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(71) Applicant: **COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH** [IN/IN]; Anusandhan Bhawan, 2 Rafi Marg, New Delhi 110 001 (IN).

(72) Inventors: **KARIM, Adnan, Asad**; Institute of Minerals and Materials Technology, Odisha 751013 (IN). **KUMAR, Manish**; Institute of Minerals and Materials Technology, Odisha 751013 (IN). **SINGH, Saroj, Kumar**; Institute of Minerals and Materials Technology, Odisha 751013 (IN). **PANDA, Chitta, Ranjan**; Institute of Minerals and Materials Technology, Odisha 751013 (IN). **MISHRA, Barada, Kanta**; Institute of Minerals and Materials Technology, Odisha 751013 (IN).

(74) Agent: **KASTURIRANGAN, Srihari, Saragur** et al.; K & S PARTNERS, Intellectual Property Attorneys, 109, Sector 44, Gurgaon, National Capital Region 122003 (IN).

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(54) Title: A METHOD FOR PRODUCTION OF POTASH ENRICHED BIOCHAR FROM WASTE BIOMASS

(57) Abstract: The present invention discloses a process for the production of potash enriched biochar. A potassium rich waste biomass preferably banana peduncle undergoes thermal treatment in an extended arc thermal plasma reactor for fixed period of time to produce potash enriched biochar. The potash rich biochar was produced in such a manner that lead to the significant enrichment of available potassium for supporting soil fertility. Laboratory grade plasma forming gases such as argon, ammonia and oxygen are used in the reactor. The prepared potash enriched biochar are porous, alkaline in nature and mainly comprises of kalicinite ($KHCO_3$) mineral and disordered graphitic structure. Kalicinite mineral in potash enriched biochar is a source of readily available potassium (water soluble and exchangeable potassium).

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"A METHOD FOR PRODUCTION OF POTASH ENRICHED BIOCHAR FROM WASTE BIOMASS"

FIELD OF THE INVENTION

The present invention relates to a method for production of potash enriched biochar from waste biomass. Particularly, the present invention relates to a field of potash enrich biochar production. More particularly, the present invention is directed to an innovative process for production of potash enriched biochar from banana peduncle waste biomass by using the extended arc thermal plasma system. Potash enriched biochar will be an alternative substitute for K-fertilizers towards maintaining soil fertility.

BACK GROUND AND PRIOR ART OF THE INVENTION

Biomass is abundant, easily available and valuable renewable resource, which supports life system on earth. But this important resource is not utilized to its full extent, due to which bio-waste such as agricultural wastes, weeds, and plant wastes can be found all around us. These wastes face disposal problem and cause environmental nuisance, pollution, and spread of pathogenic diseases. Plant residues being organic in nature are a rich source of macro and micronutrients and can be recycled to prevent their disposal in the environment, thus sustaining the balance between economic development and environmental protection. Traditional methods such as ashing and composting of waste biomass are being practiced for centuries for nutrient recycling and its utilization as a soil amendment. But composting and ashing of biomass releases greenhouse gases into the atmosphere contributing environmental pollution and global warming. Also the major limitation towards utilizing the agricultural biomass waste like farm yard manure, composted manures are due to its bulky nature, low nutrient contents, long time and large space required for composting. This organic manure sometime also adds to some unwanted problems of plant pathogen and weeds.

Recent advancement in research has introduced a novel concept of conversion of biomass into biochar. The biochar is the solid product of biomass carbonization and contains highly stable recalcitrant aromatic carbon. Its characteristics mainly depend on the chemical composition of biomass/feedstock and production method. The biochar has high nutrient retention capacity, water holding capacity, improved cation exchange property and porosity (Enders et al. 2012). Therefore, it is a benign material which enhances overall soil productivity.

Because of these aforesaid biochar characteristics, several inventions have been focused on a method for production of biochar based fertilizers. In these inventions, different nutrient rich substances, chemical fertilizers such as potassium phosphate, potassium sulphate, potassium permanganate and/or complex microbial inoculants are used as raw material to prepare biochar based fertilizers. Some examples of these inventions are disclosed in CN104876679 (coarse biochar slow release fertilizer), CN105085021 (wheat straw biochar fertilizer), CN104446691 (Micro algae-biochar composite bio-fertilizer), and CN104529636 (Biochar-based slow-release nitrogen fertilizer). These biochar based fertilizers possess several advantages such as reduce fertilizer usage, reduction of the loss of nutrients, enhancing soil health, quality improvement of agricultural products, and facilitation of the benign development of the agricultural ecologic system. But, the limitations of these inventions are, (a) the method is not focused on enrichment of inherent nutrient of biochar and it is mainly used as a carrier through which adsorbed fertilizer nutrients can be efficiently released in soil, and,
(b) use of chemical fertilizers such as potassium phosphate, potassium sulphate, potassium permanganate limits the cost-effectiveness of biochar based fertilizers. Under these backdrops, our intention and priority are to produce nutrient enriched biochar from abundantly available nutrient rich waste biomass without using any chemical additives. The enriched biochar can reduce the dependence on chemical fertilizers.

In WO2014189433 entitled "production of nutrient rich biochar from a residual material, which revealed the process comprises of a residual product material comprising, at least, phosphorous; then performing a thermal treatment of the residual product material at a temperature of 800 – 1100°C in at least a low oxygen containing environment for the separation

of volatiles in a stream probably containing at least cadmium (Cd). The process also included volatiles containing cadmium separated in the thermal treatment directed to combustion in which at least 90% of cadmium is separated in ash residue during a subsequent flue gas cleaning after the actual combustion. This invention has certain limitations: (a) need use of chemical additives and different steps to clean up the toxic volatiles generated due to pyrolysis of residual material such as sludge and digestion residues, (b) generates ash residue as a waste product having high concentration of heavy metals, which needs further management due to risk of environmental pollution and, (c) final nutrient rich biochar product might not be 100% free from toxic heavy metals and hence, its acceptance for application is questionable due to factors such as soil contamination and biomagnification.

