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(71) Applicant: **SABIC GLOBAL TECHNOLOGIES B.V.** [NL/NL]; Plasticslaan 1, 4612 PX Bergen op Zoom (NL).

(72) Inventor: **PATEL, Haresh**; P.O. Box 11669, Jubail, 31961 (SA).

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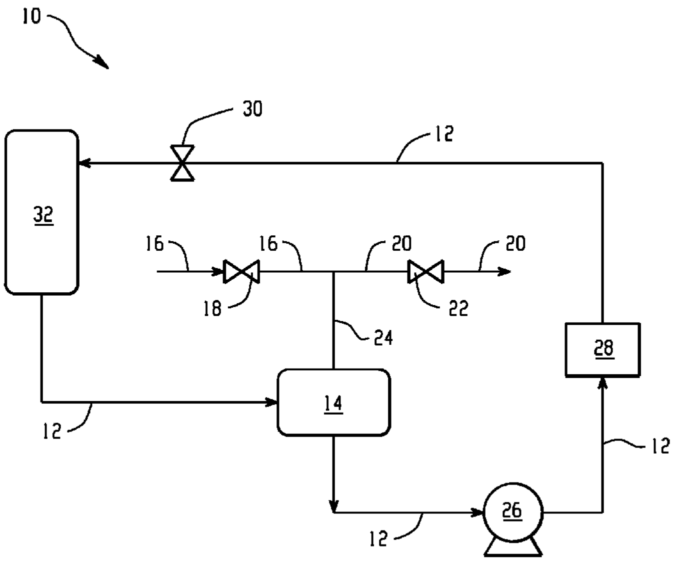
(54) Title: METHOD OF CONTROLLING PRESSURE WITHIN A PRESSURE VESSEL



(57) Abstract: A method of controlling pressure within a pressure vessel includes introducing a flushing fluid stream into a pressure vessel, wherein the pressure vessel comprises a vapor injection valve and a vapor release valve; passing a first vapor stream through the vapor injection valve and into the pressure vessel when a pressure within the pressure vessel reaches a minimum value; passing a second vapor stream through the vapor release valve and out of the pressure vessel when the pressure within the pressure vessel reaches a maximum value, wherein the minimum value and the maximum value are different.

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METHOD OF CONTROLLING PRESSURE WITHIN A PRESSURE VESSEL

BACKGROUND

[0001] Pressure vessels are used in a variety of applications in both industry and the private sector. They appear in these sectors as industrial compressed air receivers and domestic hot water storage tanks. Other examples of pressure vessels are diving cylinders, recompression chambers, distillation towers, pressure reactors, autoclaves, and many other vessels in mining operations, oil refineries and petrochemical plants, nuclear reactor vessels, submarine and space ship habitats, pneumatic reservoirs, hydraulic reservoirs under pressure, rail vehicle airbrake reservoirs, road vehicle airbrake reservoirs, and storage vessels for liquefied gases such as ammonia, chlorine, and liquid petroleum gas.

[0002] Conventional methods of pressure control often involve non-variable or static pressure control systems. These methods increase or release pressure from within the vessel whenever a certain internal pressure value is reached. This pressure value is a single, static value. These static systems result in significant inefficiencies and economic losses. For example, the pressure within the vessel must be adjusted too frequently. This results in excessive use of pressure adjustment streams and also allows significant amounts of stored material to escape from the vessel.

[0003] Especially in technologies related to oligomer and/or polymer production, such as the polymerization of ethylene, or the oligomerization of ethylene, such as the selective ethylene di-, tri- and tetramerization for producing comonomer-grade linear alpha-olefins, equipment fouling is a problem and is frequently encountered. In such processes waxes and polymers are inherent side-products which cannot be avoided completely. These waxes and polymers can lead to fouling of the reactor itself, as well as of peripheral and downstream equipment. In the worst case, part of the equipment, such as pipes, in the subsequent process sections are plugged with the consequence that the process has to be shut down.

[0004] In the polymerization of ethylene and/or other alpha-olefins, deposition of polymeric solids may as well occur in reactor and/or equipment with the various changes in pressure.

[0005] To control the polymer and wax deposits, the reactor has to be cleaned periodically. To avoid any long shut down periods, a spare reactor to prevent any production loss is required.

[0006] For cleaning a reactor bearing solid deposits (e.g. high molecular weight oligomers/polymers), the reactor has so far to be opened and usually plant personnel has to enter the reactor for mechanical cleaning. After cleaning, the reactor has to be rendered inert again. The reason is that any traces of moisture and oxygen will poison the highly sensitive organo- metallic catalyst used for oligomerization and polymerization. This procedure is very time- consuming. In conclusion, a typical reactor downtime is about 1 week or longer, given rise to a considerable overall productivity loss.

[0007] To overcome these disadvantages, a procedure to avoid any mechanical cleaning includes a hot solvent having a temperature of at least about 75°C being introduced into the reactor to dissolve the polymer deposits. After cleaning, the solvent may be recovered in a solvent recovery unit, for example by distillation, crystallization, thin- film evaporation, wiped-film evaporation and/or falling film evaporation.

