A SYSTEM TO INVESTIGATE THE REMEDIATION OF ORGANIC VAPORS USING MICROWAVE-INDUCED PLASMA WITH FLUIDIZED CARBON GRANULES

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This article describes a system to investigate the parameters for the remediation of organic vapors using microwave-induced plasma on fluidized carbon granules. The system is based on a single mode microwave apparatus with a variable power (2.45 GHz) generator. Carbon granules are fluidized in a 20 mm diameter silica tube situated in the sample section of a waveguide incorporating two additional ports to allow plasma intensity monitoring using a light sensor and imaging with a digital camera. A fluoroptic probe is used for in-situ measurement of the carbon granule temperature while the effluent gas temperature is measured with a thermocouple situated in the silica tube outside the cavity. Data acquisition and control software allow experiments using a variety of microwave power regimes while simultaneously recording the light intensity of any plasma generated within the carbon bed together with its temperature. The system was evaluated using two carbons and ethyl acetate, introduced as a vapor into the fluidizing air stream at a concentration of 1 ppm. Results indicated that significant destruction of ethyl acetate, as monitored using a mass spectrometer, was achieved only with the carbon showing high plasma activity under pulsed microwave conditions.

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INTRODUCTION

Many activated carbons can be heated using microwaves and their use to regenerate static beds of granular carbon has been shown to be effective [1-3]. Some studies have also been published on the combination of microwave heating with a fluidized bed, especially for drying applications [4, 5].

When some carbons are exposed to microwave radiation, their temperature can rise rapidly due to dielectric heating. In such cases, the mechanism responsible is space charge polarization or the Maxwell-Wagner effect [6] arising from movement of the free electrons in the carbon. Electron displacement, which occurs in the oscillating microwave electric field (E-field) is restricted by grain boundaries, giving rise to macroscopic regions of positive and negative charge, which at lower frequencies are able to follow the changing E-field. However, at higher frequencies a phase lag develops which gives rise to conversion of part of the absorbed microwave power to heat. Often, heating is accompanied by tiny discharges between granules, especially when agitated (e.g. when the bed is fluidized). This 'twinkling' effect has been reported in waste water remediation studies [7, 8]. Different carbons heat and exhibit this discharge behavior to different extents in a microwave field depending on their method of preparation. Chemical or physical activation, type of precursor and presence of trace elements are all thought to be factors responsible for this variation [9].

However, the fundamental interaction of microwave energy with fluidized carbon granules and their potential application in the remediation of airborne organic pollutants has not been studied extensively. This paper describes the design, construction and use of a system for the investigation of some of the phenomena associated with the formation of microwave-induced plasma on fluidized activated carbon granules exposed to low concentrations of organic vapor.

I. SYSTEM DESCRIPTION

A. Single mode microwave equipment

In this work, a single mode microwave heating device is used, of similar design to that described previously [10-12]. A schematic diagram of the microwave – fluidized bed (MW-FB) reactor is shown in FIG. 1. It comprises a high stability, narrow band 2.45 GHz generator (Industrial Microwave Systems), whose power output can be continuously varied up to 1000 W. From the generator, the microwaves are passed via a water-cooled circulator, used to prevent reflected power from damaging the magnetron, to a launcher incorporated into an S-band brass waveguide (rectangular cross section, width 86 mm, height 43 mm). Tuning, accomplished using a 3-stub tuner and a variable short, is used to set up a standing wave with the peak maximum of the electric component of the microwave E-field in the centre of the heating section.