Thus, the present invention is directed to a process for the production of nutrient enriched biochar to eliminate some of the aforesaid inefficiencies inherent in the prior art. We have utilized thermal plasma process and potassium rich banana peduncle waste biomass for the production of potash enriched biochar. The present invention is new because in prior art no attempts have been made so far to utilize banana peduncle waste biomass and thermal plasma process for the production of potash enriched biochar. Banana ranks first in global fruit production i.e. 106.7 million tons (FAO, 2013). India is the largest producer of banana in the entire world, produces around 29.8 million tons (Indian Horticulture Database, 2014). This information reflects and substantiates the economic significance of banana peduncle waste biomass availability for industrial production of potash enriched biochar.

OBJECTIVES OF THE INVENTION

(i) The main object of the invention is to provide a process to produce potash enriched biochar through a relatively simple and facile method which obviates the aforesaid limitations.

(ii) Another object of the invention is to produce potash enriched biochar by a novel process.

(iii) Another object of the invention is to produce potash enriched biochar from potassium rich waste biomass by a thermal plasma process.

(iv) Another object of the invention is to provide a process for producing potash enriched biochar using different plasma forming gases such as argon, ammonia and oxygen in a thermal plasma reactor.

(v) Yet another object of the invention is to enrich plant available potassium in biochar to make it useful for agricultural applications.

SUMMARY OF THE INVENTION

Accordingly the present invention provides a process for the production of potash enriched biochar by the thermal treatment of dried banana peduncle biomass for fixed period of time such as five to seven minutes in an extended arc thermal plasma reactor.

In one embodiment of the invention, any potassium rich biomass and combination of one, two or many of them can be used for the production of potash enriched biochar.

In another embodiment of the invention, the extended arc thermal plasma reactor comprises of two graphite electrodes and hearth.

In another embodiment of the invention, the gases such as oxygen, ammonia or argon but not limited to these gases are used for the generation of plasma in the extended arc thermal plasma reactor.

In yet another embodiment of the invention, the plasma gas used is of laboratory grade.

In yet another embodiment of the invention, the parameters such as gas flow rate, current, voltage, and time are regulated during the thermal treatment of banana peduncle biomass in extended arc thermal plasma system for production of potash enriched biochar.

In yet another embodiment of present invention, the produced potash enriched biochar contains readily plant available potassium and can be utilized to supplement fertilizer for agricultural application.

BRIEF DESCRIPTION OF THE DRAWING

In the drawings accompanying the specification, FIG. 1 represents a schematic of the plasma hearth, in accordance with the present invention for the preparation of potash enriched biochar.

In the drawings accompanying the specification, FIG. II illustrates the van krevelen diagram of potash enriched biochars.

In the drawings accompanying the specification, FIG. III illustrates the x-ray diffraction spectra of potash enriched biochars.

In the drawings accompanying the specification, FIG. IV illustrates the infrared spectra of potash enriched biochars.

In the drawings accompanying the specification, FIG. V illustrates the Raman spectra of potash enriched biochars.

In the drawings accompanying the specification, FIG. VI illustrates the nitrogen adsorption-desorption isotherm curve of potash enriched biochars.

DETAILED DESCRIPTION OF THE INVENTION

This invention is not limited to the specific conditions or parameters of the embodiments described herein, and that the terminology used herein for the purpose of describing particular embodiments by way of example only. In addition, any methods described herein are not intended to be limited to the sequence of steps described but can be carried out in other sequences, unless expressly stated otherwise herein. The outlook of the present invention is illustrated in FIG. 1 of the drawing.

In an embodiment of the present invention, banana peduncle waste biomass undergoes thermal treatment in an extended arc thermal plasma reactor for the production of potash enriched biochar.

In an embodiment of the present invention, potassium rich waste biomass such as banana peduncle is selected for production of potash enriched biochar because of its wide availability and high biomass. However, the present invention is not limited to banana peduncle waste biomass and can be any potassium rich biomass and/or combination of one, two or many of them for the production of potash enriched biochar.

In an embodiment of the present invention, banana peduncle biomass is chopped in pieces, sundried or oven dried in order to remove water and moisture from it. Then stored in an air tight container for its prior use in an extended arc thermal plasma system for production of potash enriched biochar.

In an embodiment of the present invention, any process or method can be employed for preparing pieces and/or powder and drying of banana peduncle biomass.

In another embodiment of the present invention, production of potash rich biochar material through extended/expanded thermal plasma reactor has several advantages such as simple procedure, very less production time, and scope for utilization of produced syngas.

In another embodiment of the present invention, the extended/expanded plasma reactor used for potash rich biochar production has following constituents. Two graphite electrodes [1, 7] are arranged in the vertical configuration in the pot type extended/expanded arc plasma reactor. The graphite crucible [5] is used as the hearth of the reactor and is connected to the bottom graphite electrode [7]. The crucible assembly constitutes the anode. The top graphite electrode [1], the cathode is having an axial hole to pass the plasma forming gas. The bottom electrode [1] and the crucible [5] is kept fixed and the formation and stabilization of the extended arc plasma are done by the movement of the top electrode [1], which is actuated by a rack and pinion mechanism.

In another embodiment of the present invention, the banana peduncle biomass undergoes thermal treatment in the extended arc thermal plasma reactor for production of potash enriched

biochar by following steps. Initially, both the electrodes of the reactor were kept in contact with each other, and then the crucible was partially filled with the biomass [3]. A graphite lid [2] with a central hole is kept as a cover on the graphite crucible. The plasma forming gas of laboratory grade was injected to the reactants present in the graphite crucible [5] through the axial hole of the top electrode. Plasma forming gas of the electrodes was regulated. As soon as the power to the reactor was switched on, the top electrode was slowly pulled up after striking the arc to form extended/expanded arc plasma in the hearth. The arc current and voltage were regulated during the course of the experiment. After fixed period of time, the power of the reactor was switched off and the gas flow rate was minimized but continued till the cooling of the reactor. Then the prepared potash enriched biochar samples were collected from the crucible and stored in air tight container. Experiments were carried out in the expected temperature range of 1500°C – 1800°C. The plasma forming gas and the graphite lid [2] on the top of the graphite hearth [5] helps in maintaining the desired atmosphere inside the hearth.

In another embodiment of the present invention, the plasma forming gas such as argon, ammonia or oxygen can be used in extended arc plasma reactor for the preparation of potash enriched biochar. All the gases used were of laboratory grade. However, the present invention is not limited to these gases and any other plasma forming gas or combination of one, two or many of them might be used in the extended/expanded arc plasma reactor.

