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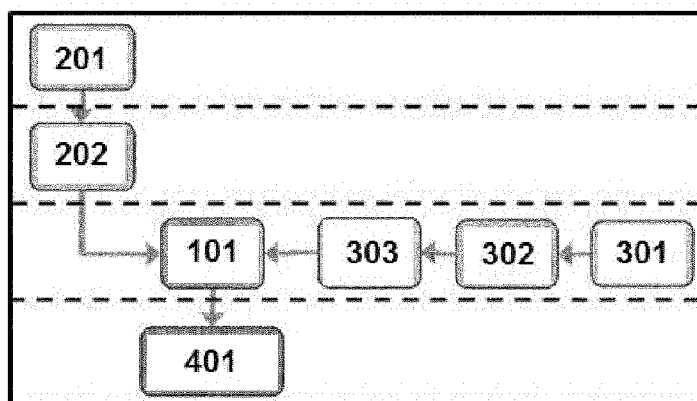
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(54) Title: CONTINUOUS PRODUCTION OF AN ADSORPTION PRODUCT OF A VITAMIN

Figure 2



(57) Abstract: The invention relates to a process for the continuous production of an adsorption product of one or more vitamins adsorbed on the surface of a particulate adsorbent material, the process comprising the steps of: continuously feeding particulate adsorbent material into an elongated cavity; continuously conveying the material within the cavity in a downstream direction; continuously spraying a liquid adsorbate onto the particulate adsorbent material, wherein the liquid adsorbate comprises one or more vitamins; continuously agitating the mixture thus obtained to form the adsorption product; and continuously removing the adsorption product from the cavity. The invention further relates to an adsorption product obtained by such process and the use of such adsorption product in nutrition and preferably animal nutrition.



Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
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Continuous production of an adsorption product of a vitamin

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The invention relates to process for the continuous production of an adsorption product of one or more vitamins adsorbed on the surface of a particulate adsorbent material. The invention further relates to an adsorption product obtained by such process and its use in nutrition and preferably animal nutrition

Vitamins are essential nutrients that an organism requires in limited amounts. An organic chemical compound is called a vitamin when the organism cannot make the compound in sufficient quantities, and it must be obtained through the diet. Vitamins have been produced as commodity chemicals and made widely available as inexpensive semisynthetic and synthetic-source multivitamin dietary and food supplements and additives since the middle of the 20th century. They also play an important role in animal nutrition.

20

Vitamin E refers to a group of compounds that include both tocopherols and tocotrienols. As a fat-soluble antioxidant, it interrupts the propagation of reactive oxygen species that spread through biological membranes or through a fat when its lipid content undergoes oxidation by reacting with more-reactive lipid radicals to form more stable products. Vitamin E is sold as a dietary supplement, either by itself or incorporated into a multi-vitamin product. It is also sold as animal food supplement.

25

For example, animal nutrition products have been developed that contain vitamins in general and vitamin E in particular in the form of an adsorption product of the one or more vitamins adsorbed on the surface of a particulate adsorbent material. These products were discontinuously produced in batch processes to be able to guarantee homogenous

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filler loadings and generally high quality. From the viewpoint of production efficiency, however, continuous process settings would be preferable.

The invention aims to provide a process for the continuous production of a high quality
5 adsorption product of one or more vitamins adsorbed on the surface of a particulate adsorbent material.

Against this background, the invention relates to a process for the continuous production
of an adsorption product of one or more vitamins adsorbed on the surface of a particulate
10 adsorbent material, the process comprising the steps of: continuously feeding particulate
adsorbent material into an elongated cavity; continuously conveying the material within
the cavity in a downstream direction; continuously spraying a liquid adsorbate onto the
particulate adsorbent material, wherein the liquid adsorbate comprises one or more
vitamins; continuously agitating the mixture thus obtained to form the adsorption product;
15 and continuously removing the adsorption product from the cavity. Such continuous
setting has been found out to yield a high quality adsorption product at increased
production efficiency as compared to state of the art methods.

In one embodiment, the one or more vitamins comprise one or more E vitamins, i.e., one
20 or more of the compounds selected from the group of α -, β -, γ - or δ -tocopherol, α -, β -, γ -
or δ -tocotrienol, or derivatives such as organic esters thereof.

