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(54) Title: SHAPED CELLULOSE ARTICLE COMPRISING ACTIVATED CARBON, IN PARTICULAR AS SUPPORT FOR CO₂ ADSORBENTS

(57) Abstract: The invention relates to a method for preparing a shaped cellulose article suitable and adapted for CO₂ capture from an air stream containing activated carbon, to the shaped article obtainable by the method, the use of the shaped cellulose article as a catalyst, a catalyst support or as an adsorbent or as an adsorbent support, preferably as an adsorbent for capturing and/or concentrating of CO₂. The method comprises the steps of contacting cellulose with an ionic liquid to form a liquid cellulose mass, forming a mixture of activated carbon in the liquid cellulose mass, optionally forming activated carbon in-situ by partial carbonization of carbonisable components in biomass like lignin, shaping the mixture or the precipitate thereof to form a shaped cellulose article containing activated carbon and removing the ionic liquid before, during or after the shaping step.



WO 2020/165048 A1

TITLE

SHAPED CELLULOSE ARTICLE COMPRISING ACTIVATED CARBON, IN PARTICULAR AS SUPPORT FOR CO₂ ADSORBENTS

5 TECHNICAL FIELD

The invention relates to a novel cost-effective method to produce a shaped article comprising activated carbon, to the shaped article obtainable by the method, the use of the shaped article as a catalyst, catalyst support or adsorbent and in particular as an adsorbent or adsorbent support for capturing and/or concentrating CO₂. The shaped article can for
10 example be a fiber, a sheet or particles like microspheres, beads, extrudates, granulates, monoliths or structured adsorbers.

PRIOR ART

Carbon containing materials are known, for example carbon coated articles such as
15 specialty paper, filters and conductive films as described in Vinay Kumar et al 2017 Flex. Print. Electron. 2 035002. Unfortunately, the process to produce these materials as described in the reference is complex and costly and therefore very few applications of these materials have been developed and/or commercialized up to now. A process for making carbon coated nanocellulose conductive films is illustrated by the 3rd Annual
20 Knowledge Exchange Day 2013 Student Video Competition submission by University of Guelph by student Yin Li (see <https://www.youtube.com/watch?v=KMESLaa4BT4>)

Further, in the area of carbon-based catalysis and sorbents, in particular for CO₂ capture, there is a need for a shaped articles comprising activated carbon, which exhibit good mechanical stability, tenacity and strength combined with good adsorbing and/or catalytic
25 activity of active carbon, in particular when used as CO₂ sorbents or as supports for CO₂ sorbents for carbon capture application.

US2014194603 (A1) relates to a method for the production of a precursor for the production of carbon- and activated carbon fibres according to the wet- or air-gap spinning method, in which a solution of lignin and a fibre-forming polymer in a suitable solvent is extruded
30 through the holes of a spinning nozzle into a coagulation bath, the formed thread is stretched and subsequently treated, dried at an elevated temperature and then wound up. The lignin-containing thread is an economical starting material for the production of carbon- and activated carbon fibres.

35 SUMMARY OF THE INVENTION

Thus, an objective underlying the invention is to provide a cost-effective method to produce

shaped articles comprising activated carbon. A further objective is to provide articles with mechanical stability and good strength combined with good adsorbing and/or catalytic activity of active carbon in particular when used as support for carbon capture chemicals.

According to the invention there is provided a method for preparing a shaped cellulose

5 article containing activated carbon comprising the following steps:

- a) contacting cellulose with an ionic liquid to form a liquid cellulose mass,
- b) forming a mixture of an activated carbon or of a carbonisable component in the liquid cellulose mass of step a),
- c) shaping the mixture to form a shaped cellulose article containing activated carbon
10 or a carbonisable component,
- d) in case the mixture comprises a carbonisable component, in-situ carbonisation of the carbonisable component in the liquid cellulose mass before or after shaping step c),
- e) optionally precipitating (in particular for removing solvent) the mixture before or after
15 shaping step c) to form a precipitate mixture comprising the activated carbon or carbonisable component and cellulose,
- f) removing the ionic liquid before, during or after said shaping step c) and after step b) or after the optional precipitation step e), preferably before said shaping step c).

Preferably the sequence is followed by at least one further step:

- 20 g) impregnating the thus obtained article(s) with an active phase capable of reversibly binding CO₂. The active phase can be a chemical that can bind CO₂ from a gas stream (flue gas, ambient air, greenhouse gas, etc.) and that can release CO₂ using apt thermodynamic conditions known by those skilled in the art. Preferably but not exclusively, the article is impregnated with at least one of an alkali or alkaline earth
25 carbonate, or with amines, or polymeric amines, or metal organic frameworks (MOFs), or a mixture or combination of such active phases in different proportions that enable or enhance the carbon capture capacity of the thus obtained article, or any other chemical or material apt for capturing or enhancing the CO₂ capture capacity of the article from a gas stream;
- 30 h) chemically modifying the article with an apt active phase such as amines, or polymeric amines, or metal organic frameworks (MOFs), or a mixture or combination of such active phases in different proportions that enable or enhance the carbon capture capacity of the thus obtained article, or any other chemical or material apt for capturing or enhancing the CO₂ capture capacity of the article from a gas stream,
35 through the formation of chemical bonds

The foregoing is schematically illustrated by example of a possible processing scheme as given in Figure 1.

An example of a process of precipitation of cellulose from such a mixture as in step e is also
5 described in US2018/0282437A1. The Cellulose formed exhibits binding properties, similar as which can be achieved with nanocellulose.

An interesting aspect of the method of the invention is that the activated carbon can be either provided from an external source and added to the liquid cellulose mass or alternatively or even additionally the activated carbon can be in-situ formed by carbonisation
10 of carbonisable components in the liquid cellulose mass.

Preferably, at least one of the cellulose, the activated carbon or the carbonisable component as used in steps a) and b) contains nitrogen in a form which is converted in one of the following steps to a chemical moiety capable of reversibly binding CO₂. This way step g) can be prepared, or supported or even omitted for providing a material which is capable of
15 reversibly binding CO₂ and suitable for CO₂ capture processes.

An important advantage of the cellulose shaped articles of the invention is that these shaped materials, for example in the form of fiber, a sheet or fiber, a sheet or particles like microspheres, beads, extrudates, granulates etc. are strong. With strength, it is meant mechanical properties that impede the destruction of the material under operating
20 conditions. Such mechanical properties are for example but not exclusively in particular crushing strength, meaning in particular that the shaped articles do not as easily attrite, break and form dust.

Because of the good strength of the cellulose shaped articles, in particular also fibers or threads can be produced with a small diameter (below 1 mm, 1000 microns, and by spinning
25 even below 0.2mm) which, is beneficial for use in adsorption applications where the adsorption processes are typically mass transfer limited and high surface area/small size adsorption materials are preferred. For example, the method allows fiber spinning to durable fibers that can be processed to yarns, fabrics and the like. Furthermore, the good strength can also be used to provide mechanical stability to structured adsorbers and monoliths
30 obtained by extrusion or by other form of shaping of the described mixture of cellulose and activated carbon.

Preferably, in the step of carbonisation d) the carbonisation is not a full carbonisation but only a partial carbonisation on the surface of the shaped cellulose article. The aim of this partial carbonisation is to maintain the structural integrity in the core but to generate
35 activated carbon on the surface to make available the corresponding functionality on the surface only. Preferably the carbonisation is partial in the sense that less than 50% of the

weight of the corresponding shaped cellulose articles are carbonised and converted into activated carbon, and/or in that on the surface layer of less than 1 mm, preferably less than 0.5 mm, more preferably less than 0.25 mm is converted to activated carbon, while the structure further below is not converted by carbonisation.