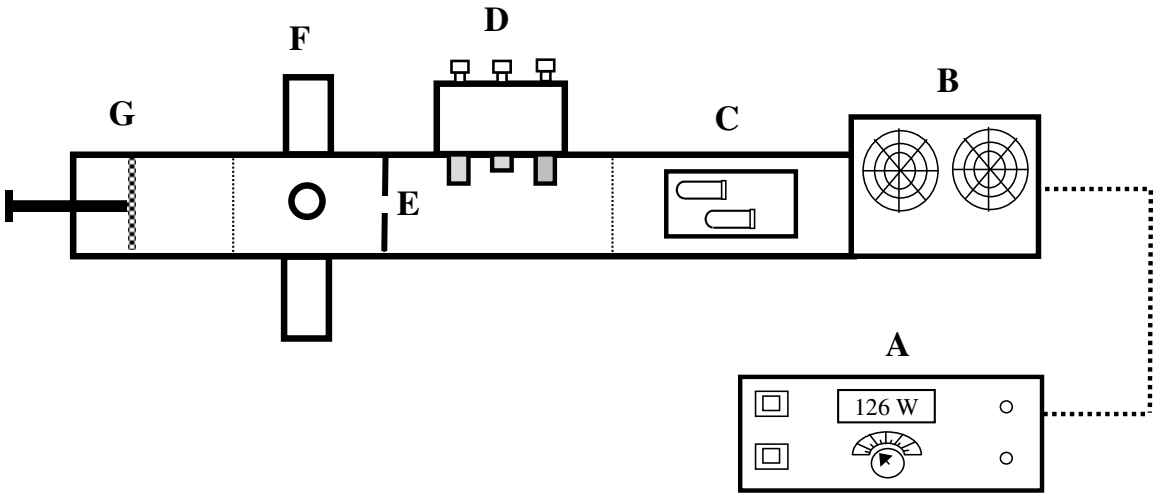


FIG. 1. Schematic diagram of the single-mode microwave system
A: 1000 W variable microwave power unit; B: air-cooled generator and launch section; C: water-cooled circulator; D: manual 3-stub unit; E: iris plate; F: 4-port heating section; G: variable short circuit (plunge tuner)

The heating section has four circular ports, two vertical larger ports (diameter 50 mm) to allow insertion/removal of the silica reaction tube and two smaller horizontal ports (diameter 30 mm) for location of a light sensor and digital camera. The ports have cylindrical extensions of over twice their diameter to prevent microwave leakage.

B. Reactor tube and fluidization system

The silica reactor tube is 10-20 mm diameter, situated vertically in the heating section of the microwave cavity and contains a porous ceramic sinter which supports the granules and a silica wool plug to trap fines. Fluidization of the granules between the sinter and the silica wool is produced by an air flow supplied by a diaphragm pump (Capex, Charles Austen) the output of which can be adjusted between 1 and 20 liters per minute, using a restricting tap and rotameter on the pump inlet. The exact flow rate necessary for fluidization varied depending on the carbon used and the tube diameter, but was set according to Equation 1 based on the work of Wen *et al.* [13].

$$u = \frac{d_p^2 \times g \times (\rho_c - \rho_g)}{1650\mu} \qquad \text{Eqn. 1}$$

Where: u = minimum air velocity for fluidization

d_p = average particle diameter

$g = 981$ cm s^{-2}

ρ_c = density of granules

ρ_g = density of air, 1.2×10^{-3} g cm^{-3}

μ = viscosity of air, 1.82×10^{-5} N s m^{-2}

For activated carbon granules of density 1.1 g cm^{-3} and diameter 0.1 cm this gives a value for u of 36 cm s^{-1} which equates to a flow rate of approximately 7 liters per minute in a tube of diameter 20 mm, or 2 liters per minute for a diameter of 10 mm. In practice, higher flow rates were used to assist in cooling the carbon granules during plasma formation.

The fluidized bed length can be varied between the ceramic sinter and the position of the quartz wool plug. However, the length of the section actually in the microwave electric field is constant and determined by internal height (43 mm) of the waveguide. The silica wool is typically positioned outside the limit of the microwave electric field and at the height limit of fluidization so, during fluidization, granules tumble in and out of the microwave field. A

volatile organic compound can be introduced as a vapor into the fluidizing air, upstream of the reactor tube, using an aspirator with a flow rate set by a mass flow controller to produce the desired concentration. For ethyl acetate at room temperature a gas flow rate of 45 cm^3 min^{-1} was shown to produce vapor with an average concentration of 1 ppm (1 mg/l) ethyl acetate in the fluidizing gas stream.