In another embodiment of the present invention, potash enriched biochar is produced in the extended arc thermal plasma reactor at a very high elevated temperature and heating rate. Under this condition, banana peduncle biomass decomposes thermolytically via depolymerization, volatilization and cracking process at a very faster rate and the complex organic compounds of biomass converted into simple molecules such as H_2, CO, and CO_2. Tar formation under aforesaid conditions might significantly reduce due to the cracking effects of the highly active plasma environment with a variety of electron, ion, atom, and activated molecule species.

In another exemplary embodiment of the present invention, prepared potash enriched biochar comprises of kalicinite (potassium bicarbonate) mineral.

In another exemplary embodiment of the present invention, the prepared potash enriched biochar are alkaline in nature, mainly macroporous or mesoporous and contains disordered graphitic structure.

In another exemplary embodiment of the present invention, the prepared potash rich biochar would be most suitable for its application in acidic soils because it can act both as a liming agent and supply plant available potassium.

In another embodiment of the present invention, the parameters such as selection of potassium rich waste biomass, the size of biomass pieces, selection of plasma forming gas, the flow rate of plasma forming gas, biomass residence time and power input can be varied to tune up the characteristics of potash enriched biochar material.

In a preferred embodiment, the present invention discloses a process for production of potash enriched biochar from waste biomass comprising the steps:

a. providing a potassium rich ligno-cellulosic waste biomass;

b. washing the biomass as obtained from step (a) and chopping it into pieces;

c. preparing dried biomass by air drying the chopped pieces of biomass as obtained from step (b), followed by oven drying at a temperature above 40 °C for a time period of 6 to 72 hrs.

d. characterised in thermally treating the dried biomass as obtained from step (c) in a plasma reactor having graphite electrodes by feeding the pieces of dried biomass obtained in step (c) into the hearth of the plasma reactor;

e. injecting the plasma generating gas with a flow rate of at least 1 litre/min into the hearth of the reactor;

f. operating the reactor with an arc voltage 30 – 90 V and an arc current 100 – 500 Amp.

g. heat treating the dried biomass in the plasma reactor of at least 1000°C and above for a time period of at least 1 minute in the hearth of the reactor;

h. cooling the product in the hearth with a continuous flow of gas till further charring ceases.

i. collecting the biochar from hearth obtained in step (h) after the reactor cools down to room temperature and processed to powder form to obtain potash enriched biochar.

In yet another embodiment, the process utilizes a potassium rich biomass, which is selected from the group of waste biomass comprising of carbohydrate polymers and lignin.

In a further embodiment, the process of the present invention utilizes the plasma forming gas used in the reactor, which is selected from the group comprising of Argon, Oxygen, Nitrogen, Ammonia, Carbon dioxide, Hydrogen, Air, Steam etc.

In yet another embodiment, the invention relates to a potash enriched biochar obtained by the process comprising the steps of :

a) providing a potassium rich ligno-cellulosic waste biomass;

b) washing the biomass as obtained from step (a) and chopping it into pieces;

c) preparing dried biomass by air drying the chopped pieces of biomass as obtained from step (b), followed by oven drying at a temperature above 40 °C for a time period of 6 to 72 hrs.

d) characterised in thermally treating the dried biomass as obtained from step (c) in a plasma reactor having graphite electrodes by feeding the pieces of dried biomass obtained in step (c) into the hearth of the plasma reactor;

e) injecting the plasma generating gas with a flow rate of at least 1 litre/min into the hearth of the reactor;

f) operating the reactor with an arc voltage 30 – 90 V and an arc current 100 – 500 A.

g) heat treating the dried biomass in the plasma reactor of at least 1000°C and above for a time period of at least 1 minute in the hearth of the reactor;

h) cooling the product in the hearth with a continuous flow of gas till further charring ceases.

i) collecting the biochar from hearth obtained in step (h) after the reactor cools down to room temperature and processed to powder form to obtain potash enriched biochar.

In another important embodiment, the potash enriched biochar of the present invention is utilizable in agricultural applications.

In another important embodiment, the potash enriched biochar of the present invention is utilizable for increasing soil productivity and carbon sequestration.

EXAMPLES

The following examples are given by way of illustration of the present invention and, therefore, should not be construed to limit the scope of the present invention.

Example 1

Here in, to illustrate the present invention, banana peduncle (*Musa species*) waste biomass is collected from different fruit vendors of local market, Bhubaneswar, Odisha. Then, the biomass thoroughly washed with tap and distilled water, manually chopped in pieces (20mm to 50mm length and 0.2 to 10 mm width), air dried and oven dried at nearly 80°C for 24 hrs. The oven dried banana peduncle was weighed and then fed to the hearth for its thermal treatment in the plasma reactor. Initially, both the electrodes were kept in contact with each other, and then the hearth was partially filled with the biomass. A graphite lid with a central hole was kept as a cover on the graphite crucible. The Plasma forming gas, argon was introduced through the axial hole of the top electrode. As soon as the power to the reactor was switched on, the top electrode was slowly pulled up after striking the arc to form extended/expanded arc plasma in the hearth. After fixed period of time, the power of the reactor was switched off and the gas flow rate was decreased but continued for few minutes till the completion of charring process and cooling of the reactor. The arc current and voltage were regulated during the course of the experiment. The experimental conditions for producing potash enriched biochar sample are as follows:

Weight of Banana peduncle biomass - 100 g

Argon gas flow rate - 1 L/min

Arc Current - 280 A

Load voltage - 50 V

Reaction Time - 8 min

Example 2

The experiment procedure was carried out as described in Example-1, for the preparation of potash rich biochar. But, banana peduncle biomass pieces of size ranges 15 mm to 40 mm length and 0.2 to 8 mm width was used and the plasma forming gas was changed to ammonia. The experimental conditions are as follows:

Weight of Banana peduncle biomass - 100 g

Ammonia gas flow rate - 1 L/min

Arc Current - 310 A

Load voltage - 60 V

Time - 7 min

Example 3

The experiment procedure was carried out as described in Example – 1. But, banana peduncle biomass of size ranges 10mm to 30mm length and 0.2 to 8 mm width was used and the plasma forming gas was oxygen. The experimental conditions are as follows:

Weight of Banana peduncle biomass - 100 g

Oxygen gas flow rate - 1 L/min

Arc Current - 300 A

Load voltage - 40 V

Time - 5 min

Example 4

In order to simplify the description of the example of the potash enriched biochar, samples prepared with argon, ammonia and oxygen plasma gas (described in example-1, 2 and 3) were abbreviatory named as ArBPB, AmBPB, and OxBPB respectively and used herewith in tables, figures, and following examples.

