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(54) **Title**: PROCESS FOR CONTROLLING AN ETHYLENE POLYMERIZATION PROCESS

(57) **Abstract**: A method for controlling a slurry polymerization for the preparation of polyethylene, where the polyethylene is formed in a polymerization reactor comprising a vapor section by contacting a Ziegler-type catalyst, ethylene, and either hydrogen or, as comonomer(s), one or more C_3 to C_{10} alpha-olefins or hydrogen and one or more C_3 to C_{10} alpha-olefins, wherein the ethylene partial pressure is maintained by adjusting the flow rate of the catalyst to the polymerization reactor and the hydrogen/ethylene and comonomer/ethylene partial pressure ratios are maintained by adjusting the flow rates of hydrogen and/or of the one or more comonomers to the polymerization reactor.

PROCESS FOR CONTROLLING AN ETHYLENE POLYMERIZATION PROCESS

FIELD OF THE INVENTION

[0001] The present disclosure relates to a method for controlling an ethylene polymerization process. More particularly, the present disclosure relates to a process for controlling an ethylene slurry polymerization process using gas-phase analysis of the reactor vapor. The present disclosure further relates to a process for the preparation of polyethylene in a slurry polymerization.

BACKGROUND OF THE INVENTION

[0002] The use of polyethylene-containing products is known. Various processes can be used to produce polyethylene, including gas phase processes, solution processes, and slurry processes. In ethylene slurry polymerization processes, diluents such as hexane or isobutane may be used to dissolve the ethylene monomer, comonomers and hydrogen, and the monomer(s) are polymerized with a catalyst. Following polymerization, the polymer product formed is present as a slurry of polyethylene particles suspended in the liquid medium.

[0003] In typical multi-reactor cascade processes, shown e.g., in WO 2005/077992 A1 or WO 2012/028591 A1, the reactors can be operated in parallel or in series, and the types and amounts of monomer and conditions can be varied in each reactor to produce a variety of polyethylene materials, including unimodal or multimodal polyethylene material. Such multimodal compositions are used in a variety of applications; e.g., WO 2012/069400 A1 discloses trimodal polyethylene compositions for blow moldings.

[0004] In processes to produce polyethylene, feeding comonomers and hydrogen along with ethylene as main monomer allows to adapt the properties of the resulting ethylene polymer to the required values. Adding comonomer reduces the density of the polyethylene and has a significant effect on stiffness, toughness and stress crack resistance. Adding hydrogen reduces the molecular weight and accordingly has a significant effect on the processability. In multi-reactor processes with different polymerization conditions in each reactor, an even more targeted adaption of the polymer properties is possible. While also in multi-reactor processes, feeding as well comonomer and hydrogen along with the ethylene to one polymerization reactor is common, there are nonetheless many possibilities to produce polyethylenes with outstanding property combinations when feeding only hydrogen together with ethylene and/or only comonomer together with ethylene to one or more reactors of a multi-reactor polymerization process.

[0005] There is a need for efficient control of multiple reactor systems for the production of polyolefins. Various approaches have been used to control continuous manufacturing processes in polymerization plants. EP 0 318 609 A1 discloses a process for producing propylene copolymers where the fraction of gas-phase produced copolymer is controlled. EP 2 336 200 A1 discloses a process to manufacture an olefin polymer in suspension in a series of two polymerization reactors.

[0006] Nevertheless, a continuing need exists for a more efficient method for controlling a slurry polymerization for the preparation of polyethylene. In particular for the operation of the reactors in series to produce bimodal or multimodal polyethylene, a more precise control of each reactor to provide a better control of the polymer properties of the final powder is desired.

SUMMARY OF THE INVENTION

[0007] The present disclosure provides methods for controlling a slurry polymerization of ethylene to produce polyethylene.

[0008] The disclosure provides methods for controlling a slurry polymerization for the preparation of polyethylene, where the polyethylene is formed in a polymerization reactor comprising, as slurry, a suspension of particulate polyethylene in a suspension medium comprising a diluent by contacting a Ziegler-type catalyst, ethylene, and either hydrogen or, as comonomer(s), one or more C_3 to C_{10} alpha-olefins or hydrogen and one or more C_3 to C_{10} alpha-olefins at a reactor temperature from 60°C to 95°C and a reactor pressure from 0.15 MPa to 3 MPa,

where a diluent, ethylene, the Ziegler-type catalyst, and either hydrogen or one or more C_3 to C_{10} alpha-olefins or hydrogen and one or more C_3 to C_{10} alpha-olefins are fed to the polymerization reactor and slurry is withdrawn from the polymerization reactor, and

