on oxidation stability of carbon-solvent systems, the amounts of adsorbed solvent per DSC sample were varied accordingly. All DSC experiments were conducted with loosely covered aluminum pans. For TGA experiments, usually 10-15 mg of adsorbate-loaded carbon was employed to yield about 1-3 carbon particle layer(s) in the pan. Sample sizes for all carbons were kept fairly constant.

DSC experimental steps employed (using parameters in Table I) to determine oxidative activity characteristics of a particular carbon-solvent system are as follows:

1. Empty, but loosely covered pans were placed on both reference and sample sides of the DSC cell module and taken through the temperature ramp in a nitrogen flow to establish instrument baseline stability.
2. The instrument was then calibrated for temperature and cell constant.
3. A test was conducted in a nitrogen atmosphere using virgin carbon of identical weight (7 mg) and particle size on both reference and sample sides in order to establish carbon baseline.
4. Subsequently, an experiment was conducted in N<sub>2</sub> atmosphere by placing virgin carbon (7 mg) on the reference side and solvent-loaded carbon (9.1 mg) on the sample side. (Weight of solvent-loaded carbon was adjusted to accommodate the solvent weight.)
5. A carbon baseline in oxygen was obtained by conducting an experiment in pure oxygen using virgin carbon of identical weight on both reference and sample sides.
6. Subsequently, an experiment was carried out in pure oxygen using virgin carbon on the reference side and solvent-loaded carbon on the sample side (adjusting for weight of solvent).

Enthalpy changes of the system were monitored. Steps 1 and 2 were carried out only once at the beginning of the study. Repeats were necessary only after several DSC experiments or instrument-prolonged idle times. Weight changes associated with carbon-solvent systems were monitored using a TGA. These were used to verify the DSC results.

**Table II. Activated Carbon Characteristics.**

Type	Supplier	Precursor Material <sup>a</sup>	Form	U.S. mesh size	AD, <sup>b</sup> kg/m <sup>3</sup>
965	Witco	PASC	granular	12 x 30	440
JXC		PASC	pellet	4 x 6	428
A-7 <sup>e</sup>	Calgon Carbon	coal	pellet	4 x 6	453
CP-IVA		coal	pellet	4 x 6	439
BPL		coal	granular	4 x 6	507
PCB		CS	granular	4 x 6	465
Sorbonorit B3	Norit	peat	pellet	4 x 10	465
Sorbonorit B4		peat	pellet	4 x 6	436
Shirasagi S	Takeda	CS	pellet	4 x 6	398

<sup>a</sup>PASC = petroleum acid sludge coke; CS = coconut shell. <sup>b</sup>AD = apparent density (weight of carbon by unit volume). <sup>c</sup>A-7 is an experimental low-reactivity carbon produced by Calgon Carbon Corp.