In one embodiment, the particulate adsorbent material is granular silica, charcoal or
zeolite material. Granular silica material is preferred in some embodiments. The average
25 grain size of the granular material may be between 10-1000 μm , preferably 50-500 μm
and more preferably between 200-400 μm as determined with laser diffraction system dry
measurement (Malvern MasterSizer 3000). The inclusive graphic standard deviation of
the granular material diameter as expressed in phi units may be smaller 1. The particulate
adsorbent material is preferably a porous material. Specifically, it is preferred that the
30 adsorbent material has a specific surface area of at least 100 m^2/g and preferably at least
200 m^2/g as determined using the BET method according to DIN ISO 9277. In one

embodiment, the particulate adsorbent material is a porous material having an oil adsorption capacity of between 100 and 300 ml/100g, as determined according to DIN ISO 19246.

5 In one embodiment, the liquid adsorbate comprises one or more liquid vitamins in their pure form. For example, E vitamins are in a liquid state at room temperature. It may be that these pure vitamins comprise some residual solvent, e.g., less than 10 wt% or less than 5 wt% or less than two wt% of solvents, e.g., organic solvents such as toluene, propylene carbonate, ethylene carbonate hexane or heptane.

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In another embodiment, a liquid solution of dissolved non-liquid vitamins may be provided as adsorbate, wherein preferably the solvent is an organic solvent.

15 In one embodiment, the average residence time of the particulate material in the cavity is adjusted to be between 5 and 20 minutes and preferably between 10 and 15 minutes. At a given cavity layout, the residence time can be adjusted by varying the particulate adsorbent material feed rate and, in the case of active conveying, the conveying speed. Depending on cavity volume, exemplary particulate adsorbent material feed rates can exceed 100, 500, 1.000 or even 5.000 kg/h.

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In one embodiment, the ratio of the introduction rate of liquid adsorbate to the introduction rate of particulate adsorbent material is between 60 and 140 ml, preferably between 80 and 120 ml of liquid adsorbate per 100 g particulate adsorbent material. These ratios may be employed in the process of the invention to obtain a product of sufficiently high and
25 homogenous load. Generally, the ratio should be balanced and consider the adsorption capacity of the material pair.

In one embodiment, the sprayed liquid adsorbent has a temperature of between 50 and 80°C and preferably between 60 and 70°C and/or wherein the liquid adsorbent is sprayed
30 through one or more nozzles and/or wherein the spray pressure of the liquid adsorbent is between 2 and 5 bar. Hence, in this embodiment the liquid is preheated, which aids the

adjustment of an appropriate viscosity and hence spraying behavior. In some applications, viscosities between 10 and 500 mPa·s and preferably between 50 and 200 mPa·s may be considered ideal.

- 5 In one embodiment, the particulate adsorbent material can be provided and conveyed at a temperature of between 15-35°C.

In one embodiment, the cavity has a tubular shape and/or wherein the L/D (length/diameter) ratio of the cavity is between 2 and 10, preferably between 3 and 7. The
10 total volume of the cavity can, in one example, be between 0,1 and 2 m³, but smaller or larger volumes are also possible. Such layouts may be used to obtain a product of sufficiently high and homogenous load. A too small ratio or too large volume may deteriorate product quality. A too large ratio or too small volume may decrease process efficiency.

15 In one embodiment, the cavity comprises an initial transport zone where the particulate adsorbent material is actively conveyed in a downstream direction, preferably by a screw conveyor, and wherein the cavity comprises a mixing zone where the liquid adsorbate is sprayed onto the particulate adsorbent material and the mixture thus obtained is agitated
20 by mixing instruments to form the adsorption product, preferably by mixing instruments such as mixing paddles that are mounted on a shaft that extends through the cavity in a longitudinal direction.

The process may be carried out in an apparatus that includes a mixing drum comprising
25 the elongated and preferably tubular cavity with an upstream adsorbent inlet, a downstream product outlet and one or more injection nozzles for spraying the liquid adsorbate. A rotating member may extend through the cavity in its longitudinal direction. It may comprise at least one helical conveying blade to form a screw conveyor in one longitudinal zone of the cavity and mixing instruments in another longitudinal zone of the
30 cavity.