where the polymerization reactor has a reactor slurry section comprising the slurry and a reactor vapor section comprising a vapor comprising ethylene, diluent, and either hydrogen or one or more C_3 to C_{10} alpha-olefins or hydrogen and one or more C_3 to C_{10} alpha-olefins,

the method comprising:

a) withdrawing vapor from the reactor vapor section;

b) analyzing the vapor to determine its composition; and

c) calculating thereof, based on the pressure within the polymerization reactor, values for the partial pressure of ethylene, for the partial pressure ratio of hydrogen to ethylene and for the partial pressure ratios of the one or more comonomers to ethylene;

d) maintaining the flow rate of the ethylene to the polymerization reactor at a constant level;

e) adjusting the flow rate of the Ziegler-type catalyst to the polymerization reactor to maintain the ethylene partial pressure at a targeted ethylene partial pressure; and

f) either adjusting the flow rate of hydrogen to the polymerization reactor to maintain the hydrogen/ethylene partial pressure ratio at a targeted hydrogen/ethylene partial pressure ratio;

or adjusting the flow rates of the one or more comonomers to the polymerization reactor to maintain the comonomer/ethylene partial pressure ratios at targeted comonomer/ethylene partial pressure ratios;

or adjusting both the flow rate of hydrogen to the polymerization reactor to maintain the hydrogen/ethylene partial pressure ratio at a targeted hydrogen/ethylene partial pressure ratio and adjusting the flow rates of the one or more comonomers to the polymerization reactor to maintain the comonomer/ethylene partial pressure ratios at targeted comonomer/ethylene partial pressure ratios.

[0009] In some embodiments, hydrogen is fed to the polymerization reactor and the flow rate of hydrogen to the polymerization reactor is adjusted to maintain the hydrogen/ethylene partial pressure ratio at a targeted hydrogen/ethylene partial pressure ratio.

[0010] In some embodiments, one or more comonomers are fed to the polymerization reactor and the flow rates of the comonomers to the polymerization reactor are adjusted to maintain the comonomer/ethylene partial pressure ratios at targeted comonomer/ethylene partial pressure ratios.

[0011] In some embodiments, wherein the comonomers are selected from the group consisting of 1-butene, 1-pentene, 1-hexene, 1-octene or mixtures thereof.

[0012] In some embodiments, the methods additionally comprise:

g) maintaining the flow rate of the diluent to the polymerization reactor at a constant level.

[0013] In some embodiments, the diluent is hexane or isobutane.

[0014] In some embodiments the vapor withdrawn from the reactor vapor section is conditioned by being cooled to a temperature of 10°C or below before being analyzed.

[0015] In some embodiments the cooling occurs by means of a heat exchanger located above the polymerization reactor and the liquid, which is obtained by partial condensing of the vapor during cooling, returns to the polymerization reactor by means of gravity.

[0016] In some embodiments, the present disclosure provides methods for controlling a slurry polymerization for the preparation of polyethylene which is carried out in a series of polymerization reactors having a first polymerization reactor and one or more subsequent polymerization reactors, where the polyethylene is formed in polymerization reactors comprising, as slurry, a suspension of particulate polyethylene in a suspension medium comprising a diluent by contacting a Ziegler-type catalyst, ethylene, and either hydrogen or, as comonomer(s), one or more C_3 to C_{10} alpha-olefins or hydrogen and one or more C_3 to C_{10} alpha-olefins at a reactor temperatures from 60°C to 95°C and a reactor pressures from 0.15 MPa to 3 MPa,

where the Ziegler-type catalyst is fed to the first polymerization reactor and a diluent, ethylene, and either hydrogen or one or more C_3 to C_{10} alpha-olefins or hydrogen and one or more C_3 to C_{10} alpha-olefins are fed to each of the polymerization reactors and slurry is withdrawn from each of the polymerization reactor, and

where the polymerization reactor each have a reactor slurry section comprising the slurry and a reactor vapor section comprising a vapor comprising ethylene, diluent, and either hydrogen or one or more C_3 to C_{10} alpha-olefins or hydrogen and one or more C_3 to C_{10} alpha-olefins, the method comprising:

a) withdrawing vapor from the reactor vapor section of the first polymerization reactor;
b) analyzing the vapor to determine its composition; and
c) calculating thereof, based on the pressure within the first polymerization reactor, values for the partial pressure of ethylene, for the partial pressure ratio of hydrogen to ethylene and for the partial pressure ratios of the one or more comonomers to ethylene;
d) maintaining the flow rate of the ethylene to the first polymerization reactor at a constant level;
e) adjusting the flow rate of the Ziegler-type catalyst to the first polymerization reactor to maintain the ethylene partial pressure at a targeted ethylene partial pressure;

f) either adjusting the flow rate of hydrogen to the first polymerization reactor to maintain the hydrogen/ethylene partial pressure ratio at a targeted hydrogen/ethylene partial pressure ratio;