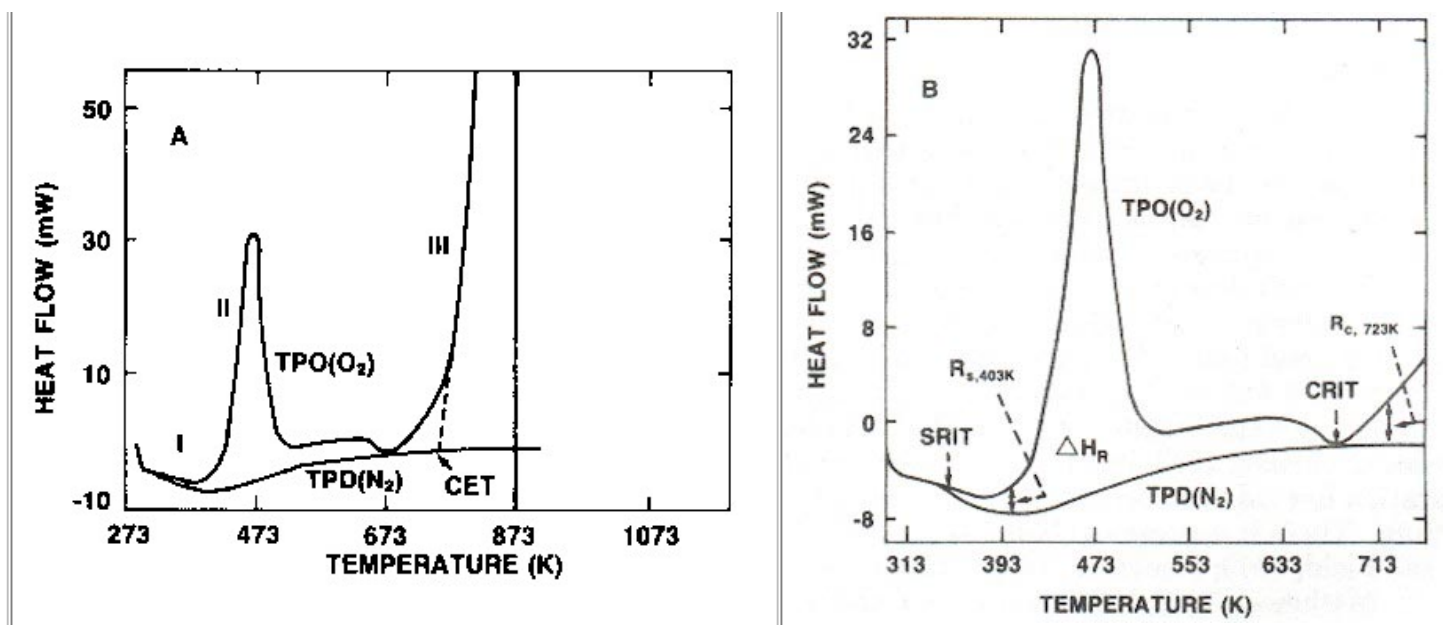


Figure 1. Oxidative behavior of carbon-solvent (BPL-MEK) system showing (A) regions of activity and (B) reactivity parameters.

## Results and Discussion

**Criteria for Determination of Oxidation Stabilities of Carbon-Solvent Systems.** The reactivities of carbon-solvent systems were determined by temperature programmed oxidation (TPO) and temperature programmed desorption (TPD) techniques (see Figure 1). Activated carbons containing oxidizable organic solvents generally showed three regions of activity as a function of temperature in the presence of air/oxygen. The sequence of activity consisted of desorption of adsorbate (region I), oxidation of adsorbate (and desorption of adsorbate and oxidation products) (region II), and oxidation of carbon skeleton (region III).

The test conditions chosen were such that the oxidation reactions were chemically controlled. Minor diffusional resistances were noted during severe oxidation reactions involving highly reactive carbon-solvent systems.

The oxidative activity characteristics of a carbon-solvent system were determined using the following parameters from DSC data (see Figures 1 and 2):

**A. Solvent reaction (oxidation) initiation temperature (SRIT).** This is the temperature of first deviation from a temperature programmed oxidation (TPO) profile (DSC step 6) and a temperature programmed desorption (TPD) profile (DSC step 4) when superimposed. It gives an indication of the temperature at which any recognizable oxidation of the adsorbate initiates on a particular adsorbent carbon. This is essential in prevention of hot-spot generation in carbon bed under stagnant conditions.

**B. Apparent (effective) heat of reaction.** This is the area under the TPO and TPD profiles to 723K: total apparent (effective) heat generated by the system [ $(\dot{H}_{R_{T=723K}})$ ]; total apparent (effective) heat generated expressed per mole of solvent adsorbed [ $(\dot{H}_R)$ ]. These parameters give a measure of the extent of oxidation reaction primarily due to the adsorbate on carbon. The importance of these parameters lies in the fact that they give an indication of the relative amounts of heat that need to be dissipated from the carbon-solvent system if solvent oxidation occurs. Large amounts of heat are less easily dissipated and more easily propagated into bed combustion. Thus, greater precautionary or preventive measures should be exercised when such carbon-solvent systems are in use, in order to prevent bed exotherm.

**C. Oxidation (heat production) rate of adsorbed solvent ( $R_{s,T}$ ).** This is measured by the difference in heat flow between TPO and TPD profiles at a given temperature of interest; s, T denotes solvent and temperature, respectively. (A temperature of 403 K was chosen.) This parameter indicates how fast the heat rise due to adsorbate oxidation will occur. This is important since the sustainment of a hot spot depends on the local thermal balance between the rate of heat generation by chemical reaction and the rate of heat removal by convective heat transfer. Awareness of the relative rates of heat production (especially when compared to well-studied carbons, such as JXC) will help prevent carbon bed exotherms as corrective or preventive actions can be implemented.

**D. Combustion/oxidation characteristics of the carbon skeleton (matrix).** Carbon reaction (oxidation) initiation temperature (CRIT) indicates the temperature at which oxidation of the carbon matrix initiates. This is important in the prevention of carbon bed combustion. Carbon excursion temperature (CET) indicates the temperature at which carbon bed combustion will occur. This temperature should be avoided when air/oxygen is present. Oxidation (heat production rate of carbon matrix ( $R_{c,T}$ ) (where c, T denotes carbon and temperature, respectively) gives a measure of how rapid the heat rise due to oxidation of carbon matrix (leading to complete bed combustion) will occur.

Since all carbons are loaded to the same level, the DSC parameters as defined represent the adsorbent's ability to catalyze oxidation of the adsorbate. The reported  $\bar{H}_R$  or  $(\bar{H}_R)_{tot}$  are effective (or observed) values and not heats of reaction due to oxidation of the total amount of adsorbate originally loaded on the carbon. For carbons loaded to saturation some of the adsorbate molecules residing at lower energy sites will desorb at lower temperatures (in accordance with Polanyi adsorption potential theory; see Figure 1) prior to reaching the adsorbate oxidation initiation temperature.

