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(54) Title: METHOD OF PREVENTING OR REDUCING AGGLOMERATION ON GRID IN FLUIDIZED-BED VESSEL

(57) Abstract: A method for preventing or reducing agglomeration and/or accumulation on or around the gas distribution grid in a fluidized-bed vessel. The method involves introducing one or more scouring balls into the vessel above the gas distribution grid, and carrying out a fluidized-bed process in the presence of the scouring balls.

METHOD OF PREVENTING OR REDUCING AGGLOMERATION ON GRID IN FLUIDIZED-BED VESSEL

FIELD OF THE INVENTION

[0001] The invention generally relates to a method of preventing or reducing agglomeration and/or accumulation on or around the gas distribution grid in a fluidized-bed vessel.

BACKGROUND OF THE INVENTION

[0002] In fluidized-bed vessels such as those used in catalytic cracking, gasification, combustion, polymerization, and drying, there is a tendency for particles to agglomerate (i.e., to stick or fuse together to form larger masses) and deposit on top of and/or around the gas distribution grid inside the vessel.

[0003] Such agglomeration and/or accumulation can block the flow of the fluidizing gas. When the fluidizing gas flow is blocked, the fluidized bed can become unstable and collapse. In which case, the vessel would have to be shut down and cleaned. Also, when temperature sensors near the grid behave abnormally, the vessel would typically have to be shut down as well. Frequent vessel shutdowns are undesirable as they can delay production and increase the cost of running the vessel. Thus, there is a need to prevent or reduce agglomeration and/or accumulation on top of and/or around the gas distribution grid in a fluidized-bed vessel.

[0004] The present invention provides a solution for solving this problem.

SUMMARY OF THE INVENTION

[0005] The invention provides a method for preventing or reducing agglomeration and/or accumulation on or around a gas distribution grid in a fluidized-bed vessel.

The method comprises:

introducing one or more scouring balls into the vessel above the gas distribution grid; and

carrying out a fluidized-bed process in the presence of the scouring balls.

DETAILED DESCRIPTION OF THE INVENTION

[0006] The present inventors have surprisingly found that agglomeration and/or accumulation including so-called “waffling” on top of or around the gas distribution grid in a fluidized-bed vessel can effectively be reduced, prevented, and/or inhibited by carrying out the fluidized-bed process in the presence of one or more scouring balls located in the vessel above the gas distribution grid.

[0007] Thus, the invention provides a method for preventing or reducing agglomeration or accumulation on and/or around a gas distribution grid in a fluidized-bed vessel. The method comprises:

introducing one or more scouring balls into the vessel above the gas distribution grid; and

carrying out a fluidized-bed process in the presence of the scouring balls.

[0008] By “scouring balls,” it is meant any object that is substantially inert, substantially non-fluidizable, and laterally movable under process conditions. The words “scouring” and “balls” themselves do not necessarily imply any particular action or shape in the context of the invention. According to the invention, the scouring balls can vary in size, shape, and density over a wide range so long as they do not become fluidized under process conditions, but rather reside primarily on or slightly above the grid.

[0009] Preferably, the balls have rounded edges to facilitate their lateral movement. Exemplary shapes for the balls include spherical or substantially spherical, oblong, or even disk-like. They can be solid or hollow.

[0010] Preferably, the balls are substantially spherical and have a size, hardness, and density such that the fluidizing gas can make them roll around and/or bounce up-and-down on top of the grid to break up and/or prevent the formation of agglomerates during the process. Also, preferably, the size, shape, and density of the balls are such that the balls cause minimal disruption to the fluidization, by leaving the grid holes as unobstructed as possible as they move.

[0011] The individual balls can have different sizes, shapes, and densities from each other. In one preferred embodiment, multiple balls are used having varying sizes, shapes, and densities so as to maximize the amount of scouring in any given area per unit of time.

[0012] The balls can be made of any material, such as wood, metal, plastic, ceramic, or combinations thereof, so long as they are substantially inert under process conditions. As conditions may vary from process to process, the precise make up of the balls may vary too, both within the same process and among different processes.

[0013] In one embodiment, the balls are substantially spherical, have a diameter ranging from 8 to 10 inches, and are made of plastic. In a preferred embodiment, the balls are made from a linear low density polyethylene having a melt index of about 0.5 and a density of about 0.926 g/cc. The balls preferably weigh about 9 to 18 lbs each. Such balls are extremely hard and durable under the conditions of most processes.

