Title of the Invention: **Derivatization of carbon**

Abstract Title: **A process for the chemical modification of elemental carbon**

A process is disclosed for the chemical modification of the surface of elemental carbon which comprises a first stage of attaching a compound with an azo group to the elemental carbon and then a second stage of decomposing the azo group in the presence of one or more compounds with an olefinic group so that decomposition of the azo group forms radicals attached to the carbon surface and a said radical forms a covalent bond to a said olefinic group. The second stage may proceed as a polymerization of a vinyl monomer with a redox active group such as ferrocene, anthracene or anthraquinone. The resulting polymer-modified carbon may be used in an electrochemical sensor.
DERIVATIZATION OF CARBON

Field of the Invention

[0001] This invention relates to the derivatization of carbon, i.e. the covalent attachment of molecules to the surface of elemental carbon.

Background of the Invention

[0002] Derivatization of carbon surfaces has attracted considerable interest in recent years, in particular in connection with attaching molecules to carbon nanotubes.

[0003] The derivatization of carbon may be carried out for a range of purposes which include modification of the surface properties of a carbon substrate, preparation of carbon-epoxy composites and attaching a molecule to a carbon electrode so that it can take part in an electrochemical reaction in an electrochemical sensor or an electrochemical catalyst.

[0004] Traditionally, carbon surfaces were modified by vigorous oxidation on the surface leading to the formation of carboxylic, quinonic, ketonic or hydroxylic groups, which were then reacted further with the target molecule.


[0006] There have also been a number of disclosures of routes for derivatization of carbon, without electrochemistry. These include the homogeneous reduction of diazonium
compounds in reducing media as described by Pandurangappa et al Analyst, vol 127, page 1568 (2002) and Leventis et al, Talanta vol 63, page 1039 (2004). Also in this category is WO2005/066618 (Schlumberger) which includes description of the diazocoupling of anthraquinonyl and nitrophenyl groups onto carbon nanotubes by means of the reduction of diazonium salts. WO2010/106404 teaches exposing the carbon to a reaction mixture in which a reactive carbene is transiently formed by reaction between a precursor and an extremely strong base.

**Summary of the Invention**

[0007] According to a first aspect of this invention, this invention provides a process for chemical modification of the surface of elemental carbon comprising attaching a compound with an azo group to the elemental carbon and then decomposing the azo group in the presence of one or more compounds with an olefinic group so that decomposition of the azo group forms radicals attached to the carbon surface and a said radical forms a covalent bond to a said olefinic group.

[0008] When the azo compound is decomposed, two radicals are formed. One of these radicals is attached to the carbon surface. Reaction of a radical with an olefinic group forms a bond, generally a carbon-carbon bond, to one atom of the olefinic group.

[0009] The immediate product of such a reaction will also be a radical. Consequently, the reaction may proceed as a polymerisation in which the compound with an olefinic group or a mixture of compounds with olefinic groups, are the monomer(s) which become converted to a polymer chain attached to the carbon surface. These monomers may be vinyl compounds and more specifically may be one or more aromatic compounds with a vinyl group attached to an aromatic ring. It is also possible that a compound containing an olefinic group will be attacked by the radical on the carbon surface but polymer chain formation will terminate instead of propagating.

[0010] The azo compound which is decomposed to radicals may be attached directly to the elemental carbon surface. This can be done with an azo compound which also has a diazonium group attached to it. The diazonium group is reduced in the presence of the
elemental carbon in accordance with the known procedure for derivatisation of carbon with a diazonium compound.

[0011] Another possibility is to begin by derivatizing the elemental carbon with a functional group which does not contain an azo group and then react this group with an azo compound. For instance, this may be accomplished using the known process for treating elemental carbon with a strong oxidising acid to introduce carboxylic acid groups attached to carbon which can be utilised for attachment of another compound.

[0012] In embodiments of this invention, the olefinic compound(s) may introduce one or more moieties which can undergo redox reactions and can be used in an electrochemical sensor. Aspects this invention includes carbon which has been derivatized by the process above, and products which incorporate such derivatized carbon.

[0013] So in another aspect this invention provides an electrochemical sensor electrode comprising elemental carbon having one or more redox-active compounds attached thereto by the process above. Such a sensor may be a constituent part of measuring apparatus which also has means to apply voltage to the electrode and measure current flow.