or adjusting the flow rates of the one or more comonomers to the first polymerization reactor to maintain the comonomer/ethylene partial pressure ratios at targeted comonomer/ethylene partial pressure ratios;

or adjusting both the flow rate of hydrogen to the first polymerization reactor to maintain the hydrogen/ethylene partial pressure ratio at a targeted hydrogen/ethylene partial pressure ratio and adjusting the flow rates of the one or more comonomers to the first polymerization reactor to maintain the comonomer/ethylene partial pressure ratios at targeted comonomer/ethylene partial pressure ratios;

h) withdrawing vapor from the reactor vapor section of the one or more subsequent polymerization reactors,

i) analyzing the vapor to determine its composition; and

j) calculating thereof, based on the pressure within the subsequent polymerization reactor, values for the partial pressure of ethylene, for the partial pressure ratio of hydrogen to ethylene and for the partial pressure ratios of the one or more comonomers to ethylene;

k) maintaining the flow rate of the ethylene to the one or more subsequent polymerization reactors at a constant level; and

l) either adjusting the flow rate of hydrogen to the one or more subsequent polymerization reactors to maintain the hydrogen/ethylene partial pressure ratio at a targeted hydrogen/ethylene partial pressure ratio;

or adjusting the flow rates of the one or more comonomers to the one or more subsequent polymerization reactors to maintain the comonomer/ethylene partial pressure ratios at targeted comonomer/ethylene partial pressure ratios;

or adjusting both the flow rate of hydrogen to the one or more subsequent polymerization reactors to maintain the hydrogen/ethylene partial pressure ratio at a targeted hydrogen/ethylene partial pressure ratio and adjusting the flow rates of the one or more comonomers to the one or more subsequent polymerization reactors to maintain the comonomer/ethylene partial pressure ratios at targeted comonomer/ethylene partial pressure ratios.

[0017] In some embodiments, the methods additionally comprise:

m) maintaining the flow rates of the diluent to the one or more subsequent polymerization reactors at a constant level.

[0018] In some embodiments, the series of polymerization reactors has two polymerization reactors.

[0019] In some embodiments, the series of polymerization reactors has three polymerization reactors.

[0020] In some embodiments, hydrogen is fed to a previous polymerization reactor; the slurry withdrawn from the previous polymerization reactor is subjected to a flashing step in a flashing vessel before being fed to the subsequent reactor; and the flow rate of hydrogen to the subsequent polymerization reactor is adjusted to maintain the hydrogen/ethylene partial pressure ratio at a targeted hydrogen/ethylene partial pressure ratio by adjusting the pressure in the flashing vessel.

[0021] In some embodiments, the present disclosure provides processes for the preparation of polyethylene in a slurry polymerization by contacting, in a suspension medium comprising a diluent, ethylene, a Ziegler-type catalyst and either hydrogen or, as comonomer(s), one or more C_3 to C_{10} alpha-olefins or hydrogen and one or more C_3 to C_{10} alpha-olefins at a reactor temperature from 60°C to 95°C and a reactor pressure from 0.15 MPa to 3 MPa.

[0022] In some embodiments, the polymerization is carried out in a series of polymerization reactors.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] To assist those of ordinary skill in the relevant art in making and using the subject matter hereof, reference is made to the appended drawings, wherein:

[0024] Figure 1a is a flow diagram of an ethylene slurry polymerization process having multiple reactors operated in series, i.e. in cascade mode.

[0025] Figure 1b is a flow diagram of an ethylene slurry polymerization process having multiple reactors operated in parallel mode.

[0026] Figure 2 is a flow diagram of an ethylene slurry polymerization process having multiple reactors operated in series illustrating control loops for operating the polymerization process.

DETAILED DESCRIPTION OF THE INVENTION

[0027] Applicants presently believe that more efficient control of ethylene slurry polymerization processes can result from obtaining a vapor sample from the polymerization reactor, analyzing the sample to determine its compositional makeup and then controlling the composition of the components in the polymerization reactor by adjusting, based on the gas sample analysis, the feed rate of the Ziegler-type catalyst and the feed rates of hydrogen and comonomers and maintaining the feed rates of ethylene.

[0028] The process of the present disclosure to produce polyethylene includes the slurry polymerization of ethylene and optionally one or more comonomers in the presence of a Ziegler-type catalyst, a diluent, such as hexane or isobutane, and optionally hydrogen. The polymerization proceeds in a suspension of particulate polyethylene in a suspension medium comprising the diluent, unreacted ethylene and optionally one or more comonomers. Polyethylene polymers obtained by the process described in the present disclosure can be ethylene homopolymers or copolymers of ethylene containing up to 40 wt. %, more preferably from 0.1 to 10 wt. % of recurring units derived from C_3-C_{10}-1-alkenes. Preferably, the comonomers are chosen from propylene, 1-butene, 1-pentene, 1-hexene, 1-octene or mixtures thereof. The slurry polymerization occurs at reactor temperatures from 60°C to 95°C, preferably from 65°C to 90°C, and more preferably from 70°C to 85°C, and at reactor pressures from 0.15 MPa to 3 MPa, preferably from 0.2 MPa to 2 MPa, more preferably from 0.25 MPa to 1.5 MPa.

