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(54) Titre : PROCEDE DE SEPARATION DU GAZ DE FLUIDISATION DE RETOUR DANS UN REACTEUR DE
POLYMERISATION D'OLEFINE A GAZ-SOLIDES
(54) Title: METHOD OF SPLITTING THE RETURN FLUIDIZATION GAS IN A GAS SOLIDS OLEFIN POLYMERIZATION
REACTOR

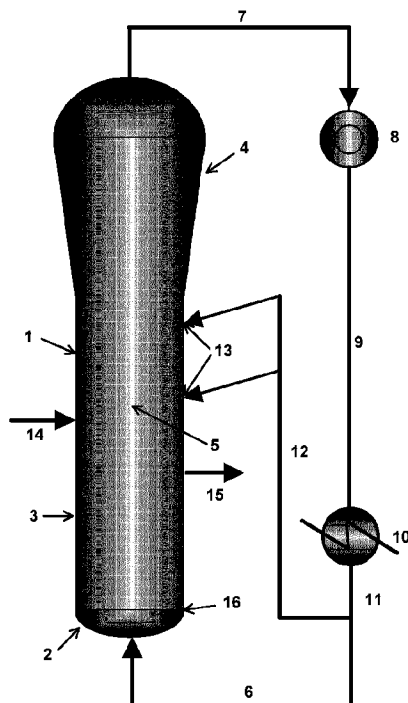


Fig 1

(57) **Abrégé/Abstract:**

The present invention relates to a process for polymerizing olefin monomer(s) in a gas solids olefin polymerization reactor wherein the fluidization gas is split and returned to the reactor into the bottom zone of the reactor and directly into the dense phase formed by particles of a polymer of the olefin monomer(s) suspended in an upwards flowing stream of the fluidization gas in the middle zone of the reactor.

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Method of splitting the return fluidization gas in a gas solids olefin polymerization reactor

The present invention is directed to the polymerization of olefins in a gas solids olefin polymerization reactor. More specifically, the present invention is directed to the polymerization of olefins in a gas solids olefin polymerization reactor with reduced polyolefin powder entrainment.

Background

Gas solids olefin polymerization reactors are commonly used for the polymerization of alpha-olefins such as ethylene and propylene as they allow relative high flexibility in polymer design and the use of various catalyst systems. A common gas solids olefin polymerization reactor variant is the fluidized bed reactor.

Typically, in gas solids olefin polymerization reactors the fluidization gas moving upwards through the dense phase in which the polymerization reaction takes place and the polyolefin particles are polymerized forms gas bubbles which entrain polyolefin powder into the disengaging zone near to the fluidization gas exit. This hydrodynamic pattern limits the filling degree of the reactor, the average bulk density and the reactor productivity. It can additionally cause difficulties related to fluidization gas circulation due to a risk of increased polyolefin powder entrainment. Further, the relatively low polyolefin powder concentration in the upper reactor zone can lead to stronger adhesion of the reactive powder at the inner reactor wall and it can generate wall sheeting and lump formation.

US 5,428,118 discloses a process for polymerizing olefins in a gas phase reactor in which hot fluidization gas withdrawn from the reactor is reintroduced into the disengaging zone via a tangential flow of gas or gas-solids in order to reduce polyolefin powder entrainment into the fluidization gas circulation system.

WO 2017/025330 A1 discloses a process for polymerizing olefins in a gas phase reactor in which a cooled stream of partially condensed fluidization gas withdrawn from the reactor is reintroduced into the disengaging zone in order to reduce polyolefin powder entrainment into the fluidization gas circulation system.

It now has been found that introducing circulation gas into the disengaging zone bears the risk of an increased polyolefin powder carry over in the circulation gas.

Thus there is still a need in the art to provide a process for polymerizing olefins with a gas solids olefin polymerization reactor with reduced powder entrainment in the circulation gas.

Summary of the invention

It has been surprisingly discovered that by cooling the circulation gas and injection of at least a part of the circulation gas into the upper half of the middle zone of a gas solids olefin polymerization reactor, the carry-over of particles of the polyolefin into the stream of disengaging fluidization gas withdrawn from the top zone of the gas solids olefin polymerization reactor is reduced and at the same time the cooling capacity of the the process is not sacrificed. In other words, a higher bulk density of the dense phase can be obtained over the whole polymerization process.

Thus, the present invention provides a process for polymerizing olefin monomer(s) in a gas solids olefin polymerization reactor comprising a top zone, a middle zone, which comprises a top end in direct contact with said top zone and which is located below said top zone, the middle zone having a generally cylindrical shape, and a bottom zone, which is in direct contact with a bottom end of the middle zone and which is located below the middle zone, comprising the following steps:

- a) introducing a first stream of fluidization gas into the bottom zone;
- b) polymerizing olefin monomer(s) in the presence of a polymerization catalyst in a dense phase formed by particles of a polymer of the olefin

monomer(s) suspended in an upwards flowing stream of the fluidization gas in the middle zone;

c) withdrawing a second stream comprising the fluidization gas from the top zone;

5 d) introducing the second stream into cooler;

e) withdrawing the cooled second stream from the cooler; and

f) splitting the cooled second stream into a cooled third stream and the first stream;

10 g) introducing the cooled third stream through one or more feeding ports in a feeding area of the middle zone at the dense phase in the middle zone of the gas solids olefin polymerization reactor;

15 wherein the feeding area of the middle zone is located on the surface of the middle zone between the top end and 50% of the total height of the middle zone, whereas the bottom end corresponds to 0% and the top end corresponds to 100% of the total height of the middle zone.

The present invention is also related to a reactor assembly for polymerizing olefin monomer(s) comprising

20 a gas-solids olefin polymerization reactor comprising a top zone, a middle zone, which comprises a top end in direct contact with said top zone and which is located below said top zone, the middle zone having a generally cylindrical shape, and a bottom zone, which is in direct contact with a bottom end of the middle zone and which is located below said middle zone,

25 a first line for withdrawing a second stream comprising fluidization gas from the top zone of the gas-solids olefin polymerization reactor,

a cooler for cooling the second stream,

a second line for withdrawing the cooled second stream from the cooler,

a third line connecting the second line and the bottom zone of the gas-solids olefin polymerization reactor for introducing a first stream of fluidization gas into the bottom zone of the gas-solids olefin polymerization reactor,

5 one or more feeding ports located in a feeding area of the middle zone,

a fourth line connecting the second line and the one or more feeding ports for introducing a cooled third stream into the middle zone of the gas-solids olefin polymerization reactor

10 wherein the feeding area of the middle zone is located on the surface of the middle zone between the top end and 50% of the total height of the middle zone, whereas the bottom end corresponds to 0% and the top end corresponds to 100% of the total height of the middle zone.

Further, the present invention is related to the use of the process according to the present invention as described above and below for
15 reducing the carry-over of particles of the polyolefin of the olefin monomer(s) into the second stream withdrawn from the top zone of the gas solids olefin polymerization reactor.

Still further, the present invention is related to the use of the process according to the present invention as described above and below for
20 increasing the bulk density of the dense phase during polymerization.

