Adsorption (2008) 14: 679–686
DOI 10.1007/s10450-008-9139-4

Statistical quantification of the influence of material properties on the oxidation and ignition of activated carbons

Thangavelu Jayabalan · Pascaline Pré · Valérie Héquet · Pierre Le Cloirec

Received: 30 April 2007 / Revised: 26 January 2008 / Accepted: 23 June 2008

Abstract The influence of material properties on the reactivities of activated carbon materials have been studied on a laboratory scale. Carbon samples having diversified origin and properties were characterized using a thermogravimetry (TG) coupled with a differential scanning calorimetry (DSC). Reactivity parameters like the Point of Initial Oxidation (PIO) representing the beginning of the oxidation reactions and the Spontaneous Ignition Temperature (SIT) where the bed combustion takes place in a self sustaining manner were experimentally determined. The intrinsic properties of the activated carbons influencing oxidation and ignition were examined qualitatively followed by quantitative statistical correlations. Results from both qualitative and statistical correlations showed that increase in the oxygen content in the form of surface oxygenated groups increased the reactivity of activated carbons. It was by far the single most influential property discriminated from the analysis. The porosity characteristics like the specific surface area and pore volume did show some vague trends but could not be validated like that of the oxygen content. The effects of these individual properties on the oxidation and ignition reactivity are discussed.

Keywords Adsorbents · Activated carbons · Thermal analysis

1 Introduction

Activated carbons (ACs) are microporous adsorbents used for instance in respiratory filters and vehicle filters for the removal of harmful gases, to treat industrial gaseous effluents for the removal of volatile organic compounds (VOCs) and odours (Bansal et al. 1988). Ignition risks are commonly found for activated carbons packed in filters, mainly caused by certain types of contaminants that are filtered or adsorbed. Extensive literature sources are available for incidents of fires and thermal runaways encountered with activated carbon beds in service, idle condition and also during the handling and regeneration of the spent carbon (Naujokas 1985; Delage et al. 2000; Zerbonia et al. 2001). Fires were also reported during transit on board ship for chemically activated carbons (Bowes and Cameron 1971).

On these contexts, a laboratory study is undertaken to evaluate how the material properties both physical and chemical contribute to the reactivity of the activated carbons. The characterization of oxidation and ignition process of activated carbons at elevated temperatures was extensively studied by Suzin et al. (1999). Two regions of interest were defined which describe the oxidation process at relatively low temperature followed by ignition at higher temperature. The first region that causes the carbon to start oxidizing significantly is denoted by the Point of Initial Oxidation (PIO). The surface properties start to change as the oxidation reaction reaches a certain value of significance. The second one where the material ignites in a self-sustaining manner is denoted by Spontaneous Ignition Temperature (SIT). Thermal analysis techniques consisting of thermogravimetry (TG)

T. Jayabalan (✉) · P. Pré · V. Héquet
GEPEA UMR-CNRS 6144, Ecole des Mines de Nantes,
BP-20722 4 Rue Alfred Kastler, Nantes 44307, France
e-mail: Thangavelu.Jayabalan@emn.fr

P. Pré
e-mail: Pascaline.Pre@emn.fr

P. Le Cloirec
Université Européene de Bretagne, Ecole de Chimie de Rennes (ENSCR), UMR CNRS 6226, “Sciences Chimiques de Rennes”, Campus de Beaulieu, Avenue du général Leclerc, 35700 Rennes, France

and Differential Scanning Calorimetry (DSC) were extensively used in his work. This test method is mainly used for the comparison of the ignition characteristics of the different activated carbons and should not be taken as the true oxidation and ignition temperatures as they are dependant on the operating conditions of activated carbons. Suzin et al. (1999) compared and correlated the SIT and PIO using different methods, the oxidation and ignition characteristics changed with the system operating conditions, physical carbon conditions and intrinsic properties of carbon.

The specific aim of this work is to establish quantitative correlation between the intrinsic properties of activated carbons and their reactivity leading to oxidation and ignition. Their reactivity is characterised by measuring PIO and SIT. The correlation is assessed by analysing a large number of activated carbon samples having diversified properties. In a first approach, oxidation and the ignition behaviours described by the PIO and SIT values were plotted against intrinsic properties of the activated carbon and global trends were underlined. In a second step, a more rigorous statistical analysis was performed and correlation between oxidation and the ignition behaviours and intrinsic characteristic of carbon were established by multiple linear regressions (MLR). This approach is contributing to the understanding of the influence of material properties and mechanisms leading to oxidation and spontaneous ignition of activated carbons.