[0029] Preferably, the polyethylene polymers produced by the polymerization process are high density polyethylene resins preferably having a density in the range from 0.935 g/cm^3 to 0.970 g/cm^3. More preferably, the density is in the range from 0.940 g/cm^3 to 0.970 g/cm^3. Most preferably, the density is in the range from 0.945 g/cm^3 to 0.965 g/cm^3. Density is measured according to DIN EN ISO 1183-1:2004, Method A (Immersion) with compression molded plaques of 2 mm thickness which were prepared with a defined thermal history: Pressed at 180°C, 20 MPa for 8 min with subsequent crystallization in boiling water for 30 min.

[0030] Preferably, the polyethylene polymers produced by the polymerization process have a melt index ($MI_{21.6}$) from 1 dg/min to 300 dg/min, more preferably from 1.5 dg/min to 50 dg/min, and most preferably from 2 dg/min to 35 dg/min. The $MI_{21.6}$ is measured according to DIN EN ISO 1133:2005, condition G at a temperature of 190°C under a load of 21.6 kg.

Catalyst

[0031] The polymerization is preferably carried out using Ziegler-type catalysts, i.e. catalysts of the Ziegler type which are at times also designated as Ziegler-Natta catalysts, comprising a compound of titanium or vanadium, a compound of magnesium and optionally a particulate inorganic oxide as support.

[0032] The titanium compounds are preferably selected from the halides or alkoxides of trivalent or tetravalent titanium, with titanium alkoxy halogen compounds or mixtures of various titanium compounds. Examples of suitable titanium compounds are $TiBr_3$, $TiBr_4$, $TiCl_3$, $TiCl_4$, $Ti(OCH_3)Cl_3$, $Ti(OC_2H_5)Cl_3$, $Ti(O\text{-}i\text{-}C_3H_7)Cl_3$, $Ti(O\text{-}n\text{-}C_4H_9)Cl_3$, $Ti(OC_2H_5)Br_3$, $Ti(O\text{-}n\text{-}C_4H_9)Br_3$, $Ti(OCH_3)_2Cl_2$, $Ti(OC_2H_5)_2Cl_2$, $Ti(O\text{-}n\text{-}C_4H_9)_2Cl_2$, $Ti(OC_2H_5)_2Br_2$, $Ti(OCH_3)_3Cl$, $Ti(OC_2H_5)_3Cl$, $Ti(O\text{-}n\text{-}C_4H_9)_3Cl$, $Ti(OC_2H_5)_3Br$, $Ti(OCH_3)_4$, $Ti(OC_2H_5)_4$ or $Ti(O\text{-}n\text{-}C_4H_9)_4$. Preference is given to using titanium compounds which comprise chlorine as the halogen. Preference is likewise given to titanium halides which comprise only halogen in addition to titanium, and among these especially titanium chlorides and in particular, titanium tetrachloride. Among the vanadium compounds, preferable are the vanadium halides, the vanadium oxyhalides, the vanadium alkoxides and the vanadium acetylacetonates. Preference is given to vanadium compounds in the oxidation states 3 to 5.

[0033] In the production of the solid component, preferably at least one compound of magnesium is used. Suitable compounds of this type are halogen-comprising magnesium compounds such as magnesium halides, and in particular the chlorides or bromides, and magnesium compounds from which the magnesium halides can be obtained in a customary way, e.g., by reaction with halogenating agents. Preferably, the halogens are chlorine, bromine, iodine or fluorine, or mixtures of two or more of the halogens. More preferably, the halogens are chlorine or bromine. Most preferably, the halogens are chlorine.

[0034] Possible halogen-containing magnesium compounds are magnesium chlorides or magnesium bromides. Magnesium compounds from which the halides can be obtained are, for example, magnesium alkyls, magnesium aryls, magnesium alkoxy compounds or magnesium aryloxy compounds or Grignard compounds. Suitable halogenating agents are, for example, halogens, hydrogen halides, $SiCl_4$ or CCl_4. Preferably, chlorine or hydrogen chloride is the halogenating agents.