The biochar yield (%) was calculated by dividing the weight of biochar to oven dried weight of biomass multiplied by 100. For pH measurement, one gram of biochar was put in a 100 ml of distilled water, stirred for 1 hour and measured using a pH meter. The proximate analysis was performed to measure moisture, ash, volatile matter, and fixed carbon content of potash enriched biochar samples. These parameters were determined by following American Society for Testing and Materials (ASTM) method D514220 using LECO Thermogravimetric analyzer (TGA701, LECO, St. Joseph, MI) on an air dried basis. Elemental composition (CHNO) of potash enriched biochar samples were determined by dry combustion using Perkin-Elmer 2400 Series II CHN analyzer (Perkin-Elmer, Shelton, CT). Total O was derived by subtraction according to the ASTM method as follows:

O (% w/w) = 100 - ash (% w/w) - C (% w/w) - N (% w/w) - H (% w/w)

Table-1 presents the biochar yield, pH, proximate and elemental properties of produced potash enriched biochar. The pH values of 8.3 to 8.6 shows the alkaline nature of potash enriched biochar and its feasibility to be used as theliming agent. The fixed carbon (5.03 - 14.33 %) represents the highly stable aromatic organic carbon in potash enriched biochar. ArBPB and AmBPB showed relatively less fixed carbon content than OxBPB. It indicates lesser stable aromatic carbon content in ArBPB and AmBPB than OxBPB. The high ash content (54.26 - 57.37 %) indicates the enrichment of inorganic components in biochar matrix mainly carbonates of potassium, as potassium can more resist decomposition at a higher temperature in comparison to calcium, sodium, magnesium and phosphorus etc. The calculated O/C and H/C atomic ratio (presented in table -1) represents the polarity and aromaticity of the potash enriched biochar. The lower O/C ratio and H/C ratio values indicate the higher carbon stability for OxBPB than ArBPB and AmBPB. The Van Krevelen diagram (FIG. 2) is also plotted from

O/C and H/C ratio to visualize the carbon stability of potash enriched biochar in the natural environment. The diagram reveals that the carbon stability of OxBPB resembles with lignite. Whereas, carbon stability of ArBPB and AmBPB resembles with biomass because of their high inorganic carbon content such as carbonates.

Table 1: Proximate and elemental analysis of biochar samples on air dried basis

Samples	Biochar Yield (%)	pH	Moisture (%)	Volatile Matter (%)	Ash (%)	Fixed Carbon (%)	C (%)	H (%)	N (%)	O (%)	H/C	O/C	C/N
ArBPB	21	8.6	18.05	19.55	57.37	5.03	17	2.4	0.09	23.04	1.67	1.01	207.36
AmBPB	20	8.4	15.95	20.31	57.21	6.53	20.3	1.87	0.51	19.96	1.09	0.73	46.44
OxBPB	15	8.3	11.33	20.08	54.26	14.33	29.3	1.28	0.07	15.02	0.52	0.38	438.06
Biomass	-	7.9	7.61	64.72	20.58	7.09	37.2	4.57	1.46	36.01	1.46	0.72	29.77

Example 5

The minerals present in potash enriched biochar samples were investigated through X-ray diffraction (XRD) analysis. The XRD patterns were recorded on a Xpert PRO, PANalytical X-ray diffractometer using Cu K alpha radiation with 2 theta value ranging from 10° to 80° at a rate of 5° min-1. FIG. 3 presents the XRD spectra showing the mineralogical composition of potash enriched biochar. The spectrum confirms that the potash enriched biochar comprises of mostly kalicinite ($KHCO_3$) and graphite minerals. The peaks position having 2 theta values (angle of diffraction) at about 24.2, 30.07, 31.3,34.09, 38.8, 40.6 and 44.4 reveal the presence of highly crystalline kalicinite as a dominant mineral phase in potash enriched biochar. The presence of graphite like structures in potash enriched biochar is confirmed by peaks having 2 theta values at about 26.7 (002 plane, high intensity) and 42.7 (100 plane). The XRD results also reveal that high ash and low fixed carbon content in potash enriched biochar are might be due to the formation of kalicinite (Potassium bicarbonate).

Example 6

The Fourier transform infrared (FTIR) analysis was performed to identify functional groups present in potash enriched biochar samples. The FTIR spectrums were recorded on a FTIR Spectrometer (PerkinElmer Spectrum GX) at 8 cm^{-1} resolution from 400 to 4000 cm^{-1} wavelength with 128 scans. FIG. 4 presents the infrared transmittance spectra of potash enriched biochar samples. The presence of absorption band above 3500 cm^{-1} in potash enriched biochar samples are due to hydroxyl stretching vibrations in COOH and/or intercalated water. The absorption bands at 3055, 2956 and 2894 cm^{-1} reveal the presence of unsaturated (C-H)n bonds. The last two bands can be assigned as Vas (asymmetric) and Vs (symmetric)stretching vibrations of CH_3 methyl groups. Due to its low intensity, the absorption bands of unsaturated C-H bonds generally appear as small peaks overlapping upon the strong band. The absorption band about 3055 cm^{-1} corresponds to the aromatic ring compound and indicates the presence of inorganic compounds. The small intensity band at 2315 cm^{-1} is from the CO_2 background. The peak at 2620 cm^{-1} can be ascribed to O-H stretching bond. The absorption band at 1655 cm^{-1} and a small intensity branched band at about 1456 cm^{-1} represent C=C and/or C=O stretching & aromatic skeletal vibrations of benzene ring respectively. weak absorption bands at 1868 cm^{-1} are also due to stretching vibrations of aromatic C=C functional groups of benzene stretching ring. The high intensity absorption bands at 1407 and 1133 cm^{-1} are due to OH bending vibrations of acid and C-OH vibrations respectively. The absorption band at 1008 cm^{-1} represents C-O stretching & deformation vibrations. The absorption bands between 900-850 cm^{-1} illustrate the substituted benzene ring with one or two isolated hydrogen atoms. The band at 830 cm^{-1} represents the presence of carbonate groups. The absorption peak at 698 cm^{-1} is assigned to the C=O in plane bending coupled with OH stretching modes. Thus, the FTIR spectra show the aromatic character of potash enriched biochar samples, comprising of hydroxyl groups, unsaturated methyl groups, substituted benzene rings and a carbonate group.