2 Experimental

2.1 Materials

Twelve different activated carbons were selected for this study based on the nature of the raw material and the mode of activation applied, as shown in Table 1. All of them were produced from the carbonisation at 800 °C to 1000 °C in the absence of oxygen of various synthetic and natural raw materials (coconut, peat, coke, wood, olive stone and polyacrylo nitrile fibre) followed by physical or chemical activation. Physical activation was carried out using steam or CO_2 gases and the chemical activation was performed using concentrated solutions of like H_3PO_4, $ZnCl_2$, and H_2SO_4. The polymer based activated carbons were prepared by blending PAN (polyacrylo nitrile fibre) and coal tar pitch CTP and carbonizing at 520 °C for 2 hours and the resultant chars were activated using steam at 800 °C. The samples having the same precursor were activated to different extent as in the case of NC with coconut shell giving rise to property differences in the samples.

2.2 Methods

2.2.1 Chemical composition

In order to point out the differences in the chemical composition of the activated carbon samples, which greatly depends on the nature of the precursor and the preparation mode, an elemental analysis of the activated carbon samples was carried out by using the Thermofinnigan Flash EA-112 analyser. The mass ratios over carbon for the components such as oxygen, hydrogen, nitrogen and sulphur were thus measured. The experimental error in the determination of the chemical composition of the activated carbons was found to be about 4% for three trials.

2.2.2 Porosity characteristics

The volume of larger pores (including macro and mesopores) of the AC samples was measured by mercury porosimetry (Micrometrics Auto pore IV 9500). The porosimeter

Table 1 General characteristics of carbon samples tested

Sample name	Manufacturer	Raw material	Mode of activation
NC-50	PICA	Coconut shell	Physical
NC-60	PICA	Coconut shell	Physical
NC-100	PICA	Coconut shell	Physical
RB-2	NORIT	Peat	Physical
BPL	CHEMVIRON	Coal	Physical
GF-40	NORIT	Olive stone	Chemical
BC-120	PICA	Wood	Chemical
PICABIOL	PICA	Wood	Chemical
CTP-A	LCSM Nancy	Coal tar pitch	Physical
CTP-PAN-3:1-A	LCSM Nancy	Coal tar pitch and polyacrylonitrile fibre	Physical
CTP-PAN-1:1-A	LCSM Nancy	Coal tar pitch and polyacrylonitrile fibre	Physical
PAN-A	LCSM Nancy	Polyacrylonitrile fibre	Physical

Table 2 Chemical and porosity characteristics of activated carbon samples

Sample	O/C (%)	H/C (%)	N/C (%)	Volume of micropores (Vmicro) ($cm^3\,g^{-1}$)	Average width of micro pores (Wmicro) (nm)	Surface area (S_{BET}) ($m^2\,g^{-1}$)	Porous volume (Vporous) ($cm^3\,g^{-1}$)
NC-50	1.72	0.52	0	0.36	1.35	1078	1.28
NC-60	3.60	0.30	0.04	0.32	0.97	1220	0.35
NC-100	3.30	0.53	0	0.27	1.11	1803	0.47
RB-2	5.90	0.32	0.20	0.35	0.92	1012	0.34
BPL	4.10	0.20	0.30	0.30	0.93	1106	0.40
GF-40	34.60	2.64	0.30	0.29	1.15	1718	0.80
BC-120	35.40	2.72	0.01	0.33	1.12	1975	1.50
PICABIOL	40.60	2.70	0	0.24	1.38	1534	1.34
CTP-A	1.72	3.08	0.70	0.04	1.30	102	0.07
CTP-PAN-3:1-A	3.10	0.86	5.70	0.20	1.32	468	0.25
CTP-PAN-1:1-A	7.20	1.22	9.20	0.21	1.11	482	0.27
PAN-A	13.40	1.12	15.5	0.26	1.15	515	0.27

enables the penetration of the mercury up to a pressure of 2050×10^5 Pa and this corresponds to an approximate pore width of 8 nm according to Washburn equation (Kenneth Sing 1998). The experiments were repeated thrice and the experimental error was found to be less than 10%.