[0035] Examples of suitable, halogen-free compounds of magnesium are diethylmagnesium, di-n-propylmagnesium, diisopropylmagnesium, di-n-butylmagnesium, di-sec-butylmagnesium, di-tert-butylmagnesium, diamylmagnesium, n-butylethylmagnesium, n-butyl-sec-butylmagnesium, n-butyloctylmagnesium, diphenylmagnesium, diethoxymagnesium, di-n-propyloxymagnesium, diisopropyloxymagnesium, di-n-butyloxymagnesium, di-sec-butyloxymagnesium, di-tert-butyloxymagnesium, diamyloxymagnesium, n-butyloxyethoxymagnesium, n-butyloxy-sec-butyloxymagnesium, n-butyloxyoctyloxymagnesium and diphenoxymagnesium. Among these, preference is given to using n-butylethylmagnesium or n-butyloctylmagnesium.

[0036] Examples of Grignard compounds are methylmagnesium chloride, ethylmagnesium chloride, ethylmagnesium bromide, ethylmagnesium iodide, n-propylmagnesium chloride, n-propylmagnesium bromide, n-butylmagnesium chloride, n-butylmagnesium bromide, sec-butylmagnesium chloride, sec-butylmagnesium bromide, tert-butylmagnesium chloride, tert-butylmagnesium bromide, hexylmagnesium chloride, octylmagnesium chloride, amylmagnesium chloride, isoamylmagnesium chloride, phenylmagnesium chloride and phenylmagnesium bromide.

[0037] As magnesium compounds for producing the particulate solids, preference is given to using, apart from magnesium dichloride or magnesium dibromide, the di(C_1-C_{10}-alkyl)magnesium compounds. Preferably, the Ziegler-type catalyst comprises a transition metal selected from titanium, zirconium, vanadium, and chromium.

[0038] The Ziegler-type catalyst is preferably added to the slurry reactor by first mixing the catalyst with the diluent used, such as hexane, in a mixing tank to form a slurry suitable for pumping. Preferably, a positive displacement pump, such as a membrane pump is used to transfer the catalyst slurry to the slurry polymerization reactor.

Cocatalyst

[0039] Catalysts of the Ziegler type are commonly used for polymerization in the presence of a cocatalyst. Accordingly, the slurry polymerization of the present disclosure is preferably carried out in the presence of a cocatalyst. Preferred cocatalysts are organometallic compounds of metals of groups 1, 2, 12, 13 or 14 of the Periodic Table of Elements, in particular organometallic compounds of metals of group 13 and especially organoaluminum compounds. Preferred organoaluminum compounds are selected from aluminum alkyls. The aluminum alkyls are preferably selected from trialkylaluminum compounds. More preferably, the aluminum alkyls are selected from trimethylaluminum (TMA), triethylaluminum (TEAL), tri-isobutylaluminum (TIBAL), or tri-n-hexylaluminum (TNHAL). Most preferably, the aluminum alkyl is TEAL. The cocatalyst(s) are preferably miscible with the diluent and thus comprised in the suspension medium.

[0040] The cocatalyst can be added to the slurry reactor as such. Preferably, the cocatalyst is added by first mixing the cocatalyst with the diluent used, such as hexane or isobutane, in a mixing tank. Preferably, a positive displacement pump, such as a membrane pump is used to transfer the cocatalyst to the slurry polymerization reactor.

[0041] The polyethylene slurry production process is carried out in at least one polymerization reactor. It may include a polymerization in a stand-alone polymerization reactor or it may include a polymerization in a polymerization reactor of a multi-reactor system. Such multi-reactor systems may be operated in parallel or in series. It is possible to operate two, three or more polymerization reactors in parallel. Preferably, the polymerization reactors of the multi-reactor system are operated in series; i.e. the reactors are arranged as cascade. Such series of polymerization reactors have a first polymerization reactor and one, two or more subsequent polymerization reactors. More preferably the polyethylene slurry production process is carried out in a series of three polymerization reactors.

[0042] The slurry polymerization occurs in the polymerization reactor by contacting the Ziegler-type catalyst, usually in combination with the cocatalyst, ethylene, and either hydrogen or, as comonomer(s), one or more C_3 to C_{10} alpha-olefins or hydrogen and one or more C_3 to C_{10} alpha-olefins. Polyethylene forms around the catalyst particles as a result of the polymerization reactions, so that the catalyst becomes part of the polymer itself. The resulting slurry is a suspension of particulate polyethylene in a liquid suspension medium.