Example 7

Raman analysis was conducted to know about the amorphous or graphitic carbon present in potash enriched biochar samples. Raman spectra were recorded in Renishaw inVia Raman Microscope (Model H33197) system and excitation line were at 513 nm from with 100-2000

spectral range with 1 cm^{-1} spectral resolution. Fig-5 presents the Raman spectra, which reveals the presence of graphite with varying disorder in potash enriched biochar samples. The absorption peaks at 1341 and 1571 cm^{-1} are assigned to D-band and G- band of graphite respectively. The absorption peak at 1054 cm^{-1} corresponds to the presence of carbonate in potash enriched biochar samples. Thus, the results of Raman analysis are in good agreement with XRD results of potash enriched biochar samples.

Example 8

The surface area of potash enriched biochar samples were measured by nitrogen adsorption isotherms at 77 K using NOVA 2000 surface area analyzer (Quantachrome, Boynton Beach, FL). Before analysis, the samples were dried in the oven followed by degassing in a vacuum. Specific surface area was determined from adsorption isotherms using BET equation. The pore size was calculated using t-plots derived from the NOVA 2000 software. The pore volume was calculated using BJH method. The morphology of biochar samples was analyzed by scanning electron microscope (Hitachi, S-34500N). Table-2 presents the surface area, pore size, and pore volume of potash enriched biochar samples. The BET surface area of potash enriched biochar samples ranges from 3.67 to 54.99 m^2/g. The ArBPB is macro-porous as its average pore diameter is 89 nm, whereas AmBPB and OxBPB are mesoporous with average pore diameter of 18 and 11 nm respectively. The relation between pore diameter and surface area is also evident from the table-2. The OxBPB has lower pore diameter and the higher surface area in comparison to AmBPB and ArBPB. The ArBPB and AmBPB surface area are lower than OxBPB due to blockage of pores by more ash. FIG. 6 presents the nitrogen adsorption-desorption isotherm curve of potash enriched biochar samples. The hysteresis occurs in curve might be due to capillary condensation and presence of mesopores with relatively strong fluid-wall forces in samples. The isotherm curve also reveals the monolayer followed by multilayer nitrogen adsorption on potash enriched biochar samples. The hysteresis loop also indicates that the structure of pores present in biochar is slit shaped. The surface area and porosity of biochar may act as active sites for water and nutrient retention. Additionally, its pores may provide habitat for beneficial soil microorganisms and metabolized labile organic compounds for their growth.

Table 2: Surface area analysis of potash enriched biochar samples

Samples	BET Surface Area (m^2/g)	BJH cumulative volume of pores (cm^3/g)	Average pore width (nm)	BJH average pore diameter (nm)
ArBPB	3.67	0.034	8	89
AmBPB	27.58	0.02	2	18
OxBPB	54.99	0.054	2	11

Example 9

The enrichment of potassium in biochar and its efficacy for agricultural application as natural fertilizer was evaluated by measuring their available potassium content. Because plant mostly uptakes the available potassium (includes both water soluble and exchangeable form of potassium) from soil and/or fertilizers. The available and water soluble form of potassium was extracted (1:100 extraction ratio (w/v)) from potash enriched biochar/ raw biomass by mixing it in neutral 1 N ammonium acetate solution and distilled water respectively. Then the mixed solutions were shaked for 30 min at room temperature and filtered through Whatman 41 filter paper for potassium measurement using flame photometer (Systronics 128). Available potassium is the sum total of water soluble and exchangeable potassium. Hence, the exchangeable potassium was calculated by subtracting water soluble potassium from available potassium content. For accuracy of the result, the blank sample was also prepared and potassium was estimated in it. Water soluble, available and exchangeable potassium in potash enriched biochars are given in Table-3. The results showed the enrichment of available potassium content in biochar. The raw banana peduncle contains66.3 g/kg i.e. about ~ 6 % (weight basis) of available potassium. Thermal treatment of banana peduncle in plasma reactor under high temperature and heating rate fastly volatilizes many of its organic components (e.g., cellulose and hemicellulose). But the potassium resists volatilization and rapidly reacts with the gases such as carbon dioxide, carbon monoxide, and hydrogen to form minerals such as kalicinite. With relative to reaction time, the kalicinite mineral formation increases and thus eventually leads to enrichment in the concentration of potassium by mass of the product. The biochar produced with argon as a plasma generating gas contains 262.5 g/kg ~ 26% of available potassium. The above result estimates that compare to raw biomass, there is about 4.3 times

increase/enrichment of available potassium in biochar. The different plasma generating gas has a diverse effect on potassium enrichment of biochar. The potash rich biochar prepared with argon gas has relatively higher available potassium.

Table-3: Different fractions of potassium potash enriched biochar and raw biomass

Samples	Water soluble K (g/kg)	Available K (g/kg)	Exchangeable K (g/kg)
ArBPB	113.7	262.5	148.7
AmBPB	90	190	100
OxBPB	82.5	162.5	80
Raw biomass	46.3	66.3	20

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ADVANTAGES

Abundantly available waste biomass is converted to potash enriched biochar.

Biochar production time is reduced from several hours (as in the case of conventional resistance heated furnace) to minutes with the use of extended arc thermal plasma reactor.

The available and water soluble potassium content enriched in biochar in comparison to raw biomass and hence the potash enriched biochar has the higher potassium nutrient contribution capacity to soil.

Additional advantages of potash rich biochar may be also on soil productivity and carbon sequestration.