- 5 Further, the active carbon in the shaped article of the invention is well distributed and well adhered in the cellulose even without chemical modification of the active carbon and/or the cellulose, which is advantageous compared to prior art methods wherein the active carbon and/or the cellulose has to be chemically modified to improve the adhesion of the active carbon on the cellulose article.
- 10 An additional advantage is that it is easier/simpler to modify the activated carbon in the shaped article of the invention for specific end uses compared to prior art methods wherein activated carbon is first modified and then added to a carrier substrate. For example, the active carbon in the shaped article of the invention can be easily modified by addition of a CO₂ adsorbent active phase to the article, for example by impregnation. The modification
- 15 of the article with an active phase can be further simplified considering that the activation of the carbonized cellulose can be obtained by addition of a strong base such as KOH in the compounding step, and that this component, besides being functional to activate the carbonized cellulose, is a precursor to the K₂CO₃ that will also be used as active phase for the capture of CO₂. The processes of activation and modification to form a CO₂ adsorbent
- 20 are thus reduced to a single step.
- In order to make the shaped article suitable and adapted for carbon dioxide capture, preferably in the form of a shaped cellulose article only having a surfacial layer of activated carbon, the shaped cellulose article is impregnated with an alkali carbonate or alkaline earth carbonate, e.g. by immersing in a corresponding solution and subsequent drying.
- 25 Preferably, the activated carbon is impregnated with at least one alkali carbonate salt selected from the group consisting of: K₂CO₃, Li₂CO₃, Na₂CO₃ as well as mixed salts thereof. For preparing the corresponding impregnated shaped articles, preferably in a first step at least one alkali carbonate salt is dissolved in a solvent, preferably water, most preferably deionized water, wherein preferably the concentration is 1-8 mmol (total) alkali
- 30 carbonate salt per ml water, preferably 1.5-4.5 mmol/ml water and wherein the corresponding shaped article with activated carbon on its surface, if need be after drying and/or purification, is added to the solution, under stirring, preferably at a temperature in the range of 5-40°C, most preferably at a temperature in the range of 20-30°C, and/or for a time span in the range of 30 minutes-100 hours, most preferably in the range of 6 hours-40
- 35 hours, and wherein subsequently at least the solid fraction is isolated and/or dried by (vacuum) evaporation.

An important advantage of the process of the invention is that the shaped articles of the invention can be produced at a low enough cost, in particular also because they can be made from inexpensive bio-based materials. The bio-based materials can be chosen in such a way that the nitrogen content is high thus pre-disposing the material to capture CO₂ by means of amines that reversibly bind CO₂, or as catalytic moieties apt to accelerate the uptake/release of CO₂ by other binding moieties.

The invention further relates to the shaped article obtainable by the methods of the invention in particular fibers, yarns, films, extruded articles, such as structured adsorbers or structured supports for adsorbers, monoliths, microspheres, beads, extrudate particles, granulates and articles made from the shaped articles, preferably fabrics and particle beds

In a further aspect the invention relates to the use of the shaped article according to the invention as a catalyst or as catalyst support or as CO₂ adsorbent or support for CO₂ adsorbent, preferably as adsorbent for capturing and/or concentrating of CO₂ from CO₂ containing sources such as flue gas, biogas and/or air.

In a particular embodiment, the invention relates to a method for CO₂ absorption comprising contacting a CO₂ containing gas with shaped articles according to the invention, preferably fibers, more preferably a fabric made of the fibers, wherein the active carbon in the shaped article preferably comprises a CO₂ adsorbent.

Further embodiments of the invention are laid down in the dependent claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention are described in the following with reference to the drawings, which are for the purpose of illustrating the present preferred embodiments of the invention and not for the purpose of limiting the same. In the drawings,

Fig. 1 in A) shows a possible preparation scheme for active carbon, and in B) a possible preparation scheme for a sorbent;

Fig. 2 in A) shows preferred scheme of this invention, in B) an alternate scheme of this invention, in C) another preferred scheme of this invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

Fig 1A depicts a possible process to produce active carbon, starting from a biomass source, which is activated to create the desired porosity, surface area and surface chemistry. Examples of activation agents are H₂O, KOH, NH₄OH and ZnCl₂.

Thereafter, the activated biomass material is carbonized via a high temperature treatment under exclusion of air, above 500°C: Pyrolysis.

Fig 1B depicts a possible process to produce a CO₂ sorbent supported or base on Active

Carbon. In Fig 1B the active carbon described by Fig 1A is functionalized to adsorb CO₂ from air and/or other CO₂ containing streams by impregnation the active carbon with a CO₂ adsorbing species. Examples are: KOH, NaOH, KHCO₃, Amines.

Note, that certain activation agents (e.g. KOH, NH₄OH) mentioned in Fig 1A can also function as functionalizing species. This can be an advantage in terms of simplicity and cost of the process if thereby the impregnation step can be skipped.

Fig 2A depicts one embodiment of this invention whereby a cellulose source (cotton, cotton waste, paper pulp, etc., ligno-cellulosic biomass) is contacted with ZnCl₂ hydrate solvent and the cellulose is dissolved forming nanocellulose. In the following, step the nanocellulose is separated from the ZnCl₂ hydrate solvent by precipitation with an anti-solvent. This anti-solvent can be organic like ethanol or tri-butyl-alcohol or water. The precipitated nanocellulose is thereafter dispersed in water.

In the following step the nanocellulose dispersion is mixed (compounded) with active carbon and/or biomass to form a viscous slurry which can then be shaped into a particle, for instance by extrusion.

In the case biomass is used a carbonization step is applied, this can be before, during or after the shaping of the particles

Thereafter the shaped particle can be impregnated and functionalized as a CO₂ adsorbing sorbent with a CO₂ adsorbing species.

Examples are: KOH, NaOH, KHCO₃, Amines

Fig 2B is a variation of Fig 2A whereby the ZnCl₂ hydrate sorbent is separated after the compounding step. Extra solvent can be added in this case to also convert the cellulose in the biomass source into nanocellulose.

It is even possible to omit the cellulose source of the first step and to only utilize the biomass source as a source of cellulose to be converted to nanocellulose. This can result in a further cost reduction.

Fig 2C is a variation of Fig 2A whereby functional sorbent components such as KOH, NH₄OH or Amines are added during the compounding step.

This can be an advantage in terms of simplicity and cost of the process if thereby the impregnation step can be skipped.

In all cases (2A,2B,2C), the use of a Nitrogen containing biomass source such as algae, seaweed etc. is also an option to introduce CO₂ sorbent species into the sorbent.

Step a)

The method of the invention starts with providing cellulose, preferably in the form of a biomass feed; preferably a low-cost waste biomass comprising cellulose and optionally also lignin and hemicellulose. Biomasses containing cellulose are for example e.g. wood pulp or

other plant material and algae. In particular biomasses that are rich in Nitrogen that can be further used in the form of amines to capture CO₂. The biomass is reduced in size to particles of about few mm size, washed to remove sand, optionally dried if needed etc. Other biomass components as for instance hemicellulose, proteins, extractives and
5 inorganic ash can be removed, for instance by a hot water wash and/or an acid treatment. In step a) of the method the cellulose is contacting with an ionic liquid to form a liquid cellulose mass. Preferably, the ionic liquid is an inorganic molten salt. Inorganic molten salts have been disclosed in WO 2010/106053 A2 as being capable of dissolving cellulose. Preferably, in the method according to the invention the ionic liquid is a molten salt,
10 preferably comprising ZnCl₂ or CaCO₃, preferably a ZnCl₂ hydrate, more preferably ZnCl₂.4H₂O.

It is preferred that in step a) of the method, the cellulose component of the biomass is delaminated but not dissolved by the ionic liquid (also referred to as dissolved). In this way a liquid cellulose mass is formed that can be shaped for example by extrusion, but wherein
15 the cellulose in the liquid mixture retains semi-crystalline structure and reduction of the molecular weight is minimized, which is important for the strength properties. Reference is made to WO2017055407 describing details of the above process. Cellulose obtained by the process comprise semi-crystalline cellulose and have a nano-crystalline structure, which results in good strength and a higher resistance against carbonization during carbonization
20 step d).

This delamination or dissolution is preferably done by choosing in step a), an inorganic molten salt that is substantially proton-free, so in substantial absence of protic acid. It is further preferred to make the molten salt substantially proton-free. There are various methods for making an inorganic molten salt medium substantially proton-free. For
25 example, the solvent medium may be passed through a column of cation-exchange material, in which protons from the solvent are replaced with alkaline cations, such as lithium, sodium, potassium, calcium, magnesium, and the like. An alternative and preferred method for making an inorganic molten salt solvent medium substantially proton-free is the addition of a proton scavenger (also referred to as acid scavenger). The advantage is that
30 hydrolysis of the cellulose due to the presence of protons is reduced, thus maintaining high molecular weight, high crystallinity and strength properties of the shaped article.