[0008] As long as the polymeric solid material features a sufficiently short carbon chain length, this process works in a satisfying manner. This is especially true for the use of zirconium-based catalyst systems, which usually provide only relatively short chain length polyethylene and waxes. However, the situation changes if trace-levels of impurities are inherently (via feedstock impurities) or inadvertently (caused by upset process conditions) introduced into the oligomerization reactor. Especially traces of moisture, air and/or corrosion products may induce the formation of long chain and potentially branched polyethylene with relatively poor solubility in aromatic solvents.

[0009] This situation aggravates considerably with the use of other catalyst systems, for example chromium-based catalyst systems for the selective tri- or tetramerization of ethylene. Although only traces of polyethylene are formed under on- spec conditions, Cr-induced polymer tends to feature a longer chain length and a morphology that slows down the dissolution process considerably.

[0010] Conventional methods of pressure control in flushing system involve non-variable or static pressure control systems. These methods increase or release pressure from within the vessel whenever a certain internal pressure value is reached. These static systems result in significant inefficiencies and economic losses. For example, the pressure within the vessel must be adjusted too frequently. This results in excessive use of pressure adjustment streams and also allows significant amounts of stored material to escape from the vessel.

[0011] Thus, there is a need for an efficient method of controlling the pressure within a pressure vessel that significantly reduces the use of pressure adjustment streams and the amount of stored material lost due to frequent pressure adjustments.

SUMMARY

[0012] Disclosed, in various embodiments, are methods of controlling pressure within a pressure vessel and methods of flushing a reactor.

[0013] A method of controlling pressure within a pressure vessel, comprises: introducing a flushing fluid stream into a pressure vessel, wherein the pressure vessel comprises a vapor injection valve and a vapor release valve; passing a first vapor stream through the vapor injection valve and into the pressure vessel when a pressure within the pressure vessel reaches a minimum value; passing a second vapor stream through the vapor release valve and out of the pressure vessel when the pressure within the pressure vessel reaches a maximum value, wherein the minimum value and the maximum value are different.

[0014] A method of flushing a reactor, comprises: introducing a flushing fluid stream into a pressure vessel, wherein the pressure vessel comprises a vapor injection valve and a vapor release valve; passing a first vapor stream through the vapor injection valve and into the pressure vessel when a pressure within the pressure vessel reaches a minimum value; passing a second vapor stream through the vapor release valve and out of the pressure vessel when the pressure within the pressure vessel reaches a maximum value, wherein the minimum value and the maximum value are different; withdrawing a portion of the flushing fluid stream from the pressure vessel; and passing the portion of the flushing fluid stream through a reactor to flush the reactor.

[0015] These and other features and characteristics are more particularly described below.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] The following is a brief description of the drawings wherein like elements are numbered alike and which are presented for the purposes of illustrating the exemplary embodiments disclosed herein and not for the purposes of limiting the same.

[0017] FIG. 1 is a simplified schematic diagram representing a pressure control method in accordance with the present disclosure.

DETAILED DESCRIPTION

[0018] The method disclosed herein can provide an efficient method of controlling the pressure within a pressure vessel that reduces the use of pressure adjustment streams and the amount of stored material lost due to frequent pressure adjustments. For example, the method disclosed herein can include a variable pressure control system. For example, the method can include the use of a variable pressure between two set minimum and maximum points. This can be advantageous compared to static pressure, since the use of static pressure generally results in the use of more nitrogen and the loss of more toluene as the pressure valve opens and closes to equilibrate the static pressure. With the inventive method, a different type of control other than the static control can be used to reduce the amount of stored material lost because of the pressure adjustments. The method can reduce the frequency of required pressure adjustments. The method disclosed can reduce the amount of material injected into a pressure vessel for pressure adjustment purposes. For example, the method disclosed herein can reduce the amount of nitrogen consumed by greater than or equal to 90%. The method can also reduce the amount of stored material that is lost from the vessel during frequent pressure adjustments. For example, the method disclosed herein can reduce the amount of toluene lost from a pressure vessel by greater than or equal to 45%.

[0019] The method disclosed herein for pressure control can include introducing a flushing fluid stream into a pressure vessel. The pressure vessel can comprise a vapor injection valve and a vapor release valve. A first vapor stream can then be passed through the vapor injection valve and into the pressure vessel when a pressure within the pressure vessel reaches a minimum value. A second vapor stream can be released through the vapor release valve and out of the pressure vessel when the pressure within the pressure vessel reaches a maximum value. The minimum value and the maximum value can be the same or different. A portion of the flushing fluid stream can be withdrawn from the pressure vessel and passed through a reactor to flush the reactor.