The mixing instruments such as mixing paddles are preferably distributed over the length of the mixing zone. The distribution can be regular or irregular. In one embodiment, the operative surfaces of the paddles are slanted backwards. In other words, the operative surfaces of the paddles are not parallel to the longitudinal direction cavity but are slanted to effect reverse movement of the particulate material. Such reverse mixing can beneficially influence adsorption quality and homogeneity. Other suitable mixing instruments that may be used alternatively to or in conjunction with mixing paddles comprise screw fragments.

In one embodiment, the cavity comprises an intermediate transport zone within the mixing zone, where premixed material is actively conveyed in a downstream direction from a primary to a secondary mixing zone, preferably by another screw conveyor. In this embodiment, the liquid adsorbate is sprayed onto the particulate adsorbent material in the primary mixing zone prior intermediate transport.

In an alternative embodiment, the secondary mixing zone can be replaced by a resting zone without mixing paddles.

In one embodiment, the cavity comprises a terminal transport zone where product material is actively conveyed in a downstream direction from the mixing zone to the outlet, preferably by another screw conveyor.

Indications as made above regarding the cavity altogether, such as average residence times, L/D ratio, cavity volume, or the like may in one embodiment more specifically apply to the mixing zone or mixing zones of the cavity.

In one embodiment, the screw conveyor and/or shaft-mounted mixing elements are operated at a rotational speed such that the peripheral speed of the screw conveyor and/or shaft-mounted mixing elements is 1 m/s or less. These low peripheral speeds can be preferred to avoid excessive frictional heat that may negatively affect potentially heat-sensitive vitamin compounds and unwanted dust formation due to grinding of the

particulate materials. The explosion risk of smoldering, fires and dust explosions can thereby be minimized. The peripheral speed as defined above relates to the point of highest radial extension. Depending on the radius of the cavity, such can correspond to rotational speeds of, e.g., less than 50 rpm.

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In one embodiment, the cavity is inclined in downstream direction, wherein the incline angle is preferably between 15 and 45° and/or wherein the cavity is partially filled with material, wherein preferably the mixing zone comprises a subsection that is fully filled with material and a subsection that is partially filled with material. It can be provided that the incline angle and the length and diameter of the mixing zone are such that there are longitudinal positions within the mixing zone whose entire cross-section remains below the level of product removal, and preferably such that longitudinal positions whose entire cross-section remains below the level of product removal account for at least 30% of all longitudinal positions within the mixing zone.

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In one embodiment, the liquid adsorbate is sprayed onto the particulate adsorbent material at a longitudinal position of the cavity where it is fully filled with particulate adsorbent material and/or wherein the cavity volume unoccupied by the particulate material is filled with ambient air. In other words, no inert gas blanket is introduced to the cavity. Dust formation and flammable vapor may largely be avoided by the continuous process where the liquid adsorbate is directly sprayed onto the adsorbent material and the mixture is conveyed through an elongated cavity. Inert gas may hence not be needed to avoid any explosion risk, even when using flammable materials.

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25 The invention further relates to an adsorption product of one or more vitamins adsorbed on the surface of a particulate adsorbent obtained by the process of the invention and the use of such adsorption product in nutrition and preferably animal nutrition.

Further details and advantages of the invention will be explained in the following with reference to the figures and working examples. The figures show:

30

Figure 1: a longitudinal section of a mixing drum that may be used to carry out a process of the invention; and

Figure 2: a flow diagram illustrating the process of the invention.

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In Figure 1 a mixing drum that may be used to carry out a process of the invention is schematically illustrated. The mixing drum 11 is generally tubular in shape and has an elongated tubular cavity 12 of essentially circular cross-section for receiving the particulate granular adsorbent material. On the upstream end of the cavity 12, an adsorbent inlet opening 13 is provided on the upper side of the cavity wall. On the downstream end of the cavity 12, a product outlet opening 14 is provided on the lower side of the cavity wall. The mixing drum 11 is made of stainless steel and consists of two halves, a base 11a and a lid 11b. The inlet opening 13 is arranged at the lid 11b. The outlet opening 14 is arranged at the base 11a. The overall length L of the cavity 12 is 140 cm and the diameter D is 20 cm, accounting for an L/D ratio of 7,0 and a total chamber volume of 0,044 m³.