The microporous structure of the AC samples was determined from nitrogen adsorption isotherms at 77 K (Micrometrics ASAP 2010 adsorption instrument). Prior to the analysis, the carbon samples were degassed at 150 °C for about 48 hours. The specific surface area was measured using the BET model from the adsorption of gases on the surface of the material. The volume of the micropores was measured from the t-plot or De Boer method that provide a simple means of comparing the shape of a given adsorption isotherm with that of a standard non-porous solid (Lecloux 1971; Olivier 1995a). The average width of the micropore was evaluated from the Density Functional Theory (DFT), based on the molecular models of adsorption giving accurate description of the adsorption phenomena particularly on the intermolecular fluid-fluid and fluid-solid interactions (Olivier 1995b; Lastoskie et al. 1993). Repeatability tests showed that the specific surface area, as well as the volume and the width of the micropores were determined with an accuracy of about 10%. The results of the porosity characteristics can be found in Table 2.

2.2.3 *Thermogravimetry-differential scanning calorimetry*

The instrument ATG-DSC, SETARAM-111 was used for the determination of the Point of Initial Oxidation (PIO) and the Spontaneous Ignition Temperature (SIT). In order to remove the effect of external size of the AC particles on the properties measured, the samples to be tested were first crushed and finely sieved to have a uniform size (average diameter: 50 µm). The experiment was carried out under a continuous flow of an oxygen/helium mixture (0.21–0.79) at the rate of 1 L/h. A mass of 3.5 mg of the crushed carbonaceous material was loaded in the measure cell, whilst the reference cell was empty. In order to remove the adsorbed moisture from the samples, an isotherm was primarily maintained at 105 °C during 30 min. An increasing temperature ramp was afterwards applied at a rate of 5 °C per minute, to heat the sample up to 650 °C. The heat flux released as well as the mass variations resulting from the carbon consumption was then continuously recorded. In order to cancel the effect of the calorific capacity of the solid materials on the measurements of the heat flux release, and the effect of Archimedes pressure on the mass changes, blank tests were conducted under a flow of inert gas (helium), and the TG-DSC signals observed were subtracted from the previous ones.

Figure 1 shows an example of the shape of the net heat flux measured. The TG-DSC thermograms describe a continuous exothermic oxidation process ended by complete combustion of the sample. The mass variation taking place along the temperature programmation can be seen in Fig. 2.

According to Suzin et al. (1999), the SIT was determined from the net heat flux curve measured, and corresponds to the temperature where the tangent to the point of inflection intersects the baseline DSC value. The SIT determined by this method was indicated on the Fig. 1. The SIT defines the limit beyond which the combustion of the sample takes place, and leads to the consumption of the carbon matrix as observed on the mass curve in Fig. 2. The PIO represents the point at which the exothermic reaction is significant: a low oxidation process takes place with partial oxidation