Downstream from the reactor tube, the exhaust gas is sampled by a mass spectrometer (Hiden, HPR20) fitted with a secondary electron multiplier detector and heated capillary inlet to allow the concentration of reactants and products to be continuously monitored. The gas flow diagram is shown in Fig, 2 and the reactor tube and heating cavity in Fig. 3.

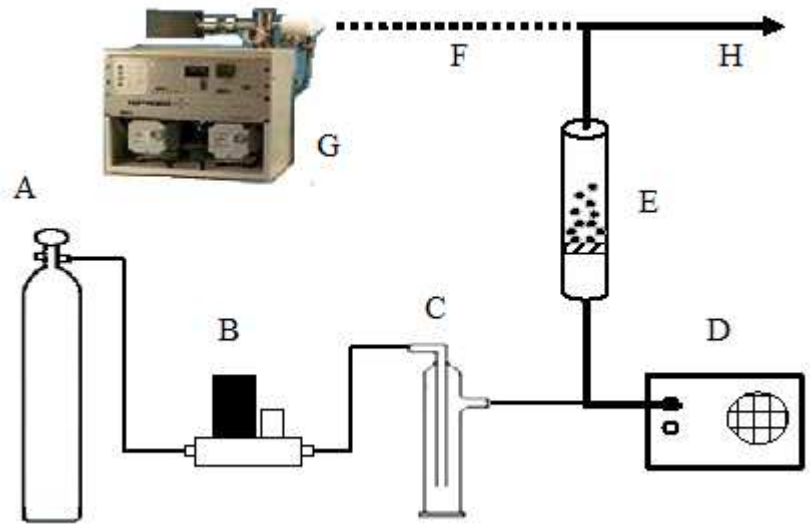


FIG. 2. Gas flow diagram
(A) Air cylinder, (B) mass flow controller, (C) bubbler, (D) diaphragm pump, (E) reactor tube, (F) heated capillary line, (G) mass spectrometer and (H) vent

C. Temperature measurement

Temperature measurement within a microwave cavity is difficult as conventional thermocouples must be thin, shielded [3, 14] and precisely located normal to the E-field if they are not to act as an antenna [11, 12]. An alternative approach is to use fluoroptic probes, which do not interact with microwaves and can be placed directly in the cavity, but these are not generally very robust. In this system, the fluoroptic probe (STF type probe, Luxtron) is contained in a ceramic sheath (alumina, 3 mm old.) whose tip is located above the ceramic

sinter in the reactor tube in contact with those granules which are momentarily at rest. This arrangement affords the probe protection in the somewhat aggressive experimental conditions produced by the fluidized carbon granules. The validity of the temperatures recorded in a fluidized bed where the granules are heated by microwaves has been proved in a study [15] which concluded that the solid and gas temperatures are equal when the system is in equilibrium (steady state).