The inlet opening 13 may be connected to a feeding apparatus for continuously introducing a controlled amount of granular adsorbent material to the cavity 12, such as a suitable gravimetric loss-on-weight type powder feeder. Such is apparent from the flow diagram of Figure 2, where the mixing step 101 that is carried out in the apparatus 10 is preceded, on the one hand, by a step 201 of charging a feeder from a granular adsorbent material reservoir and a step 202 of feeding the granular adsorbent material to the inlet 13.

25

A rotating shaft 15 extends through the cavity in longitudinal direction. The shaft 15 is arranged in the center of the circle defined by the cross-section of the cavity 12 and is operably connected to an electric motor for driving the shaft 15 at a desired rotation speed. The regular rotation direction of the shaft 15 is counterclockwise, when looking in the direction of the product flow.

30

The rotating shaft 15 comprises two types of rotating annexes that are distributed over the length of the cavity 12, namely helical conveying blades 17a, 17c and 17e as well as mixing instruments 18-1 and 18-2b. The helical conveying blade 17a is arranged around the shaft 15 in the initial transport section 12a of the cavity 12 that is adjacent to the inlet opening 13. The mixing instruments 18-1 and 18-2 are distributed within a mixing zone 12b that follows the initial transport section 12a. The mixing zone 12b is separated from a resting zone 12d by an intermediate transport zone 12c, where the helical conveying blade 17c is arranged around the shaft 15. The intermediate transport zone 12c is rather short and the number of full rotations of the helical conveying blade 17c around the shaft 15 is less than two. The resting zone 12d is followed by a terminal transport zone 12e, where the helical conveying blade 17e is arranged around the shaft 15.

The mixing instruments comprise a number of pairs of mixing paddles 18-1, wherein the individual paddles 18-1 of the pairs are slightly offset in longitudinal direction. Specifically, in the mixing zone 12b, two helical mixing blade fragments 18-2 are arranged between the pairs. In contrast to the helical conveying blades 17a, 17c or 17e, the blade fragments 18-2 do not comprise a closed surface but rather an open construction such as to limit the feeding forward action.

The resting zone 12d is devoid of any mixing instruments or helical blades.

In an alternative embodiment, the resting zone 12d can be replaced by a secondary mixing zone comprising mixing paddles and/or blade fragments.

The apparatus 10 further comprises injection nozzles 19 for injecting a liquid adsorbate to the cavity 12, and more specifically to an early position within the mixing zone 12b. Specifically, the nozzles 19 are arranged at a longitudinal position corresponding to the upstream pair of mixing paddles 18. The injection nozzles 19 are connected to a suitable liquid supply that includes a tank, a heating, a liquid pump and a volume flow meter whose signal is used to regulate pump operation. Such, again, is apparent from the flow diagram of Figure 2, where the mixing step 101 is also preceded by a step 301 of suctioning liquid

adsorbate from a liquid adsorbate tank and, optionally, preheating the liquid adsorbate to a desired temperature, a step 302 of pumping the liquid adsorbate to the nozzles 19 and a step 303 of measuring the volume flow towards the nozzles 19.

- 5 The rotating shaft 15 and the rotating annexes 17a, 17c, 17e, 18-1 and 18-2 are all made of stainless steel. The injection nozzles 19 are arranged at the lid 11b. The rotating shaft 15 and motor are arranged at the base 11a.

10 The outlet opening 14 can be connected to a suitable packaging apparatus for weighting and packaging the product. Also this is apparent from the flow diagram of Figure 2, where the mixing step 101 is followed by a packaging step 401.

15 A lifting means including, for example, suitable swivel joints and a hydraulic cylinder may be used to lift the end section of the tubular mixing drum 11 to adjust a certain incline of the tubular cavity 12. In consideration of such incline, the mixing and resting zones 12b and 12d can further be subdivided in fully filled sections and partially filled sections. Specifically, owing to the essentially fluid behavior of suitable granular adsorbent materials, the materials will form an essentially planar surface within the cavity 12. The surface level corresponds essentially to the level of the lowest points of action of the
20 helical conveying blades 17c and 17e, respectively, as any fluidly behaving material that reaches these levels will be transported further by the blade 17c or 17e. The longitudinal position of the boundary between the fully filled and partially filled sections hence depends on the ratio of length to diameter of the mixing and resting zones 12b and 12d as well as on the incline angle of the cavity 12. In this regard, the incline angle is preferably set such
25 that the injection nozzles 19 are arranged at an early position within the mixing zone 12b that is fully filled in operation.