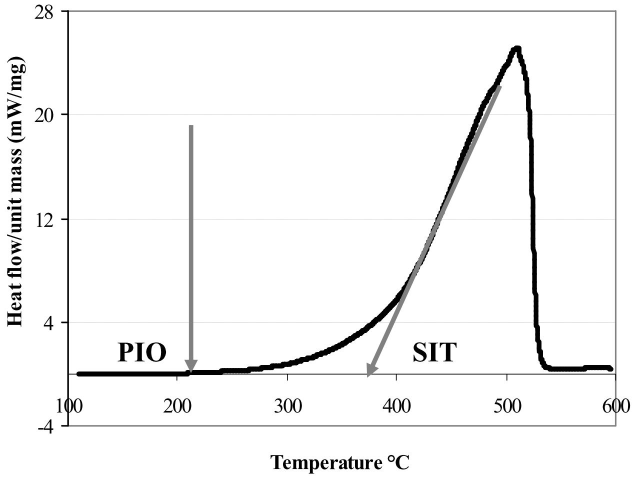

Fig. 1 DSC thermogram of a physically activated carbon sample NC-60

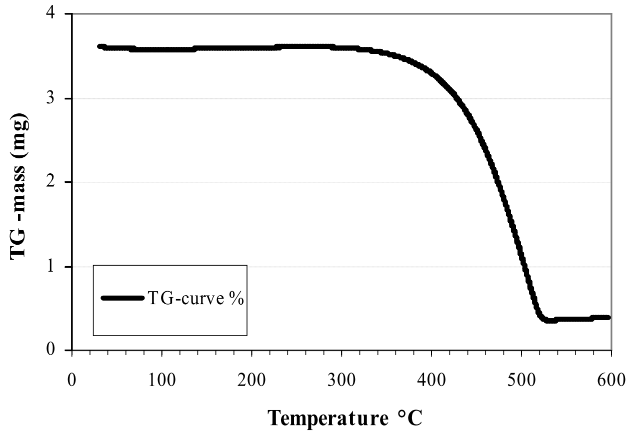

Fig. 2 Example of TG curve for physically activated carbon sample NC-60

of the carbon and the organic components. The PIO was extracted from the net heat flux curve by locating the initial point of deviation from the baseline (deviation of 2% from the running average of the prior 5 points). Using this method the relative errors for the experimental determination of the SIT and PIO were estimated respectively to be less than 5 and 10%.

3 Results and discussion

3.1 Influence of chemical composition

Looking at the elemental analysis results, it is shown that all the chemically activated carbon samples contain more oxygen content than the physically activated ones. The PICABIOL sample contains the highest oxygen to carbon ratio of 45% in comparison with that of the physically activated carbon samples ranging from 1–15%. Nitrogen is found in significant quantities in the activated carbons manufactured from coal tar pitch and polyacrylo nitrile fibres. The maximum N/C ratio is thus measured for the CTP-PAN sample and is as high as 15%. Hydrogen is found to be present in small quantities in the activated carbon samples, less than 3%. No sulphur was detected in the elemental analysis for the samples selected for this study.

3.1.1 Oxygen content

The influence of oxygen to carbon ratio of activated carbons on the reactivity can be studied from the Fig. 3 with a plot of log (O/C) versus PIO and (O/C) versus SIT. Firstly there is an increase in the reactivity (lower PIO and SIT values) of the activated carbons samples with an increase in the oxygen to carbon ratio. The main reason is being attributed to the reactivity of the oxygenated surface functional groups with air. The oxygen content in activated carbons is present in the form of surface oxygenated groups like carboxyl, hydroxyl, carbonyl and ether groups. Some of the oxygen content may come from the material itself or from its activation mode. When activated carbons are exposed to air and heated, the surface oxygenated groups reacts with air to form desorbable products like CO_2, CO, H_2O, intermediate complexes accompanied by exothermic heat (Hardman et al. 1983). Further the oxygenated groups are bonded to the edge sites which have a greater reactivity than the basal plane of the graphene layers and hence react rapidly on exposure to air.

Looking at Fig. 3, there are exceptions to these trends found in activated coconut shell samples which have lower PIO and SIT values than expected. The deviation of the three activated coconut shell samples is shown in Fig. 3. A good regression coefficient of 0.96 and 0.97 for SIT and PIO were obtained without the presence of these samples, but with the presence of the coconut shell activated carbons the regression coefficients were less significant with R^2 values of 0.58 and 0.47 for PIO and SIT respectively. Many reasons can be attributed for the deviation in behaviour, which may be due to higher affinity for the chemisorption of oxygen and also the presence of higher potassium content in these samples which catalyses the oxidation reactions and enhances the reactivity of the material (van der Merwe and Bandosz 2005).