Suitable proton scavengers are the oxide or hydroxide of any metal being a stronger reducing agent than hydrogen. Suitable proton scavengers include the oxides and hydroxides of alkali metals and alkaline earth metals, and the oxides and hydroxides of non-
35 noble transition metals. It is desirable to use the oxide or hydroxide of the corresponding molten salt. For example, if a hydrate of zinc chloride is used as the inorganic molten salt,

preferred proton-scavengers are ZnO and Zn(OH)₂.

The cellulose containing biomass can be dissolved or delaminated in the solvent medium by stirring for about 20 to about 60 minutes, at a temperature in the range of from room temperature to 120°C, preferably in the range of from 70°C to 100°C.

- 5 If in the method of the invention a biomass is used, the amount of cellulose in the biomass comprising cellulose and carbonisable components is preferably more than 50 wt.% relative to total dry solids of the biomass.

Step b)

- 10 In step b) a mixture is formed of an activated carbon or a carbonisable component in the liquid cellulose mass of step a).

It is believed that by mixing with activated carbon before shaping, the activated carbon is more evenly distributed along the cellulose fibers and distributed evenly throughout the final article or particle. This provides a benefit in that it allows for more structural integrity and durability, compared to an external coating of activated carbon on a shaped cellulose article
15 or nanocellulose fiber.

- In step b) the activated carbon can be provided from an external source and added to the liquid cellulose mass. In principle any commercially available activated carbon powder can be used. Suitable commercially available activated carbon is for example NORIT PK1-3, which is a granular carbon activated by steam activation. This can be ground to the desired
20 size for use in the method of the invention.

Preferably, the activated carbon is obtained by carbonisation of carbonisable components from a cellulose containing biomass, preferably lignin, hemicellulose or peptides or combinations thereof. This makes effective and more economical use of the biomass starting material and results in less waste.

- 25 In a preferred embodiment, the method comprises after contacting step a), a separation step wherein carbonisable components are separated from cellulose containing biomass, subjected to a separate (ex-situ) carbonisation step to form activated carbon, which then is provided to form the mixture in step b).

In preferred ionic liquids the cellulose and carbonisable components, in particular lignin,
30 separate in two separate phases allowing for easy separation. Separate carbonization, as opposed to in-situ carbonization, has the advantage that higher temperatures to be used and that better quality control is possible, as the activated carbon can be screened before being provided to form the mixture. It can also be favourable to separate, carbonise and then re-add the activated carbon, as it allows for more precise ratio control.

- 35 Alternatively, the method according to the invention comprises step a) wherein biomass comprising cellulose and carbonisable components is contacted with ionic liquid and in step

b) the mixture comprises cellulose and carbonisable components. The active carbon is then formed in-situ in a step d) by carbonisation of the carbonisable components in the presence of the cellulose, preferably in a later step. This is more economic from process point of view.
Step c) shaping step

- 5 The shape can be a fiber, a sheet, extrudate or particles like microspheres, beads, cut extrudates, granulates. The mixture of step b) or the precipitate of step e) can be shaped according to any method known in the art, including extruding, spinning, moulding, prilling, granulating etc. Preferably, the shaped article is shaped by extrusion or spinning, preferably to elongate or particulate shaped articles.
- 10 In a particular embodiment the shaped article is immersed in a bath comprising an alcohol to coagulate and precipitate the cellulose comprising the activated carbon or carbonisable component. The advantage of using an alcohol in the bath, compared to for example water, is that a smaller amount of active carbon or carbonisable component is removed from the extrudate in the bath.
- 15 The spinning can also be done in a bath to extract and remove the ionic liquid (i.e step f) which may also result in precipitation of the cellulose containing the activated carbon or a carbonisable component (step e). Spinning can mean, but is not limited to fibrous spinning electrospinning, spin-coating and/or forms of extrusion.

Step d) optional in-situ carbonization

- 20 In a special embodiment, the mixture in step b) comprises a carbonisable component and the process comprises a step d) comprising carbonisation of carbonisable components in the presence of the cellulose before or after shaping step c). In the presence of cellulose implies that the cellulose experiences substantially the same carbonization conditions, for example when carbonization is done in the same reactor. This process is advantageous
- 25 because this excludes a separation step and furthermore the carbonization can also be done in the same reactor as used in step a) and b). This can be preferable as only one reactor can be used and it can be used in both batch processes as continuous processes. The in-situ carbonisation step d) can be done in the mixture after step a) and before precipitation step b) or in the precipitate after precipitation step b) and before shaping or on
- 30 the shaped article after shaping step c) and preferably before ionic liquid removal step f). In-situ-carbonization can for example be done after shaping step c), for example by shaping a lignin and cellulose containing liquid mass followed by carbonization. As the carbonization temperature of the carbonisable components in the mixture is lower than the carbonization temperature of cellulose, in-situ carbonization is possible and attractive.
- 35 The active carbon can be obtained by carbonisation of carbonisable components of a cellulose containing biomass by heating the carbonisable components to a temperature of

above 100°C, preferably above 150, 200 or even 250°C and in case of in-situ carbonisation step d), by heating the carbonisable component in the presence of the cellulose preferably under 500°C, more preferably under 400, 300, 250 or even under 200°C. In case of in-situ carbonization, the carbonization temperatures are preferably lower than in separate
5 carbonization in view of the presence of the cellulose to prevent carbonization of the cellulose. When temperatures are chosen above 250°C the exposure times are preferably sufficiently short to prevent substantial carbonization of the cellulose.

It was found advantageous that in step a) the cellulose component of the biomass is delaminated but not dissolved in substantially proton-free ionic liquid as the cellulose is less
10 affected by the carbonization conditions and/or relatively higher carbonisation temperatures can be used.

It is preferred that the carbonation step is performed in the presence of an activator, preferably ZnCl₂, KOH, K₂CO₃, Fe₂O₃, ZnO, KHCO₃, Mg-Al or a mixture thereof (See also for instance Reference: Preparation of activated carbon from lignin by chemical activation
15 by J. Hayashi Volume 38, Issue 13, 2000, Pages 1873-1878). An activators allows lower temperatures to be used to carbonize the carbonizable components. Preferably, an activator is present when using carbonisation temperatures between 100 and 350 °C, preferably between 100 and 300 °C, more preferably between 150 and 250 °C.

In a preferred method activated carbon is made with KOH as activator. An advantage of
20 that method is that the residual KOH in the activated carbon forms K₂CO₃ in contact with air, which is a preferred CO₂ adsorbent, so no or less separate K₂CO₃ needs to be added to the activated carbon after the shaped article preparation for making the shaped article suitable for use in a CO₂ adsorption process.

At the carbonisation temperature within the above described ranges a good conversion of
25 the carbonisable components, preferably lignin and/or hemicellulose, can be achieved while not substantially affecting the integrity of the cellulose. Generally, the higher the temperature, the faster and higher conversion of the carbonisable components to activated carbon. However, not all carbonisable components need to be converted in the process according to the invention. The lower the temperature, the less cellulose is converted into
30 activated carbon, and as such the temperature is preferably kept below the carbonization temperature of cellulose and above the carbonization temperature of the carbonisable components.

Preferably, the carbonisable component is lignin and in the process step d) the lignin is activated by carbonization by heating the mixture to above 100°C but below approximately
35 250°C.

Hemicellulose can also be carbonised together with the lignin at conditions not affecting

(semi crystalline) cellulose, but it is preferred however, that hemicellulose is separated in a manner known in the art and the carbonisable component in the mixture is lignin. It was found that an additional advantage of only delaminating and not dissolving the cellulose in step a) is that the cellulose in the liquid mixture is more resistant to the in-situ carbonisation conditions and also the in-situ conversion of the carbonisable component to active carbon can be higher.

Step e) optional precipitation

In the optional precipitation step e) the cellulose and activated carbon or carbonisable component are together precipitated from the mixture before or after shaping step c).