30 In an experimental setup, the mixing drum as shown in Figure 1 was loaded with a particulate silica material with a nominal median particle size of between 200-400 μm and a liquid of essentially pure E vitamins (TATG, tocopheryl acetate technical grade) having a viscosity of approx. 1000 mPa·s at 37°C as liquid adsorbent material.

The weight ratio of the granular silica material and the liquid adsorbent material was 48/52. The inclination of the cavity 12 was set to 33°. The rotation speed of the shaft was set to 45 rpm, which led to a peripheral speed of the rotating annexes 17a, 17c, 17e, 18-1 and 18-2 of around 0,5 m/s. Nozzle pressure was 4,5 bar. Silica temperature was 27°C.

Using these settings, the filled chamber volume was determined at 0,015 m³, corresponding to approx. 34% of the total chamber volume. The feed rates (granular material) necessary to attain certain average residence times (standard deviation is about 40%) as determined in this experiment are outlined in Table 1 below.

Table 1:

Residence time	Feed rate
10 min	52 kg /h
15 min	35 kg / h
20 min	26 kg /h

Where the mean residence time was set to 15 minutes, a dry product of good homogeneity was obtained. It can thus be expected that a 10-15 minutes residence time would be sufficient in the given setting. Accordingly, scaling calculations would suggest that an output of several tons of product per hour would be attainable with bigger mixers having a chamber volume of, for example, between 0,1 and 2 m³. Such scaling calculations for commercially available mixers are shown in Table 2 below.

Table 2

	Pilot Mixer	Ruberg DLM 350-1500	Ruberg DLM 800-3000
L [m]	1,4	1,5	3,0
D [m]	0,2	0,35	0,8
L/D	7,0	4,3	3,8

chamber [m ³] volume	0,0044	0,144			1,507		
filled [%]	34	34	50	75	34%	50%	75%
chamber [m ³] volume	0,015	0,049	0,072	0,108	0,512	0,754	1,130
feed rate at residence time [kg/h]							
5 min	104	342	502	752	3.566	5.246	7.868
10 min	52	171	251	376	1.783	2.623	3.934
15 min	35	114	167	251	1.189	1.748	2.623
20 min	26	85	125	188	892	1.311	1.967

Claims

1. A process for the continuous production of an adsorption product of one or more vitamins adsorbed on the surface of a particulate adsorbent material, the process comprising the steps of:
 - continuously feeding particulate adsorbent material into an elongated cavity;
 - continuously conveying the material within the cavity in a downstream direction;
 - continuously spraying a liquid adsorbate onto the particulate adsorbent material, wherein the liquid adsorbate comprises one or more vitamins;
 - continuously agitating the mixture thus obtained to form the adsorption product; and
 - continuously removing the adsorption product from the cavity.
2. The process of claim 1, wherein the vitamins comprise one or more E vitamins.
3. The process of any preceding claim, wherein the particulate adsorbent material is granular silica, charcoal or zeolite material, preferably granular silica material, wherein the average grain size of the granular material is preferably between 10-1000 μm , more preferably between 50-500 μm and further preferably between 200-400 μm .
4. The process of any preceding claim, wherein the particulate adsorbent material is a porous material having a specific surface area of at least 100 m^2/g and preferably at least 200 m^2/g and/or an oil adsorption capacity of between 100 and 300 $\text{ml}/100\text{g}$.
5. The process of any preceding claim, wherein the liquid adsorbate comprises one or more liquid vitamins in their pure form.