[0014] Such apparatus may be used for determining presence or concentration of an analyte, and in a further aspect this invention provides a method of determining presence or concentration of an analyte in a liquid, comprising contacting the liquid with at least two electrodes, at least one of which is an electrode comprising elemental carbon having a redox-active group covalently attached thereto through a process as above and carrying out electrochemical measurement with the electrodes. The liquid which contains the analyte may be an aqueous solution but it may also be a non-aqueous liquid such as acetonitrile. A method of determining analyte concentration may comprise applying a potential to the sensor electrode(s) in a sweep over a range sufficient to bring about at least one oxidation and/or reduction of the redox active compound; measuring potential or potentials corresponding to one or more said oxidation and/or reductions; and then processing the measurements to give a determination of analyte concentration.
[0015] Within the broad range of possibilities, the redox active groups which may be attached to carbon include aromatic quinones, aromatic nitro compounds and metallocenes all of which have previously been disclosed for use in electrochemical sensors.

**Brief description of the drawings**

[0016] Fig 1 is a diagrammatic illustration of the parts of an electrochemical sensor;

[0017] Fig 2 shows another electrode construction;

[0018] Fig 3 illustrates the geometrical surface layout of the surface of a sensor;

[0019] Fig 4 is a perspective view, partially cut-away, of an electrochemical sensor incorporating the surface of Fig 3;

[0020] Fig 5 illustrates a working electrode covered at least in part by a polymer layer, in accordance with an embodiment of the present invention;

[0021] Fig 6 is a diagrammatic illustration of a cable-suspended tool for testing water; and

[0022] Fig 7 illustrates an example of an electrochemical sensor, in accordance with an embodiment of the present invention, as part of a wireline formation testing apparatus in a wellbore.

**Detailed description**

[0023] The first stage in derivization of carbon in accordance with embodiments of this invention is the attachment of a compound which contains an azo group which will be decomposed in a subsequent step. Such a compound may be represented by a general formula

\[ R_1-N=N-R_2 \]
where the groups $R_1$ and $R_2$ are aromatic groups and one of them may also carry a functional group for attachment carbon. Thus the compound may be represented by a formula

$$X-R_1-N=N-R_2$$

where $X$ is a functional group. One possibility is that $X$ is a diazonium group and a specific possibility is that the compound is 2,5-dimethoxy-4-([4-nitrophenyl]azo)benzenediazonium chloride which is the commercially available dyestuff fast black K. The attachment of such a compound to elemental carbon, by decomposition of the diazonium group has been documented in the literature, notably in a review by Downard at Electroanalysis vol 12 pages 1085-96 (2000). The scheme of the reaction is

[0024] Elemental carbon to which an azo compound is attached may have a variety of forms including graphite powder, glassy carbon, carbon fibres, carbon black or carbon paste, boron doped diamond and carbon epoxy. A further form of carbon, to which the invention may be applied, is the carbon nanotube (CNT) which was discovered in 1991. The structure of carbon nanotubes approximates to rolled-up sheets of graphite and can be formed as either single or multi-walled tubes. Single-walled carbon nanotubes (SWCNTs) constitute a single, hollow graphite tube. Multi-walled carbon nanotubes (MWCNTs) on the other hand consist of several concentric tubes fitted one inside the other. A further form of carbon which may be derivatized is graphene which may be in the form of graphene flakes and after derivatization these may be immobilized on a conductive substrate.
The elemental carbon may be conductive and may be for use in an electrode. Forms of conducting carbon used in electrode manufacture are glassy carbon, carbon fibres, carbon black, various forms of graphite, carbon paste, boron doped diamond and carbon epoxy. Carbon nanotubes may also be used as part of an electrode and may be immobilized on the surface of another form of conducting carbon.