The criteria for determining oxidative activity of a solvent-carbon system using DSC data are described with a "reactivity-criteria correlation scheme" shown in Figure 2. This sketch (which does not imply any linear relationship) shows the general trend in classification of the relative oxidative stabilities of carbon-solvent systems. Carbon-solvent systems with lower SRIT, CRIT, and CET and higher  $\bar{H}_R$ ,  $(\bar{H}_R)_{tot}$ ,  $R_{s,T}$ , and  $R_{c,T}$  exhibit high oxidative activity and, thus, greater potential for carbon bed exotherms. The converse is also true, as shown in Figure 2.

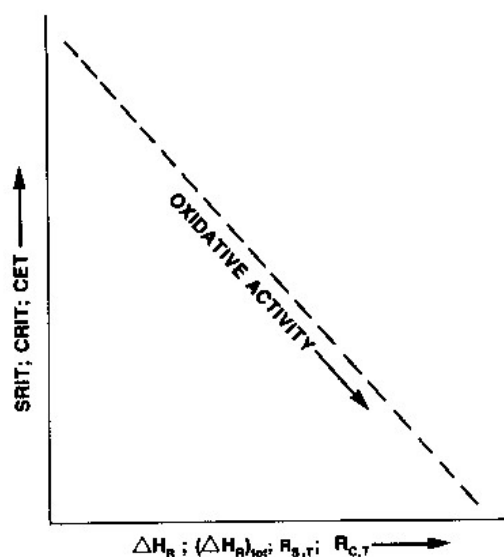


Figure 2. Reactivity-criteria correlation scheme.

The TGA-TPD profile in nitrogen gave the desorption characteristics of a particular solvent from activated carbon. While in an oxidizing atmosphere, the TGA-TPO profile yielded some information on the oxidation characteristics of the carbon-solvent system. This included the desorption and/or accumulation behavior of the oxidation products.

The DSC/TGA data obtained may be compared to a given carbon-solvent system for which process data exist, in order to establish relative performance. The test method developed is useful in screening carbon-solvent systems. A range of carbon-solvent systems can be evaluated in a short period of time.

**Optimization of Test Procedure.** A number of variables were studied in order to optimize test conditions. Conditions which allowed determination of oxidative stability of carbon-solvent systems in the absence of diffusional limitations and also amplified oxidative activity were chosen. The variables and/or parameters investigated include oxygen level, adsorbate composition, bed depth, particle size, heating rate, and gas flow rate. The test parameters were standardized to those listed in Table I.

**Behavior of Carbon-solvent Systems under Various Conditions.** A number of conditions (discussed below) were studied in order to monitor behavior of carbon-solvent systems under such environments. Carbon-solvent systems employed comprised BPL and A-7 carbons and methyl ethyl ketone (MEK).

**Gas Environment.** To determine the influence of oxygen concentration, the behavior of the carbon-solvent systems was monitored in atmospheres of nitrogen, air, and pure oxygen using the DSC, in a temperature-programmed mode. In this case, the concentrations of MEK and carbon were kept constant while oxygen concentration varied. The results (Figure 3) show that no oxidative activity occurred in nitrogen atmosphere. Only desorption of the adsorbed MEK was observed. As the concentration of oxygen increased, the oxidative activity of the carbon-solvent system increased. These results indicate that, to minimize the oxidative activity of a carbon-solvent system, and, therefore, decrease the potential for bed combustion, oxygen levels should be reduced substantially. Also, in recovery of solvents for reuse, oxygen levels should be minimized at, or close to, the solvent reaction initiation temperature in order to avoid excessive solvent decomposition to oxidation products. These results are consistent with those previously reported by Naujokas (1985).

**Solvent Concentration.** To determine the role of solvent level on the oxidative activity of carbon-solvent system, four concentration

levels - 4, 10, 19, and 30% MEK - were investigated. Oxygen concentration and carbon loading were kept constant while MEK concentration was varied as shown in Table III. As in the case of oxygen concentration, the oxidative activity of the system increased as the total amount of adsorbed MEK increased. Also, the total apparent heat of reaction, ( $\Delta H_{R,tot}$ ), generated by the system increased with amount of MEK adsorbed. This indicates that more frequent regeneration cycles may be needed to avoid large amounts of reactive adsorbates on carbon and, thus, minimize the potential for bed combustion.