The Claims:

1. A process for production of potash enriched biochar from waste biomass comprising the steps:

   a. providing a potassium rich ligno-cellulosic waste biomass;

   b. washing the biomass as obtained from step (a) and chopping it into pieces;

   c. preparing dried biomass by air drying the chopped pieces of biomass as obtained from step (b), followed by oven drying at a temperature above 40 °C for a time period of 6 to 72 hrs.

   d. characterised in thermally treating the dried biomass as obtained from step (c) in a plasma reactor having graphite electrodes by feeding the pieces of dried biomass obtained in step (c) into the hearth of the plasma reactor;

   e. injecting the plasma generating gas with a flow rate of at least 1 litre/min into the hearth of the reactor;

   f. operating the reactor with an arc voltage 30 – 90 V and an arc current 100 – 500 A.

   g. heat treating the dried biomass in the plasma reactor of at least 1000°C and above for a time period of at least 1 minute in the hearth of the reactor;

   h. cooling the product in the hearth with a continuous flow of gas till further charring ceases.

   i. collecting the biochar from hearth obtained in step (h) after the reactor cools down to room temperature and processed to powder form to obtain potash enriched biochar.

2. The process of claim 1, wherein potassium rich biomass is selected from the group of waste biomass comprising of carbohydrate polymers and lignin.
3. The process of claim 1, wherein the plasma forming gas used in the reactor is selected from the group comprising of Argon, Oxygen, Nitrogen, Ammonia, Carbon dioxide, Hydrogen, Air, Steam etc.
4. A potash enriched biochar obtained by the process as claimed in Claim 1, comprising:

   a) providing a potassium rich ligno-cellulosic waste biomass;

   b) washing the biomass as obtained from step (a) and chopping it into pieces;

c) preparing dried biomass by air drying the chopped pieces of biomass as obtained from step (b), followed by oven drying at a temperature above 40 °C for a time period of 6 to 72 hrs.

d) characterised in thermally treating the dried biomass as obtained from step (c) in a plasma reactor having graphite electrodes by feeding the pieces of dried biomass obtained in step (c) into the hearth of the plasma reactor;

e) injecting the plasma generating gas with a flow rate of at least 1 litre/min into the hearth of the reactor;

f) operating the reactor with an arc voltage 30 – 90 V and an arc current 100 – 500 Amp.

g) heat treating the dried biomass in the plasma reactor of at least 1000°C and above for a time period of at least 1 minute in the hearth of the reactor;

h) cooling the product in the hearth with a continuous flow of gas till further charring ceases.

i) collecting the biochar from hearth obtained in step (h) after the reactor cools down to room temperature and processed to powder form to obtain potash enriched biochar.

5. The potash enriched biochar obtained by the process as claimed in Claim 4, wherein the potash enriched biochar contains readily available potassium.

6. Use of the potash enriched biochar obtained by the process as claimed in Claim 4 in agricultural applications.

7. Use of the potash enriched biochar obtained by the process as claimed in Claim 4 for increasing soil productivity and carbon sequestration.

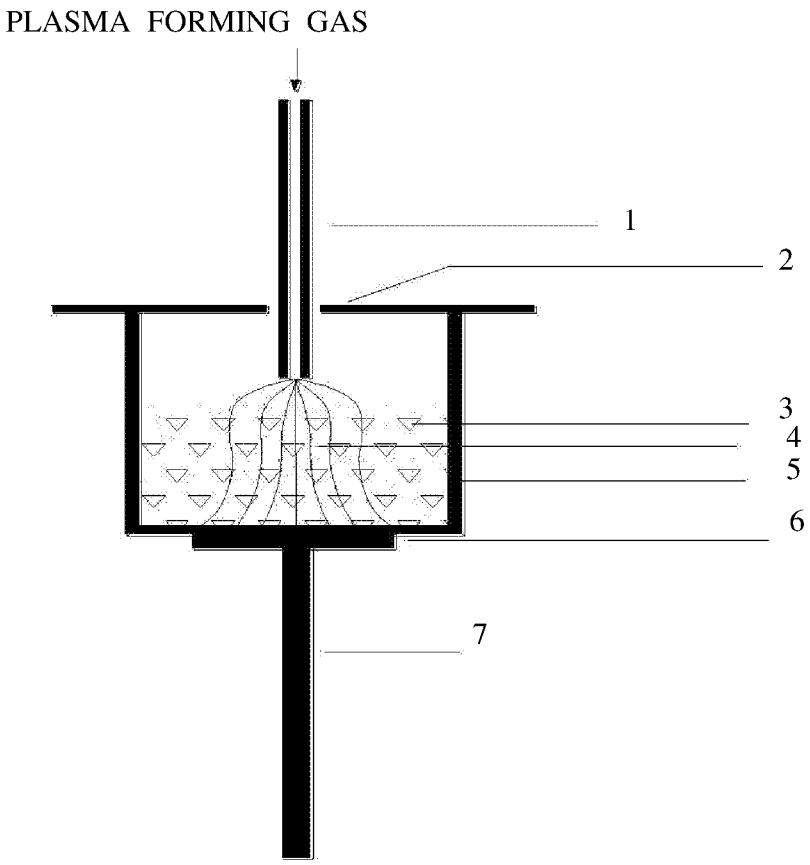


FIG. 1

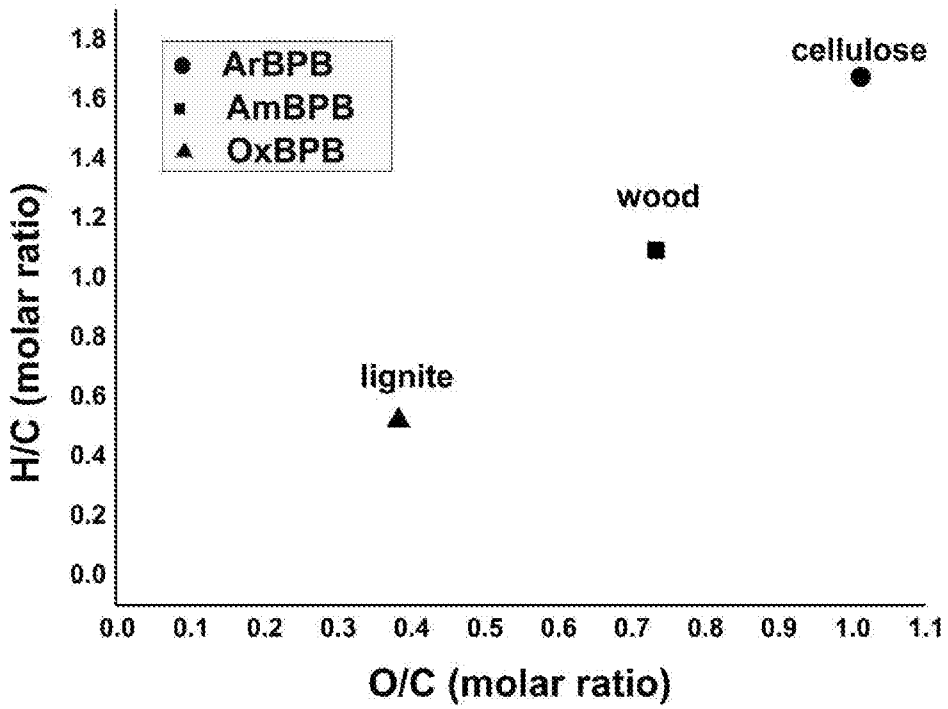

ArBPB
AmBPB
OxBPB
cellulose
wood
lignite
H/C (molar ratio)
O/C (molar ratio)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1