Detailed Description

Definitions

The present text refers to diameter and equivalent diameter. In case of non-spherical objects the equivalent diameter denotes the diameter of a
25 sphere or a circle which has the same volume or area (in case of a circle) as the non-spherical object. It should be understood that even though the present text sometimes refers to diameter, the object in question needs not be spherical unless otherwise specifically mentioned. In case of non-

spherical objects (particles or cross-sections) the equivalent diameter is then meant.

As it is well understood in the art the superficial gas velocity denotes the velocity of the gas in an empty construction. Thus, the superficial gas velocity within the middle zone is the volumetric flow rate of the gas (in m^3/s) divided by the cross-sectional area of the middle zone (in m^2) and the area occupied by the particles is thus neglected.

By fluidization gas is meant the gas comprising monomer, and eventual comonomers, chain transfer agent and inert components which form the upwards flowing gas in the gas solids olefin polymerization reactor and in which the polymer particles are suspended, e.g. in the fluidized bed of a fluidized bed reactor. The unreacted gas is collected at the top of the reactor, compressed, cooled and returned to the reactor. As it is understood by the person skilled in the art the composition of the fluidization gas is not constant during the cycle. Reactive components are consumed in the reactor and they are added into the circulation line for compensating losses.

A gas solids olefin polymerization reactor is a polymerization reactor for heterophasic polymerization of gaseous olefin monomer(s) into polyolefin powder particles, which comprises three zones: in the bottom zone the fluidization gas is introduced into the reactor; in the middle zone, which usually has a generally cylindrical shape, the olefin monomer(s) present in the fluidization gas are polymerized to form the polymer particles; in the top zone the fluidization gas is withdrawn from the reactor. In certain types of gas solids olefin polymerization reactors a fluidization grid (also named distribution plate) separates the bottom zone from the middle zone. In certain types of gas solids olefin polymerization reactors the top zone forms a disengaging or entrainment zone in which due to its expanding diameter compared to the middle zone the fluidization gas expands and the gas disengages from the polyolefin powder.

The dense phase denotes the area within the middle zone of the gas solids olefin polymerization reactor with an increased bulk density due to the formation of the polymer particles. In certain types of gas solids olefin polymerization reactors, namely fluidized bed reactors, the dense phase is formed by the fluidized bed.

“Entrained polyolefin powder” or “carry-over of particles” denotes polyolefin particles which are withdrawn together with the fluidization gas in the second stream of fluidization gas from the top zone of the gas solids olefin polymerization reactor.

“Circulation gas line” denotes the system of lines or tubes through which the second stream of fluidization gas is reintroduced into the gas solids olefin polymerization reactor as first stream of fluidization gas and as cooled third stream.

“Bulk density” (or “bed density” for fluidized bed polymerization reactors) denotes mass of polymer powder divided by the volume of the reactor, excluding the optional disengaging zone.

In the present invention the different streams are measured as volume streams so that also the split of these streams is meant as volume split measured in v/v.

Differences in pressure ΔP are measured in bar if not noted otherwise.

Polymerization

The olefin monomer(s) polymerized in the process of the present invention are typically alpha-olefins having from 2 to 12 carbon atoms, preferably from 2 to 10 carbon atoms. Preferably, the olefin monomer(s) are ethylene or propylene, optionally together with one or more other alpha-olefin monomer(s) having from 2 to 8 carbon atoms. Especially preferably the process of the present invention is used for polymerizing ethylene, optionally with one or more comonomers selected from alpha-olefin monomer(s) having from 4 to 8 carbon atoms; or propylene, optionally

together with one or more comonomers selected from ethylene and alpha-olefin monomer(s) having from 4 to 8 carbon atoms.

Thus, the polymer material is preferably selected from alpha-olefin homo- or copolymers having alpha-olefin monomer units of from 2 to 12 carbon atoms, preferably from 2 to 10 carbon atoms. Preferred are ethylene or propylene homo- or copolymers. The comonomer units of ethylene copolymers are preferably selected from one or more comonomers selected from alpha-olefin monomer(s) having from 4 to 8 carbon atoms. The comonomer units of propylene copolymers are preferably selected from one or more comonomers selected from ethylene and alpha-olefin monomer(s) having from 4 to 8 carbon atoms.

In one preferred embodiment of the invention, in the method according to the invention a polypropylene homo- or copolymer is polymerized from the olefin monomer(s) and optional comonomer(s). Preferably, in this embodiment, the polymerization is carried out at a temperature of 50-100 °C under a pressure of 15-25 barg. Preferably, the molar ratios of the reactants are adjusted as follows: a C_2/C_3 ratio of 0–0.05 mol/mol for random polypropylenes, and a molar C_2/C_3 ratio of 0.2–0.7 mol/mol for block polypropylenes. Generally, the H_2/C_3 molar ratio in this embodiment is adjusted to 0–0.05 mol/mol. Moreover, in this embodiment, the propylene feed is preferably adjusted to 20-40 t/h, whereby the comonomer feed is 0–15 t/h and hydrogen feed is 1-10 kg/h.

In a second preferred embodiment of the invention, in the method according to the invention a polyethylene homo- or copolymer is polymerized from the olefin monomer(s) and optional comonomer(s). Preferably, in this embodiment, the polymerization is carried out at a temperature of 50-100 °C under a pressure of 15-25 barg. Preferably, the molar ratios of the reactants are adjusted as follows: a C_4/C_2 ratio of 0.1-0.8 mol/mol for polyethylene-1-butene copolymers and a C_6/C_2 ratio of 0-0.1 mol/mol for polyethylene-1-hexene copolymers. Generally, the H_2/C_2 molar ratio in this embodiment is adjusted to 0–0.05 mol/mol. Moreover, in

this embodiment, the ethylene feed is preferably adjusted to 15-20 t/h, whereby the comonomer feed is adjusted to 0– 20 t/h for 1-butene and to 0–7 t/h for 1-hexene. Preferably, hydrogen feed is 1-100 kg/h and diluent feed (propane): 30–50 t/h.

5 Polymerization catalyst

The polymerization in the gas-solids olefin polymerization reactor is conducted in the presence of an olefin polymerization catalyst. The catalyst may be any catalyst which is capable of producing the desired olefin polymer. Suitable catalysts are, among others, Ziegler – Natta
10 catalysts based on a transition metal, such as titanium, zirconium and/or vanadium catalysts. Especially Ziegler – Natta catalysts are useful as they can produce olefin polymers within a wide range of molecular weight with a high productivity.

Suitable Ziegler – Natta catalysts preferably contain a magnesium
15 compound, an aluminium compound and a titanium compound supported on a particulate support.

The particulate support can be an inorganic oxide support, such as silica, alumina, titania, silica-alumina and silica-titania. Preferably, the support is silica.

20 The average particle size of the silica support can be typically from 6 to 100 μm . However, it has turned out that special advantages can be obtained if the support has median particle size from 6 to 90 μm , preferably from 10 to 70 μm .

25 The magnesium compound is a reaction product of a magnesium dialkyl and an alcohol. The alcohol is a linear or branched aliphatic monoalcohol. Preferably, the alcohol has from 6 to 16 carbon atoms. Branched alcohols are especially preferred, and 2-ethyl-1-hexanol is one example of the preferred alcohols. The magnesium dialkyl may be any compound of magnesium bonding to two alkyl groups, which may be the same or

different. Butyl-octyl magnesium is one example of the preferred magnesium dialkyls.