Precipitation is preferably done by adding an anti-solvent. Any liquid that does not dissolve nanocellulose and that is miscible with the inorganic molten salt medium can be used as an anti-solvent. Examples include water and alcohols having from 1 to 6 carbon atoms, for example tertiary-butyl alcohol (TBA). The mixture of step b) can be precipitated to form a precipitate comprising the activated carbon or carbonisable component in cellulose, but the precipitation can also be done after shaping as for example by spinning in a coagulation bath described above. Hereafter, step d) can be performed for forming the activated carbon by carbonization of the carbonisable components in-situ. A benefit of this method can be that it only requires heating the precipitate.

Step f) removing the ionic liquid

The ionic liquid is removed before, during or after shaping c) and after step b) or after the optional precipitation step e). The precipitation step and solvent removal step can be combined in a single step for example if precipitation takes place to some extent as a result of a solvent removal step.

In a preferred embodiment the method comprises forming a mixture of an activated carbon in the liquid cellulose mass, then shaping the obtained mixture, for example by spinning, then precipitating the cellulose and activated carbon, for example by immersing the shaped article in a coagulation/cooling bath, wherein ionic liquid removal step f) takes place simultaneous with or after precipitation step e) for example by extraction with water followed by drying. This process uses separately prepared activated carbon and comprises consecutive steps a, b, c, e/f.

For example, a fiber can be formed by extrusion spinning a mixture comprising 30 wt.% cellulose, 10 wt.% activated carbon and 60 wt.% of an ionic liquid comprising 70 wt.% ZnCl₂ in water. The extruded fiber is immersed in an acetone bath to precipitate the cellulose. The formed fiber is washed with water and dried.

In an alternative embodiment, the method comprises steps a) and b) followed by a precipitation step e) and the ionic liquid removal step f) is done directly after the precipitation

step e) and before shaping step c). So the consecutive steps are a, b, e, f, c.

Removing the ionic liquid can be done by decanting supernatant ionic liquid, centrifugation, filtration or combinations thereof, subsequent washing the ionic liquid from the precipitate with water in one or more steps until sufficiently low ionic liquid concentration is reached.

- 5 Optional precipitation coagulant can be washed or evaporated. The suspension of cellulose in water can then be dried and shaped or wet shaped and dried.

As described above, the process can also involve in-situ prepared activated carbon and thus the method comprises for example consecutive steps a, b, c, e/f, d or consecutive steps a, b, d, c, e/f.

- 10 In one embodiment the cellulose is precipitated from the ionic liquid together with the carbonisable components, the ionic liquid is removed and isolated and the resulting article is shaped and carbonised (example A3)

Alternatively, the carbonization is done after step a) on the liquid mixture comprising cellulose and carbonisable components and the cellulose is subsequently precipitated,

- 15 separated from the ionic liquid and the resulting precipitated product is then shaped (example A2).

The shaped article

- The invention also relates to shaped article obtainable by a process according to the
20 invention as described above in particular fibers, yarns, films and extruded articles, microspheres, beads, extrudate particles, monoliths, structured adsorbers, granulates and articles made from the shaped articles, preferably fabrics, catalyst particle beds.

- In a preferred embodiment, the obtained shaped article is an elongate shaped article, in particular a fiber or film, having a long axis and having a smallest diameter of a cross-section
25 perpendicular to the long axis smaller than 0.5 mm, preferably smaller than 0.2 mm and more preferably smaller than 0.1 mm. Preferably, the elongate shaped article is a fiber, yarn, film or extruded article such as a particle, pellet, monolith, structured adsorber.

- The amount of activated carbon in the mixture and in the resulting shaped article can in principle vary between wide ranges, the choice of the amount is also determined by the
30 requirements of the envisaged application. For adsorption purposes the amount of activated carbon is preferably high, but for strength and durability the amount of cellulose on total may need to be higher. The amount of activated carbon relative to the total weight of the shaped article is between 1 and 90 wt.%, preferably between 5 and 80 wt.%, more preferably between 10 and 70 wt.%.

- 35 It has been observed that in a fiber of the invention, the activated carbon is in particles segregated from the cellulose and apparently more concentrated at the outside of the

shaped cellulose article where they are most effective for adsorption purposes. Good results can be obtained with lower amounts, for example when in the fiber the amount of active carbon is between 1 and 30 wt.%, more preferably 5 and 25 wt.%.

In case the activated carbon is in-situ formed from lignin and/or hemicellulose, the conversion to activated carbon may not be 100%, so there may be some residual lignin and/or hemicellulose in the mixture after the carbonisation step. The skilled person can easily determine the amount of carbonisable component in the mixture such as to arrive at the envisaged amount of activated carbon in the shaped article. The residual cellulose content can also be established by XRD and NMR.

10 The shaped articles can be used as a catalyst, as catalyst support or as adsorbent or adsorbent support. Preferably, the shaped articles are used as a sorbent or adsorbent support for capturing and/or concentrating of CO₂ from CO₂ containing source such as flue gas, biogas, and/or air.

Preferably, the shaped article comprises a CO₂ absorbent, preferably a carbonate, preferably a potassium bicarbonate or one or more nitrogen containing compounds, preferably amine compounds, Nitrogen containing biomass, or combinations thereof. The CO₂ absorbent can be added to the mixture in step b) or be adsorbed into the formed active carbon containing cellulose article. It is thought that by adding the adsorbent to the mixture in step b) a more even distribution of the adsorbent on the shaped cellulose article can be obtained. In a particular preferred embodiment, the active carbon in step b) and d) comprises KOH which acts as CO₂ adsorbant in the final product. In some cases it may be preferred to contact (impregnate) the shaped cellulose article with the CO₂ adsorbent so that more of the CO₂ adsorbent can be adsorbed on the shaped cellulose article.

In a preferred embodiment, the activation of the carbon source and the functionalization into a CO₂ adsorbent is achieved in one single process step. For example, the carbon source is activated by the reaction with KOH, ZnCl₂ or NH₄OH and the residual reactants incorporated into the activated carbon are CO₂ adsorbing species.

The invention also relates to the use of the shaped article according to the invention as a catalyst or as catalyst support or as adsorbent or as a support for a CO₂ adsorbent, preferably as a sorbent for capturing and/or concentrating of CO₂ from CO₂ containing sources such as flue gas, biogas and/or air.

In a preferred embodiment, the biomass source used to form activated carbon contains Nitrogen, as for instance Seaweed, Algae and/or Alginate. See for reference Saha et al. "Synthesis of Nitrogen and Sulfur codoped Nanoporous Carbons from Algae: Role of CO₂ separation" in ACS Omega 2018, 3, p 18592-18602.

The invention also relates to a method for CO₂ absorption comprising contacting a CO₂

containing gas with a shaped article according to the invention wherein the active carbon comprises a CO₂ adsorbant. More preferably, the shaped article is a fabric made of fibre shaped articles of the invention or a bed of particles according to the invention.

Prior to carbonization, the raw biomass material is impregnated with certain chemicals. The chemical is typically an acid, strong base or a salt (phosphoric acid, potassium hydroxide, sodium hydroxide, calcium chloride, and zinc chloride). Then, the raw material is carbonized. It is believed that the carbonization / activation step proceeds simultaneously with the chemical activation. Chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating material.

- 5 The strength of the finished particle can be determined using commonly used mechanical strength test, such as ball-mill hardness, abrasion strength, impact hardness, ball-pan hardness, T-bar hardness, crushing strength and impact-hardness. Preferably, the particle is defined by its crushing strength, which is defined as the pressure needed to be applied to crush a granule of activated carbon. Apparatus for this test is commercially available.
- 10 Particles according to the invention can have a crushing strength equivalent to commercially available activated carbon granules, Norit PK 1-3.

DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

The following is a description of certain embodiments and examples of the invention, given by way of example only.

EXAMPLE A.1: A biomass composition consisting of mainly cellulose and lignin is treated with a ZnCl₂.4H₂O solution.

EXAMPLE A.2: The solution of EXAMPLE A.1 is heated above 100 degrees Celsius whereby at least part of the lignin present is carbonized. Any cellulose dissolved is precipitated and the solution is decanted.