[0020] The method disclosed herein for pressure control can include a fluid stream. For example, the fluid stream can comprise a solvent, for example, an aromatic solvent. For example, the fluid stream can comprise toluene for use as a solvent in an oligomerisation reaction. The fluid stream can comprise a flushing fluid. For example, the fluid stream can comprise toluene for flushing reactors and heat exchangers. The flushing fluid stream can comprise any aromatic solvent. The fluid stream can comprise any organic liquid with a boiling point less than or equal to 300°C at atmospheric pressure. For example, the fluid stream can comprise an aromatic solvent, an organic liquid with a boiling point less than or equal 300°C, or a combination comprising at least one of the foregoing.

[0021] The method described herein for pressure control can include a pressure vessel. For example, a fluid stream can be passed through the pressure vessel. For example, the pressure vessel can be a toluene storage vessel. The pressure vessel can comprise steel, composite materials, polymeric materials, or a combination comprising at least one of the foregoing. A temperature within the vessel can be greater than or equal to 50°C. For example, a temperature within the vessel can be greater than or equal to 80°C. For example, a temperature within the vessel can be 80°C to 250°C. The pressure vessel can comprise a valve. For example, the pressure vessel can comprise greater than or equal to one valve. For example, the pressure vessel can comprise 2 valves. The valves can be injection valves, release valves, or a combination comprising at least one of the foregoing. For example, the pressure vessel can comprise one injection valve and one flare depressurization valve.

[0022] The method disclosed herein for pressure control can include passing a stream through a valve and into a pressure vessel. For example, a vapor stream can be passed through a vapor injection valve and into the pressure vessel. The vapor stream can comprise an inert gas. For example, the vapor stream can comprise nitrogen gas, methane gas, ethane gas, or a combination comprising at least one of the foregoing. The vapor stream can pass through the injection valve and into the pressure vessel when a pressure within the pressure vessel reaches a minimum value. The injection of the vapor stream can increase the pressure within the pressure vessel.

[0023] The method disclosed herein for pressure control can include passing a stream through a valve, releasing the stream from a pressure vessel. For example, a vapor stream can be passed through a flare depressurization valve, releasing the vapor stream from the pressure vessel. The vapor stream being released from the pressure vessel can comprise the vapor phase of the fluid being stored in the pressure vessel, an inert gas, or a combination comprising at least one of the foregoing. For example, the vapor stream being released from the pressure vessel can comprise nitrogen gas and vapor phase toluene. A vapor stream can be released from the pressure vessel through the flare depressurization valve when a pressure within the pressure vessel reaches a maximum value. The release of the vapor stream can decrease the pressure within the pressure vessel.

[0024] The method disclosed herein for pressure control can include a variable, non-static pressure control system. For example, the minimum pressure value and the maximum pressure value within the pressure vessel can be different values. For example, the minimum pressure value can be 10 kiloPascals to 500 kiloPascals. For example, the minimum pressure value can be 300 kiloPascals to 400 kiloPascals. For example, the minimum pressure value can be 350 kiloPascals. The maximum pressure value can be 50 kiloPascals to 1000 kiloPascals. For example, the maximum pressure value can be 600 kiloPascals to 700 kiloPascals. For example, the maximum pressure value can be 650 kiloPascals. The minimum pressure value and the maximum pressure value can differ, for example, by greater than or equal to 10 kiloPascals. For example, the values can differ by greater than or equal to 300 kiloPascals.

[0025] The method disclosed herein for pressure control can include withdrawing a fluid stream from the pressure vessel. For example, the method disclosed herein can comprise withdrawing a flushing fluid stream comprising toluene from the pressure vessel. The fluid stream can be passed through greater than or equal to one pump. For example, the fluid stream can be propelled by greater than or equal to one pump. For example, the fluid stream can be propelled by 2 pumps. The pump can operate independently of the pressure within the pressure vessel. For example, a change in pump suction pressure will not impact the flow of the fluid stream being withdrawn from the pressure vessel (a change in pressure within the pressure vessel will also have no impact on pump performance). The fluid stream can be passed through a heat exchanger. For example, the fluid stream can be passed through a heater and the temperature of the fluid stream can be increased.

[0026] The method disclosed herein for pressure control can include passing a fluid stream through a reactor or heat exchanger for flushing purposes. The fluid stream can be used as a solvent stream. For example, the fluid stream can be used as a solvent stream for an oligomerization reactor. The fluid stream can be returned to the pressure vessel after passing through a reactor or heat exchanger as part of a closed loop system. The flow of the fluid stream can be controlled by a flow controller.

[0027] The method can be used for cleaning reactors and/or equipment used in oligomerization or polymerization. Oligomerization shall comprise di-, tri- and tetramerization of olefins, e.g., ethylene to produce linear alpha-olefins. Polymerization includes polymerization of ethylene and other alpha-olefins, as well as copolymerization thereof.

[0028] In the oligomerization, polymer residues are inherently formed as side-products which may form deposits in the reactor and/or equipment. In the polymerization process, the product as such (polymer) can form respective deposits. In both, oligomerization and polymerization process, reactor and/or equipment have to be cleaned to avoid plugging thereof.