The aluminium compound is chlorine containing aluminium alkyl. Especially preferred compounds are aluminium alkyl dichlorides and aluminium alkyl sesquichlorides.

The titanium compound is a halogen containing titanium compound, preferably chlorine containing titanium compound. Especially preferred titanium compound is titanium tetrachloride.

The catalyst can be prepared by sequentially contacting the carrier with the above mentioned compounds, as described in EP-A-688794 or WO-A-99/51646. Alternatively, it can be prepared by first preparing a solution from the components and then contacting the solution with a carrier, as described in WO-A-01/55230.

Another group of suitable Ziegler – Natta catalysts contains a titanium compound together with a magnesium halide compound acting as a support. Thus, the catalyst contains a titanium compound on a magnesium dihalide, like magnesium dichloride. Such catalysts are disclosed, for instance, in WO-A-2005/118655 and EP-A-810235.

Still a further type of Ziegler-Natta catalysts are catalysts prepared by a method, wherein an emulsion is formed, wherein the active components form a dispersed, i.e. a discontinuous phase in the emulsion of at least two liquid phases. The dispersed phase, in the form of droplets, is solidified from the emulsion, wherein catalyst in the form of solid particles is formed. The principles of preparation of these types of catalysts are given in WO-A-2003/106510 of Borealis.

The Ziegler – Natta catalyst is used together with an activator. Suitable activators are metal alkyl compounds and especially aluminium alkyl compounds. These compounds include alkyl aluminium halides, such as ethylaluminium dichloride, diethylaluminium chloride, ethylaluminium sesquichloride, dimethylaluminium chloride and the like. They also include

trialkylaluminium compounds, such as trimethylaluminium, triethylaluminium, tri-isobutylaluminium, trihexylaluminium and tri-n-octylaluminium. Furthermore they include alkylaluminium oxy-compounds, such as methylaluminiumoxane (MAO), hexaisobutylaluminiumoxane (HIBAO) and tetraisobutylaluminiumoxane (TIBAO). Also other aluminium alkyl compounds, such as isoprenylaluminium, may be used. Especially preferred activators are trialkylaluminiums, of which triethylaluminium, trimethylaluminium and tri-isobutylaluminium are particularly used. If needed the activator may also include an external electron donor. Suitable electron donor compounds are disclosed in WO-A-95/32994, US-A-4107414, US-A-4186107, US-A-4226963, US-A-4347160, US-A-4382019, US-A-4435550, US-A-4465782, US 4472524, US-A-4473660, US-A-4522930, US-A-4530912, US-A-4532313, US-A-4560671 and US-A-4657882. Also electron donors consisting of organosilane compounds, containing Si-OCOR, Si-OR, and/or Si-NR₂ bonds, having silicon as the central atom, and R is an alkyl, alkenyl, aryl, arylalkyl or cycloalkyl with 1-20 carbon atoms are known in the art. Such compounds are described in US-A-4472524, US-A-4522930, US-A-4560671, US-A-4581342, US-A-4657882, EP-A-45976, EP-A-45977 and EP-A-1538167.

The amount in which the activator is used depends on the specific catalyst and activator. Typically triethylaluminium is used in such amount that the molar ratio of aluminium to the transition metal, like Al/Ti, is from 1 to 1000, preferably from 3 to 100 and in particular from about 5 to about 30 mol/mol.

Also metallocene catalysts may be used. Metallocene catalysts comprise a transition metal compound which contains a cyclopentadienyl, indenyl or fluorenyl ligand. Preferably the catalyst contains two cyclopentadienyl, indenyl or fluorenyl ligands, which may be bridged by a group preferably containing silicon and/or carbon atom(s). Further, the ligands may have substituents, such as alkyl groups, aryl groups, arylalkyl groups, alkylaryl groups, silyl groups, siloxy groups, alkoxy groups or other heteroatom

groups or the like. Suitable metallocene catalysts are known in the art and are disclosed, among others, in WO-A-95/12622, WO-A-96/32423, WO-A-97/28170, WO-A-98/32776, WO-A-99/61489, WO-A-03/010208, WO-A-03/051934, WO-A-03/051514, WO-A-2004/085499, EP-A-1752462 and EP-A-1739103.

Prior polymerization stages

The polymerization in the gas-solids olefin polymerization reactor may be preceded by prior polymerization stages, such as prepolymerization or another polymerization stage conducted in slurry or gas phase. Such polymerization stages, if present, can be conducted according to the procedures well known in the art. Suitable processes including polymerization and other process stages which could precede the polymerization process of the present invention are disclosed in WO-A-92/12182, WO-A-96/18662, EP-A-1415999, WO-A-98/58976, EP-A-887380, WO-A-98/58977, EP-A-1860125, GB-A-1580635, US-A-4582816, US-A-3405109, US-A-3324093, EP-A-479186 and US-A-5391654. As it is well understood by the person skilled in the art, the catalyst needs to remain active after the prior polymerization stages.

Gas-solids olefin polymerization

In the gas-solids olefin polymerization reactor polymerization is conducted using gaseous olefin monomer(s) in which the polymer particles are growing.

The present process is suitable for any kind of gas-solids olefin polymerization reactors suitable for the polymerization of alpha-olefin homo- or copolymers. Suitable reactors are e.g. continuous-stirred tank reactors or fluidized bed reactors. Both types of gas-solids olefin polymerization reactors are well known in the art.

Preferably the gas-solids olefin polymerization reactor is a fluidized bed reactor.

In a fluidized bed reactor the polymerization takes place in a fluidized bed formed by the growing polymer particles in an upwards moving gas stream. In the fluidized bed the polymer particles, containing the active catalyst, come into contact with the reaction gases, such as monomer, comonomer(s) and hydrogen which cause polymer to be produced onto the particles.

Thereby, in one preferred embodiment the fluidized bed reactor can comprise a fluidization grid which is situated below the fluidized bed thereby separating the bottom zone and the middle zone of the reactor. The upper limit of the fluidized bed is usually defined by a disengaging zone in which due to its expanding diameter compared to the middle zone the fluidization gas expands and the gas disengages from the polyolefin powder. Fluidized bed reactors with disengaging zone and fluidization grid are well known in the art. Such a fluidized bed reactor suitable for the process of the present invention is shown in Fig. 1.

In another preferred embodiment the fluidized bed reactor does not comprise a fluidization grid. The polymerization takes place in a reactor including a bottom zone, a middle zone and a top zone. The bottom zone, which has a generally conical shape, forms the lower part of the reactor in which the base of the fluidized bed is formed. The base of the bed forms in the bottom zone with no fluidization grid, or gas distribution plate, being present. Above the bottom zone and in direct contact with it is the middle zone, which has a generally cylindrical shape. The middle zone and the upper part of the bottom zone contain the fluidized bed. Because there is no fluidization grid there is a free exchange of gas and particles between the different regions within the bottom zone and between the bottom zone and the middle zone. Finally, above the middle zone and in direct contact therewith is the top zone which has a generally conical shape tapering upwards.