6. The process of any preceding claim, wherein the average residence time of the particulate material in the cavity is between 5 and 20 minutes, preferably between 10 and 15 minutes.
- 5 7. The process of any preceding claim, wherein the ratio of the introduction rate of liquid adsorbate to the introduction rate of particulate adsorbent material is between 60 and 140 ml, preferably between 80 and 120 ml of liquid adsorbate per 100 g particulate adsorbent material.
- 10 8. The process of any preceding claim, wherein the sprayed liquid adsorbent has a temperature of between 50 and 80°C and preferably between 60 and 70°C and/or wherein the liquid adsorbent is sprayed through one or more nozzles and/or wherein the spray pressure of the liquid adsorbent is between 2 and 5 bar.
- 15 9. The process of any preceding claim, wherein the cavity has a tubular shape and/or wherein the L/D (length/diameter) ratio of the cavity is between 2 and 10, preferably between 3 and 7.
- 20 10. The process of any preceding claim, wherein the cavity comprises an initial transport zone where the particulate adsorbent material is actively conveyed in a downstream direction, preferably by a screw conveyor, and wherein the cavity comprises a mixing zone where the liquid adsorbate is sprayed onto the particulate adsorbent material and the mixture thus obtained is agitated by mixing instruments to form the adsorption product, preferably by mixing instruments such as mixing
25 paddles that are mounted on a shaft that extends through the cavity in a longitudinal direction.
- 30 11. The process of claim 10, wherein the screw conveyor and/or shaft-mounted mixing elements are operated at a rotational speed such that the peripheral speed of the screw conveyor and/or shaft-mounted mixing elements is 1 m/s or less.

12. The process of any preceding claim, wherein the cavity is inclined in downstream direction, wherein the incline angle is preferably between 15 and 45° and/or wherein the cavity is partially filled with material, wherein preferably the mixing zone comprises a subsection that is fully filled with material and a subsection that is partially filled with material.
13. The process of claim 12, wherein the liquid adsorbate is sprayed onto the particulate adsorbent material at a longitudinal position of the cavity where it is fully filled with particulate adsorbent material and/or wherein the cavity volume unoccupied by the particulate material is filled with ambient air.
14. An adsorption product of one or more vitamins adsorbed on the surface of a particulate adsorbent obtained by the process of any preceding claim.
15. Use of an adsorption product of claim 14 in nutrition and preferably animal nutrition.