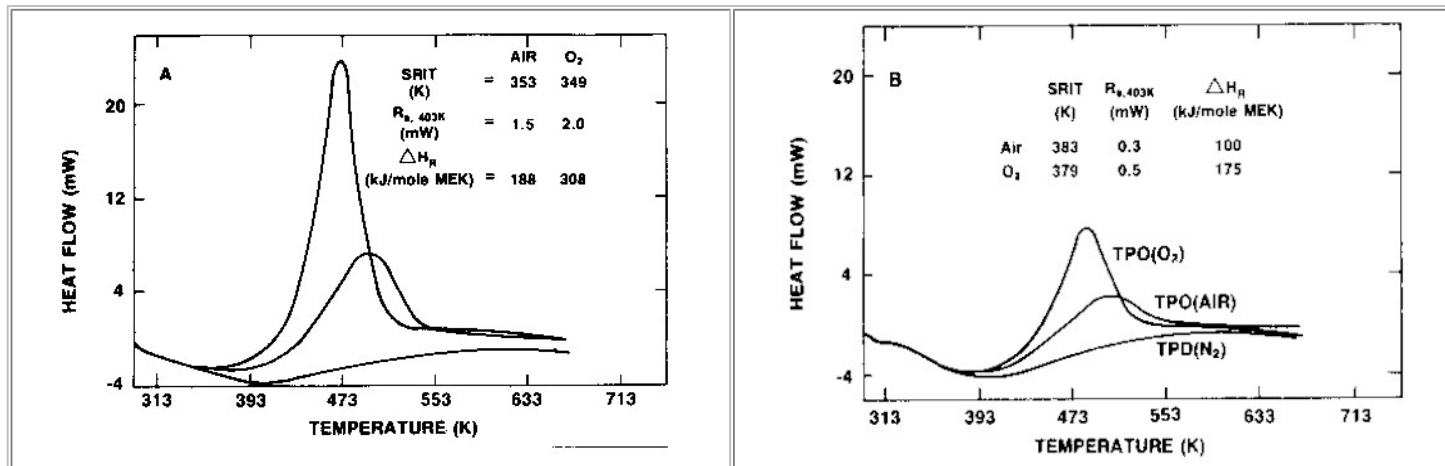


Figure 3. Effect of oxygen concentration on oxidative behavior of carbon-solvent systems: (A) BPL-MEK and (B) A-7-MEK

Table III. Effects of MEK Concentration on Reactivities of Various Activated Carbons

Carbon	Concn, %	SRIT, K	$R_{s,403K}$ , mW	$(\Delta H_{R,tot})^a$ , J
BPL	4	350	1.2	4.7
	10	351	1.7	7.2
	19	349	2.0	8.8
	30	349	2.0	9.0
A-7	4	379	0.3	2.9
	10	380	0.5	4.6
	19	380	0.5	5.5
	30	379	0.5	5.4
965	4	383	0.4	3.2
	10	382	0.5	5.0
	19	382	0.6	6.1
	30	383	0.6	6.4

<sup>a</sup> Total apparent heat of reaction (total area under TPO and TPD profiles) generated by system.

**Carbon-Solvent Size.** The effect of size of solvent-laden carbon on oxidative activity was determined using four different carbon loadings. In this case, the concentration of oxygen was kept constant while the amount of solvent-laden carbon was varied. As shown in Figure 4, the overall oxidative activity of the system increased as the amount of solvent-laden carbon increased. This indicates that more effective heat dissipation capability will be necessary in large adsorbers if solvent oxidation should occur, in order to avoid severe carbon bed exotherms. These observations are consistent with those reported by Mathewes (1986) on carbon adsorbers.

**Effects of DSC Pan and Cover.** A solid-to-liquid transition is sharp (as in the case of indium fusion) and independent of pressure. Such a process is generally considered instantaneous and, thus, can be carried out in an open system. On the other hand, a liquid-to-vapor transition is controlled by pressure and will only occur at a constant temperature if the vapor pressure over the liquid is kept constant. Processes such as boiling or other vaporization or desorption processes require mass transfer from the liquid surface to the vapor phase. As a consequence, the peak shape will depend on the rate of vaporization, which is a function of temperature and of the rate at which vapor is removed. Accordingly, the surface area of the liquid and the size of the opening through which the vapor escapes to the surroundings are, therefore, important factors.

In this study the DSC experiments compared the behavior of carbon-solvent systems in open and loosely covered pan configurations. One such result is shown in Figure 5. The open pan system exhibited a lower oxidative activity, with heat of reaction that is about a factor of 5 less than that of loosely covered pans. Also, the observed rate of solvent oxidation, measured by  $R_{s,T}$  at  $T = 403$  K, showed lower values for the open system. However, the SRIT's were fairly similar. The loosely covered pans exhibited higher oxidative activity due to decrement in the rate of solvent vaporization. Thus, more solvent vapor was present in the system at the temperature of solvent oxidation on that particular carbon. This gives an indication of the high degree of oxidative activity which would be generated in an adsorber, if there was a buildup of pressure or solvent vapor during in situ oxidation at low temperatures.

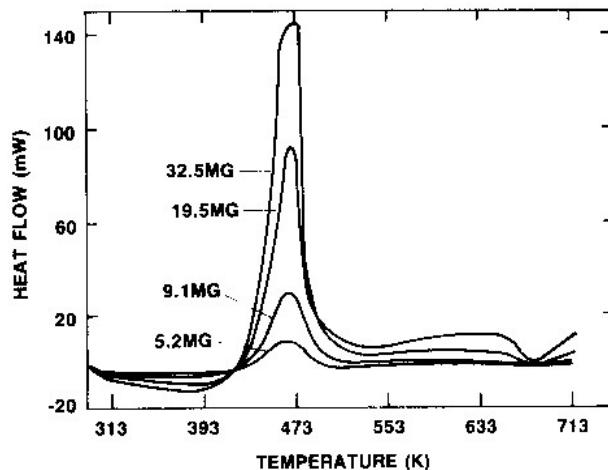


Figure 4. Effect of carbon-solvent size on oxidative<sup>a</sup>

To determine the variability and reproducibility of the test procedure, two sets of experiments were conducted. The first set of experiments investigated the effects of reusing a particular set of DSC sample pan and cover after use in several runs. The results are shown in Table IV. It was observed that reuse of the DSC sample pan had not significant effect on oxidative activity characteristics of carbon-solvent systems. The second set of experiments investigated the effects of using different sets of pan and cover (from the same manufacturing lot) for a particular carbon-solvent system. Results indicated only negligible effects on carbon-solvent system behavior (Table IV).