The bottom zone of the reactor has a generally conical shape tapering downwards. Because of the shape of the zone, the gas velocity gradually

decreases along the height within said bottom zone. The gas velocity in the lowest part is greater than the transport velocity and the particles eventually contained in the gas are transported upwards with the gas. At a certain height within the bottom zone the gas velocity becomes smaller than the transport velocity and a fluidized bed starts to form. When the gas velocity becomes still smaller the bed becomes denser and the polymer particles distribute the gas over the whole cross-section of the bed. Such a fluidized bed reactor without fluidization grid is described in EP-A-2 495 037 and EP-A-2 495 038.

In a gas solids olefin polymerization reactor the upwards moving gas stream is established by withdrawing a fluidization gas stream as second gas stream from the top zone of the reactor, typically at the highest location. The second gas stream withdrawn from the reactor is then usually cooled and re-introduced to the bottom zone of the reactor as first stream of fluidization gas. In a preferred embodiment, the fluidization gas of the second gas stream is also compressed in a compressor. More preferably, the compressor is located upstream of the cooler. Preferably, the gas is filtered before being passed to the compressor. Additional olefin monomer(s), eventual comonomer(s), hydrogen and inert gas are suitably introduced into the circulation gas line. It is preferred to analyze the composition of the circulation gas, for instance, by using on-line gas chromatography and adjust the addition of the gas components so that their contents are maintained at desired levels.

The polymerization is generally conducted at a temperature and pressure where the fluidization gas essentially remains in vapour or gas phase. For olefin polymerization the temperature is suitably within the range of 30 to 110 °C, preferably 50 to 100 °C. The pressure is suitably in the range of 1 to 50 bar, preferably 5 to 35 bar.

In order to remove entrained polyolefin powder, the circulation gas line, i.e. the line for withdrawing the second stream, preferably comprises at least one cyclone. The cyclone has the objective of removing the

entrained polymer material from the circulation gas. The polymer stream recovered from the cyclone can be directed to another polymerization stage, or it may be returned into the gas-solids olefin polymerization reactor or it may be withdrawn as the polymer product.

5 In the case the polymer stream recovered from the cyclone is returned into the gas-solids polymerization reactor the polymer stream is returned through one or more feedings ports, which are different feeding ports as the one or more feeding ports for introducing the cooled third stream into the dense phase in the middle zone of the gas-solids olefin polymerization
10 reactor.

Preferably, the cooled third stream comprises not more than 5 wt% solid polymer with respect to the total weight of the cooled third stream, more preferably not more than 3 wt% solid polymer, even more preferably not more than 2 wt% solid polymer and most preferably not more than 1 wt%
15 solid polymer.

Circulation of the fluidized gas

According to the present invention the fluidization gas is withdrawn from the top zone of the reactor as second stream, optionally compressed by a compressor, introduced into a cooler, withdrawn from the cooler as cooled
20 second stream and split into a cooled third stream and the first stream. The first stream is introduced into the reactor into the bottom zone whereas the cooled third stream is introduced into the reactor through one or more feeding ports at a feeding area of the middle zone into the dense phase in the middle zone of the reactor. Thereby, the third stream is not
25 mixed with particles of the polymer of the olefin monomer(s) before entering the reactor and thus is not introduced into the reactor through feeding ports for reintroducing particles of the polymer of the olefin monomer(s) into the gas solids olefin polymerization reactor.

No advantageous effect of the invention has been found, if the cooled
30 third stream is introduced in a feeding area of the middle zone, which is

only located on the surface of the middle zone between the *bottom* end and 50% of the total height of the middle zone, whereas the bottom end corresponds to 0% and the top end corresponds to 100% of the total height of the middle zone.

5 Hence, the the feeding area of the middle zone is located on the surface of the middle zone between the *top* end and 50% of the total height of the middle zone, whereas the bottom end corresponds to 0% and the top end corresponds to 100% of the total height of the middle zone. Preferably, the feeding area of the middle zone is located on the surface of the middle
10 zone between the *top* end and 70% of the total height of the middle zone.

Preferably, the cooled third stream is introduced through the one or more feeding ports into the dense phase in the middle zone of the gas solids olefin polymerization reactor in an introduction angle α of 5° to 75°, preferably 10° to 65°, most preferably 15° to 60°. The introduction angle is
15 the angle between a projection and a perpendicular line, whereas the projection is the projection of the direction of the cooled third stream after introduction into the reactor on a projection plane, which crosses the tangent plane of the generally cylindrical shape of the middle zone at the location of the one or more feeding ports and along an intersection line
20 between the tangent plane and the generally cylindrical surface of the middle zone, whereas the projection plane is located perpendicular to the tangent plane and whereas the perpendicular line crosses the generally cylindrical surface of the middle zone at the location of the one or more feeding ports, is parallel to the projection plane and is perpendicular to the
25 tangent plane (cf. Figure 2). Most preferably, the optimal introduction angle for introducing the cooled third stream has been found to be about 20°.

The number of feeding ports for introducing the cooled third stream is in the range of preferably 1 to 15, more preferably 2 to 10 and most
30 preferably 2 to 5.

The feeding ports are preferably distributed across the middle zone of the gas solids olefin polymerization reactor in axial and/or radial direction with the proviso that the cooled third stream is introduced into the dense phase.

- 5 Preferably, the fluidization gas of the cooled third stream is compressed by a compressor. The compressor could either be located upstream or downstream of the cooler. Even more preferably, before being introduced into the cooler, the second stream is introduced into a compressor; withdrawn from the compressor as the compressed second stream and
10 introduced as compressed second stream into the cooler.

In the cooler the second stream is preferably cooled as such that the cooled second stream, and as a consequence also the cooled third stream and/or the first stream, comprise condensed fluidization gas preferably together with gaseous fluidization gas. Preferably, the cooled second
15 stream and as a consequence also the cooled third stream and/or the first stream, comprise from 1 to 30 wt% condensed fluidization gas, more preferably from 3 to 25 wt% condensed fluidization gas and most preferably from 5 to 20 wt% condensed fluidization gas, based on the total weight of the cooled second stream and as a consequence also the
20 cooled third stream and/or the first stream. The remaining weight of the cooled second stream and as a consequence also the cooled third stream and/or the first stream preferably consists of gaseous fluidization gas.

In another embodiment the cooled second stream is not condensed or partly condensed and does not comprise condensed fluidization gas. As a
25 consequence also the cooled third stream and the first stream in said embodiment do not comprise condensed fluidization gas.

The cooled second stream is split into the cooled third stream and the first stream at a ratio of 5:95 (v/v) to 75:25 (v/v), preferably 7:93 (v/v) to 65:35 (v/v), most preferably 10:90 (v/v) to 50:50 (v/v).

Depending on the volume split between the cooled third stream and the first stream the cooled third stream has a certain pressure and contributes to the superficial gas velocity of the upwards flowing stream in the middle zone of the reactor.

5 The pressure difference between the cooled third stream and the polymerization pressure in the gas solids polymerization reactor, ΔP , is at least 0.1 bar, preferably at least 0.3 bar, most preferably at least 0.5 bar. The upper limit for the pressure difference is usually not higher than 10 bar, preferably not higher than 7 bar.

10 It is further preferred that the superficial gas velocity of the upwards flowing stream of the fluidization gas in the middle zone of the reactor is from 0.3 to 1.2 m/s, more preferably from 0.4 to 1.0 m/s, most preferably from 0.5 to 0.9 m/s.