The effect of oxygen to carbon ratio can be well explained in the coal tar pitch and polyacrylo nitrile fibre blend samples. The coal tar pitch (CTP) sample has scarce O/C ratio of about 1.7% with a high PIO and SIT. On the other hand PAN-A has nearly 13.4% O/C ratio approximately 8 times that of CTP sample with a lower PIO and SIT. The blend of these two samples takes the behaviour of either of the 2 depending upon their amount in the blend. For example CTP-PAN-3:1-A having 3 parts of CTP and one part

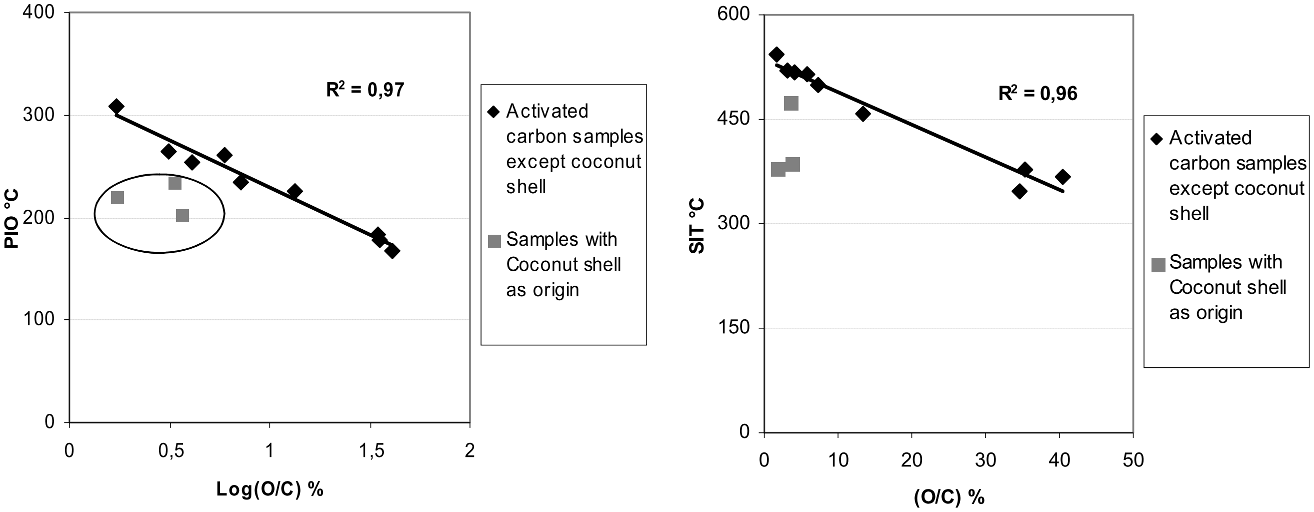

Fig. 3 Influence of oxygen to carbon ratio on PIO and SIT

of PAN in the sample has lower oxygen to carbon ratio of about 3.1% compared to the activated carbon sample having 1 part of CTP and 1 part of PAN in the blend having relatively higher oxygen to carbon ratio of about 7.2%. From the graph it is evident that the reactivity of CTP-PAN-1:1-A is higher than that of CTP-PAN-3:1-A which shows that the presence of large proportion of CTP sample stabilizes the blend.

When the nitrogen rich activated carbons namely coal tar pitch and polyacrylonitrile fibre samples are compared with samples containing less nitrogen content, we find a global trend that the nitrogen rich samples are more stable and found to have higher PIO and SIT values (Fig. 4). But since the nitrogen to carbon ratio is also associated with the oxygen to carbon ratio particularly for the CTP and PAN samples, it is difficult to show a tendency just only for the nitrogen to carbon ratio versus PIO and SIT. The main reason for their stability is the high temperature treatment involved in the activated carbon preparation makes them thermally stable.

In order to verify the interpretation, that the increase of oxygen content in the carbon matrix increases the reactivity of the activated carbons, a complementary Temperature Programmed Desorption (TPD) was carried out. The activated carbon samples were heated under an inert atmosphere like helium to about 750 °C to remove a part of the surface oxygenated groups. The oxygen content of the samples were then measured without exposing them to air, this was followed by Temperature Programmed Oxidation (TPO) in an atmosphere of oxygen. The TPD results are shown in Fig. 5.