EXAMPLE A.3: Dissolved cellulose present in Example A.1 is precipitated in the presence of the lignin and the solution is decanted.

EXAMPLE A.4: The sample of EXAMPLE A.3 is heated above 100 degrees Celsius.

EXAMPLE A.5: The sample of EXAMPLE A.3 is heated above 100 degrees Celsius in the presence of an activator, being KOH, KHCO₃, Fe₂O₃, ZnO and/or a mixture thereof.

EXAMPLE B.1 The sample of EXAMPLE A.5 is used to prepare a shaped particle by extrusion, which can be applied for the capturing of CO₂ from CO₂ containing gasses.

In a specific embodiment the shaped materials are produced by spinning out to produce thread and make fabrics, whereby very small diameter bundles or threads can be produced in the order of 0.1 - 0.2 mm.

EXAMPLE C: Nanocellulose

A solution of nanocellulose (20% solids in water) is prepared (NCC) according to the following recipe:

20 g cellulose are placed into a 1 l glass vessel and mixed with 200 gr 70 wt% $ZnCl_2$ solution in water. The mixture was kept under continuous stirring (200 rpm) at 50 C until a transparent solution was obtained (20 min). Than 500 gr cold water was added to the reactor under continuous stirring. Stirring was kept for additional 15 min at room temperature to allow precipitates to be formed. The obtained slurry were separated from liquid by centrifugation (5000 rpm; 10 min), nanocellulose was washed 5 times with water (1:10). After last washing solid cellulose was diluted with water to get a solution of nanocellulose with 20 % solids in water.

EXAMPLE D: The following samples of CO_2 sorbent particles are prepared:

A sample of commercially available Chopped Carbon fiber impregnated with 20% $KHCO_3$ (CF-K)

A sample of commercially available activated carbon granules Norit PK 1-3 impregnated with 20% $KHCO_3$ (AC-K)

A sample prepared according to this invention containing 20% Cellulose and 80% of a powdered active carbon impregnated with 20% $KHCO_3$ (AC-NCC-K) extruded into granulates of 0.5-1.5mm.

This is illustrated here by 4 examples – first NCC precipitation then mixing with AC, extrusion and impregnation; second NCC precipitation than mixing with AC, adding $KHCO_3$ and extrusion; third making solution, adding AC, precipitating, extrusion and impregnation; and 4th - making solution, adding AC, precipitating, adding $KHCO_3$, extrusion .

Option 1:

20 g cellulose are placed into a 1 l glass vessel and mixed with 200 gr 70 wt% $ZnCl_2$ solution in water. The mixture was kept under continuous stirring (200 rpm) at 50 C until a transparent solution was obtained (20 min). 500 gr cold water was added to the reactor under continuous stirring. Stirring was kept for additional 15 min at room temperature to allow precipitates to be formed. The obtained slurry was separated from liquid by centrifugation (5000 rpm; 10 min), nanocellulose solids were washed 5 times with water (1:10). After last washing NCC was mixed with 50 gr AC and water to get a slurry with appropriate extrusion properties. The slurry was extruded to particle size 0.5 -1.5 mm, dried at 90°C and impregnated with 15 gr $KHCO_3$ dissolved in 60 ml water. Water was evaporated and the sample was dried at 90°C.

Option 2:

20 g cellulose are placed into a 1 l glass vessel and mixed with 200 gr 70 wt% $ZnCl_2$ solution in water. The mixture was kept under continuous stirring (200 rpm) at 50 C until a

transparent solution was obtained (20 min). 500 gr cold water was added to the reactor under continuous stirring. Stirring was kept for additional 15 min at room temperature to allow precipitates to be formed. The obtained slurry was separated from liquid by centrifugation (5000 rpm; 10 min), nanocellulose solids were washed 5 times with water (1:10). After last washing NCC was mixed with 50 gr AC and 15 gr KHCO_3 dissolved in 60 ml water. Water was evaporated until the slurry applicable for extrusion was obtained. Extrusion of granulates of 0.5 – 1.5 mm was performed. Finally the sample was dried at 90°C.

Option 3:

20 g cellulose are placed into a 1 l glass vessel and mixed with 200 gr 70 wt% ZnCl_2 solution in water. The mixture was kept under continuous stirring (200 rpm) at 50 C until a transparent solution was obtained (20 min). 50 gr of AC was mixed with the solution and 500 gr cold water was added to the reactor under continuous stirring. Stirring was kept for additional 15 min at room temperature to allow precipitates to be formed. The obtained slurry were separated from liquid by centrifugation (5000 rpm; 10 min), nanocellulose/AC solids were washed 5 times with water (1:10). After last washing NCC/AC mixture was extruded to particle size 0.5 – 1.5 mm and dried at 90°C. The granules were mixed with 15 gr KHCO_3 dissolved in 60 ml water. Water was removed by evaporation and the sample was dried at 90 C.

Option 4:

20 g cellulose are placed into a 1 l glass vessel and mixed with 200 gr 70 wt% ZnCl_2 solution in water. The mixture was kept under continuous stirring (200 rpm) at 50 C until a transparent solution was obtained (20 min). 50 gr of AC was mixed with the solution and 500 gr cold water was added to the reactor under continuous stirring. Stirring was kept for additional 15 min at room temperature to allow precipitates to be formed. The obtained slurry were separated from liquid by centrifugation (5000 rpm; 10 min), nanocellulose/AC solids were washed 5 times with water (1:10). After last washing NCC/AC mixture was mixed with 15 gr KHCO_3 dissolved in 60 ml water. Water was evaporated until the slurry applicable for extrusion was obtained. Extrusion of granulates of 0.5 – 1.5 mm was performed and they were dried at 90°C.

A sample prepared according to this invention containing 20% Cellulose and 80% of Lignin, was extruded into granulates of 0.5-1.5mm. Whereby the lignin is subsequently carbonized by heating at 300°C for 3 hours in a closed vessel and the sample is thereafter impregnated with 20% KHCO_3 (AC-NCC-K) extruded into granulates of 0.5-1.5mm

Option 1 lignin:

20 g cellulose are placed into a 1 l glass vessel and mixed with 200 gr 70 wt% ZnCl_2 solution

in water. The mixture was kept under continuous stirring (200 rpm) at 50 C until a transparent solution was obtained (20 min). 500 gr cold water was added to the reactor under continuous stirring. Stirring was kept for additional 15 min at room temperature to allow precipitates to be formed. The obtained slurry was separated from liquid by centrifugation (5000 rpm; 10 min), nanocellulose solids were washed 5 times with water (1:10). After last washing NCC was mixed with 50 gr lignin and water to get a slurry with appropriate extrusion properties. The slurry was extruded to particle size 0.5 -1.5 mm, dried at 90°C, carbonized by heating at 300°C for 3 hours in a closed vessel and impregnated with 15 gr KHCO₃ dissolved in 60 ml water. Water was evaporated and the sample was dried at 90 C.

Option 2 lignin:

20 g cellulose are placed into a 1 l glass vessel and mixed with 200 gr 70 wt% ZnCl₂ solution in water. The mixture was kept under continuous stirring (200 rpm) at 50 C until a transparent solution was obtained (20 min). 50 gr of lignin was mixed with the solution and 500 gr cold water was added to the reactor under continuous stirring. Stirring was kept for additional 15 min at room temperature to allow precipitates to be formed. The obtained slurry was separated from liquid by centrifugation (5000 rpm; 10 min), nanocellulose/lignin solids were washed 5 times with water (1:10). After last washing NCC/lignin mixture was extruded to particle size 0.5 – 1.5 mm and dried at 90°C, carbonized by heating at 300°C for 3 hours in a closed vessel and impregnated with 15 gr KHCO₃ dissolved in 60 ml water. Water was removed by evaporation and the sample was dried at 90 C.

EXAMPLE E: CO₂ Adsorption Capacity

The samples of Example D are tested to establish CO₂ adsorption from Air. The samples containing Activated Carbon showed a significant and fast adsorption of CO₂; while the Carbon Fiber based sorbent (CF-K) hardly adsorbed any CO₂.