15 Thereby, the superficial gas velocity of the first stream of fluidization gas introduced into the bottom zone is preferably lower than the superficial gas velocity of the upwards flowing stream of the fluidization gas in the middle zone and is preferably in the range of from 0.1 to 1.3 m/s, more preferably of from 0.15 to 1.1 m/s, most preferably of from 0.2 to 1.0 m/s.

20 The bulk density of the dense phase during polymerization is in the range of from 100 to 500 kg/m³, preferably of from 120 to 470 kg/m³, most preferably of from 150 to 450 kg/m³.

Benefits of the invention

25 It has been found that in the process of the present invention a higher bulk density of the dense phase can be obtained over the whole polymerization process.

As a consequence with the process of the present invention the gas solids olefin polymerization reactor can be run under higher space-time yield or volume based production rate increasing the throughput or capacity of the reactor.

Without being bound by theory it is believed that the increase of bulk density results from a reduction of gas bubbles in the bottom and middle zone of the reactor

Further, the axial motion of the polyolefin powder in the top zone of the gas solids olefin polymerization reactor is disturbed by the feed of the cooled third stream as such that the gaseous (and optional solid) content in the upper part of the middle zone and the top zone of the reactor is permanently accelerated in one direction. The introduced cooled third stream accelerates the downward flow of polymer solids close to the wall of the middle zone. This effect allows destruction of the axially moving polyolefin powder fountains and contributes to separating gas and solids, with solids moving downwards along the wall, "scraping" the wall permanently such that adhesive powder is washed away and wall sheeting can be suppressed thereby improving the reactor operability.

As a consequence the carry-over of particles of the polyolefin of the olefin monomer(s) into the second stream withdrawn from the top zone of the gas solids olefin polymerization reactor is reduced thereby increasing the gas-solids separation efficiency and at the same time the cooling capacity of the the process is not sacrificed.

Figures

Fig. 1 shows an embodiment of the polymerization process according to the present invention in a fluidized bed reactor with a fluidization grid.

Reference signs

- 1 fluidized bed reactor
- 2 bottom zone
- 3 middle zone
- 4 top zone (disengaging zone)
- 5 fluidized bed (dense zone)

- 6 first stream of fluidized gas
- 7 second stream of fluidized gas
- 8 compressor
- 9 compressed second stream of fluidized gas
- 5 10 cooler
- 11 cooled second stream of fluidized gas
- 12 cooled third stream of fluidized gas
- 13 feeding ports for the cooled third stream of fluidized gas
- 14 feeding port for polymerization catalyst
- 10 15 polymer withdrawal
- 16 fluidization grid

Description of Figure 1

Fig. 1 shows an embodiment of the gas solids olefin polymerization reactor system according to the present invention. The fluidized bed reactor (1) comprises a bottom zone (2), a middle zone (3) and a disengaging zone as top zone (4). The middle zone (3) and the bottom zone (2) are separated by the fluidization grid (16). The first stream of fluidized gas (6) enters the fluidized bed reactor (1) through the bottom zone (2) and flows upwards, thereby passing the fluidization grid (16) and entering the middle zone (3). Due to the substantially cylindrical shape of the middle zone (3) the gas velocity is constant so that above the fluidization grid (16) the fluidized bed (5) is established in the middle zone (3). Due to the conical shape of the disengaging zone (4) the gas entering the disengaging zone (4) expands so that the gas disengages from the polyolefin product of the polymerization reaction so that the fluidized bed (5) is confined in the middle zone (3) and the lower part of the disengaging zone (4). The polymerization catalyst together with optional polyolefin powder polymerized in previous polymerization stage(s) is

introduced into the fluidized bed reactor (1) through feeding port (14) directly into the fluidized bed (5). The polyolefin product of the polymerization process is withdrawn from the fluidized bed reactor through outlet (15).

- 5 The fluidized gas is withdrawn from the disengaging zone (4) as second stream of fluidization gas (7) and introduced into a compressor (8). The compressed second stream (9) is withdrawn from the compressor (8) and introduced into a cooler (10). The cooled second stream (11) is withdrawn from the cooler (10) and split into a third cooled stream (12) and the first stream (6). The cooled third stream (12) is introduced into fluidized bed (5) of the fluidized bed reactor (1) through one or more feeding ports (13) as such that the fluidized gas of the cooled third stream (12) is directed into the fluidized bed (5).

15 Figure 2 shows the definition of the introduction angle of the cooled third stream.

Reference signs

- a projection of the direction of the cooled third stream
- b perpendicular line
- c projection plane
- 20 d tangent plane
- e location of the feeding port
- f intersection line
- g generally cylindrical surface of the middle zone
- α introduction angle
- 25 γ angle between planes (c) and (d)

Description of Figure 2

Fig. 2 demonstrates the definition of the introduction angel α of the cooled third stream. Said introduction angle (α) is the angle between a projection

(a) and a perpendicular line (b), whereas the projection (a) is the projection of the direction of the cooled third stream after introduction into the reactor on a projection plane (c), which crosses the tangent plane (d) of the generally cylindrical shape (g) of the middle zone at the location of the one or more feeding ports (e) and along an intersection line (f) between the tangent plane (d) and the generally cylindrical surface (g) of the middle zone, whereas the projection plane (c) is located perpendicular to the tangent plane (d) ($\gamma = 90^\circ$) and whereas the perpendicular line (b) crosses the generally cylindrical surface (g) of the middle zone at the location of the feeding port (e), is parallel to projection plane (c) and is perpendicular to tangent plane (d).

Examples

A gas phase reactor equipped with a fluidization grid and a disengaging zone was employed to assess the effect of splitting the recirculation gas in the solids carry over. The reactor had a diameter equal to 0.3 m and height equal to 1.5m. The following experimental procedure steps were followed for all the gas experiments:

- i) Starting to inject fluidization gas (FG) into the bottom of the fluidized bed reactor to form the bottom of the fluidized bed (FB)
- ii) Feeding polyolefin powder with a powder feed of 7.65 kg/min through the catalyst feeding port to form the fluidized bed (FB)
- iii) Increasing the bulk density (BD) of the fluidized bed in the middle zone of the fluidized bed reactor (bulk density = mass of polymer powder divided by the volume of the reactor, excluding the disengaging zone) to about 300 kg/m³
- iv) Starting to inject fluidization gas (i.e. jet gas (JG)) through one feeding port situated in the middle zone of the fluidized bed reactor at an introduction angle of 20° directly into the fluidized bed (FB)
- v) Stopping polymer powder feed

- vi) Keeping fluidization gas (FG) feed constant while the bulk density (BD) decreases over time due to polymer powder entrainment

Reference Example 1

In this example a fluidization experiment following the procedure described above was performed without using jet gas (JG) so that all fluidization gas was injected from the bottom of the fluidized bed reactor. The conditions and results for the reference fluidization experiment (i.e. fluidization gas split, superficial gas velocity of the fluidization gas (FG) just above the fluidization grid (SGV_{FG}), the combined superficial gas velocity of the fluidization gas (FG) and the jet gas (JG) in the middle zone (SGV_{total}), FG flow and BD) are illustrated in Table 1.

Table 1: Experimental fluidization conditions without jet gas (JG).