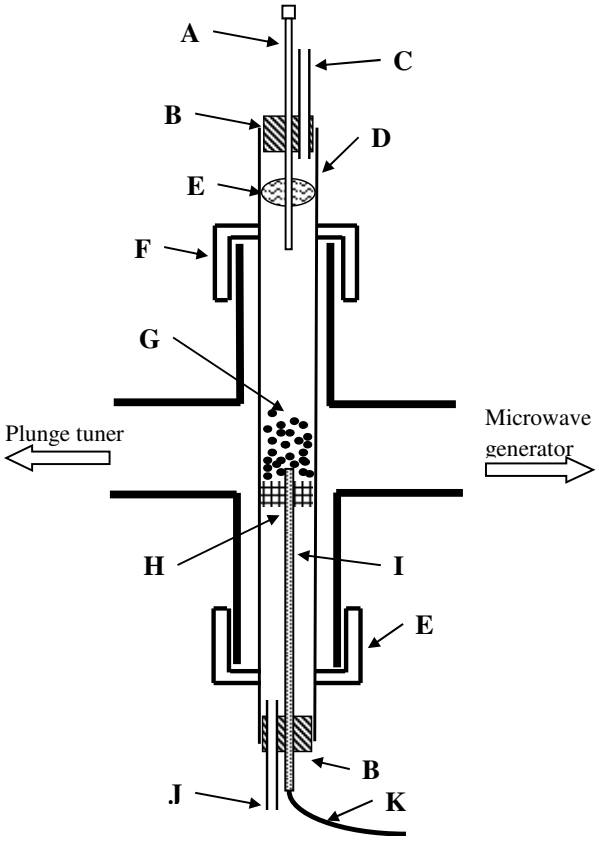


FIG. 3. Schematic cross-section of heating section with reactor tube and fluidised carbon
(A) stainless steel sheathed thermocouple, (B) rubber bung; (C) gas outlet tube; (D) quartz reactor tube; (E) quartz wool plug, (F) reactor tube placement cap/light seal, (G) fluidised carbon granules, (H) ceramic sinter, (I) ceramic coated temperature probe, (J) gas inlet tube, (K) fluoroptic temperature probe

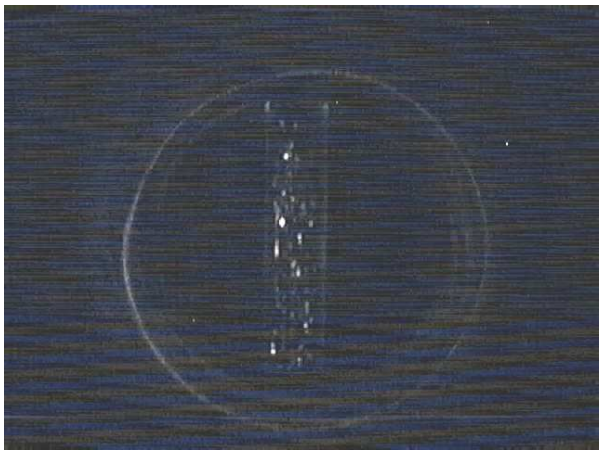
D. Plasma intensity monitoring using a light sensor

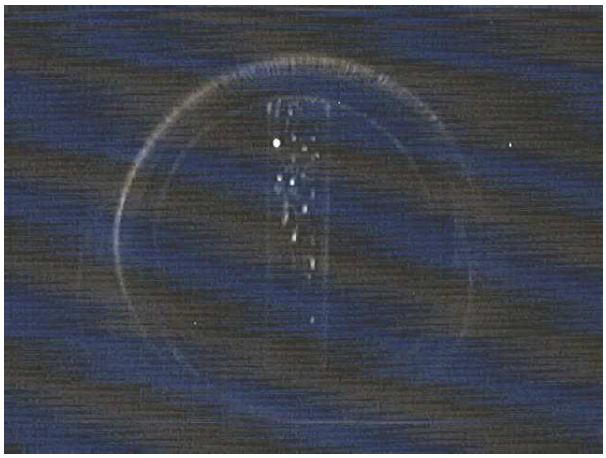
The intensity of any transient plasma formed in the fluidized carbon bed while subjected to microwaves was monitored using a simple light sensor based on a light dependent resistor (LDR) whose resistance falls as a function of the intensity of light falling on it. This was connected to an amplifier circuit which converted the changing resistance into

a voltage for interfacing to an ADC (Weeder Technologies). This voltage was designated the plasma discharge signal.

E. Digital imaging of the fluidized bed

Visual monitoring of the carbon fluidization and any plasma discharge is achieved using a CCD webcam (Logitech) positioned in the side port of the microwave heating cavity opposite the light sensor. Extraneous light is excluded from the microwave heating section using black plastic end caps on the vertical ports and from the exposed lengths of the sample cell by black adhesive tape.