FIG. 2

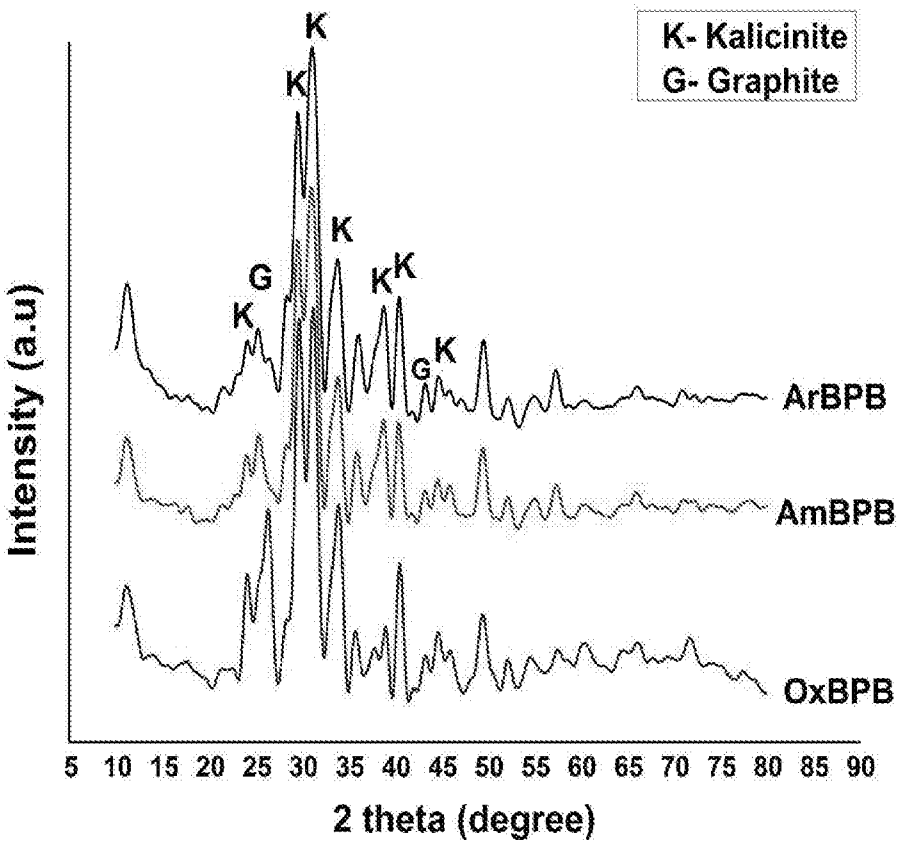

K- Kalicinite
G- Graphite
Intensity (a.u)
2 theta (degree)
5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90
ArBPB
AmBPB
OxBPB
K
K
K
G
K
K
K
G
K

FIG. 3

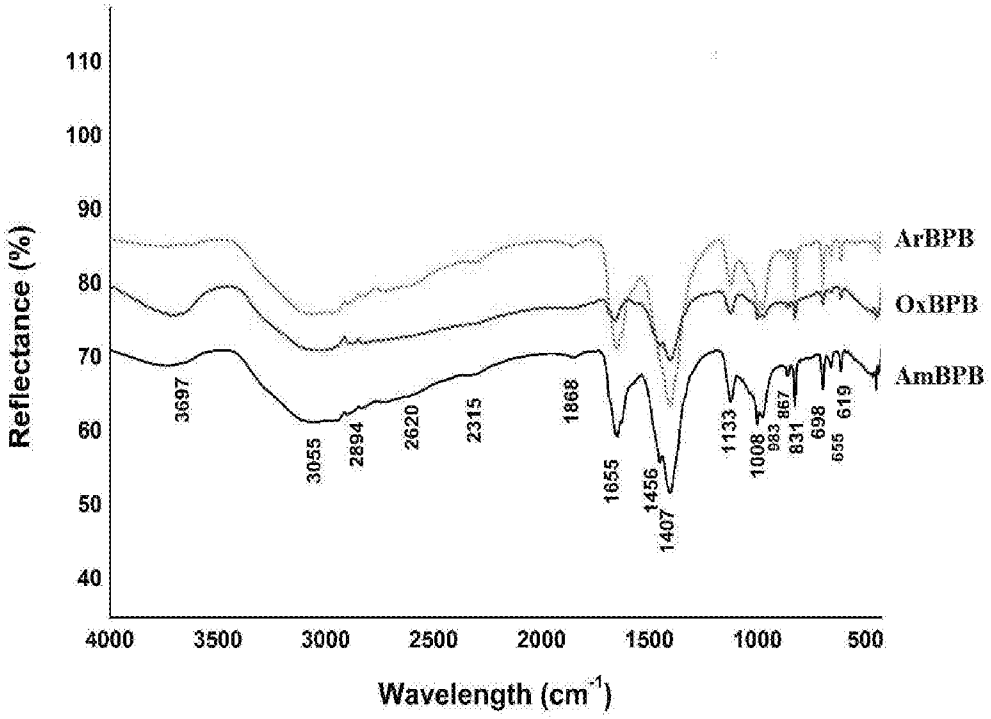

Reflectance (%)
110
100
90
80
70
60
50
40
4000
3500
3000
2500
2000
1500
1000
500
Wavelength (cm-1)
ArBPB
OxBPB
AmBPB
3697
3055
2894
2620
2315
1868
1655
1456
1407
1133
1008
983
867
831
698
655
619