The oxygen content of activated carbons after TPD were then analysed using an elementary analyser. It was found that there was a decrease in the oxygen content of the activated carbon samples due to the liberation of the oxygenated groups from the surface. There was approximately 10% decrease in the oxygen content for the chemically activated

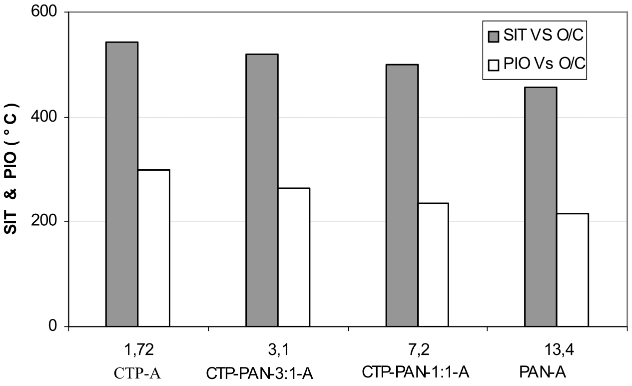

Fig. 4 Influence of oxygen to carbon ratio on PIO and SIT values for coal tar pitch and polyacrylo nitrile fibre blend samples

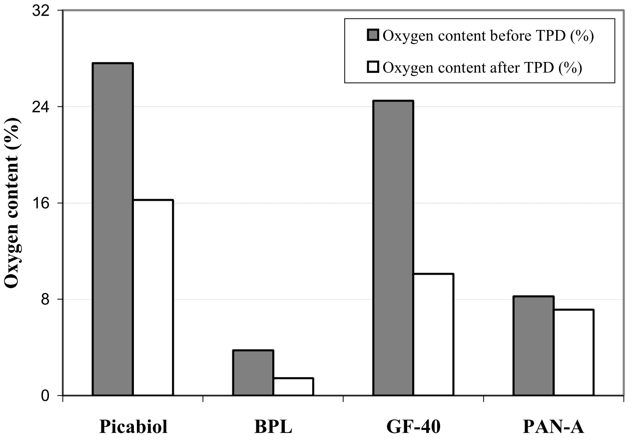

Fig. 5 Oxygen content of carbon samples before and after temperature programmed desorption

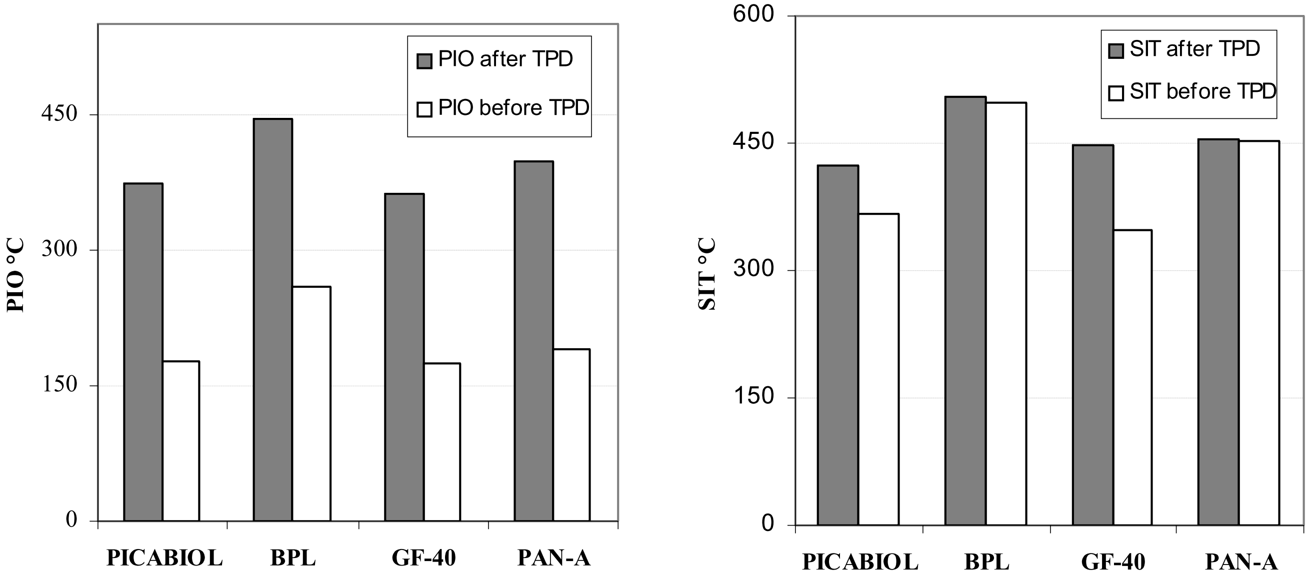

Fig. 6 Results of Temperature Programmed Desorption followed by oxidation of activated carbons

carbons. The samples were then subjected to oxidation in air which showed an increase in the PIO and SIT values shown in Fig. 6. A considerable increase in the PIO and SIT were noticed for the chemically activated carbons particularly in the PIO values as shown in Fig. 6 which indicates that the surface oxygenated groups initiate an early oxidation reaction in air.