Table IV. Variability and Reproducibility of Test Procedure<sup>a</sup>

Conditions <sup>b</sup>	Expt. No.	SRIT, K	$R_{s,403\text{K}}$ , mW	$\Delta H_R$ , kJ/mol MEK
I. Same set (pan and cover)	1	349	2.0	310
	2	350	2.0	306
	3	348	2.1	314
II. Different set (pan and cover)	1	349	2.0	310
	4	347	2.1	319
	5	351	1.8	302

<sup>a</sup> The BPL-MEK system was employed in this study. <sup>b</sup> Same set (pan and cover): The same set of DSC pan and cover employed in several experiments of oxidative activity evaluation was used. Variability and reproducibility tests were conducted at different times during the entire study. Different sets (pan and cover): Different (but similar) sets of pan and cover were used to evaluated oxidative activity of a particular batch of carbon-solvent system.

Several carbon-solvent systems were evaluated using the same DSC sample pan and cover in order to keep the size of the opening constant and, thus, minimize variability. This allowed carbon-solvent systems to be evaluated under similar conditions.

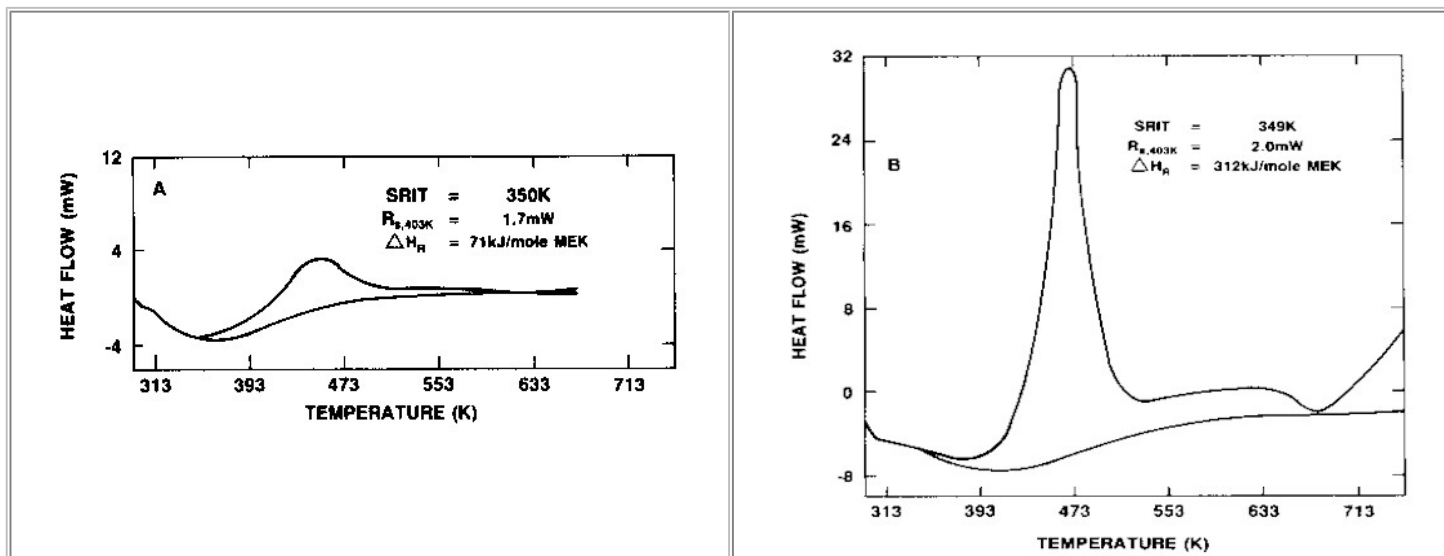


Figure 5. Comparison of sample pan configuration on oxidative behavior of carbon-solvent (BPL-MEK) system: (A) open and (B) loosely covered sample pan.

Table V. Initial Oxidative Activity Characteristics of Various Activated Carbons Containing MEK

Carbon	SRIT, K	$R_{s,403\text{ K}}$ , mW	$\bar{H}_R$ , kJ/mol MEK
Calgon Carbon A-7	380	0.5	175
Witco 965	383	0.6	218
Witco JXC	378	0.7	211
Takeda Shirasagi S	371	1.0	305
Calgon Carbon BPL	349	2.0	310
Calgon Carbon CP-IV A	343	2.3	295
Norit Sorbonorit B3	332	3.5	>850
Norit Sorbonorit B4	329	3.2	>850
Calgon Carbon PCB	331	6.6	>850

**Behavior of Various Activated Carbons Containing Adsorbed Organic Solvents.** The oxidative activity characteristics of various activated carbons containing oxidizable organic solvent were investigated. MEK was chosen as the oxidizable solvent for this comparison study since it has been studied extensively by other investigators and also had been implicated in carbon bed combustion (Nauokas, 1985; Wildman, 1988).