[0014] The scouring balls can even be made of agglomerates that are obtained from prior process runs and intentionally placed or left in the reactor before the process is resumed.

[0015] The scouring balls may be introduced into the fluidized-bed vessel at anytime that is safe and via any port, existing or newly created. Preferably, the balls are introduced through a "man-way" in the vessel before the process begins by placing them on a clean gas distribution grid prior to the seed bed being loaded.

[0016] The method of the present invention may be employed in any process that uses a fluidized-bed vessel. Such processes include but are not limited to catalytic cracking, gasification, combustion, polymerization, and drying. The method of the present invention is particularly suitable for application in connection with olefin polymerization processes. Such polymerization processes are discussed below.

[0017] Olefin polymerization may be carried out using a gas-phase, fluidized-bed polymerization reactor. This type reactor and means for operating the reactor are well known and described in the literature such as U.S. Patent Nos. 3,709,853; 4,003,712; 4,011,382; 4,302,566; 4,543,399; 4,882,400; 5,436,304; and 5,541,270; Canadian Patent No. 991,798; and Belgian Patent No. 839,380. These patents disclose gas-phase polymerization processes wherein the polymerization medium is fluidized by the continuous flow of the gaseous monomer and diluent. The entire contents of these patents are incorporated herein by reference.

[0018] In general, the fluidized-bed reactor comprises a gas distribution grid, a reaction zone, and a so-called velocity reduction zone. The reaction zone comprises a bed of growing polymer particles, formed polymer particles, and a minor amount of catalyst particles fluidized by the continuous flow of the gaseous monomer and diluent to remove heat of polymerization through the reaction zone. Optionally, some of the recirculated gases may be cooled and compressed to form liquids that increase the heat removal capacity of the circulating gas stream when readmitted to the reaction zone. A suitable rate of gas flow may be readily determined by simple experimentation. Make-up gaseous monomer may be added to the circulating gas stream at a rate equal to the rate at which particulate polymer product and monomer associated therewith is withdrawn from the reactor, and the composition of the gas passing through the reactor is adjusted to maintain an essentially steady-state gaseous composition within the reaction zone. The gas leaving the reaction zone is passed to the velocity reduction zone where entrained particles are removed. Finer entrained particles and dust may be removed in a cyclone and/or fine filter. The gas can be passed through a heat exchanger to remove the heat of polymerization, compressed in a compressor, and then returned to the reaction zone.

[0019] The fluidized-bed reactor temperature can range from about 30°C to about 150°C. In general, the reactor temperature is operated at the highest temperature that is feasible taking into account the sintering temperatures of the polymer product within the reactor.

[0020] The polymerization may be conducted with one or more olefins. Olefins suitable for polymerization may contain, for example, from 2 to 16 carbon atoms. Included herein are homopolymers, copolymers, terpolymers, and the like of the olefin monomeric units. Particularly preferred for preparation herein is polyethylenes. Such polyethylenes can be homopolymers of ethylene and copolymers of ethylene and at least one alpha-olefin wherein the ethylene content is at least about 50% by weight of the total monomers involved. Exemplary alpha-olefins that may be utilized herein are propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 4-methyl-1-pentene, 1-decene, 1-dodecene, 1-hexadecene, and the like. Also utilizable herein are polyenes such as 1,3-hexadiene, 1,4-hexadiene, 1,5-hexadiene, cyclopentadiene, dicyclopentadiene, 4-vinylcyclohex-1-ene, 1,5-

cyclooctadiene, 5-vinylidene-2-norbornene, 5-vinyl-2-norbornene, and olefins formed in situ in the polymerization medium. When olefins are formed in situ in the polymerization medium, the formation of polyethylenes containing long chain branching may occur.

[0021] Any catalyst known for polymerizing olefins may be used. Preferably, the olefin polymerization catalyst comprises at least one metal selected from Groups 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 and 13 of the Periodic Table of the Elements, as defined herein. Exemplary metals are titanium, zirconium, vanadium, iron, chromium, nickel and aluminum. The olefin polymerization catalyst may be neutral or cationic.