3.2 Influence of porosity characteristics

The porosity characteristics constitute important parameters like the specific surface area (S_{BET}), the porous volume (Vporous), the width of the micropore (Wmicro) and volume of micropores (Vmicro). The S_{BET} of the carbon samples used in the study varies from 102 $\mathrm{m^2\,g^{-1}}$ to 2000 $\mathrm{m^2\,g^{-1}}$ approximately. The chemically activated carbon samples have high surface area with an average of about 1700 $\mathrm{m^2\,g^{-1}}$ and 865 $\mathrm{m^2\,g^{-1}}$ for the physically activated carbons. The coal tar pitch activated samples have a low S_{BET} with an average of 300 $\mathrm{m^2\,g^{-1}}$. The volume of micropores varies from 0.04–0.4 $\mathrm{cm^3\,g^{-1}}$. The width of the micropores was evenly distributed among the activated carbon samples with an average value of 1 nm. The average porous volume is about 0.60 $\mathrm{cm^3\,g^{-1}}$ with chemically activated carbons having a large porous volume compared to the physically activated carbons.

Out of these properties, a global trend is observed from the graphical analysis but with a low value of R^2. We could think that the porous properties may aid in the diffusion of oxygen to the interior of the activated carbons and also the presence of the active sites on their surface, but the surface oxygenated groups may be more dominant than the porosity characteristics.

In order to be able to conclude, that oxygen composition is more influent than the porosity characteristics it was necessary to deepen our analysis. This is the reason why, a statistical modelling approach was carried out in the next step.

4 Statistical modelling

Multiple Linear Regression (MLR) was used for carrying out the quantitative analysis which attempts to model the relationship between two or more explanatory or predictor variables and a response variable by fitting a linear equation to observed data. All the physical and chemical properties of the activated carbons furnished in Table 2 were taken into account. The principle response variables are the Point of Initial Oxidation (PIO) representative of the low temperature oxidation region and the Spontaneous Ignition Temperature (SIT) representative of the ignition region at higher temperature are utilised for the regression analysis. The main predictor variables are oxygen to carbon ratio log(O/C) % and (O/C) % (since PIO correlates well with log(O/C) and SIT correlates well with (O/C), nitrogen to carbon ratio (N/C) %, specific surface area (S_{BET}) $\mathrm{m^2\,g^{-1}}$, porous volume (Vporous) $\mathrm{cm^3\,g^{-1}}$, volume of micropore (Vmicro) $\mathrm{cm^3\,g^{-1}}$ and width of the micropore (Wmicro) nm.

The MLR analysis was carried out using MINITAB software. Multicollinearity among the predictor variables was checked before carrying out the regression analysis. It represents the interdependence among the predictor variables and increases the statistical errors in regression analysis. The

Table 3 Matrix of correlation for predictor variables

	S_{BET} ($m^2\,g^{-1}$)	H/C (%)	N/C (%)	Vporous ($cm^3\,g^{-1}$)	Log (O/C) (%)	Wpore (nm)	O/C (%)
H/C (%)	0.39						
N/C (%)	−0.56	0.09					
Vporous ($cm^3\,g^{-1}$)	0.82	0.60	−0.40				
Log (O/C) (%)	0.54	0.88	−0.083	0.57			
Wpore (nm)	−0.17	0.41	0.010	0.12	0.003		
O/C (%)	0.60	0.93	−0.13	0.68	0.94	−0.22	
Vmicro ($cm^3\,g^{-1}$)	0.63	−0.062	−0.22	0.48	0.22	−0.44	0.15

multicollinearity character was tested by the use of correlation of matrix (Brasquet 1998; Giraudet et al. 2006). From the Table 3, it was found that two pairs of predictor variables are highly correlated namely oxygen and hydrogen composition followed by Vporous and S_{BET}. The oxygen in the surface oxygenated groups are mostly associated with hydrogen than any other heteroatom in the form of carboxylic groups, phenol and water, hence there is a strong correlation between oxygen and hydrogen composition in the activated carbon samples. There is collinearity between the porous volume and the specific surface area in the activated carbons. Therefore only one predictor variable from the highly correlated pairs is considered at a time while performing the regression analysis.