[0029] A more complete understanding of the components, processes, and apparatuses disclosed herein can be obtained by reference to the accompanying drawings. These figures (also referred to herein as "FIG.") are merely schematic representations based on convenience and the ease of demonstrating the present disclosure, and are, therefore, not intended to indicate relative size and dimensions of the devices or components thereof and/or to define or limit the scope of the exemplary embodiments. Although specific terms are used in the following description for the sake of clarity, these terms are intended to refer only to the particular structure of the embodiments selected for illustration in the drawings, and are not intended to define or limit the scope of the disclosure. In the drawings and the following description below, it is to be understood that like numeric designations refer to components of like function.

[0030] Referring now to FIG. 1, the method disclosed herein for pressure control 10 can include passing a fluid flushing stream 12 through a pressure vessel 14. For example, the fluid flushing stream 12 can comprise toluene and the pressure vessel 14 can be a toluene storage vessel. The method disclosed herein can include passing a first vapor stream 16 through a vapor injection valve 18. For example, the first vapor stream 16 can comprise nitrogen. The first vapor stream 16 can be passed through the vapor injection valve 18 and into the pressure vessel 14 via a combined line 24. For example, the first vapor stream 16 can be passed into the pressure vessel 14 when a pressure within the pressure vessel 14 reaches a minimum value.

[0031] The method disclosed herein for pressure control can include passing a second vapor stream 20 through a vapor release valve 22. For example, the second vapor stream 20 can comprise gaseous nitrogen and gaseous toluene. For example, the second vapor stream 20 can exit the pressure vessel 14 via the combined line 24 and pass through the vapor release valve 22. For example, the second vapor stream 20 can exit the pressure vessel 14 when a pressure within the pressure vessel 14 reaches a maximum value. For example, the maximum pressure value and the minimum pressure value can be different values.

[0032] The method disclosed herein for pressure control can include withdrawing the fluid flushing stream 12 from the pressure vessel 14. The fluid flushing stream 12 can then be passed through a pump 26. For example, the fluid flushing stream 12 can be propelled by the pump 26. The pump 26 can operate independently of the pressure within the pressure vessel 14. The fluid flushing stream 12 can also be passed through a heater 28. The pressure control method 10 can be a closed loop system.

[0033] The method disclosed herein for pressure control can include passing the fluid flushing stream 12 through a reactor 32 to flush the reactor 32. The flow of the fluid flushing stream 12 to the reactor 32 can be controlled by a flow controller 30. The fluid flushing stream 12 can pass through the reactor 32 and be fed back to the pressure vessel 14 as part of the closed loop pressure control method 10.

[0034] The following examples are merely illustrative of the pressure control method disclosed herein and are not intended to limit the scope hereof.

EXAMPLES

Comparative Example 1

[0035] A conventional method of pressure control within a pressure vessel was used for the purposes of this comparative example. A static, non-variable pressure control system was used. A toluene storage pressure vessel was operated at a fixed pressure of 510 kiloPascals. Nitrogen was injected into the vessel to increase pressure within the vessel and a release valve was opened to decrease the pressure. Two separate trials, Trial 1 and Trial 2, were conducted using this method. The trials were conducted one month apart. The results from the two trials are presented in Table 1. The total amount of nitrogen consumed is presented in kilograms per day. The total ventilation flowrate is presented in kilograms per day. The toluene concentration is presented in mass percent. The total amount of toluene consumed is presented in kilograms per day. Temperature was held constant at 155°C.

Example 1

[0036] A pressure control method according to the present disclosure, and as depicted in FIG. 1, was used for the purposes of this example. A variable, non-static pressure control system was used. Nitrogen injection was used to increase pressure within a toluene vessel. Pressure was decreased using a pressure release valve. The maximum pressure value was set at 650 kiloPascals and a minimum pressure value was set at 350 kiloPascals. The available net positive suction head of the vessel was 20 meters and the required net positive suction head was 5.3 meters. A temperature within the vessel was 155°C. The results are presented in Table 1 as Trial 3. As can be seen, the method disclosed herein (Trial 3) significantly reduces the amount of material that must be injected into a pressure vessel for pressure adjustment purposes (as compared to Trial 1 and Trial 2). For example, the method disclosed herein can reduce the amount of nitrogen consumed by greater than or equal to 90%. The method disclosed herein can also significantly reduce the amount of stored material that is lost from the vessel during frequent pressure adjustments. For example, the method disclosed herein can reduce the amount of toluene lost from a pressure vessel by greater than or equal to 45%.