Conditions	Values
JG Pressure difference [bar]	0
JG Flow [m^3/h] (% Split (v/v))	0 (0% split)
JG Velocity [m/h]	0
FG Flow [m^3/h] (% Split (v/v))	150.6 (100% Split)
Overall Gas Feed [m^3/h]	150.6
SGV_{FG} [m/s]	0.61
SGV_{total} [m/s]	0.61

It was found that at a constant FG flow the bulk density decreases from about 300 kg/m^3 to about 110 kg/m^3 over a time of about 40 min due to polymer powder entrainment.

Inventive Example 2

Example 1 was repeated by splitting the fluidization gas flow into a jet gas (JG) flow and a fluidization gas (FG) flow with a split of 45:55 (v/v). The conditions and results for the reference fluidization experiment (i.e. fluidization gas split, superficial gas velocity of the fluidization gas (FG) just above the fluidization grid (SGV_{FG}), the combined superficial gas velocity of the fluidization gas (FG) and the jet gas (JG) in the middle zone (SGV_{total}), FG flow and BD) are illustrated in Table 2.

Table 2: Experimental fluidization conditions with a JG:FG split of 45:55 (v/v).

Conditions	Values
JG Pressure difference [bar]	5
JG Flow [m ³ /h] (% Split (v/v))	68.0 (45.3% split)
JG Velocity [m/h]	1053
JG Temperature [°C]	25
FG Flow [m ³ /h] (% Split (v/v))	82.1 (54.7% Split)
Overall Gas Feed [m ³ /h]	150.1
SGV_{FG} [m/s]	0.33
SGV_{total} [m/s]	0.61

It was found that at a constant FG flow the additional JG flow minimizes the polymer powder entrainment which can be seen in the bulk density that only decreases from about 300 kg/m³ to about 200 kg/m³ over a time of about 44 min.

Inventive Example 3

Example 1 was repeated by splitting the fluidization gas flow into a jet gas (JG) flow and a fluidization gas (FG) flow with a split of 15:85 (v/v). The conditions and results for the reference fluidization experiment (i.e. fluidization gas split, superficial gas velocity of the fluidization gas (FG) just above the fluidization grid (SGV_{FG}), the combined superficial gas velocity of the fluidization gas (FG) and the jet gas (JG) in the middle zone (SGV_{total}), FG flow and BD) are illustrated in Table 3.

Table 3: Experimental fluidization conditions with a JG:FG split of 15:85 (v/v).

Conditions	Values
JG Pressure difference [bar]	1
JG Flow [m ³ /h] (% Split (v/v))	23.3 (15.3% split)
JG Velocity [m/h]	515
JG Temperature [°C]	25
FG Flow [m ³ /h] (% Split (v/v))	129.1 (84.7% Split)
Overall Gas Feed [m ³ /h]	152.3
SGV_{FG} [m/s]	0.52
SGV_{total} [m/s]	0.62

It was found that at a constant FG flow even a lower amount of JG flow minimizes the polymer powder entrainment which can be seen in the bulk density that only decreases from about 320 kg/m³ to about 160 kg/m³ over a time of about 46 min.

Additional experiments:

The gas phase reactor mentioned above was further employed with the following experimental procedure steps:

- i) Starting to inject fluidization gas (FG) into the bottom of the fluidized bed reactor to form the bottom of the fluidized bed (FB)
- ii) Feeding polyolefin powder with a powder feed of 7.65 kg/min through the catalyst feeding port to form the fluidized bed (FB)
- iii) Increasing the bulk density (BD) of the fluidized bed in the middle zone of the fluidized bed reactor (bulk density = mass of polymer powder divided by the volume of the reactor, excluding the disengaging zone) to about 350 kg/m³
- iv) Starting to inject fluidization gas (i.e. jet gas (JG)) through one feeding port situated in the disengaging zone of the fluidized bed reactor having an introduction angle of 20°. As the disengaging zone does not have a cylindrical shape, the introduction angle is defined in that the perpendicular line (b) is not perpendicular to the tangent plane (d), but to a line crossing the location of the one or more feeding ports (e) and extending parallel to the generally cylindrical surface (g) of the middle zone.
- v) Stopping polymer powder feed
- vi) Keeping fluidization gas (FG) feed constant while the bulk density (BD) decreases over time due to polymer powder entrainment

Reference Example 4

In this example a fluidization experiment following the procedure described above was performed without using jet gas (JG) so that all fluidization gas was injected from the bottom of the fluidized bed reactor. The conditions and results for the reference fluidization experiment (i.e. fluidization gas split, superficial gas velocity of the fluidization gas (FG) just above the fluidization grid (SGV_{FG}), the combined superficial gas

velocity of the fluidization gas (FG) and the jet gas (JG) in the middle zone (SGV_{total}), FG flow and BD) are illustrated in Table 4.

Table 4: Experimental fluidization conditions without jet gas (JG).

Conditions	Values
JG Pressure difference [bar]	0
JG Flow [m ³ /h] (% Split (v/v))	0 (0% split)
JG Velocity [m/h]	0
FG Flow [m ³ /h] (% Split (v/v))	150 (100% Split)
Overall Gas Feed [m ³ /h]	150
SGV_{FG} [m/s]	0.60
SGV_{total} [m/s]	0.60

It was found that at a constant FG flow the bulk density decreases from about 350 kg/m³ to about 150 kg/m³ over a time of about 30 min due to polymer powder entrainment.

Comparative Example 5

Example 4 was repeated by splitting the fluidization gas flow into a jet gas (JD) flow and a fluidization gas (FD) flow with a split of 16:84 (v/v). The conditions and results for the reference fluidization experiment (i.e. fluidization gas split, superficial gas velocity of the fluidization gas (FG) just above the fluidization grid (SGV_{FG}), the combined superficial gas velocity of the fluidization gas (FG) and the jet gas (JG) in the middle zone (SGV_{total}), FG flow and BD) are illustrated in Table 5.

Table 5: Experimental fluidization conditions with a JG:FG split of 16:84 (v/v). Injection port of JG is located at the disengaging zone in downwards direction towards the bottom part of that zone.

Conditions	Values
JG Pressure difference [bar]	1
JG Flow [m ³ /h] (% Split (v/v))	24 (16% split)
JG Velocity [m/h]	156
JG Temperature [°C]	25
FG Flow [m ³ /h] (% Split (v/v))	126 (84% Split)
Overall Gas Feed [m ³ /h]	150
SGV _{FG} [m/s]	0.504
SGV _{total} [m/s]	0.60

It was found that at a constant FG flow the addition of the JG flow maximizes the polymer powder entrainment which can be seen in the bulk density that further decreases from about 350 kg/m³ to about 110 kg/m³ over a time of about 30 min. It was made clear that introducing the JG flow into the disengaging zone of the gas phase reactor has a negative effect of solids carry over.