Figs. 5 and 6. Typical CCD images showing plasma formation
on fluidized carbon granules in a microwave field

Typical pictures of the granular discharges are given in Figs. 5 and 6, which show the internal microwave heating cavity and the fluidized section of the sample cell with the carbon granules moving through the microwave field. The random nature of the generation of the plasma is clearly seen. A schematic diagram of the analogue and digital electrical connections of the system is shown in Fig 7.

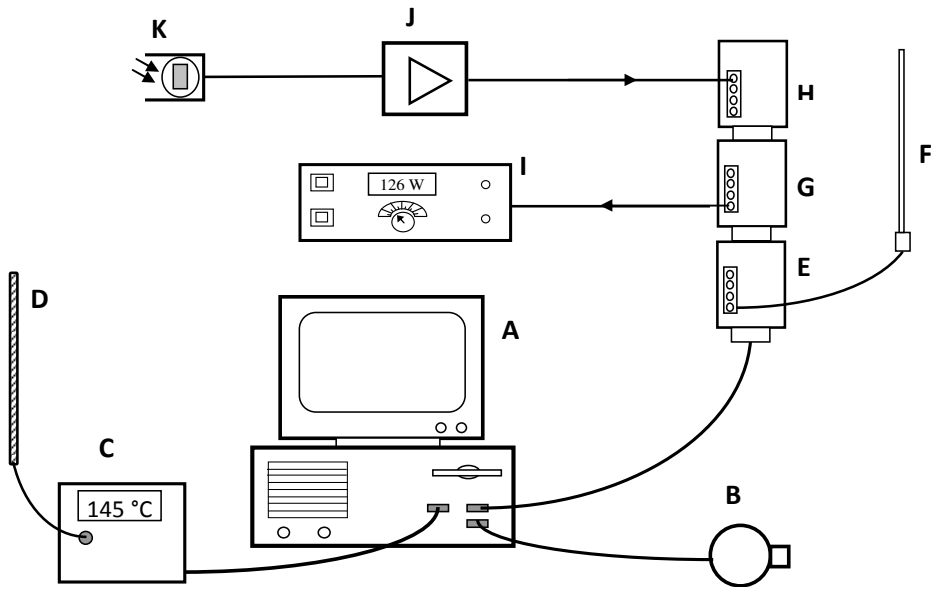


FIG. 7. Schematic diagram of electrical and computer connections
(A) computer, (B) CCD camera, (C) Luxtron control unit, (D) ceramic sheathed fluoroptic temperature probe, (E) thermocouple module, (F) stainless steel sheathed thermocouple, (G) DAC module, (H) ADC module, (I) 1000 W variable microwave power unit, (J) light sensor amplifier unit, (K) LDR light sensor

F. Control and acquisition software

Proprietary data acquisition and control software was developed using Visual Basic 6 running under Windows XP (Microsoft). The software continuously monitors the fluoroptic temperature probe (via an RS232C connection to the control unit) and the outputs of the LDR light sensor and thermocouple via 12-bit ADC modules (Weeder Technologies). Control of the microwave power is effected via a 0 – 5 V analogue signal fed to the generator via an 8-bit DAC (Weeder Technologies) and equating to 0 – 1000 W of power. Acquisition and control is performed on a 1 second cycle. The software permits a variety of experimental modes including constant power, linearly increasing or decreasing power and pulsed power.

II. SYSTEM EVALUATION

A. Determination of temperature and plasma discharge levels

Initial experiments were performed to compare the relative temperature and plasma discharge levels of two different carbon samples (BPL and AR1, Chemviron). These carbons were selected because, according to the manufacturer, both are suitable for adsorption of

organic vapors [16]. Samples (1 g) were fluidized with an air flow of 2 liters per minute, in the silica reactor tube (10 mm o.d.). The microwave power was linearly increased to 400 W at a rate of 50 W/min and the temperature of the granules and their plasma discharge signal recorded. The results of this experiment are shown in Fig. 8. The plasma discharge signals are very noisy, partly as a result of their transient nature within the fluidized bed, and are shown in the form of 2nd order polynomial fitted curves. It can be seen that, although the AR1 carbon became only slightly hotter than BPL carbon, it showed a much higher plasma activity which increased with microwave power.