Table 1

	Trial 1	Trial 2	Trial 3
Nitrogen Consumption (kg/day)	309	402	4
Ventilation Flow Rate (kg/day)	1133	1310	558
Toluene Concentration (mass %)	75.2	75.1	78.9
Toluene Consumption (kg/day)	852	984	440

[0037] The processes disclosed herein include(s) at least the following embodiments:

[0038] Embodiment 1: A method of controlling pressure within a pressure vessel, comprising: introducing a flushing fluid stream into a pressure vessel, wherein the pressure vessel comprises a vapor injection valve and a vapor release valve; passing a first vapor stream through the vapor injection valve and into the pressure vessel when a pressure within the pressure vessel reaches a minimum value; and passing a second vapor stream through the vapor release valve and out of the pressure vessel when the pressure within the pressure vessel reaches a maximum value, wherein the minimum value and the maximum value are different.

[0039] Embodiment 2: The method of Embodiment 1, wherein the flushing fluid stream comprises an aromatic solvent, an organic liquid with a boiling point less than or equal to 300°C, or a combination comprising at least one of the foregoing, preferably wherein the flushing fluid comprises toluene.

[0040] Embodiment 3: The method of any of the preceding embodiments, wherein the first vapor stream comprises an inert gas, preferably wherein the first vapor stream comprises nitrogen gas, methane gas, ethane gas, or a combination comprising at least one of the foregoing.

[0041] Embodiment 4: The method of any of the preceding claims, wherein the second vapor stream comprises the flushing fluid in a vapor phase.

[0042] Embodiment 5: The method of any of the preceding embodiments, wherein a temperature within the pressure vessel is 80°C to 250°C.

[0043] Embodiment 6: The method of any of the preceding embodiments, wherein the minimum value for the pressure within the pressure vessel is 10 kiloPascals to 500 kiloPascals.

[0044] Embodiment 7: The method of any of the preceding embodiments, wherein the maximum value for the pressure within the pressure vessel is 50 kiloPascals to 1000 kiloPascals.

[0045] Embodiment 8: The method of any of the preceding embodiments, wherein the minimum value for the pressure within the pressure vessel and the maximum value for the pressure within the pressure vessel differ by greater than or equal to 10 kiloPascals.

[0046] Embodiment 9: The method of any of the preceding embodiments, wherein the flushing fluid stream is propelled by a pump, wherein the pump operates independently of the pressure within the pressure vessel.

[0047] Embodiment 10: The method of any of the preceding embodiments, wherein the pressure vessel comprises steel, composite materials, polymeric materials, or a combination comprising at least one of the foregoing.

[0048] Embodiment 11: A method of flushing a reactor, comprising: introducing a flushing fluid stream into a pressure vessel, wherein the pressure vessel comprises a vapor injection valve and a vapor release valve; passing a first vapor stream through the vapor injection valve and into the pressure vessel when a pressure within the pressure vessel reaches a minimum value; passing a second vapor stream through the vapor release valve and out of the pressure vessel when the pressure within the pressure vessel reaches a maximum value, wherein the minimum value and the maximum value are different; withdrawing a portion of the flushing fluid stream from the pressure vessel; and passing the portion of the flushing fluid stream through a reactor to flush the reactor.

[0049] Embodiment 12: The method of Embodiment 11, wherein the withdrawn portion of the flushing fluid is monitored by a flow controller prior to passing through the reactor.

[0050] Embodiment 13: The method of Embodiment 11 or Embodiment 12, wherein flushing the reactor is a closed loop system.

[0051] Embodiment 14: The method of any of Embodiments 11-13, wherein the flushing fluid stream comprises an aromatic solvent, an organic liquid with a boiling point less than or equal to 300°C, or a combination comprising at least one of the foregoing, preferably wherein the flushing fluid comprises toluene.

[0052] Embodiment 15: The method of any of Embodiments 11-14, wherein the first vapor stream comprises an inert gas, preferably wherein the first vapor stream comprises nitrogen gas, methane gas, ethane gas, or a combination comprising at least one of the foregoing.

[0053] Embodiment 16: The method of any of Embodiments 11-15, wherein a temperature within the pressure vessel is 80°C to 250°C.

[0054] Embodiment 17: The method of any of Embodiments 11-16, wherein the minimum value for the pressure within the pressure vessel is 10 kiloPascals to 500 kiloPascals.

[0055] Embodiment 18: The method of any of Embodiments 11-17, wherein the maximum value for the pressure within the pressure vessel is 50 kiloPascals to 1000 kiloPascals.

[0056] Embodiment 19: The method of any of Embodiments 11-18, wherein the minimum value for the pressure within the pressure vessel and maximum value for the pressure within the pressure vessel differ by greater than or equal to 10 kiloPascals.

[0057] Embodiment 20: The method of any of Embodiments 11-19, wherein the flushing fluid stream is propelled by a pump, wherein the pump operates independently of the pressure within the pressure vessel.

[0058] Embodiment 21: The method of any of Embodiments 11-20, wherein the amount of toluene lost per month is reduced by greater than or equal to 45% as compared to a reactor flushed by a different method.

[0059] Embodiment 22: The method of any of Embodiments 11-21, wherein the amount of nitrogen consumed by the reactor is reduced by greater than or equal to 90% compared to a reactor flushed by a different method.