As previously noted, the solvent reaction initiation temperature (SRIT), apparent heat of reaction [ $\bar{H}_R$ , ( $\bar{H}_R$ )<sub>tot</sub>], solvent oxidation (heat production) rate  $R_{s,T}$ , and oxidation characteristics of the carbon matrix (CRIT, CET,  $R_{c,T}$ ) were used to define oxidative activity. Carbon-solvent systems showing higher SRIT, CRIT, and CET and lower  $\bar{H}_R$ , ( $\bar{H}_R$ )<sub>tot</sub>,  $R_{s,T}$ , and  $R_{c,T}$  exhibit low oxidative activity (high oxidation stability) and, thus, lower potential for carbon bed exotherms. The converse is also true. The solvent oxidation (heat production) rate was measured at a temperature of 403 K [designated as  $R_{s,403\text{ K}}$ ] in order to compare the results obtained in this study to previously reported column studies (Naujokas, 1979, 1985).

The initial oxidative activity characteristics of the carbons evaluated are summarized in Table V. The carbons are listed in order of decreasing oxidation stability, as shown by the decreasing SRIT values and increasing  $R_{s,403\text{ K}}$  and  $\bar{H}_R$  values. Carbons A-7, 965, and JXC exhibited the least oxidative activity to adsorbed MEK and, thus, the least potential for carbon bed combustion. (Carbon A-7, which showed the least oxidative activity, is an experimental low-reactivity carbon developed by Calgon Carbon Corp.) PCB, Sorbonorit B3, and Sorbonorit B4 showed the highest oxidative activity toward adsorbed MEK. Figure 6 shows the thermograms of two carbon-MEK systems and their relative oxidative activity characteristics. Figure 6B shows that, in addition to high adsorbate oxidation initiation temperature, high exothermic heat, and the large rate of heat generation due to solvent oxidation, oxidation of the carbon matrix initiates at a lower temperature. Carbon-solvent systems exhibiting this type of behavior are more easily propagated into carbon bed combustion, compared to carbon-solvent systems of the type depicted in Figure 6A, where low exothermic heat, low rate of heat generation, and high temperature for oxidations of solvent and carbon matrix are observed.

The results obtained on the initial oxidative activity of various activated carbons were compared to those obtained from column studies previously reported by Naujokas (1985). The comparison is shown in Table VI. In Naujokas' column studies measurements of time and position of hot generation in the carbon column and associated temperature and CO concentration changes were used to define oxidative activity of the carbon-solvent systems. The higher the values of time and position of hot-spot generation in the carbon column, the lower the oxidative activity. Carbon-solvent systems exhibiting steady state temperature gradients along the bed showed the least oxidative behavior toward adsorbed organic solvents. Given the oxidative activity criteria for this study and Naujokas' study (Naujokas, 1985), Table VI shows the two test methods to predict similar trends in oxidative behavior of various activated carbons containing oxidizable organic solvent, such as MEK.

It is obvious that various activated carbons exhibit different levels of oxidative behavior toward adsorbed oxidizable solvents. Thus, proper choice of carbons for systems recovering reactive solvents can help minimize the potential for carbon bed combustion.

Table VI. Comparison of Initial Oxidative Activity Trends of Carbons Containing MEK

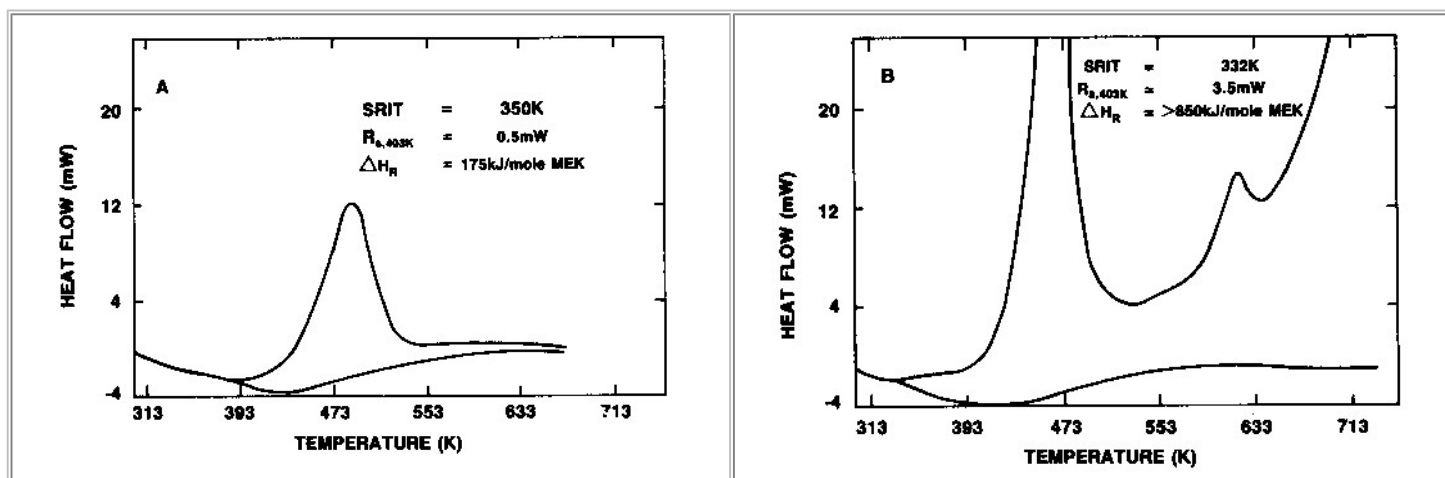
this study				Column studies (Naujokas, 1985) <sup>a</sup> hot spot parameters		
				non-steady state		steady state
Carbon	SRIT, K	$R_{s,403\text{ K}}$ , mW	$\bar{H}_R$ , kJ/mol MEK	time, min	position, cm	$\bar{T}_K$ , K
Witco JXC	378	0.7	211			33
Takeda Shirasagi S	371	1.0	305	23	85	
Calgon Carbon BPL	349	2.0	310	9	45	