Another approach begins by reaction of elemental carbon to introduce functional groups. One possibility is to treat the elemental carbon with strong oxidizing acid, for instance by placing the carbon in a solution containing a mixture of H₂SO₄ (3M) and HNO₃ (1M) for a period of 24 hours as described by Liu et al Science vol280 page 1253 (1998). This treatment produces surface bound carboxylic acid groups at the edge plane defects of the elemental carbon surface. Carbon which has been modified with acidic groups can then be reacted with an azo compound of general formula

\[ X_2-R_1-N=N-R_2 \]

where \( X_2 \) is a functional group which may be an amino group which becomes converted to an amide on reaction with an acidic group on the elemental carbon. One specific possibility is reaction with phenylazoaniline, thus:

![Diagram of reaction between carboxylic acid and phenylazoaniline](image)

A further approach for attaching an azo compound to elemental carbon is shown below. This begins by reacting the elemental carbon with 4-Benzoylamino-2,5-dimethoxybenzenediazonium chloride which is the dye “fast blue RR salt” in the same manner as for attachment of fast black K above. The resulting derivatised carbon is then heated to break the amide linkage resulting in the formation of 1,4-dimethoxyaniline derivatised carbon. This newly formed derivatised carbon is then reacted with an azo compound having a carboxylic acid group such as 5-(4-nitrophenylazo)salicylic acid which is the dye alizarin yellow R, also termed Mordant Orange 1.
Decomposition of an azo compound which has been attached to elemental carbon may be brought about with ultraviolet light, heat (which may be supplied as microwave energy) or energy supplied as ultrasound. The decomposition is brought about in the presence of an olefinic compound which can react with the radicals generated by decomposition at the azo group.
Possible olefinic compounds include vinyl ferrocene, vinyl anthracene and vinylanthraquinone. These can be incorporated into a polymer chain extending from the residue of the decomposed azo compound attached to elemental carbon as illustrated by the following scheme in which a poly(vinylferrocene) chain attached to carbon is created:

The procedures discussed above can be used to provide polymer chains which incorporate redox active groups and are attached to elemental carbon, which may be in a particulate form. The particulate carbon may be immobilized on an electrode and used in electrochemistry. Such an electrode may be used in an electrochemical sensor.

Elaborating further on the nature and function of redox-active groups which may be included in a polymer chain and thereby immobilized on an electrode, there are a number of redox active groups which are sensitive to pH, so that when observed by voltammetry, the voltage at which there is maximum current flow (ie the voltage of the peak of the voltammetric wave) is dependent on pH. An electrode with such a group attached to it can be used as a pH sensor.
[0032] Aromatic quinones which have such redox reactions are disclosed in WO2005/066618. The use of aromatic nitrogen compounds, which undergo irreversible reduction to hydroxylamine and thereafter undergo pH dependent reversible oxidation from hydroxylamine to nitroso compounds are disclosed in WO2010/001082.

[0033] In contrast, the oxidative and reductive peaks for ferrocene are substantially independent of applied voltage, so an electrode with a ferrocene group immobilised on it can serve as a reference when measuring pH, as mentioned in WO2005/066618.

[0034] An electrochemical reaction of a redox active group may couple to a reaction of an analyte species of interest and act as a catalyst for its reaction. This analyte species can be determined by means of an amperometric measurement to measure any increase in the electric current which flows when the species is present: the magnitude of the increase in current provides a measure of the concentration of the species of interest.

[0035] One instance of this is determination of oxygen. If oxygen is present in an aqueous electrolyte, the electrochemical reduction of a quinone can couple to the reduction of that oxygen to water. The quinone then serves as a catalyst in the electrochemical reduction of oxygen and the concentration of oxygen can be determined from the increase in electric current compared with the current which flows in the absence of oxygen. The reactions can be represented as

\[
\begin{align*}
AQ + 2H_2O + 2e^- &\rightarrow AQH_2 + 2OH^- \\
AQH_2 + \frac{1}{2}O_2 &\rightarrow AQ + H_2O
\end{align*}
\]

[0036] Under alkaline conditions, oxygen can be converted to hydrogen peroxide, the second step of the above reaction scheme then becoming:

\[
AQH_2 + O_2 \rightarrow AQ + H_2O_2
\]

[0037] If the electrochemical sensor is in contact with a non-aqueous liquid such as acetonitrile, the electrochemical reduction of a quinone can again couple to the reduction of oxygen, but the oxygen is reduced to superoxide, thus:
AQ + e⁻ → AQ⁻⁻
AQ⁻⁻ + O₂ → AQ + O₂⁻⁻

The redox reaction of ferrocene can couple to the oxidation of hydrogen sulphide to sulphur, so that the concentration of hydrogen sulphide can be determined from the increase in current compared to the current which flows in the absence of hydrogen sulphide. The use of ferrocene in the determination of hydrogen sulfide has been mentioned in WO2004/063743 and WO2010/001082. The reactions can be written as

Fc → Fc⁺ + e⁻
Fc⁺ + HS⁻ → Fc + S + H⁺

Ferrocene compounds can also be used in the determination of other analytes, as mentioned by Lawrence in Electroanalysis vol 18 pp1658-1663 (2006).