[0060] Embodiment 23: A system for controlling pressure within a pressure vessel, comprising: a pressure vessel comprising comprises a vapor injection valve and a vapor release valve, wherein pressure vessel is configured to: accept a flushing fluid stream introduced into the pressure vessel; pass a first vapor stream through the vapor injection valve and into the pressure vessel when a pressure within the pressure vessel reaches a minimum value; and pass a second vapor stream through the vapor release valve and out of the pressure vessel when the pressure within the pressure vessel reaches a maximum value, wherein the minimum value and the maximum value are different.

[0061] In general, the invention may alternately comprise, consist of, or consist essentially of, any appropriate components herein disclosed. The invention may additionally, or alternatively, be formulated so as to be devoid, or substantially free, of any components, materials, ingredients, adjuvants or species used in the prior art compositions or that are otherwise not necessary to the achievement of the function and/or objectives of the present invention. The endpoints of all ranges directed to the same component or property are inclusive and independently combinable (e.g., ranges of "less than or equal to 25 wt%, or 5 wt% to 20 wt%," is inclusive of the endpoints and all intermediate values of the ranges of "5 wt% to 25 wt%," etc.). Disclosure of a narrower range or more specific group in addition to a broader range is not a disclaimer of the broader range or larger group. "Combination" is inclusive of blends, mixtures, alloys, reaction products, and the like. Furthermore, the terms "first," "second," and the like, herein do not denote any order, quantity, or importance, but rather are used to denote one element from another. The terms "a" and "an" and "the" herein do not denote a limitation of quantity, and are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. "Or" means "and/or." The suffix "(s)" as used herein is intended to include both the singular and the plural of the term that it modifies, thereby including one or more of that term (e.g., the film(s) includes one or more films). Reference throughout the specification to "one embodiment", "another embodiment", "an embodiment", and so forth, means that a particular element (e.g., feature, structure, and/or characteristic) described in connection with the embodiment is included in at least one embodiment described herein, and may or may not be present in other embodiments. In addition, it is to be understood that the described elements may be combined in any suitable manner in the various embodiments.

[0062] The modifier "about" used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context (e.g., includes the degree of error associated with measurement of the particular quantity). The notation "$\pm$ 10%" means that the indicated measurement can be from an amount that is minus 10% to an amount that is plus 10% of the stated value. The terms "front", "back", "bottom", and/or "top" are used herein, unless otherwise noted, merely for convenience of description, and are not limited to any one position or spatial orientation. "Optional" or "optionally" means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where the event occurs and instances where it does not. Unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this invention belongs. A "combination" is inclusive of blends, mixtures, alloys, reaction products, and the like.

[0063] Unless otherwise indicated, each of the foregoing groups can be unsubstituted or substituted, provided that the substitution does not significantly adversely affect synthesis, stability, or use of the compound. The term "substituted" as used herein means that at least one hydrogen on the designated atom or group is replaced with another group, provided that the designated atom's normal valence is not exceeded. When the substituent is oxo (i.e., =O), then two hydrogens on the atom are replaced. Combinations of substituents and/or variables are permissible provided that the substitutions do not significantly adversely affect synthesis or use of the compound. Exemplary groups that can be present on a "substituted" position include, but are not limited to, cyano; hydroxyl; nitro; azido; alkanoyl (such as a C_{2-6} alkanoyl group such as acyl); carboxamido; C_{1-6} or C_{1-3} alkyl, cycloalkyl, alkenyl, and alkynyl (including groups having at least one unsaturated linkages and from 2 to 8, or 2 to 6 carbon atoms); C_{1-6} or C_{1-3} alkoxys; C_{6-10} aryloxy such as phenoxy; C_{1-6} alkylthio; C_{1-6} or C_{1-3} alkylsulfinyl; C1-6 or C_{1-3} alkylsulfonyl; aminodi(C_{1-6} or C_{1-3})alkyl; C_{6-12} aryl having at least one aromatic rings (e.g., phenyl, biphenyl, naphthyl, or the like, each ring either substituted or unsubstituted aromatic); C_{7-19} arylalkyl having 1 to 3 separate or fused rings and from 6 to 18 ring carbon atoms; or arylalkoxy having 1 to 3 separate or fused rings and from 6 to 18 ring carbon atoms, with benzyloxy being an exemplary arylalkoxy.

[0064] All cited patents, patent applications, and other references are incorporated herein by reference in their entirety. However, if a term in the present application contradicts or conflicts with a term in the incorporated reference, the term from the present application takes precedence over the conflicting term from the incorporated reference

[0065] While particular embodiments have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or may be presently unforeseen may arise to applicants or others skilled in the art. Accordingly, the appended claims as filed and as they may be amended are intended to embrace all such alternatives, modifications variations, improvements, and substantial equivalents.