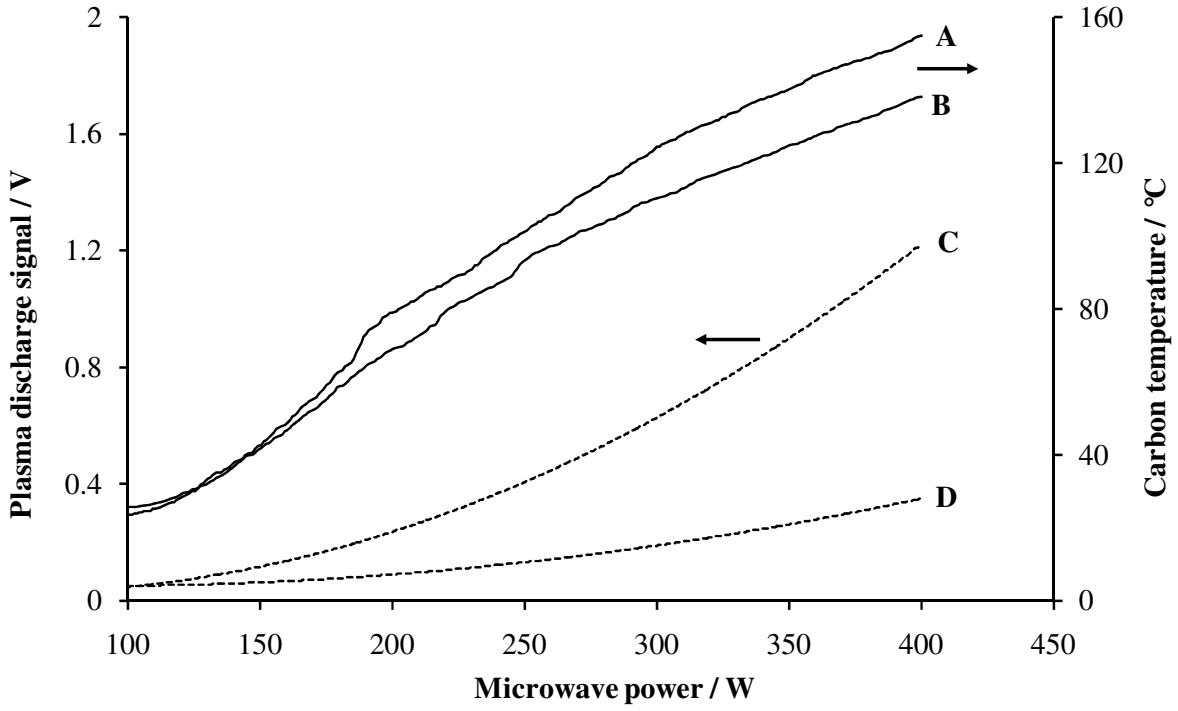


FIG. 8. Temperature and 2nd order polynomial fitted curves for the plasma discharge signal recorded for fluidized granular activated carbons under increasing microwave power. Temperature: (A) AR1, (B) BPL; Plasma discharge signal: (C) AR1, (D) BPL

B. Destruction of ethyl acetate

The instrument described was then used to study the effect of a MW pulsing regime on these two different granular activated carbons and relate their observed characteristics to their ability to promote the destruction of a low concentration of ethyl acetate in the fluidizing air stream. Samples (2 g, 12 × 30 ASTM) were dried overnight at 120 °C and placed in the reactor tube (20 mm o.d.) as described previously. Before fluidization, the carbons gave a

stationary bed depth of 2 cm in the silica tube and during fluidization with a flow of 16 liters per minute, 15 cm.