Claims

1. A process for polymerizing olefin monomer(s) in a gas solids olefin polymerization reactor comprising:

- a top zone;
- 5 – a middle zone, which comprises a top end in direct contact with said top zone and which is located below said top zone, the middle zone having a generally cylindrical shape; and
- a bottom zone, which is in direct contact with a bottom end of the middle zone and which is located below the middle zone;

10 comprising the following steps:

- a) introducing a first stream of fluidization gas into the bottom zone;
- b) polymerizing olefin monomer(s) in the presence of a polymerization catalyst in a dense phase formed by particles of a polymer of the olefin monomer(s) suspended in an upwards
- 15 flowing stream of the fluidization gas in the middle zone;
- c) withdrawing a second stream comprising the fluidization gas from the top zone;
- d) introducing the second stream into a cooler;
- e) withdrawing the cooled second stream from the cooler; and
- 20 f) splitting the cooled second stream into a cooled third stream and the first stream; and
- g) introducing the cooled third stream through one or more feeding ports in a feeding area of the middle zone at the dense phase in the middle zone of the gas solids olefin polymerization reactor

25 wherein

the feeding area of the middle zone is located on the surface of the middle zone between the top end and 50% of the total height of the

middle zone, whereas the bottom end corresponds to 0% and the top end corresponds to 100% of the total height of the middle zone.

2. The process according to claim 1, wherein the feeding area of the middle zone is located in between the top end of the middle zone and 70% of the height of the middle zone in relation to the top end of the middle zone.

3. The process according to claims 1 or 2, wherein the cooled third stream is introduced through the one or more feeding ports into the dense phase in the middle zone of the gas solids olefin polymerization reactor in an introduction angle of 5° to 75°, preferably 10° to 65°, most preferably 15° to 60°, whereas the introduction angle is the angle between

– the projection of the direction of the cooled third stream after introduction into the reactor on a projection plane, which crosses a tangent plane of the generally cylindrical shape of the middle zone at the location of the one or more feeding ports and along an intersection line between the tangent plane and the generally cylindrical surface of the middle zone, whereas the projection plane is located perpendicular to the tangent plane, and

– a perpendicular line, which

- crosses the generally cylindrical surface of the middle zone at the location of the one or more feeding ports,
- is located parallel to the projection plane, and
- is perpendicular to the tangent plane.

4. The process according to any of the preceding claims wherein number of feeding ports for introducing the cooled third stream is in the range of 1 to 15, preferably 2 to 10, more preferably 2 to 5.

5. The process according to any of the preceding claims wherein the feeding ports are distributed across the feeding area of the middle zone of the gas solids olefin polymerization reactor in axial and/or radial direction with the proviso that the cooled third stream is introduced into the dense phase.
6. The process according to any of the preceding claims wherein the cooled second stream is split into the cooled third stream and the first stream at a ratio of 5:95 (v/v) to 75:25 (v/v), preferably 7:93 (v/v) to 65:35 (v/v), most preferably 10:90 (v/v) to 50:50 (v/v).
7. The process according to any of the preceding claims wherein the pressure difference between the cooled third stream and the polymerization pressure in the gas solids polymerization reactor, ΔP , is at least 0.1 bar, preferably at least 0.3 bar, most preferably at least 0.5 bar.
8. The process according to any of the preceding claims wherein the superficial gas velocity of the upwards flowing stream of the fluidization gas in the middle zone is from 0.35 to 1.2 m/s, preferably from 0.4 to 1.0 m/s, more preferably from 0.5 to 0.9 m/s.
9. The process according to claim 8 wherein the superficial gas velocity of the first stream of fluidization gas introduced into the bottom zone is lower than the superficial gas velocity of the upwards flowing stream of the fluidization gas in the middle zone and is in the range of from 0.1 to 1.3 m/s, preferably of from 0.15 to 1.1 m/s, more preferably of from 0.2 to 1.0 m/s.
10. The process according to any of the preceding claims wherein the bulk density of the dense phase during polymerization is in the range of from 100 to 500 kg/m³, preferably of from 120 to 470 kg/m³, most preferably of from 150 to 450 kg/m³.
11. A reactor assembly for polymerizing olefin monomer(s) comprising a gas-solids olefin polymerization reactor (1) comprising:

a top zone (4);

a middle zone (3), which comprises a top end in direct contact with said top zone (4) and which is located below said top zone (4), the middle zone (3) having a generally cylindrical shape; and

5 a bottom zone (2), which is in direct contact with a bottom end of the middle zone (3) and which is located below said middle zone (3);

10 a first line (7) for withdrawing a second stream comprising fluidization gas from the top zone (4) of the gas-solids olefin polymerization reactor (1),

a cooler (10) for cooling the second stream;

a second line (11) for withdrawing the cooled second stream from the cooler (10);

15 a third line (6) connecting the second line (11) and the bottom zone (2) of the gas-solids olefin polymerization reactor (1) for introducing a first stream of fluidization gas into the bottom zone (2) of the gas-solids olefin polymerization reactor (1),

one or more feeding ports (13) located in a feeding area of the middle zone;

20 a fourth line (12) connecting the second line (11) and the one or more feeding ports (13) for introducing a cooled third stream into the middle zone (3) of the gas-solids olefin polymerization reactor (1)

wherein

25 the feeding area of the middle zone is located on the surface of the middle zone between the top end and 50% of the total height of the middle zone, whereas the bottom end corresponds to 0% and the top end corresponds to 100% of the total height of the middle zone.

12. The reactor assembly according to claim 11 wherein the gas solids olefin polymerization reactor is a fluidized bed reactor comprising a fluidization grid.
- 5 13. The reactor assembly according to claim 11 wherein the gas solids olefin polymerization reactor is a fluidized bed reactor comprising a top zone having a generally conical shape, a middle zone in direct contact and below said top zone having a generally cylindrical shape, a bottom zone in direct contact with and below the middle zone and having a generally conical shape which does not contain a
10 fluidization grid.
14. Use of the process according to any of the preceding claims for reducing the carry-over of particles of the polyolefin of the olefin monomer(s) into the second stream withdrawn from the top zone of the gas solids olefin polymerization reactor.
- 15 15. Use of the process according to any of claims 1 to 10 for increasing the bulk density of the dense phase during polymerization.