Thus, electrodes carrying carbon to which polymer chains have been attached, where the polymer chains include quinone groups, or include ferrocene groups, can be used as electrochemical sensors. Measurement of pH may be carried out using polymer chains which include a quinone. Polymer chains which include ferrocene groups may serve as a reference and it is possible that a polymer chain could be copolymeric, incorporating both quinone and ferrocene groups.

Electrodes carrying carbon to which are attached polymer chains containing ferrocene groups may be used for measurement of H₂S or thiols, in analogous manner to use of ferrocene in documents above.

Particulate carbon may be deposited on an electrode surface, for instance by evaporation of a suspension of the particles in a volatile solvent. Another possibility is to pack such derivatized particulate carbon into a recessed cavity in an electrode. The empty recess might be filled with the derivatized carbon powder which would be mechanically compacted. The resulting void in the recess would then be refilled and compacted again. This would be repeated several times until the recess is full. The material would be pressed such that the carbon particles are packed into a dense matrix.
A further possibility is that derivatized carbon particles may be screen printed onto a substrate which may be an insulating material. Carbon particles derivatized with a second redox active compound which is insensitive to analyte/ pH and which acts as a reference may be screen printed onto the same or another substrate. The particulate carbon may be combined with a binding material, which may be a conductive binding material such as a graphite-containing ink, and then screen printed onto the electrode. An external reference electrode may possibly be used with such a screen-printed electrode. One possible external reference is a silver/silver-chloride electrode. A screen-printed electrode may possibly carry such an external reference electrode on a portion of an insulating substrate. Particulate carbon derivatized with a redox active compound, mixed with a binder may also be applied to a working electrode by an inkjet-type process as an alternative to screen printing.

A screen-printed electrode may possibly be covered with a polymer film or coating. The polymer film or coating may, among other things, make the electrode more robust, prevent external adverse effects of the redox active compound(s), and allow for sterilization of the electrode without affecting the functionality of the electrode.

Some embodiments of electrochemical sensor in accordance with this invention include a temperature probe for measuring a temperature of the fluid, wherein the temperature measurement may be used to calibrate the electrochemical sensor.

An electrochemical sensor could be incorporated into a wide variety of tools and equipment. Possibilities include use in tools which are located permanently downhole, use in tools which are conveyed downhole, for instance at the head of coiled tubing or by drillpipe or on a wireline, use in underground, undersea or surface pipeline equipment to monitor liquid flowing in the pipeline, and use in a wide variety of process plant at the Earth’s surface, including use in water treatment.

Fig 1 diagrammatically illustrates apparatus which may be used in pH measurement. A working electrode 32 has carbon particles with polymer chains incorporating a pH-sensitive redox active groups such as anthaquinone groups attached to the surface of the carbon particles. A reference electrode 34 has carbon particles with polymer chains incorporating a ferrocene compound attached to the surface of the carbon particles.
There is also counter electrode 36. All the electrodes are connected by cable or other wiring indicated at 38 to a potentiostat 62 or other control unit which provides electric power and measurement. This arrangement avoids a need for a standard reference electrode such as a standard calomel electrode. However, another possibility would be to provide such a standard electrode, as shown by broken lines at 35 and possibly dispense with the electrode 34 using ferrocene groups. The various electrodes are immersed in or otherwise exposed to fluid whose pH is to be measured.

Measuring apparatus may comprise electrode(s) which utilize derivatized graphite and also a control unit providing both electrical power and measurement. A control unit such as 62 may comprise a power supply, voltage supply, potentiostat and/or the like for applying an electrical potential to the working electrode 32 and a detector, such as a voltmeter, a potentiometer, ammeter, resistometer or a circuit for measuring voltage and/or current and converting to a digital output, for measuring a potential between the working electrode 32 and the counter electrode 36 and/or potential between the working electrode 32 and the reference electrode 34 or 35 and for measuring a current flowing between the working electrode 32 and the counter electrode 36 (where the current flow will change as a result of the oxidation/reduction of a redox species). The control unit may in particular be a potentiostat. Suitable potentiostats are available from Eco Chemie BV, Utrecht, Netherlands.