CLAIMS

What is claimed is:

1. A method of controlling pressure within a pressure vessel, comprising:

introducing a flushing fluid stream into a pressure vessel, wherein the pressure vessel comprises a vapor injection valve and a vapor release valve;

passing a first vapor stream through the vapor injection valve and into the pressure vessel when a pressure within the pressure vessel reaches a minimum value; and

passing a second vapor stream through the vapor release valve and out of the pressure vessel when the pressure within the pressure vessel reaches a maximum value, wherein the minimum value and the maximum value are different.

2. The method of Claim 1, wherein the flushing fluid stream comprises an aromatic solvent, an organic liquid with a boiling point less than or equal to 300°C, or a combination comprising at least one of the foregoing, preferably wherein the flushing fluid comprises toluene.

3. The method of any of the preceding claims, wherein the first vapor stream comprises an inert gas, preferably wherein the first vapor stream comprises nitrogen gas, methane gas, ethane gas, or a combination comprising at least one of the foregoing.

4. The method of any of the preceding claims, wherein the second vapor stream comprises the flushing fluid in a vapor phase.

5. The method of any of the preceding claims, wherein a temperature within the pressure vessel is 80°C to 250°C.

6. The method of any of the preceding claims, wherein the minimum value for the pressure within the pressure vessel is 10 kiloPascals to 500 kiloPascals and wherein the maximum value for the pressure within the pressure vessel is 50 kiloPascals to 1000 kiloPascals.

7. The method of any of the preceding claims, wherein the minimum value for the pressure within the pressure vessel and the maximum value for the pressure within the pressure vessel differ by greater than or equal to 10 kiloPascals.

8. The method of any of the preceding claims, wherein the flushing fluid stream is propelled by a pump, wherein the pump operates independently of the pressure within the pressure vessel.

9. The method of any of the preceding claims, wherein the pressure vessel comprises steel, composite materials, polymeric materials, or a combination comprising at least one of the foregoing.

10. A method of flushing a reactor, comprising:

introducing a flushing fluid stream into a pressure vessel, wherein the pressure vessel comprises a vapor injection valve and a vapor release valve;

passing a first vapor stream through the vapor injection valve and into the pressure vessel when a pressure within the pressure vessel reaches a minimum value;

passing a second vapor stream through the vapor release valve and out of the pressure vessel when the pressure within the pressure vessel reaches a maximum value, wherein the minimum value and the maximum value are different;

withdrawing a portion of the flushing fluid stream from the pressure vessel; and

passing the portion of the flushing fluid stream through a reactor to flush the reactor.

11. The method of Claim 10, wherein the withdrawn portion of the flushing fluid is monitored by a flow controller prior to passing through the reactor.

12. The method of Claim 10 or Claim 11, wherein flushing the reactor is a closed loop system.

13. The method of any of Claims 10-12, wherein the flushing fluid stream comprises an aromatic solvent, an organic liquid with a boiling point less than or equal to 300°C, or a combination comprising at least one of the foregoing, preferably wherein the flushing fluid comprises toluene.

14. The method of any of Claims 10-13, wherein the first vapor stream comprises an inert gas, preferably wherein the first vapor stream comprises nitrogen gas, methane gas, ethane gas, or a combination comprising at least one of the foregoing.

15. The method of any of Claims 10-14, wherein a temperature within the pressure vessel is 80ºC to 250ºC, wherein the minimum value for the pressure within the pressure vessel is 10 kiloPascals to 500 kiloPascals and wherein the maximum value for the pressure within the pressure vessel is 50 kiloPascals to 1000 kiloPascals.

16. The method of any of Claims 10-15, wherein the minimum value for the pressure within the pressure vessel and maximum value for the pressure within the pressure vessel differ by greater than or equal to 10 kiloPascals.

17. The method of any of Claims 10-16, wherein the flushing fluid stream is propelled by a pump, wherein the pump operates independently of the pressure within the pressure vessel.

18. The method of any of Claims 10-17, wherein the amount of toluene lost per month is reduced by greater than or equal to 45% as compared to a reactor flushed by a different method.

19. The method of any of Claims 10-18, wherein the amount of nitrogen consumed by the reactor is reduced by greater than or equal to 90% compared to a reactor flushed by a different method.