[0022] Exemplary of such polymerization catalysts are:

[0023] 1. Any compound containing a Group 6 element. Preferred are chromium containing compounds. Exemplary are chromium oxide catalysts which polymerize ethylene to high molecular weight high density polyethylenes (HDPE) having a broad molecular weight distribution. These catalysts are typically based on Cr(6+) and are supported on a carrier. Further exemplary are organochromium catalysts such as bis(triphenylsilyl)chromate supported on silica and activated with organoaluminum compounds, and bis(cyclopentadienyl)chromium supported on silica.

[0024] 2. Ziegler-Natta catalysts which typically consist of a transition metal component and an organometallic co-catalyst that is typically an organoaluminum compound.

[0025] 3. An olefin polymerization catalyst that polymerizes olefins to produce interpolymers of olefins having a molecular weight distribution (MWD) of from 1 to 2.5.

[0026] 4. Metallocene catalysts which consist of a transition metal component having at least one moiety selected from substituted or unsubstituted cyclopentadienyl, substituted or unsubstituted pentadienyl, substituted or unsubstituted pyrrole, substituted or unsubstituted phosphole, substituted or unsubstituted arsole, substituted or unsubstituted boratabenzene, and substituted or unsubstituted carborane, and an organometallic co-catalyst that is typically alkyl aluminoxane, such as methyl aluminoxane, or an aryl substituted boron compound.

[0027] 5. Any compound containing a Group 13 element. Preferred are aluminum containing compounds. Exemplary are catalysts of the type described in

U.S. Patent No. 5,777,120, such as cationic aluminum alkyl amidinate complexes with an organometallic co-catalyst that is typically alkylaluminumoxane, such as methylaluminumoxane, or an aryl substituted boron containing compound.

[0028] 6. Any compound containing a Group 10 element. Preferred are nickel containing compounds. Exemplary are catalysts of the type described in U.S. Patent No. 5,866,663, such as cationic nickel alkyl diimine complexes with an organometallic co-catalyst that is typically alkylaluminumoxane, such as methylaluminumoxane, or an aryl substituted boron containing compound. Further exemplary are catalysts of the type described in *Organometallics*, 1998, Volume 17, pages 3149-3151, such as neutral nickel alkyl salicylaldiminato complexes.

[0029] 7. Any compound containing a Group 8 element. Preferred are iron containing compounds. Exemplary are catalysts of the type described in the *Journal of the American Chemical Society*, 1998, Volume 120, pages 7143-7144, such as cationic iron alkyl pyridinebisimine complexes with an organometallic co-catalyst that is typically alkylaluminumoxane, such as methylaluminumoxane, or an aryl substituted boron containing compound.

[0030] 8. Any compound containing a Group 4 element. Preferred are titanium and zirconium containing compounds. Exemplary are catalysts of the type described in the *Journal of the American Chemical Society*, 1996, Volume 118, pages 10008-10009, such as cationic titanium alkyl diamide complexes with an organometallic co-catalyst that is typically alkylaluminumoxane, such as methylaluminumoxane, or an aryl substituted boron containing compound.

[0031] The above catalysts are, or can be, supported on inert porous particulate carriers.

[0032] The above olefin polymerization catalysts can be introduced in the process in any manner. For example, the catalyst component(s) can be introduced directly into the polymerization medium in the form of a solution, a slurry or a dry free flowing powder. The catalyst if requiring a co-catalyst can be premixed to form an activated catalyst prior to addition to the polymerization medium, or the components can be added separately to the polymerization medium, or the components can be premixed and then contacted with one or more olefins to form a prepolymer and then added to the polymerization medium in prepolymer form. When the catalyst components are

premixed prior to introduction into the reactor, any electron donor compound may be added to the catalyst to control the level of activity of the catalyst. Furthermore, during the polymerization reaction being carried out in the presence of the olefin polymerization catalyst, as above described, there may be added additional organometallic compound(s). The additional organometallic compounds may be the same or different from that used as co-catalyst.

[0033] Any or all of the components of the olefin polymerization catalysts can be supported on a carrier. The carrier can be any particulate organic or inorganic material. Preferably the carrier particle size should not be larger than about 200 microns in diameter. The most preferred particle size of the carrier material can be easily established by experiment. Preferably, the carrier should have an average particle size of 5 to 200 microns in diameter, more preferably 10 to 150 microns and most preferably 20 to 100 microns.