[0043] When operated in series, diluent, the catalyst system, i.e., the Ziegler-type catalyst and usually the cocatalyst, ethylene, and either hydrogen or one or more C_3 to C_{10} alpha-olefins or hydrogen and one or more C_3 to C_{10} alpha-olefins are fed to the first polymerization reactor. The catalyst remains active within the polyethylene particles when the slurry is withdrawn from the first polymerization reactor polymer and fed to the subsequent reactor of the series of polymerization reactors. The slurry fed to the subsequent polymerization reactor not only contains particulate polyethylene but also diluent, non-reacted ethylene and, when fed, non-reacted comonomer(s) and hydrogen. Additional catalyst and cocatalyst are usually not fed to the subsequent reactor or to the subsequent reactors. Instead, catalyst and cocatalyst used in the previous reactor flows with the slurry to the subsequent reactors. This sequence can be repeated up to the total number of reactors in use. For the final polymerization reactor in the series, the slurry produced is fed to a separation system where the liquid is separated from the polymer. The liquid, composed primarily of diluent, is recycled back to the reactors. The polymer is then dried, mixed with additives and compounded. Comonomer(s) may be fed to all the polymerization reactors, to none or to some of the polymerization reactors in any combination. Preferably, no comonomer is fed to the first polymerization reactor so that an ethylene homopolymer is produced. Preferably, comonomer(s) along with ethylene are fed to the subsequent polymerization reactors. By varying the types of ethylene polymers produced in each polymerization reactor, a wide range of properties in the final polymer can be obtained.

[0044] When operated in parallel mode, catalyst, usually cocatalyst, diluent, and either hydrogen or one or more C_3 to C_{10} alpha-olefins or hydrogen and one or more C_3 to C_{10} alpha-olefins are fed to each of the polymerization reactors. The resultant product slurries are fed to a separation device where the liquid is separated from the polymer. The liquid, composed primarily of diluent, is recycled back to the polymerization reactors. The polyethylene is then dried, mixed with additives and compounded.

[0045] The polymerization reactors include cylindrical walls, bottom and top reactor heads, and an agitator for mixing the contents of the internal reactor volume. During operation, the reactor also includes a reactor slurry section and a reactor vapor section. The reactor slurry section is that volume of the reactor that contains the suspension of the particulate polyethylene in the suspension medium, and extends from the bottom head of the reactor to the level of slurry in the reactor. The reactor vapor section is that portion of the reactor extending from above the liquid level in the reactor up to the top head. The vapor in the reactor vapor section is substantially in equilibrium with the suspension medium in the reactor slurry section at the operating temperature and pressure.

[0046] The method of controlling according to the present disclosure can be carried out in any polymerization reactors for the preparation of polyethylene in slurry having a reactor vapor section, to which polymerization reactors Ziegler-type catalysts are fed. Such polymerization reactors may be stand-alone polymerization reactors; such polymerization reactors may be all reactors of a multi-reactor system operated in parallel; or such polymerization reactors may be the first reactors of multi-reactor systems operated in series. For operating multi-reactor systems in series, the method of controlling according to the present disclosure may include further steps for additionally controlling also the polymerization in subsequent polymerization reactors to which no fresh Ziegler-type catalysts are fed but solely slurry having polyethylene particles comprising still active catalysts.

Reactor Control

[0047] Direct measurement of the composition of the slurry is very difficult due to its multiphase composition. However, by determining the concentration of components in the reactor vapor, it is possible to estimate the concentration of components in the suspension medium. Thus, the method of the present disclosure comprises, as step a), that vapor is withdrawn from the reactor vapor section. Therefore, a sample point for taking a reactor vapor sample is provided on the reactor or the reactor head.

[0048] In step b), the vapor is analyzed to determine its composition. Therefore the reactor vapor sample is routed from the reactor to an analyzer for measurement of the vapor components. The composition of the vapor may be determined according to well-known methods. It is possible to determine the composition in one measurement. Preferably, different measurements, possibly according to different methods, are carried out for examining the different components of the vapor.

[0049] Based on the determined composition of the vapor and the pressure within the polymerization reactor, values for the partial pressure of ethylene, for the partial pressure ratio of hydrogen to ethylene and for the partial pressure ratios of the one or more comonomers to ethylene are calculated in step c).

[0050] According to an embodiment of the present disclosure, the vapor withdrawn from the reactor vapor section is conditioned by being first cooled to a temperature of 10°C or below, more preferably to a temperature in the range from 0°C to 10°C before being analyzed. By cooling the reactor vapor to a temperature of 10°C or below, a part of the vapor, which is mainly diluent like hexane, condenses and the analysis of the vapor can be carried out on a cooled vapor having a lower content of diluent. Thus, condensation of diluent on the line to the analyzer, which could result in erroneous results, is avoided and the analyses of the vapor is always done under same conditions, i.e. at the same temperature. Typically, the amount of diluent in the vapor withdrawn from the reactor vapor section reactor is prior to cooling

50 wt. % to 80% wt. %, based on the weight of the reactor vapor sample. The amount of diluent in the conditioned reactor vapor is preferably 0 wt. % to 10 wt. %, and more preferably, 5 wt. % to 10 wt. %, based on the weight of the reactor vapor sample.