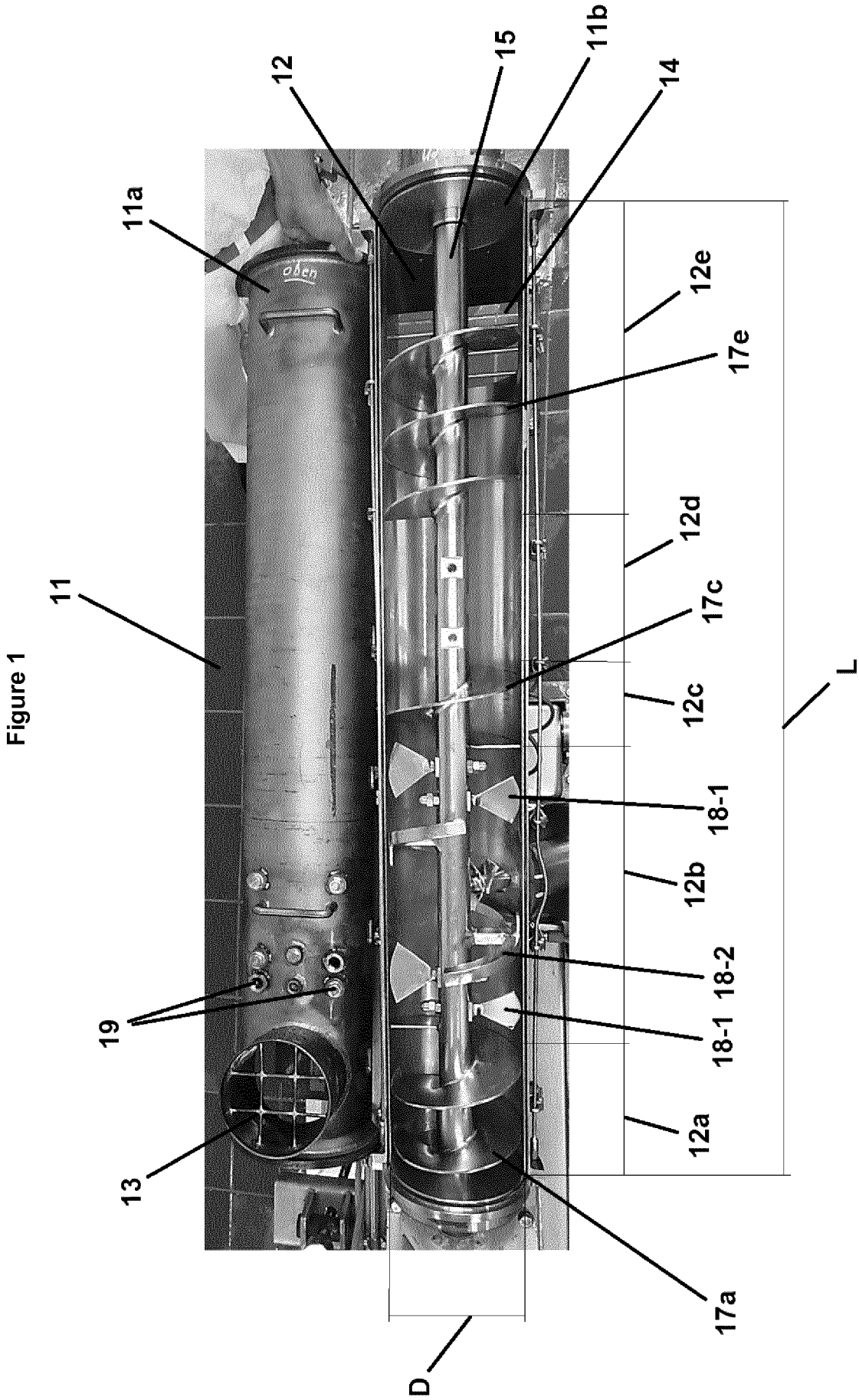
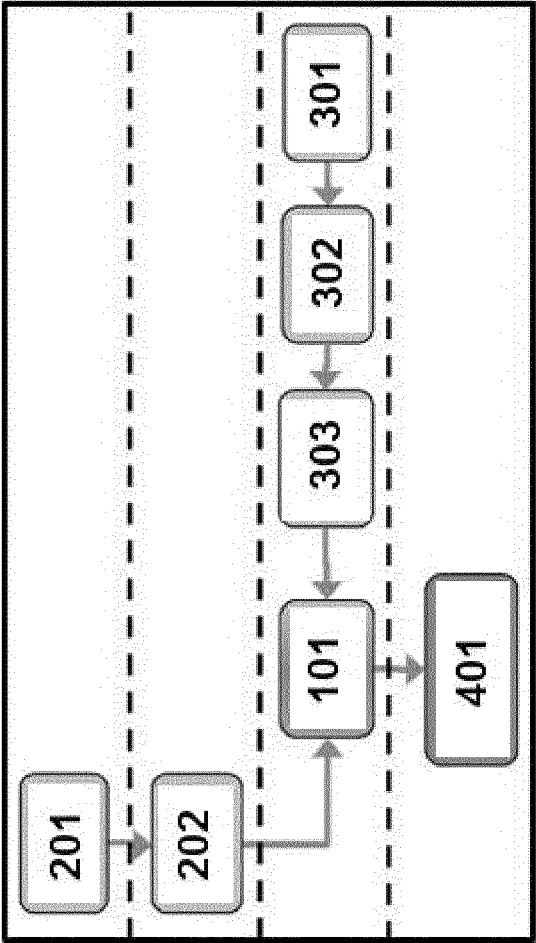


Figure 2



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/068776

A. CLASSIFICATION OF SUBJECT MATTER

INV. A61K9/14 A61K31/355 A23K20/174 A23L33/15 A23K20/28
A23K40/10 A23K40/30

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)

A61K C11C A23L A23K

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

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Y	paragraphs [0003], [0014] - [0016], [0021], [0022], [0025] paragraph [0041] - paragraph [0049] paragraph [0157] - paragraph [0160] paragraph [0163] - paragraph [0170] paragraph [0225] - paragraph [0227] paragraph [0241] - paragraph [0246] paragraph [0248] - paragraph [0258] paragraph [0277] - paragraph [0285]; claims 1-3, 10-12, 26-30 ----- -/-	4



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

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16/09/2019

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

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