[0034] Examples of suitable inorganic carriers include metal oxides, metal hydroxides, metal halogenides or other metal salts, such as sulphates, carbonates, phosphates, nitrates, and silicates. Exemplary of inorganic carriers suitable for use herein are compounds of metals from Groups 1 and 2 of the Periodic Table of the Elements, such as salts of sodium or potassium and oxides or salts of magnesium or calcium, for instance the chlorides, sulfates, carbonates, phosphates or silicates of sodium, potassium, magnesium or calcium and the oxides or hydroxides of, for instance, magnesium or calcium. Also suitable for use are inorganic oxides such as silica, titania, alumina, zirconia, chromia, boron oxide, silanized silica, silica hydrogels, silica xerogels, silica aerogels, and mixed oxides such as talcs, silica/chromia, silica/chromia/titania, silica/alumina, silica/titania, silica/magnesia, silica/magnesia/titania, aluminum phosphate gels, silica co-gels and the like. The inorganic oxides may contain small amounts of carbonates, nitrates, sulfates and oxides such as Na_2CO_3 , K_2CO_3 , CaCO_3 , MgCO_3 , Na_2SO_4 , $\text{Al}_2(\text{SO}_4)_3$, BaSO_4 , KNO_3 , $\text{Mg}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, Na_2O , K_2O , and Li_2O . Carriers containing at least one component selected from the group consisting of SiO_2 , Al_2O_3 or mixtures thereof as a main component are preferred.

[0035] Examples of suitable organic carriers include polymers such as, for example, polyethylene, polypropylene, interpolymers of ethylene and alpha-olefins, polystyrene, and functionalized polystyrene.

[0036] The Ziegler-Natta catalysts utilized herein are well known in the industry. The Ziegler-Natta catalysts in the simplest form are comprised of a component comprising at least one transition metal and a co-catalyst comprising at least one organometallic compound. The metal of the transition metal component is a metal selected from Groups 4, 5, 6, 7, 8, 9 and/or 10 of the Periodic Table of the Elements, as published in "Chemical and Engineering News", 63(5), 27, 1985. In this format, the groups are numbered 1-18. Exemplary of such transition metals are titanium, zirconium, vanadium, chromium, manganese, iron, cobalt, nickel, and the like, and mixtures thereof. In a preferred embodiment the transition metal is selected from the group consisting of titanium, zirconium, vanadium and chromium, and in a still further preferred embodiment, the transition metal is titanium. The Ziegler-Natta catalyst can optionally contain magnesium and/or chlorine. Such magnesium and chlorine containing catalysts may be prepared by any manner known in the art.

[0037] The co-catalyst can be any organometallic compound, or mixtures thereof, that can activate the transition metal component in a Ziegler-Natta catalyst in the polymerization of olefins. In particular, the organometallic co-catalyst compound that is reacted with the transition metal component contains a metal selected from Groups 1, 2, 11, 12, 13 and/or 14 of the above described Periodic Table of the Elements. Exemplary of such metals are lithium, magnesium, copper, zinc, boron, silicon and the like, or mixtures thereof.

[0038] Typically, the co-catalyst is an organoaluminum compound such as, for example, trimethylaluminum and triethylaluminum.

[0039] Furthermore, there may be added to the Ziegler-Natta catalysts any internal electron donor. The internal electron donor compound can be selected from the group consisting of ethers, thioethers, esters, thioesters, amines, amides, ketones, nitriles, phosphines, silanes, acid anhydrides, acid halides, acid amides, aldehydes, and organic acid derivatives. Internal electron donors also include compounds containing from 1 to 50 carbon atoms and from 1 to 30 heteroatoms of an element,

or mixtures thereof, selected from Groups 14, 15, 16 and 17 of the Periodic Table of Elements.