Calgon Carbon CP-IVA	343	2.3	295	7	70
Norit Sorbonorit B3	332	3.5	>850	4	22
Norit Sorbonorit B4	329	3.2	>850	3	32
Calgon Carbon PCB	331	6.6	>850	3	25

<sup>a</sup> Conducted at 398K

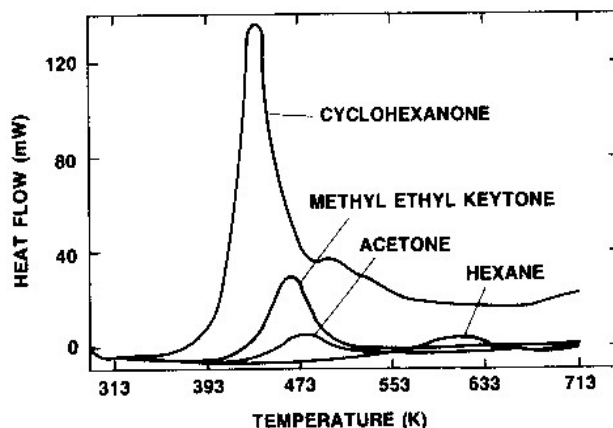
**Table VII. Oxidation Characteristics of Selected Organic Solvents on Activated Carbon (Calgon Carbon BPL)**

Solvent	bp, K	mol wt, kg/kg-mol	SRIT, K	$R_{s,403\text{K}}$ , mW	$(\bar{H}_R)_{\text{tot}}$ , J	$\bar{H}_R$ , kJ/mol solvent
Toluene	383.6	92.1	453	0	3.8	169
Hexane	342.0	86.2	451	0	3.8	157
Acetone	329.5	58.1	398	0.05	3.8	105
MEK	352.6	72.1	349	2.0	9.0	310
Cyclohexanone	428.6	98.1	338	20.0	48.9	2286



**Figure 6.** Oxidative behavior of various activated carbons toward adsorbed MEK: (A) A-7-MEK and (B) Sorbonorit B3-MEK

**Behavior of Selected Organic Solvents on Activated Carbon.** To determine the impact of adsorbed organic solvents on the oxidative activity characteristics of a carbon-solvent system, a few solvents selected from the alkane and ketone classes were tested. BPL carbon was used as the adsorbent. The results are summarized in Table VII. The temperature programmed oxidation (TPO) profiles are shown in Figure 7.



**Figure 7.** Oxidative behavior of various organic solvents adsorbed on activated carbon (BPL).

Table VII shows that toluene and hexane exhibited negligible oxidative behavior with high SRIT and very low  $\bar{H}_R$  values. There were no detectable solvent oxidation (or heat production) rates as shown by a  $R_{s,403\text{K}}$  value of 0. On the other hand, all of the ketones evaluated exhibited oxidative activity to various extents. The reactivities appeared to have increased with molecular weight and/or boiling point of the solvents in the order acetone < methyl ethyl ketone < cyclohexanone. Cyclohexanone displayed a very high

oxidative activity, with a heat of reaction that was more than a factor of 5 greater than that of MEK and more than 1 order of magnitude greater than that of acetone. Note from Figure 7 that cyclohexanone shows multiple exothermic (oxidation) peaks, indicating more than one partial oxidation step and/or oxidation of intermediate products at higher temperatures.

It is clear that various organic solvents behave differently on activated carbon. Thus, the nature of the solvent plays an important role in the oxidative activity of the carbon-solvent system.

The results obtained on solvent reactivities were compared to those reported by Naujokas (1985). The comparison is shown in Table VIII. Given the reactivity criteria for both studies described previously, Table VIII shows that while the carbon adsorbents employed in the two studies were different, similar ranking in solvent reactivities was observed. This similarity in predictive capability establishes the validity and reliability of the test method developed in this study.