A control unit 62 which is a potentiostat may sweep a voltage difference across the electrodes and carry out voltammetry so that, for example, linear sweep voltammetry, cyclic voltammetry, or square wave voltammetry may be used to obtain measurements of the analyte using the electrochemical sensor. The control unit 62 may include signal processing electronics.

Fig 2 shows a possible variation. A conductive paste containing carbon particles with polymer chains incorporating pH sensitive redox groups is printed on one area 46 of an insulating substrate 45 to provide an electrode 32. A second conductive paste containing carbon particles with polymer chains incorporating pH insensitive ferrocene groups is printed on an area 47 as a reference electrode. The two areas 46, 47 are connected together and connected to a cable 38 leading to a control unit by conductive tracks 48 on the substrate 45.
[0051] The electrodes 46, 47 may be screen printed using stencil designs to delineate the areas of the electrode. To form the working electrode, the derivatized carbon particles may be mixed within a carbon-graphite ink and deposited on area 46 of a substrate 45 which may comprise polyester or other insulating polymer. To form the reference electrode a carbon-graphite ink may be deposited on area 47 of the substrate, then a reference electrode material, such as silver/silver-chloride may be deposited as a paste onto the area of deposited carbon. In some embodiments of electrode, a polymer coating may be applied on top of deposited materials (including deposited derivatized carbon). A polymer coating which is permeable to water and other small molecules may prevent derivatized carbon particles from becoming detached from the working electrode, but still allow for interactions between an analyte and redox active groups on the working electrode. For example a polymer coating may comprise a polysulphone polymer or a polystyrene polymer.

[0052] Fig 3 shows a possible geometric configuration or layout for the surface 40 of a sensor which is exposed to the fluid to be tested, which may, merely by way of example be a wellbore fluid. The surface includes a disk shaped working electrode 32, a second electrode 43, which may be a electrode using ferrocene groups or an external reference electrode such as a silver/silver chloride electrode, and a counter electrode 36.

[0053] A schematic of a microsensor 50 incorporating such a surface is shown in Fig 4. The body 51 of the sensor is fixed into the end section of an opening 52. The body carries the electrode surface 511 and contacts 512 that provide connection points to voltage supply and measurement through a small channel 521 at the bottom of the opening 52. A sealing ring 513 protects the contact points and electronics from the fluid to be tested that passes under operation conditions through the sample channel 53.

[0054] Fig 5 shows a substrate 45 carrying a working electrode on an area 46 and a reference electrode on an area 47. These are not connected together but are connected by separate conductors within a cable 64 to a potentiostat 62 which may be a handheld device. After deposition of electrode materials onto the substrate 45, the substrate and deposited materials were coated with a permeable polymer layer indicated by reference 66. Methods to deposit the polymer in a generally uniform layer include spin coating, dip coating and application using solvent evaporation. One end of the coated substrate has an impermeable covering 68 which merges with the sheath 69 of the cable 64.
One application of an electrochemical sensor may lie in the monitoring of underground bodies of water for the purposes of resource management. Using monitoring wells drilled into the aquifers, one or more sensors may be deployed on a cable from the surface. The sensor(s) may be in place for a relatively short duration (as part of a logging operation) or a longer term (as part of a monitoring application). Fig 6 illustrates a tool for investigating subterranean water. This tool has a cylindrical enclosure 72 which is suspended from a cable 75. A sensor unit such as the sensor 50 shown in Fig 4 is accommodated within the enclosure 72 so that its surface 40 is exposed to the subterranean water. The tool also encloses also encloses a unit 62 for supplying voltage to the electrodes of the sensor 50, measuring the current which flows and transmitting the results to the surface.

The sensor may be a pH sensor. Suspending such a device on a cable within producing wells may provide information on produced water quality. Also, the pH sensor may be deployed in injection wells, e.g. when water is injected into an aquifer for later retrieval, where pH may be used to monitor the quality of the water being injected or retrieved.