[0040] In carrying out a polymerization process, an external electron donor may be used. Exemplary external electron donors include tetrahydrofuran, diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, dioctyl ether, tert-butyl methyl ether, trimethylene oxide and tetrahydropyran. The external electron donor may be added to the preformed catalyst, to the prepolymer during the prepolymerization step, to the preformed prepolymer and/or to the polymerization medium. The external electron donor may optionally be premixed with the co-catalyst. The external electron donor can be added in any amount sufficient to effect production of the desired polyolefin. The external electron donor can be used in a molar ratio of external electron donor to transition metal component of the Ziegler-Natta catalyst ranging from about 0.01:1 to about 100:1. In another embodiment, the molar ratio of external electron donor to transition metal component ranges from about 0.1:1 to about 50:1.

[0041] The Ziegler-Natta catalyst may be prepared by any method known in the art. The catalyst can be in the form of a solution, a slurry or a dry free flowing powder. The amount of Ziegler-Natta catalyst used is that which is sufficient to allow production of the desired amount of the polyolefin.

[0042] Metallocene catalysts are well known in the industry and are typically comprised of a transition metal component and a co-catalyst. The transition metal component has at least one moiety selected from substituted or unsubstituted cyclopentadienyl, substituted or unsubstituted pentadienyl, substituted or unsubstituted pyrrole, substituted or unsubstituted phosphole, substituted or unsubstituted arsole, substituted or unsubstituted boratabenzene, and substituted or unsubstituted carborane. The transition metal is selected from Groups 3, 4, 5, 6, 7, 8, 9 and 10 of the Periodic Table of the Elements. Exemplary of such transition metals are titanium, zirconium, hafnium, vanadium, chromium, manganese, iron, cobalt, nickel, and the like, and mixtures thereof. In an embodiment, the transition metal is selected from Groups 4, 5 or 6 such as, for example, titanium, zirconium, hafnium, vanadium and chromium, and in a still further embodiment, the transition metal is titanium or zirconium or mixtures thereof.

[0043] The co-catalyst component of the metallocene catalyst can be any compound, or mixtures thereof, that can activate the transition metal component of the metallocene catalyst in olefin polymerization. Typically, the co-catalyst is an alkylaluminum compound such as, for example, methylaluminumoxane (MAO) and aryl substituted boron compounds such as, for example, tris(perfluorophenyl)borane and the salts of tetrakis(perfluorophenyl)borate.

[0044] There are many references describing metallocene catalysts in great detail. For example, metallocene catalyst are described in U.S. Patent Nos. 4,564,647; 4,752,597; 5,106,804; 5,132,380; 5,227,440; 5,296,565; 5,324,800; 5,331,071; 5,332,706; 5,350,723; 5,399,635; 5,466,766; 5,468,702; 5,474,962; 5,578,537; and 5,863,853.

[0045] In carrying out the polymerization process, the co-catalyst(s), if utilized, is added to the polymerization medium in any amount sufficient to effect production of the desired polyolefin. The co-catalyst(s) can be used in a molar ratio of co-catalyst(s) to metal component(s) of the olefin polymerization catalyst ranging from about 0.5:1 to about 10000:1. In another embodiment, the molar ratio of co-catalyst(s) to metal component(s) ranges from about 0.5:1 to about 1000:1.

[0046] In carrying out an polymerization process, an ether may be used to reduce the electrostatic charge in the polymerization medium. Exemplary ethers include tetrahydrofuran, diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, dioctyl ether, tert-butyl methyl ether, trimethylene oxide, and tetrahydropyran. The ether may be added to the preformed catalyst, to the prepolymer during the prepolymerization step, to the preformed prepolymer, and/or to the polymerization medium. The ether may optionally be premixed with the co-catalyst when utilized. The ether is added in any amount sufficient to reduce the electrostatic charge in the polymerization medium to a level lower than would occur in the same polymerization process in the absence of the ether. The ether can be used in a molar ratio of compound to metal component of the olefin polymerization catalyst ranging from about 0.001:1 to about 100:1. In another embodiment, the molar ratio of the ether to metal component ranges from about 0.01:1 to about 50:1.