[0051] Preferably the cooling of the reactor vapor is carried out in the vicinity of the polymerization reactor from which it was withdrawn, in a way that the condensed components of the vapor can be returned to the polymerization reactor. Accordingly, in a preferred embodiment the cooling occurs by means of a heat exchanger located above the polymerization reactor and the liquid, which is obtained by partial condensing of the vapor during cooling, returns to the polymerization reactor by means of gravity. The heat exchanger is preferably cooled using chilled hexane.

[0052] The method of controlling according to the present disclosure is configured in a way that, as step d), the flow rate of the ethylene to the polymerization reactor is maintaining at a constant level. The ethylene flow rate to the polymerization reactor is targeted to be constant; however the amount of ethylene fed per time to an individual polymerization reactor may be different for different slurry polymerizations producing different polyethylene grades or may even be different for different polymerizations producing the same polyethylene grades if these different polymerizations producing the same polyethylene grades differ in the targeted production rate because the flow rate of ethylene to an individual polymerization reactor determines the production rate of for this polymerization reactor. The ethylene feed rate to a polymerization reactor corresponds to the polyethylene production rate in this reactor.

[0053] In the ethylene slurry polymerization reactors to which Ziegler-type catalyst is fed, the measurement of the ethylene partial pressure in the conditioned reactor vapor is used to adjust the catalyst injection rate. As the catalyst injection rate is increased, there is a corresponding increase in ethylene polymerization rate, with a related decrease in ethylene concentration and accordingly a decrease in the ethylene partial pressure. The opposite occurs when catalyst injection rate is decreased. Accordingly, in step e), the flow rate of the Ziegler-type catalyst to the polymerization reactor is adjusted to maintain the ethylene partial pressure at a targeted ethylene partial pressure.

[0054] To adapt the properties of the produced polyethylene to the needs of the specific application, usually hydrogen or one or more C_3 to C_{10} alpha olefins as comonomer(s) or both hydrogen and one or more C_3 to C_{10} alpha olefins are fed to the polymerization reactors. To ensure that the targeted property combination is maintained, a control of the hydrogen/ethylene partial pressure ratio and the comonomer/ethylene partial pressure ratios is required. Consequently, the method of the present disclosure comprises, as step f), that either the flow rate of hydrogen to the polymerization reactor is adjusted to maintain the hydrogen/ethylene partial pressure ratio at a targeted hydrogen/ethylene partial pressure ratio; or the flow rates of the one or more comonomers to the polymerization reactor is adjusted to maintain the comonomer/ethylene partial pressure ratios at targeted comonomer/ethylene partial pressure ratios; or both the flow rate of hydrogen and the flow rates of the one or more comonomers to the polymerization reactor are adjusted to maintain the hydrogen/ethylene partial pressure ratio at a targeted hydrogen/ethylene partial pressure ratio and to maintain the comonomer/ethylene partial pressure ratios at targeted comonomer/ethylene partial pressure ratios.

[0055] In a preferred embodiment of the present disclosure, the method includes as step g) that the flow rate of the diluent to the polymerization reactor is maintained at a constant level.

[0056] Preferably the method of the present disclosure is carried out in series, i.e. in cascades of polymerization reactors and comprises further steps h) to l) for additionally controlling also the polymerizations in subsequent polymerization reactors to which no fresh Ziegler-type catalyst is fed. These additional steps can be carried out in some or in all of the subsequent polymerization reactors. Preferable these further steps h) to l) are carried out in all of the subsequent polymerization reactors. The method for controlling the polymerization in subsequent polymerization reactors is similar to the method for controlling the polymerization in subsequent polymerization reactors, to which Ziegler-type catalyst is fed, but does not include a step that a flow rate of a Ziegler-type catalyst the polymerization reactor is adjusted. Accordingly, steps h), i) and j) are identical to steps a), b) and c); step k) is identical to step d); and step l) is identical to step f).

[0057] The measurement of the comonomer and ethylene partial pressures in the conditioned reactor vapor and the corresponding calculation of the comonomer/ethylene ratios are used to adjust the comonomer feed rates to each reactor. The amount of comonomer in the produced polymer influences its properties, so that targeting a particular comonomer/ethylene ratio will produce a polyethylene having particular properties. In this way, by targeting a comonomer/ethylene ratio, as the ethylene flow rate changes, for example as a result of a change in the targeted polyethylene production rate, the comonomer flow rate will also automatically change.