FIG. 4

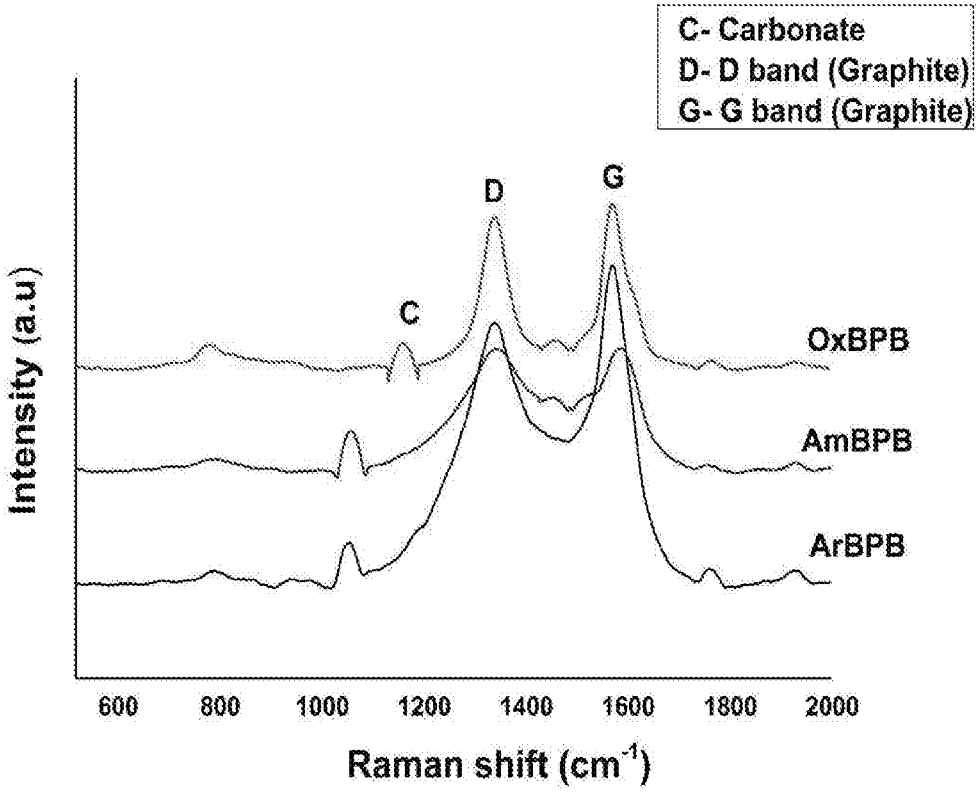

C- Carbonate
D- D band (Graphite)
G- G band (Graphite)
D
G
C
OxBPB
AmBPB
ArBPB
Intensity (a.u)
600
800
1000
1200
1400
1600
1800
2000
Raman shift (cm-1)

FIG. 5

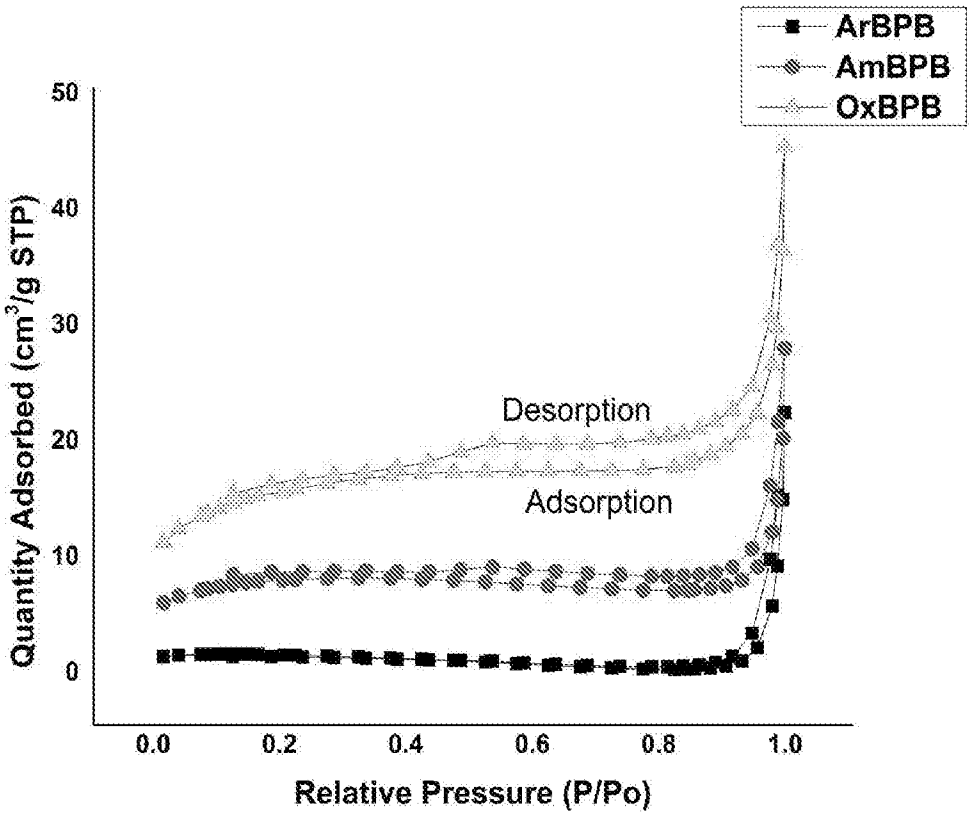

ArBPB
AmBPB
OxBPB
Quantity Adsorbed (cm3/g STP)
50
40
30
20
10
0
Desorption
Adsorption
0.0
0.2
0.4
0.6
0.8
1.0
Relative Pressure (P/Po)

FIG. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2017/050196

A. CLASSIFICATION OF SUBJECT MATTER
INV. C05F11/02 C01B32/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C05F C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, COMPENDEX, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	DATABASE WPI Week 201561 Thomson Scientific, London, GB; AN 2015-42045B XP002774786, & CN 104 610 987 A (UNIV SUN YAT-SEN) 13 May 2015 (2015-05-13) abstract ----- -/--	1-7

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 October 2017	17/11/2017

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Schut, Robert

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INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2017/050196

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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		WO 2012069448 A1	31-05-2012