Before microwave power was applied, the carbon was allowed to equilibrate in the ethyl acetate/air flow until a steady state was reached and a constant reading for m/z 43 (ethyl acetate base peak) registered by the mass spectrometer.

Pulsed microwave power was then applied. Four-second pulses at 400 W were separated by eight seconds at zero power and this regime continued until the ethyl acetate equilibrium was re-established. At this stage, the MW power was set to zero and the ethyl acetate level allowed stabilizing, at which point the experiment was terminated. In addition to the mass spectrometer data, the temperatures of the carbon granules and the effluent air stream, together with the plasma discharge signal were recorded.

Fig. 9 shows the result of the experiment using BPL carbon. It can be seen that throughout the period when the pulsed microwave power was applied the ethyl acetate concentration is unaffected. In contrast, the experiment with AR1 carbon (Fig. 10) shows a significant (27 %) drop in ethyl acetate concentration during the period when the pulsed microwave power was applied. Apart from CO_2 no other species were detected by the mass spectrometer, suggesting that complete oxidation of the ethyl acetate had occurred. Normally, ozone and NOx are formed when plasmas are produced in air but reaction with carbon in the presence of microwaves is thought to reduce these species as the results of Kong and Cha suggest [17, 18].

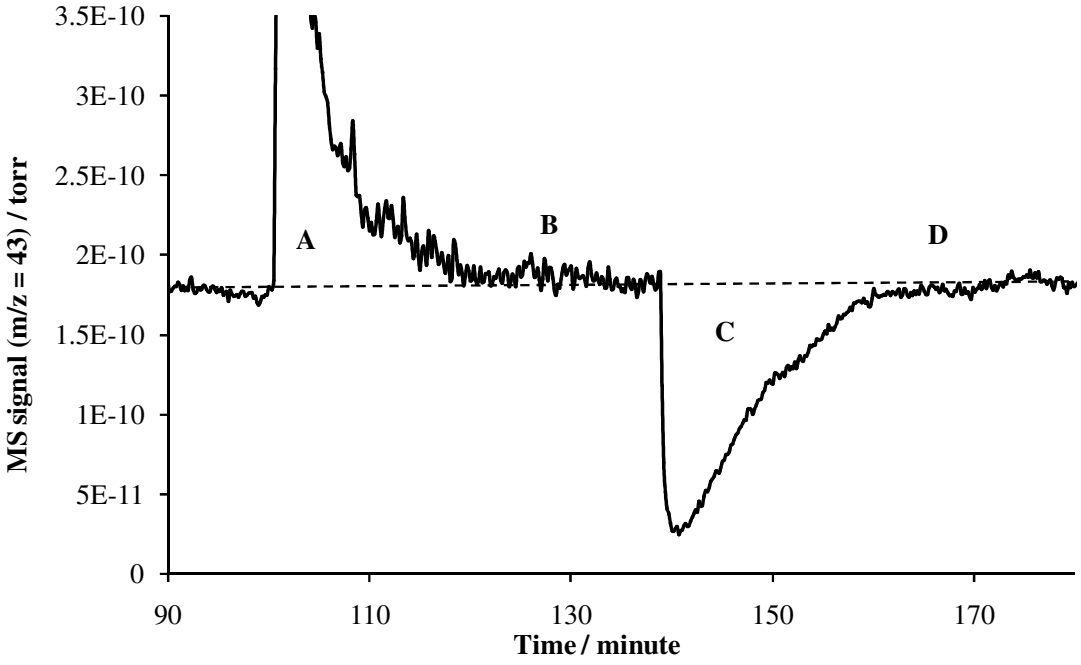


FIG. 9. Fluidized BPL carbon: effect of microwave pulsing (4/8 s on/off) on the breakthrough of ethyl acetate vapor, (A) initial desorption as microwave heating occurs, (B) no significant change in concentration during application of the microwave power, (C) re-adsorption on the cooling carbon when the microwaves are switched off and (D) return to original concentration