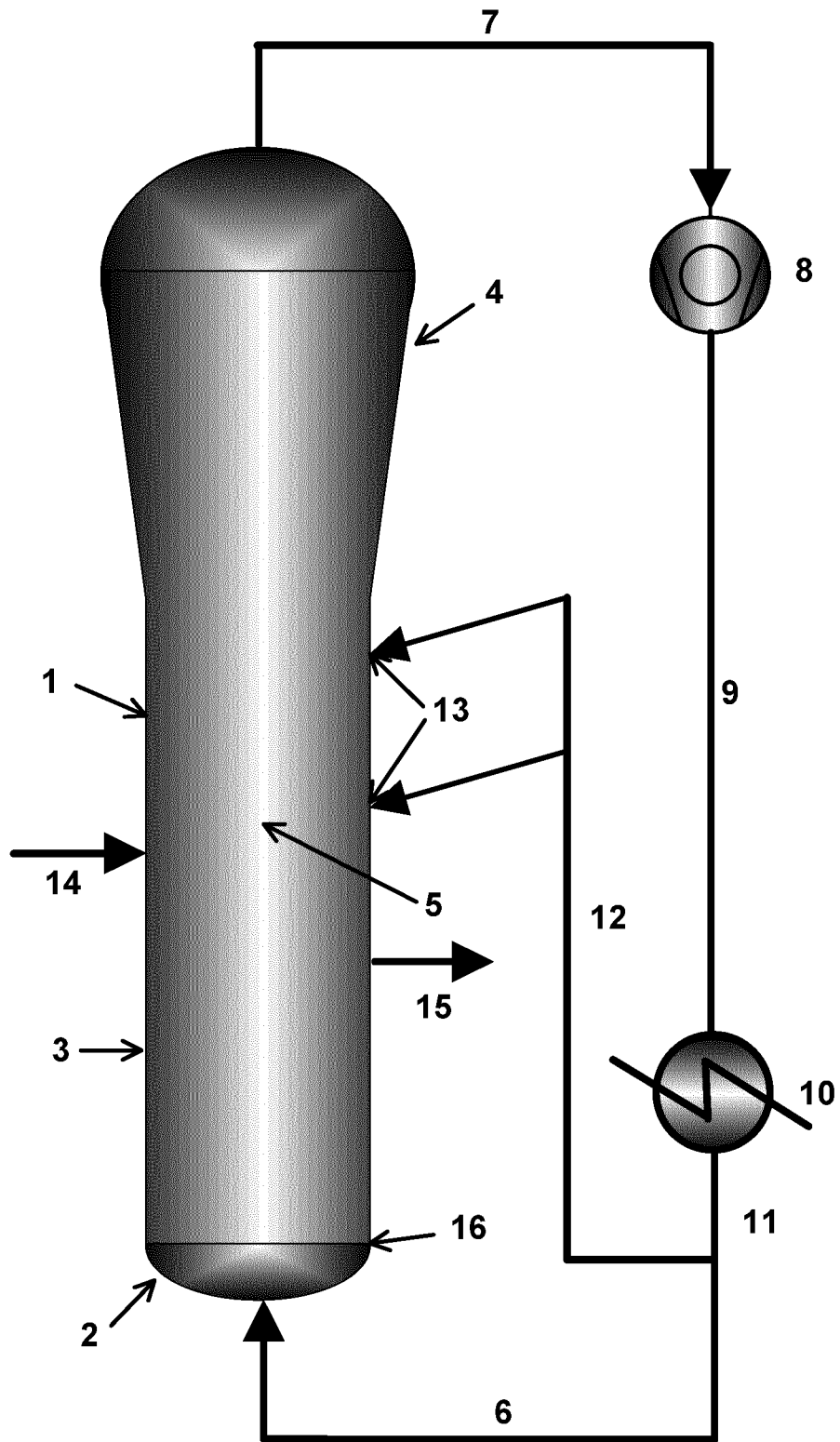


Fig 1

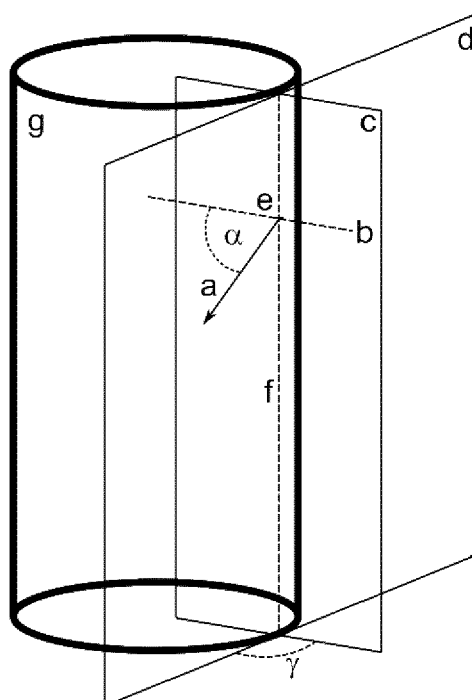


Fig. 2

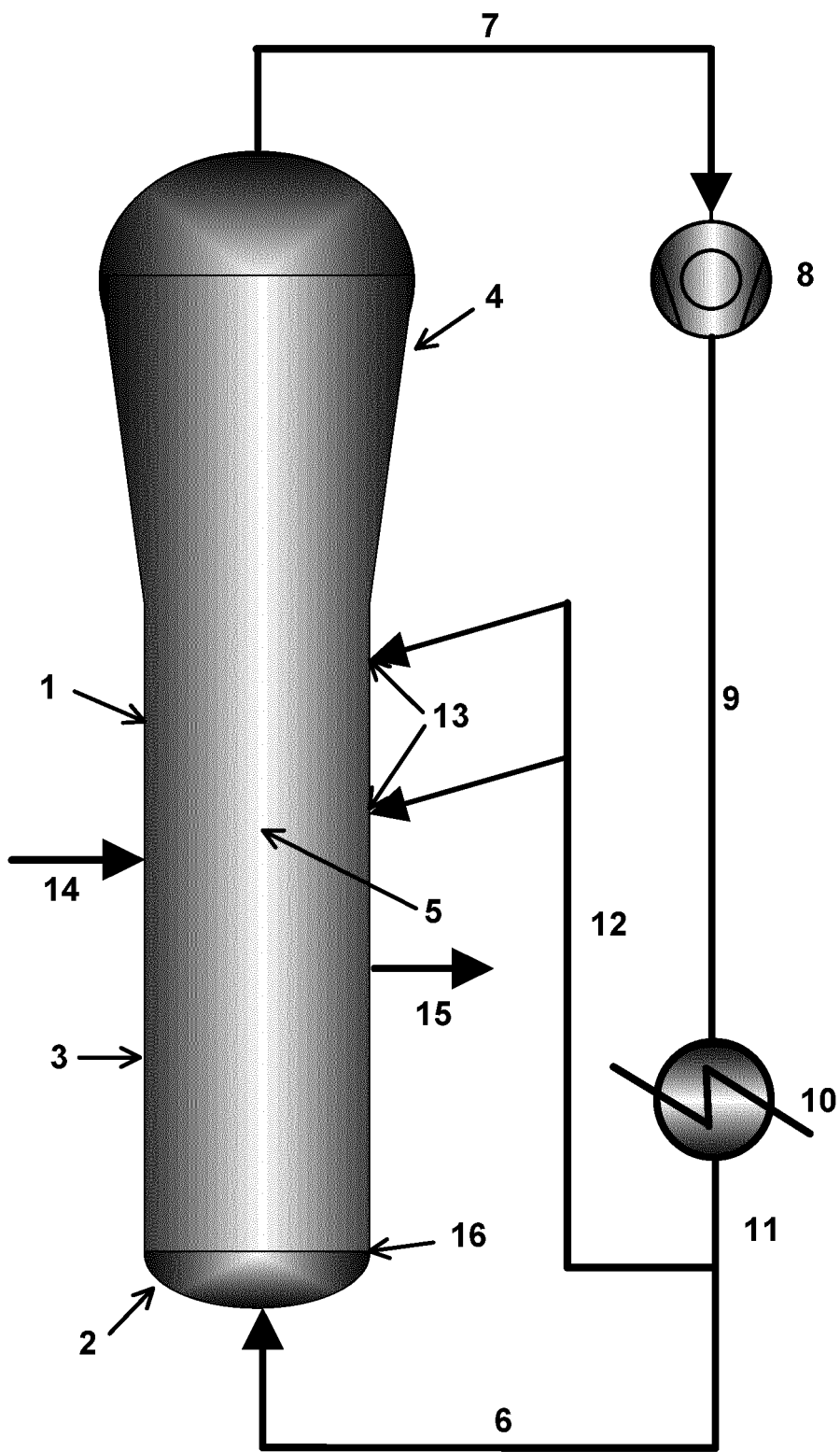


Fig 1