EXAMPLE F: Particle strength

The particles from EXAMPLE D are tested during 5 cycles whereby the conditions varied from T= 30°C to T=120°C in the presence of air (at 30°C) and steam. After 5 cycles the sample of commercially available activated carbon granules (AC-K) exhibits a significant amount (> 10%) of attrition forming fines (< 500 microns), while this is not observed in the case of the samples containing Carbon Fiber and the samples according to this invention

EXAMPLE G:

A sample is prepared according to this invention containing 20% Cellulose and 80% Alginate containing basic Nitrogen species.

CLAIMS

1. A method for preparing a shaped cellulose article containing activated carbon, preferably suitable and adapted for CO₂ capture from an air stream by contacting the article with CO₂ from an air stream, then releasing the captured CO₂ by a temperature and/or pressure swing, comprising the following steps:

- a) contacting cellulose with an ionic liquid to form a liquid cellulose mass,
- b) forming a mixture of an activated carbon or a carbonisable component in the liquid cellulose mass of step a),
- c) shaping the mixture to form a shaped cellulose article containing activated carbon or a carbonisable component,
- d) In case the mixture comprises a carbonisable component, in-situ carbonisation of the carbonisable component in the liquid cellulose mass before or after shaping step c),
- e) optionally precipitating the mixture before or after shaping step c) to form a precipitate mixture comprising the activated carbon or carbonisable component and cellulose,
- f) removing the ionic liquid before said shaping step c) followed, if needed, by chemical modification for CO₂ capture .

2. The method according to claim 1 wherein in step a) the ionic liquid is a molten salt, preferably comprising ZnCl₂ or CaCO₃, preferably a ZnCl₂ hydrate, more preferably ZnCl₂.4H₂O, preferably in substantial absence of protic acid, more preferably further comprising a proton scavenger, preferably ZnO, and wherein preferably the cellulose component of the biomass is delaminated but not dissolved by the ionic liquid.

3. The method of claim 1 or 2, wherein in step b) the activated carbon is provided from an external source, preferably the activated carbon being obtained by carbonisation of carbonisable components from a cellulose containing biomass, preferably lignin, hemicellulose or peptides or combinations thereof and wherein the method more preferably comprises after contacting step a), a separation step wherein carbonisable components are separated from cellulose containing biomass, subjected to a separate carbonisation step to form activated carbon, which then is provided to form the mixture in step b).

4. The method according to claims 1 or 2, wherein in step a) biomass comprising cellulose and carbonisable components is contacted with ionic liquid and the active carbon is formed in-situ in a step d) by preferably partial carbonisation of the carbonisable components in the presence of the cellulose.

5. The method according to anyone of claims 1 - 4, wherein the active carbon is obtained by preferably partial carbonisation of carbonisable components of a cellulose containing biomass by heating the carbonisable components to a temperature of above 100°C, preferably above 150, 200 or even 250°C and in case of in-situ carbonisation step d) according to the method of claim 4, heating the carbonisable component in the presence of the cellulose preferably under 500°C, more preferably under 400, 300, 250 or even under 200°C.

6. The method according to anyone of claims 3 - 5, wherein the carbonisation is done in the presence of an activator preferably $ZnCl_2$, KOH, K_2CO_3 , Fe_2O_3 , ZnO, $KHCO_3$, Mg-Al or a mixture thereof and preferably the activator is present when using carbonisation temperatures between 100 and 350°C, preferably between 100 and 300°C, more preferably between 150 and 250°C.

7. The method according to anyone of claims 3 - 6, wherein in-situ carbonisation step d) is done in the mixture after step a) and before precipitation step b) or in the precipitate after precipitation step b) and before shaping or on the shaped article after shaping step c).

8. The method according to anyone of claims 1 to 7, wherein in step c) the shaped article is shaped by extrusion or spinning, preferably to elongate or particulate shaped articles.

9. The method according to anyone of claims 1 – 8 wherein a CO_2 adsorbent is added to the mixture before shaping step c), preferably adsorbed in the activated carbon, or wherein the CO_2 adsorbent is added to the shaped cellulose article comprising activated carbon and the CO_2 adsorbent is adsorbed in the active carbon in the shaped cellulose article,

and/or wherein the activation of the carbon and the functionalization as a CO_2 adsorbent is achieved in one process step.

10. A shaped article obtainable by anyone of the methods of claims 1 to 9, preferably fibers, yarns, films, extruded articles, microspheres, beads, extrudate particles, granulates and articles made from the shaped articles, preferably fabrics or particle beds.

11. The shaped article according to claim 10 in the form of an elongate shaped article, in particular a fiber or film, having a long axis and having a smallest diameter of a cross-section perpendicular to the long axis smaller than 0.5 mm, preferably smaller than 0.2 mm and more preferably smaller than 0.1 mm.

12. The shaped article according to anyone of claims 10 – 11 comprising a CO₂ adsorbent, preferably a carbonate, preferably potassium bicarbonate or one or more Nitrogen containing compounds preferably amine compounds or combinations thereof.

13. The shaped article according to anyone of claims 10 - 12 comprising an amount of activated carbon relative to the total weight of the shaped article between 1 and 90 wt.%, preferably between 5 and 80 wt.%, more preferably between 10 and 70 wt.% and in case of elongate shaped articles of claim 17 the amount of active carbon is preferably between 1 and 30 wt.%, more preferably 5 and 25 wt.%.

14. Use of the shaped article according anyone of claims 10 - 13 as a catalyst, a catalyst support or as an adsorbent or adsorbent support, preferably as an adsorbent or adsorbent support for capturing and/or concentrating of CO₂ from CO₂ containing sources such as flue gas, biogas and/or air.

15. A method for CO₂ adsorption comprising contacting a CO₂ containing gas with a shaped article according to anyone of claims 10 – 13 wherein the active carbon comprises a CO₂ adsorbent and wherein the shaped article preferably is in the form of fibers, more preferably a fabric made of the fibers, or in the form of a bed of particles or in the form of structured adsorbers, or in the form of monoliths.