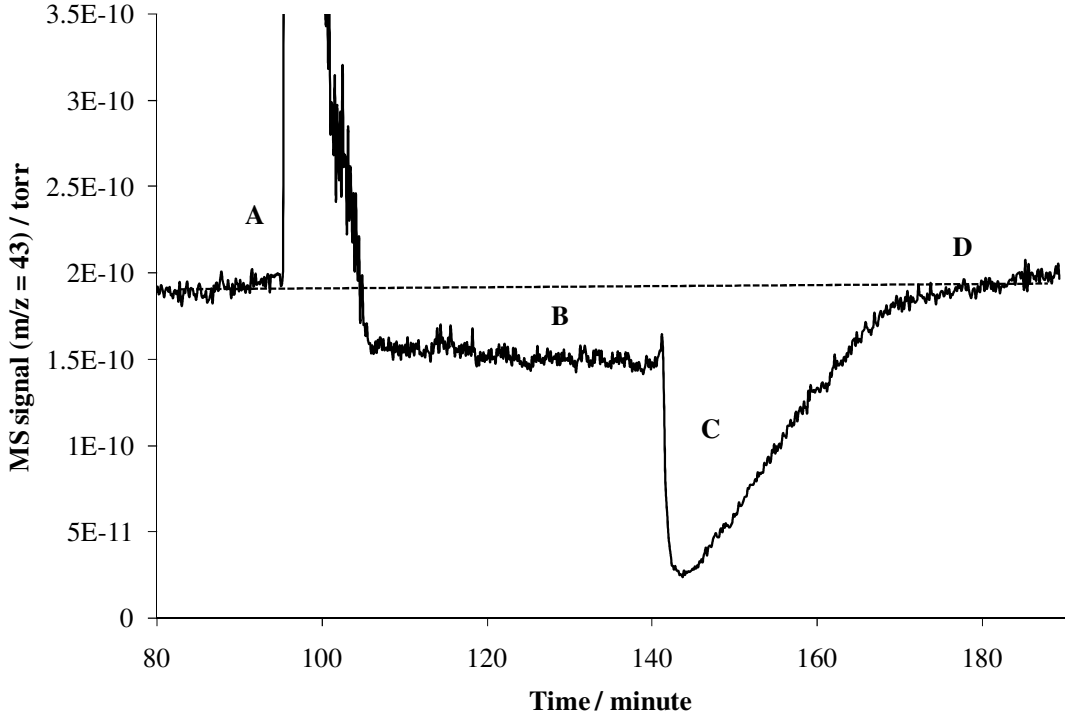


FIG. 10. Fluidized AR1 carbon: effect of microwave pulsing (4/8 s on/off) on the breakthrough of ethyl acetate vapor. (A) initial desorption as microwave heating occurs, (B) establishment of a lower concentration during application of microwave power, (C) re-adsorption on the cooling carbon when the microwaves are switched off and (D) return to original concentration

As a result of the high air flow rate, the carbon granule temperature was similar for both experiments, averaging at 73 °C, as was the exhaust gas temperature which averaged 50 °C. However, the plasma discharge signals are very different with AR1 carbon producing a much higher average value (1.9 V) than the BPL (0.05 V).

III. CONCLUSION

An instrument has been developed to study the behavior of microwave-induced plasma on fluidized granular carbons and their effectiveness in destroying organic vapors in flowing air.

Initial experiments have shown that the intensity of the transient plasma discharges (under the pulsed microwave and fluidization conditions used) is highly dependent on the carbon but does not appear to correlate with the extent of heating of the bed. Partial destruction of ethyl acetate has also been demonstrated, through oxidation by the plasma, with no detectable NOx or ozone formation.

Current research is focused on tuning the instrument to identify the experimental conditions, such as the microwave power regime, the fluidization flow rate, the carbon used, etc., that produce the greatest plasma intensity and are most effective at destroying the target vapor. Future work will evaluate the response of the system to a range of organic vapors, including species with hetero atoms, and explore the potential of scale-up.

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