[0047] In carrying out a polymerization process, a halogenated hydrocarbon may be added to the polymerization medium in any amount sufficient to effect production

of the desired polyolefin. Typical of such halogenated hydrocarbons are monohalogen and polyhalogen substituted saturated or unsaturated aliphatic, alicyclic, or aromatic hydrocarbons having 1 to 12 carbon atoms. Exemplary halogenated hydrocarbons for use in the process of the present invention include dichloromethane, chloroform, carbon tetrachloride, chlorofluoromethane, chlorodifluoromethane, dichlorodifluoromethane, fluorodichloromethane, chlorotrifluoromethane, fluorotrifluoromethane and 1,2-dichloroethane. The halogenated hydrocarbon can be used in a molar ratio of halogenated hydrocarbon to metal component of the olefin polymerization catalyst ranging from about 0.001:1 to about 100:1. In another embodiment, the molar ratio of halogenated hydrocarbon to metal component ranges from about 0.001:1 to about 10:1.

[0048] The molecular weight of the polyolefin produced can be controlled in any known manner, for example, by using hydrogen. The molecular weight control of polyethylene, for example, may be evidenced by an increase in the melt index (I_2) of the polymer when the molar ratio of hydrogen to ethylene in the polymerization medium is increased.

[0049] Any conventional additive may be added to the polyolefins obtained. Examples of the additives include nucleating agents, heat stabilizers, antioxidants of phenol type, sulfur type and phosphorus type, lubricants, antistatic agents, dispersants, copper harm inhibitors, neutralizing agents, foaming agents, plasticizers, anti-foaming agents, flame retardants, crosslinking agents, flowability improvers such as peroxides, ultraviolet light absorbers, light stabilizers, weathering stabilizers, weld strength improvers, slip agents, anti-blocking agents, antifogging agents, dyes, pigments, natural oils, synthetic oils, waxes, fillers, and rubber ingredients.

[0050] The polyolefins, particularly polyethylenes, may be fabricated into films by any technique known in the art. For example, films may be produced by the well known cast film, blown film and extrusion coating techniques.

[0051] Further, the polyolefins, particularly polyethylenes, may be fabricated into other articles of manufacture, such as molded articles, by any of the well known techniques.

[0052] This invention can be further illustrated by the following examples of preferred embodiments thereof, although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention.

EXAMPLES

Comparative Example 1

[0053] For 17 days, a commercial fluidized-bed, ethylene polymerization reactor was operated with no balls. The run was conducted under typical polymerization conditions in all respects, preceded by manual entry into the reactor in order to remove all material (loose powder, agglomerates, etc.) from the grid and to unplug any plugged grid holes. Three different reactor grades of polyethylene were produced (Melt Index / Density - 0.5 MI / 0.9160 g/cc, 1.0 MI / 0.9190 g/cc, and 0.6 MI / 0.9250 g/cc).

[0054] The run was characterized by very little temperature spiking of "grid TIs" (internal thermocouples near grid level, with spiking being a sign of moving agglomerates), but experienced severe grid TI "wandering," a phenomenon in which these thermocouples run considerably colder than expected (due to abnormal flow patterns of cold inlet gas). This type of "wandering" grid TI behavior has come to be associated particularly with polymer buildup on the surface of the grid and the surrounding wall surface around the grid perimeter.

[0055] On Day 18, the reactor was shutdown for prior scheduled maintenance.

[0056] The reactor grid was inspected on Day 19, and found to have a thick layer of polymer (1" to 4") built up on approximately 70% of the grid, as well as a buildup on the surrounding wall surface. No loose agglomerates were found. The polymer buildup was removed with some degree of difficulty, because it tightly adhered to the reactor surfaces.

Example 1

[0057] For 16 days, the same reactor as in Comparative Example 1 was operated with 10 substantially spherical balls and 7 agglomerates intentionally placed on the grid prior to startup. Five 8" and five 10" balls were used; the agglomerates were of

similar size and had a generally rounded shape. The balls were made from linear low density polyethylene having a melt index of 0.5 and a density of 0.926 g/cc. The balls weighed from 9 to 18 lbs each.

[0058] This run was similar to the run in Comparative Example 1, making the same 3 polyethylene formulas in the same order. The run was characterized by very slight temperature spiking of the grid TIs (interpreted to be due to the presence and movement of these balls) and no grid TI wandering.

[0059] The reactor was shutdown on Day 16 in order to perform maintenance on a plugged filter.

[0060] On entering the reactor on Day 17, 10 balls and 5 agglomerates were found intact (2 agglomerates apparently broke up and exited via the withdrawal system). The grid and surrounding wall were completely free of any buildup, with only a very small amount (1" to 2" wide strip) of buildup being found in the "crevice" where the grid meets the reactor wall, in an area too small for the balls to touch.