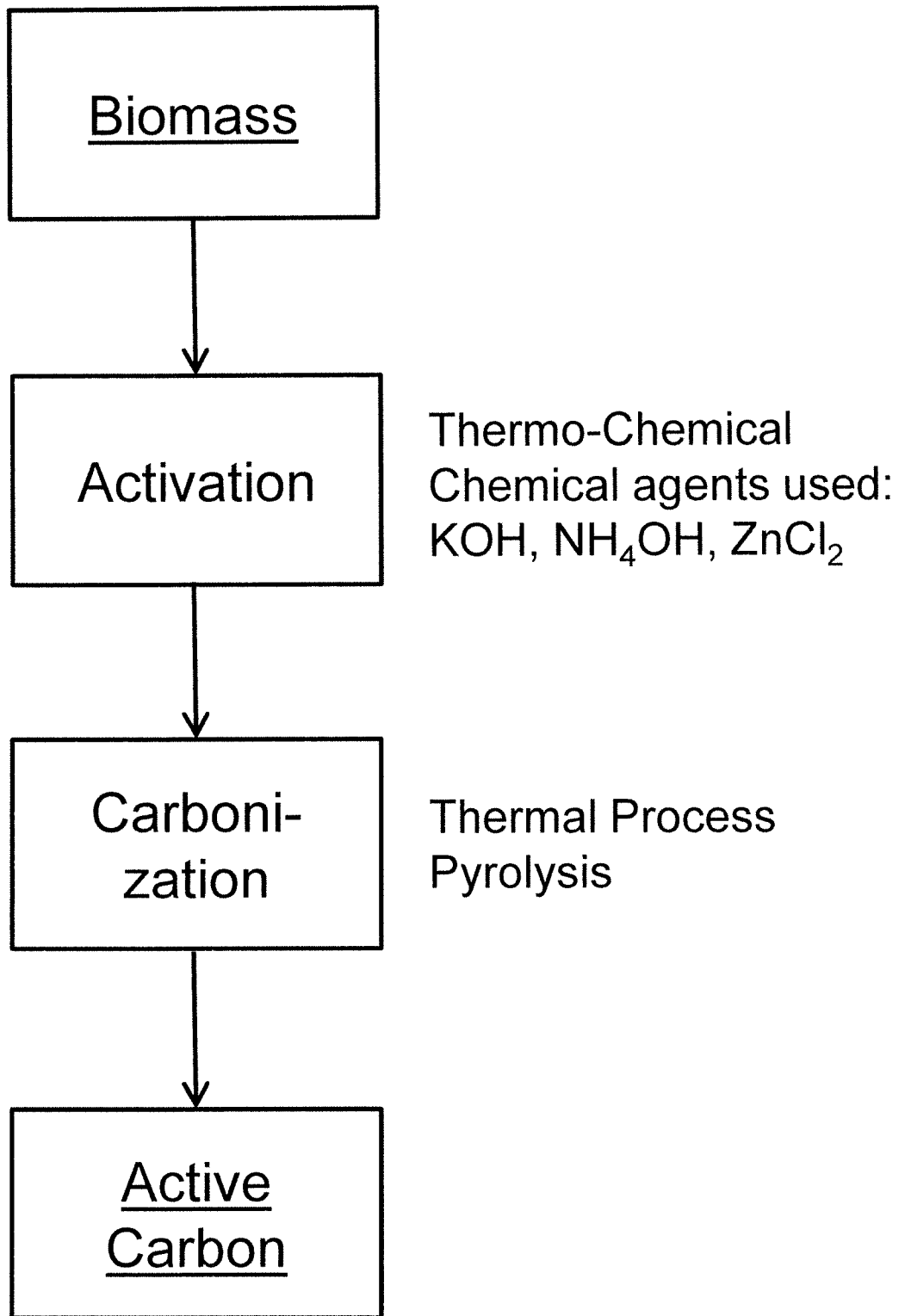
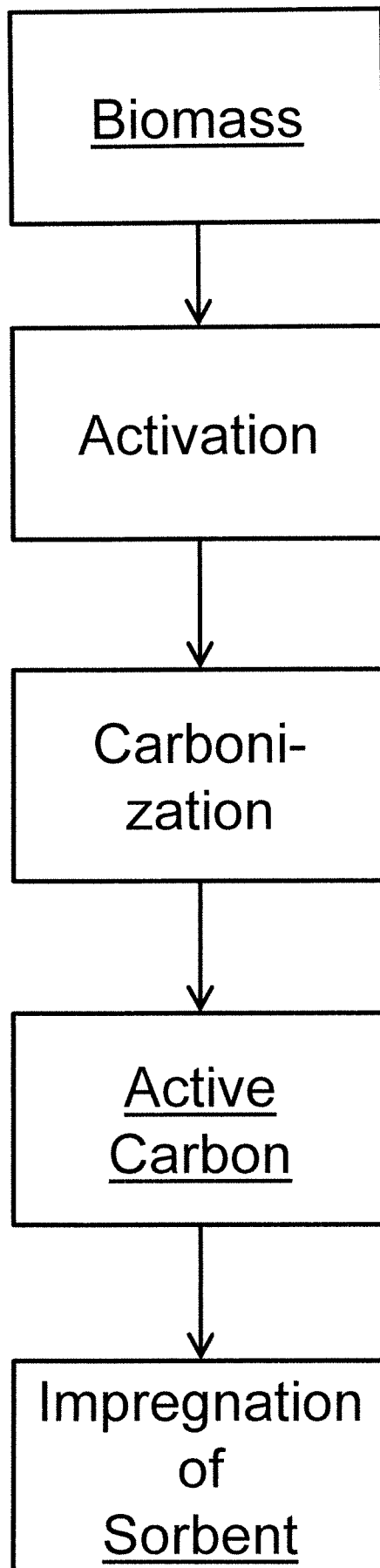