The type of the multiple linear regression carried out here is the *stepwise multiple regression* which consists in successive addition of the predictor variables one by one at each stage to get a better regression coefficient satisfying all the statistical conditions (Brasquet 1998; Giraudet et al. 2006).

The regression equation for the response variable PIO is as follows with 12 activated carbon samples

$$\mathrm{PIO} = 277 - 60.7\,\mathrm{Log}\,(\mathrm{O/C})\ \% \tag{1}$$

The accuracy of the model is given by its coefficient of determination, (R^2) which is 0.58 and it standard deviation (S) of about 27 °C. The coefficient of determination 0.58 is not significant which may be due to the effect of deviations incorporated by the presence of activated coconut shell samples. Hence the regression analysis is carried out without these samples where the following regression equation is obtained

$$\mathrm{PIO} = 315 - 89.1\,\mathrm{Log}\,(\mathrm{O/C})\ \% \tag{2}$$

The coefficient of determination in this case is 0.97 with a standard deviation of 7 °C which is better when compared to the regression equation with twelve samples containing activated coconut shell samples. In the same manner the regression equation for the response variable SIT was calculated and obtained as

$$\mathrm{SIT} = 492 - 3.33\ (\mathrm{O/C})\ \% \tag{3}$$

Here we obtain a R^2 value of 0.47 with high standard deviation of about 54 °C which may be due to deviations incorporated by the activated coconut shell samples and the regression is recalculated ignoring them.

$$\mathrm{SIT} = 537 - 4.70\ (\mathrm{O/C})\ \% \tag{4}$$

Now we obtain, R^2 of 0.96 and standard deviation (S) of about 16 °C for the recalculated regression equation.

From the statistical correlation results, it is found that oxygen to carbon ratio influences both PIO and SIT. Their influence is felt more in PIO than in SIT evident from the accuracy of determination of both the equations; hence we can say that the oxidation and ignition reactions start early for the activated carbons having higher surface oxygenated groups. The porosity characteristics like S_{BET} and Vporous also found to influence them in less significant way and have not been put into evidence as the addition of the porosity characteristics deteriorated the coefficient of determination in the regression equation.

5 Conclusion

The oxidation and ignition characteristics of a large number of activated carbons having diversified origin and properties with different mode of activation were studied using TG-DSC techniques. Based on the qualitative and quantitative results, it was found that the oxygen to carbon ratio was the most important parameter influencing the oxidation and ignition of activated carbons. The porosity parameters like the porous volume and the specific surface area also influence the reactivity but in a smaller magnitude which is not significant. Since the reactivities could not be explained with these properties, an important perspective will be added to this work by studying the textural properties using methods like image analysis adding a new dimension which might well complement the physical and porosity characteristics. Though the properties of oxidation and ignition may change with experimental conditions, the results obtained here enable us to assess the properties influencing the reactivity of activated carbons under a given condition and not to measure the exact oxidation and ignition temperatures.

Acknowledgements The authors thank Professor Guy Furdin, Laboratoire de Chimie du Solide Mineral, University Henri Poincare, Nancy, France for supplying nitrogenated activated carbon samples.

Nomenclature

DFT	Density Functional Theory
MLR	Multiple Linear Regression
PIO	Point of Initial Oxidation (°C)
TPD	Temperature Programmed Desorption
S_{BET}	Specific surface area ($m^2\ g^{-1}$)
SIT	Spontaneous Ignition Temperature (°C)
Vmicro	volume of micropores ($cm^3\ g^{-1}$)
Vporous	volume of pores greater than 8 nm ($cm^3\ g^{-1}$)
Wpore	width of the micropore (nm)
(O/C)	Oxygen to carbon ratio (%)
H/C	Hydrogen to carbon ratio (%)
N/C	Nitrogen to carbon ratio (%)
Log (O/C)	Logarithm of oxygen to carbon ratio (%)

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