[0061] The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

CLAIMS

We claim:

1. A method for preventing or reducing agglomeration or accumulation on or around a gas distribution grid in a fluidized-bed vessel, said method comprising:
introducing one or more scouring balls into the vessel above the gas distribution grid; and
carrying out a fluidized-bed process in the presence of said scouring balls.
2. The method according to claim 1, wherein said scouring balls are substantially spherical.
3. The method according to claim 1, which comprises introducing two or more scouring balls into the vessel, and said scouring balls have different shapes, sizes, or both.
4. The method according to claim 1, wherein said scouring balls are made of wood, metal, plastic, ceramic, or combinations thereof.
5. The method according to claim 1, wherein said fluidized-bed process is selected from catalytic cracking, gasification, combustion, polymerization, and drying.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/032082

A. CLASSIFICATION OF SUBJECT MATTER		
INV. B01J8/18	B01J8/24	B01J8/32 C08F2/00
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 C08F		
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 practical, 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 2005/089808 A1 (HAUZENBERGER FRANZ [AU]) 28 April 2005 (2005-04-28) abstract; figure 1A page 1, paragraph 5 page 1, paragraph 11 page 1, paragraph 17 page 2, paragraph 23; figure 2	1-5
Y	US 3 905 900 A (GULYAS JAMES W ET AL) 16 September 1975 (1975-09-16) abstract column 3, line 20 - line 34; figure 4	1-5
Y	US 2004/194805 A1 (REISINGER CLAUS-PETER [DE] ET AL) 7 October 2004 (2004-10-07) abstract page 1, paragraph 13 - page 2, paragraph 17	1-5
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PCT/US2009/032082

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 2 103 329 A (STEINMUELLER GMBH L & C [DE]) 16 February 1983 (1983-02-16) abstract; figure 1 page 1, line 23 - line 31 page 1, line 73 - line 83 page 2, line 2 - line 11; figure 4	1-5
Y	EP 0 053 355 A (ALSTHOM ATLANTIQUE [FR]) 9 June 1982 (1982-06-09) abstract; figure 1 page 2, line 6 - line 24	1-5
Y	GB 1 513 152 A (BP CHEM INT LTD) 7 June 1978 (1978-06-07) page 1, line 10 - line 32 page 2, line 23 - line 41 page 2, line 55 - line 81; examples 1,2 claims 1,6	1-5

INTERNATIONAL SEARCH REPORT

 International application No
 PCT/US2009/032082

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2005089808	A1	28-04-2005	AT 411264 B 25-11-2003
			BR 0307065 A 28-12-2004
			CA 2472720 A1 21-08-2003
			CN 1633332 A 29-06-2005
			DE 50301674 D1 22-12-2005
			WO 03068380 A1 21-08-2003
			EP 1474227 A1 10-11-2004
			JP 2005516765 T 09-06-2005
			KR 20040098644 A 20-11-2004
			RU 2310501 C2 20-11-2007
			UA 80817 C2 12-11-2007
ZA 200405551 A 13-07-2005			
US 3905900	A	16-09-1975	NONE
US 2004194805	A1	07-10-2004	CN 1533310 A 29-09-2004
			DE 10135318 A1 30-01-2003
			WO 03008116 A1 30-01-2003
			EP 1412104 A1 28-04-2004
			JP 2004538135 T 24-12-2004
			TW 583019 B 11-04-2004
GB 2103329	A	16-02-1983	AT 376496 B 26-11-1984
			DE 3213988 A1 20-10-1983
			FI 822107 A 17-10-1983
			FR 2525338 A1 21-10-1983
			JP 1643192 C 28-02-1992
			JP 3003878 B 21-01-1991
			JP 58182099 A 24-10-1983
			NL 8202464 A 16-11-1983
			SE 8203533 A 17-10-1983
			ZA 8204548 A 27-04-1983
EP 0053355	A	09-06-1982	CA 1193108 A1 10-09-1985
			DE 3161804 D1 02-02-1984
			ES 8300518 A1 01-02-1983
			FR 2495028 A1 04-06-1982
			JP 57122299 A 30-07-1982
			PT 74054 A 01-12-1981
GB 1513152	A	07-06-1978	NONE