FIG. 1A



Functionalization:
Adding the
sorbent species

FIG. 1B

3/5

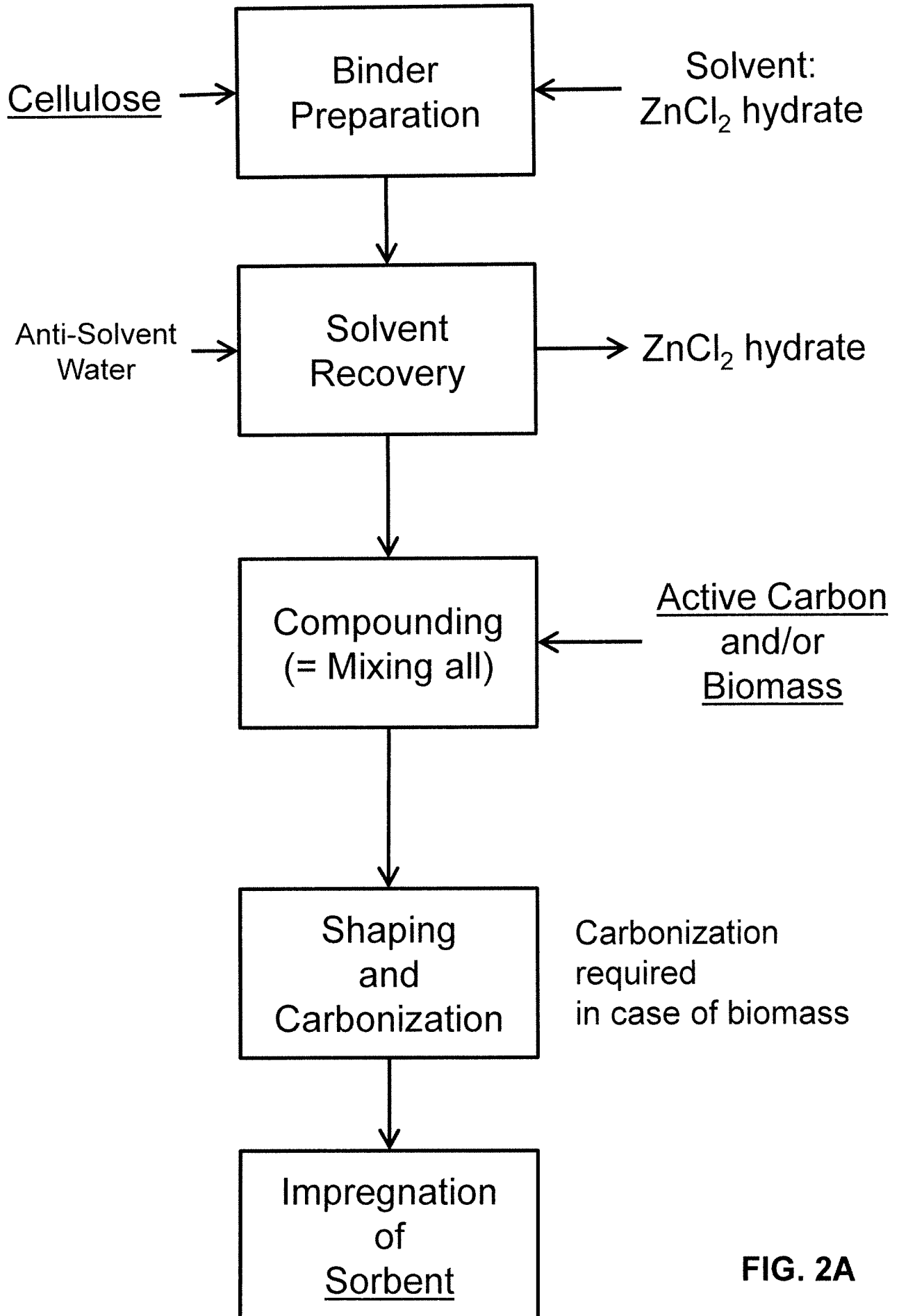


FIG. 2A

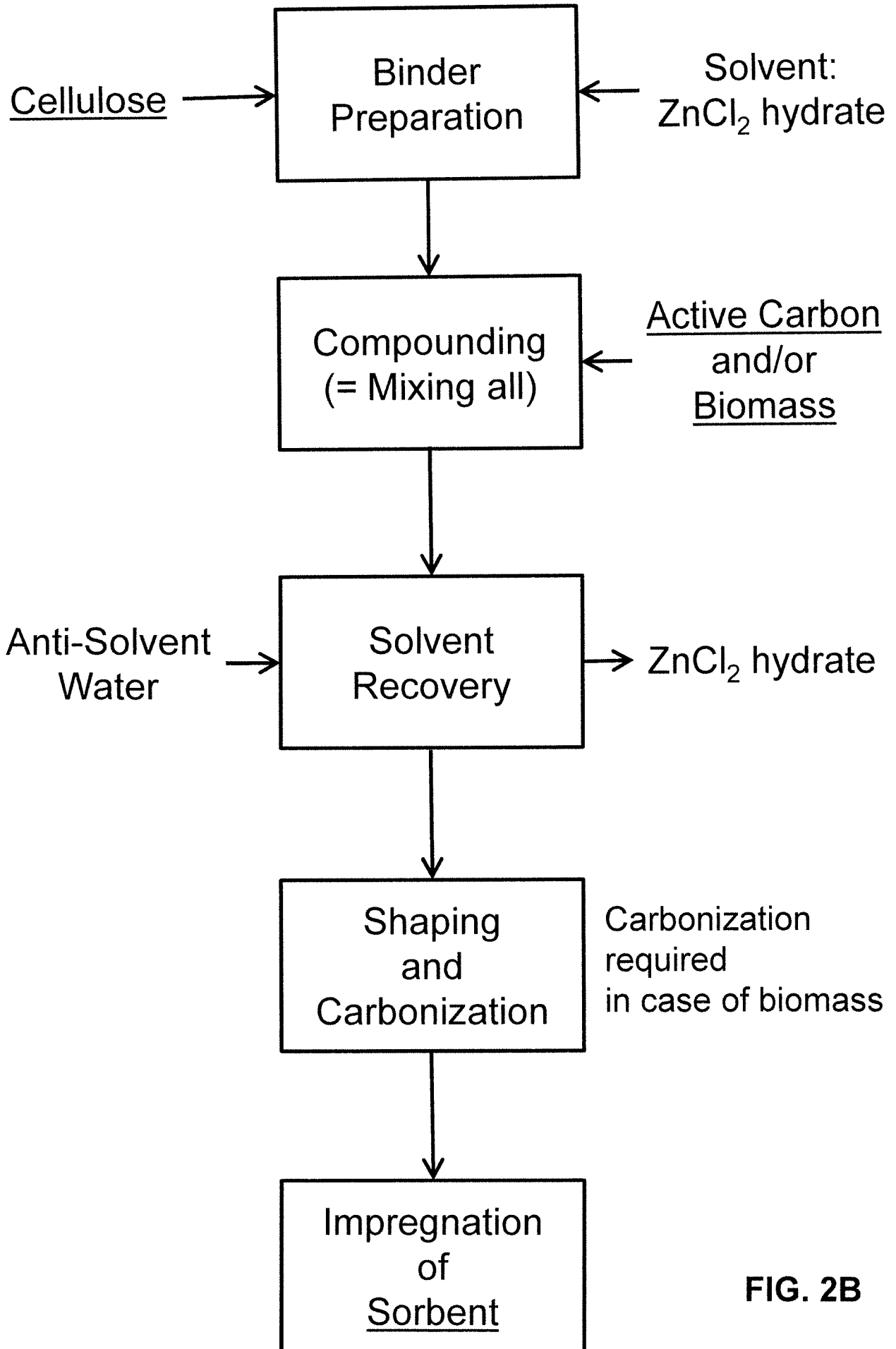


FIG. 2B

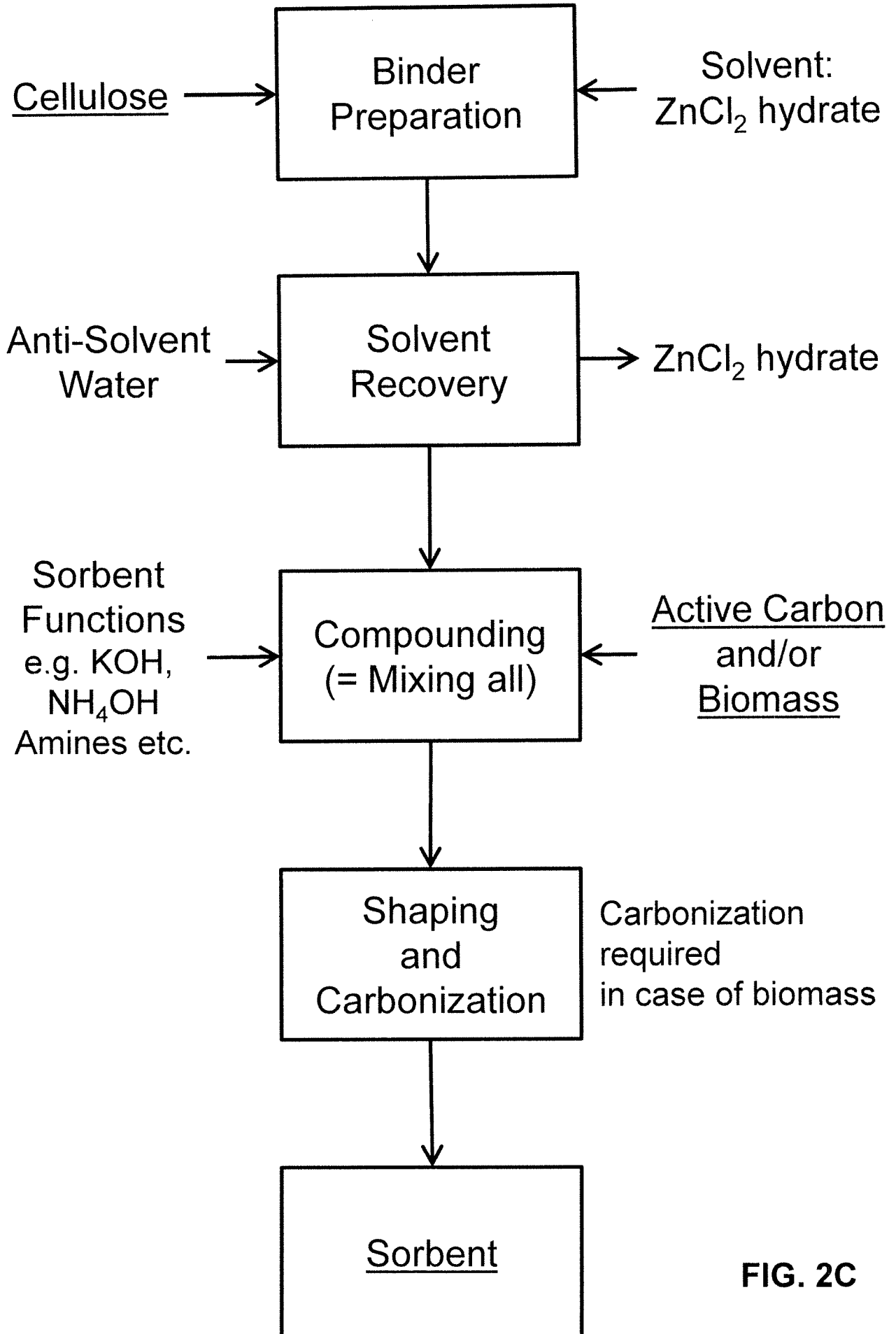


FIG. 2C

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/053155

A. CLASSIFICATION OF SUBJECT MATTER
 INV. B01J20/20 B01J20/24 B01D53/02 B01J20/28 B01J20/30
 C08L1/02 C08B1/00
 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)
 B01J B01D C09J C08L C08B 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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2014/194603 A1 (LEHMANN ANDRE [DE] ET AL) 10 July 2014 (2014-07-10) paragraph [0053] - paragraph [0054]; example 1 paragraph [0040] - paragraph [0041]; claims 16, 17, 30	1-13
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A	WO 2017/055407 A1 (BIOECON INT HOLDING N V [NL]) 6 April 2017 (2017-04-06) cited in the application the whole document	1-15
X,P	WO 2019/229030 A1 (CLIMeworks AG [CH]) 5 December 2019 (2019-12-05) the whole document	1-15

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"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
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 14 February 2020	Date of mailing of the international search report 25/02/2020
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Klemps, Christian
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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