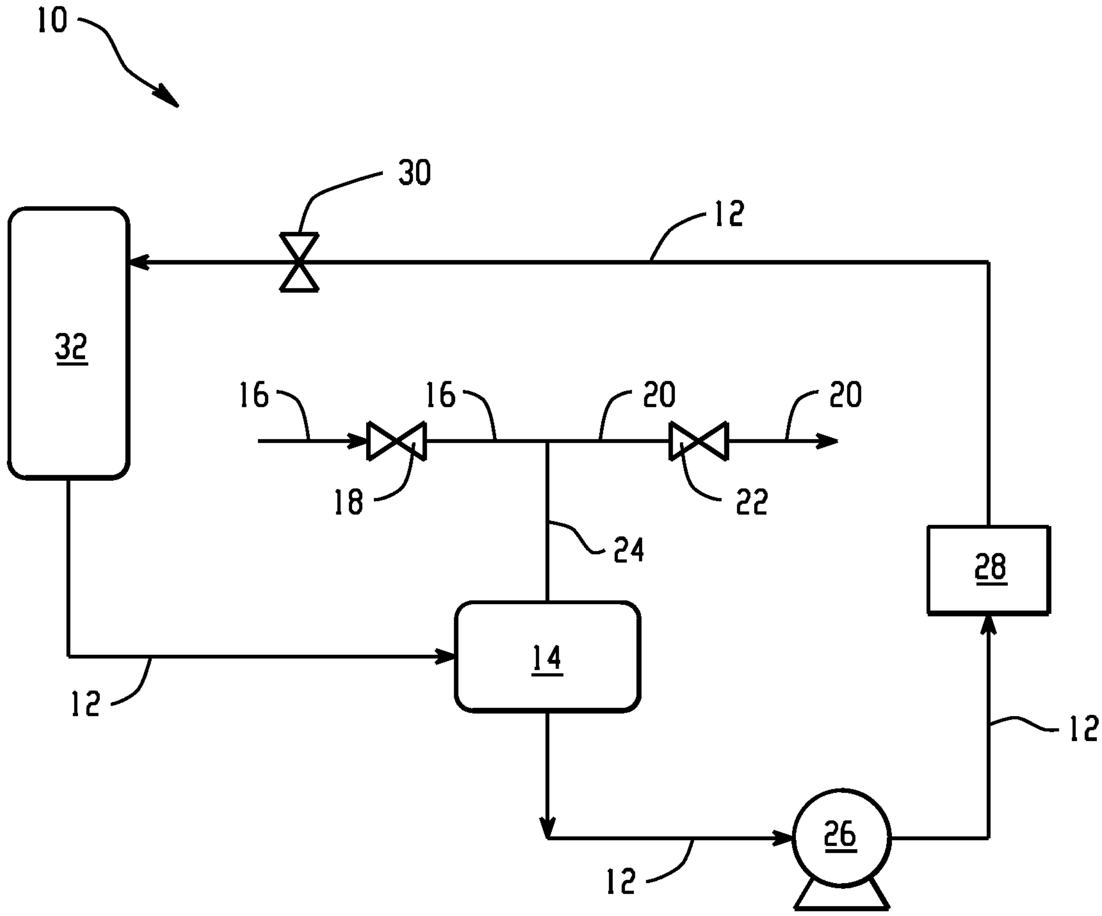
20. A system for controlling pressure within a pressure vessel, comprising:

a pressure vessel comprising comprises a vapor injection valve and a vapor release valve, wherein pressure vessel is configured to:

accept a flushing fluid stream introduced into the pressure vessel;

pass a first vapor stream through the vapor injection valve and into the pressure vessel when a pressure within the pressure vessel reaches a minimum value; and

pass a second vapor stream through the vapor release valve and out of the pressure vessel when the pressure within the pressure vessel reaches a maximum value, wherein the minimum value and the maximum value are different.



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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2016/057735

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J19/24
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/289843 A1 (JORGENSON ROGER [US]) 1 December 2011 (2011-12-01) abstract paragraph [0045] - paragraph [0047]; figure 4 claim 1 -----	1-20
X	WO 2007/122452 A1 (BURKE WILLIAM ROLAND [ZA]) 1 November 2007 (2007-11-01) abstract page 4, line 4 - line 27 page 5, line 28 - line 32 page 6, line 20 - page 7, line 6; figure 1 page 9, line 11 - page 10, line 4 claims 1, 13, 14, 15 -----	1-20

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

[X] See patent family annex.

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Date of the actual completion of the international search

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

Authorized officer

Thomasson, Philippe

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2016/057735

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2006/224033 A1 (HOVIS KEITH W [US] ET AL) 5 October 2006 (2006-10-05) abstract paragraph [0049] - paragraph [0054]; figure 1 claim 1 -----	1-20
X	US 5 667 758 A (MATSUGI NOBUO [JP] ET AL) 16 September 1997 (1997-09-16) abstract column 7, line 42 - line 60; figure 9 claim 1 -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2016/057735

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011289843 A1	01-12-2011	NONE	
WO 2007122452 A1	01-11-2007	EP 2021122 A1	11-02-2009
		WO 2007122452 A1	01-11-2007
US 2006224033 A1	05-10-2006	AR 053852 A1	23-05-2007
		EP 1883613 A2	06-02-2008
		US 2006224033 A1	05-10-2006
		US 2010129265 A1	27-05-2010
		WO 2006107485 A2	12-10-2006
US 5667758 A	16-09-1997	CN 1108965 A	27-09-1995
		DE 69418007 D1	27-05-1999
		DE 69418007 T2	23-09-1999
		EP 0659475 A1	28-06-1995
		JP 2975832 B2	10-11-1999
		JP H07185314 A	25-07-1995
		MY 122548 A	29-04-2006
		TW 255873 B	01-09-1995
		US 5667758 A	16-09-1997