Fig 7 shows a formation testing apparatus 810 held on a wireline 812 within a wellbore 814. The apparatus 810 is a well-known modular dynamic tester (MDT, Trade Mark of Schlumberger) as described in the co-owned U.S. Pat. No. 3,859,851 to Urbanosky, U.S. Pat. No. 3,780,575 to Urbanosky and U.S. Pat. No. 4,994,671 to Safinya et al., with this known tester being modified by introduction of an electrochemical analyzing sensor 816 substantially similar to sensor 50 of Fig 4. The modular dynamics tester comprises body 820 approximately 30m long and containing a main flowline bus or conduit 822. The analysing tool 816 communicates with the flowline 822 via opening 817. In addition to the novel sensor system 816, the testing apparatus comprises an optical fluid analyser 830 within the lower part of the flowline 822. The flow through the flowline 822 is driven by means of a pump 832 located towards the upper end of the flowline 822. Hydraulic arms 834 and counterarms 835 are attached external to the body 820 and carry a sample probe tip 836 for sampling fluid. The base of the probing tip 836 is isolated from the wellbore 814 by an o-ring 840, or other sealing devices, e.g. packers.

Before completion of a well, the modular dynamics tester is lowered into the well on the wireline 812. After reaching a target depth, i.e., the layer 842 of the formation which
is to be sampled, the hydraulic arms 834 are extended to engage the sample probe tip 836
with the formation. The o-ring 840 at the base of the sample probe 836 forms a seal between
the side of the wellbore 844 and the formation 842 into which the probe 836 is inserted and
prevents the sample probe 836 from acquiring fluid directly from the borehole 814.

[0059] Once the sample probe 836 is inserted into the formation 842, an electrical signal
is passed down the wireline 812 from the surface so as to start the pump 832 and the sensor
systems 816 and 830 to begin sampling of a sample of fluid from the formation 842. The
electrochemical sensor 816 can then measure the pH or concentration of another analyte such
as hydrogen sulfide in the formation effluent.

[0060] While the preceding uses of an electrochemical sensor are in the hydrocarbon and
water industries, embodiments of electrochemical sensor incorporating derivatized carbon
may be used for detecting an analyte in a whole host of industries, including food processing,
pharmaceutical, medical, water management and treatment, and biochemical industries, as
well as research laboratories. A polymer coating may prevent escape of derivatized carbon
particles from an electrode into the fluid around it, but still allow for interactions between an
analyte and one or more redox active compounds on the electrode.
CLAIMS

1. A process for chemical modification of the surface of elemental carbon comprising attaching a compound with an azo group to the elemental carbon and then decomposing the azo group in the presence of one or more compounds with an olefinic group so that decomposition of the azo group forms radicals attached to the carbon surface and a said radical forms a covalent bond to a said olefinic group.

2. A process according to claim 1 wherein the compound with an azo group has a formula

\[ \text{R}_1\text{N=N-R}_2 \]

where the groups \( \text{R}_1 \) and \( \text{R}_2 \) are aromatic groups.

3. A process according to claim 1 wherein the compound with an azo group has a formula

\[ \text{X-R}_1\text{N=N-R}_2 \]

where \( \text{X} \) is a diazonium group.

4. A process according to claim 1 claim 2 or claim 3 wherein the olefinic compound comprises vinylferrocene.

5. A process according to claim 1 claim 2 or claim 3 wherein the olefinic compound comprises vinylanthracene or vinylanthraquinone.

6. A process according to claim 1 or any one of claims 2 to 5 wherein the elemental carbon is in particulate form and the process further comprises immobilizing the derivatized elemental carbon on an electrode.
7. Elemental carbon substituted by the process of claim 1 or any one of claim 2 to 5.

8. Use of derivatized elemental carbon according to claim 7 for measuring the concentration of an analyte in a liquid.

9. Use of derivatized elemental carbon according to claim 7 for measuring the pH of water or other aqueous liquid.
Application No: GB1122058.9
Claims searched: 1-6

**Examiner:** Nicholas Mole
**Date of search:** 25 April 2012

### Patents Act 1977: Search Report under Section 17

**Documents considered to be relevant:**

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<th>Category</th>
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- **&** Member of the same patent family
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### Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC:

Worldwide search of patent documents classified in the following areas of the IPC

- **B01J:** B82B; B82Y; C01B; C25B; D01F; H01G

The following online and other databases have been used in the preparation of this search report:

- WPI
- EPODOC
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