**Table VIII. Comparison of Reactivity Trends of Organic Solvents Contained on Activated Carbon**

This study <sup>a</sup>				Column studies (Naujokas, 1985) <sup>b</sup>			
Solvent	SRIT, K	$R_{s,403\text{ K}}$ , mW	$(\bar{H}_R)_{tot}$ , J	Time, min	Position, cm	Temp rise, K	Max carbon monoxide, ppm
Toluene	453	0	3.8 (169)	4	20	3 33 >200	25 2700 >10000
Acetone	398	0.05	3.8 (105)				
MEK	349	2.0	9.0 (310)				
Cyclohexanone	338	20.0	48.9 (2286)				

<sup>a</sup> Calgon Carbon BPL was used as adsorbent. <sup>b</sup> Witco JXC was used as adsorbent. Test was conducted at 398K. <sup>c</sup>Values in parentheses are  $\bar{H}_R$  expressed in kJ/mol solvent.

**Practical Implications.** Detailed quantitative considerations of system dynamics - mass and heat transfer and chemical kinetics (in an adsorber) - are not fully discussed in this paper. Nonetheless, these properties are important in the consideration of carbon bed combustion. As indicated by Naujokas (1979, 1985), fast-changing temperature and concentration gradients (associated with continuous desorption and readsorption of adsorbates and reaction products) exist during hot-spot generation and/or carbon bed combustion. These generally result in system perturbations under appropriate conditions. The rapidly changing temperature and concentration gradients, with associated nonlinearity of chemical reaction kinetics and non-homogeneity of carbon bed, tend to make the carbon-solvent system somewhat difficult to characterize.

Since in an adsorber hot spots are generally localized, monitoring of bed temperatures alone may not always reveal onset of bed combustion. Measurements of changes in amounts and rates of solvent and carbon decomposition products (CO, CO<sub>2</sub>, etc.) above the bed and exhaust stack, in conjunction with bed temperature measurements, provide for more reliable means of detecting bed combustion. Detection of unusually high levels of decomposition products generally signifies onset of bed exotherm. Carbon-solvent systems with lower SRIT, CRIT, and CET and higher  $\bar{H}_R$ ,  $(\bar{H}_R)_{tot}$ ,  $R_{s,T}$ , and  $R_{c,T}$  exhibit high oxidative activity and, thus, are more prone to generation of high levels of decomposition products. Systems of this type exhibit high potential for bed combustion and, therefore, should be monitored more regularly. More detailed discussions on precautionary and corrective measures can be seen elsewhere (Naujokas, 1985).

In the comparison of results of this study to those of Naujokas' column studies (Naujokas, 1979, 1985), SRIT and  $R_{s,403\text{ K}}$  values generally correlated to time and position of hot-spot generation in the carbon column, while  $\bar{H}_R$  and  $(\bar{H}_R)_{tot}$  (which define the extent of reaction) generally correlated to the degree of  $\bar{T}$  and carbon monoxide concentration changes in the carbon column.

This paper provides some insights and awareness of some of the conditions and/or system behavior that might effect carbon bed exotherms. This allows for implementation of adequate corrective and/or preventive measures which, in turn, provides for safer operation of carbon adsorbents. It must be emphasized that while appropriate choice of carbons can help minimize the potential for carbon bed combustion for systems recovering oxidizable (reactive) solvents, proper bed design, operation, and maintenance are also very important. Furthermore, though some of the carbons evaluated exhibited some degree of oxidative activity toward adsorbed oxidizable solvents, these carbons are, nonetheless, suitable or good adsorbents for recovery of non-reactive (non-oxidizable) solvents or, in some cases, less reactive solvents such as acetone (see Tables VII and VIII).

## Conclusions

A comparatively simple and rapid test method has been developed to evaluate the relative oxidative activity characteristics of carbon-solvent systems. The test method predicts trends in carbon and solvent reactivities similar to those determined from column studies reported in the literature. Carbon-solvent systems generally showed three regions of activity as a function of temperature in the presence of oxygen. These regions consist of desorption of adsorbate, oxidation of adsorbate, and oxidation of carbon matrix. Various carbons exhibit different levels of oxidative activity. The nature of the solvent plays an important role in the oxidative behavior of the system. While appropriate choice of carbons can help alleviate the potential for carbon bed combustion in systems recovering oxidizable solvents, proper bed design, operation, and maintenance are also very important. Though some of the carbons evaluated exhibited some degree of oxidative activity toward adsorbed oxidizable solvents, these carbons are, nevertheless, suitable or good

adsorbents for recovery of non-reactive (non-oxidizable) solvents or, in some cases, less reactive solvents such as acetone or similarly ranked solvents.

Registry No. MEK, 78-93-3; C, 7440-44-0; PhMe, 108-88-3; C<sub>6</sub>H<sub>14</sub>, 110-54-3; MeC(O)Me, 67-64-1; cyclohexanone, 108-94-1.

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