[0058] It is possible that the desirable polyethylene product will require a combination of ethylene polymers components having different comonomer content. That demands that the polymerizations in the different polymerization reactors are carried out with different targeted comonomer/ethylene ratio. Moreover, it is possible that the desired combination of polymers components can require ethylene polymer component(s) with no comonomer at all. In this case, the targeted comonomer/ethylene ratio in the respective polymerization reactor would be zero. Preferably, no comonomer is fed to the first reactor so that an ethylene homopolymer is produced, while comonomer is fed to subsequent reactors to produce ethylene comonomers.

[0059] The measurement of the hydrogen and ethylene partial pressures in the reactor vapor and the corresponding calculation of the hydrogen/ethylene ratios are used to adjust the hydrogen feed rates to each reactor. The level of hydrogen in the reactors influences the amount of hydrogen transfer reactions that occur, which in turn determines the molecular weight, melt index and molecular weight distribution of the ethylene polymer produced. In this way, by targeting a hydrogen/ethylene ratio, as the ethylene flow rate changes, the hydrogen flow rate will also automatically change.

[0060] In the first reactor, a control valve on the hydrogen flow is adjusted to maintain the targeted hydrogen/ethylene ratio. In subsequent reactors, the ratio can also be maintained by subjecting the slurry withdrawn from the previous polymerization reactor to a flashing step in a flashing vessel such as a flash drum before being fed to the subsequent reactor and adjusting the position of a valve on the flashing vessel that controls the pressure in the flashing vessel. This valve essentially controls the amount of hydrogen transferred from the previous to the subsequent polymerization reactor. When both control valves are used to control the hydrogen/ethylene ratio, the control valve on the hydrogen flow can be configured to open as the valve on the flashing vessel becomes closed, to prevent a conflict in the control loops.

[0061] In a preferred embodiment of the present disclosure, the method includes as steps m) that the flow rates of the diluent to the polymerization reactor are maintained at a constant level.

[0062] Reference is now made to Figures 1a and 1b which illustrate an ethylene slurry polymerization process where the ethylene slurry polymerization reactors are operated in series and in parallel. Figure 1a illustrates an ethylene slurry polymerization process where the reactors are operated in series, i.e. in a cascade. Monomers, i.e. ethylene and comonomers, diluent, catalyst and hydrogen are fed to slurry polymerization reactor 100. Product from reactor 100 flows to flash drum 103 through line 106. Gas flows out of flash drum 103 through line 108. Slurry flows out of flash drum 103 through line 107 to reactor 101. Additional monomers, i.e. ethylene or preferably ethylene and comonomers, and hydrogen are fed to reactor 101. Product from reactor 101 flows to flash drum 104 through line 109. Gas flows out of the flash drum 104 through line 111. Slurry flows out of flash drum 104 through line 110 to reactor 102. Additional monomers, i.e. ethylene or preferably ethylene and comonomers, and hydrogen are fed to reactor 102. Product from reactor 102 flows to flash drum 105 through line 112. Gas flows out of flash drum 105 through line 113. Slurry flows out of flash drum 105 through line 114 to separation system 115, which separates diluent stream 116 from polymer stream 117. Diluent stream 116 is preferably either recycled to the reactors directly or processed to remove waxes and low boiling impurities, and then recycled. Polymer stream 117 is usually further dried and then compounded with additives.

[0063] Figure 1b illustrates an ethylene slurry polymerization process where the reactors are operated in parallel. Hydrogen, monomers, i.e. ethylene and comonomers, diluent and catalyst are separately fed to slurry polymerization reactors 200, 201 and 202. Product from reactors 200, 201 and 202 exit the reactors through lines 206, 209, and 212, respectively, and are routed to flash drums 203, 204 and 205. Gas flows out of flash drums 203, 204, and 205 through lines 208, 211 and 213. Slurry exits flash drums 203, 204, and 205 through lines 207, 210, and 214 respectively, and are routed to separation system 215, which separates diluent stream 216 from polymer stream 217. Diluent stream 216 is either recycled to the reactors directly or processed to remove waxes and low boiling impurities, and then recycled. Polymer stream 217 is further dried and then compounded with additives.

[0064] Reference is now made to Figure 2, which illustrates a control scheme for ethylene slurry polymerization reactors 300A, 300B, and 300C, operating in series (cascade). Each of reactors 300A, 300B, and 300C has a reactor slurry section 301A, 301B, and 301C and a reactor vapor section 302A, 302B, and 302C. For the purposes of the Figures 2, unless otherwise indicated, the suffixes "A", "B", and "C", appending the same three-digit number refer to identical elements associated with different reactors.

[0065] Slurry exits the reactors 300A, 300B, and 300C through lines 303A, 303B, and 303C and flows to flash drum 304A, 304B, and 304C. Vapor exits flash drum 304A, 304B, and 304C through lines 305A, 305B, and 305C. Slurry from flash drum 304A flows to reactor 300B via line 306A. Slurry from flash drum 304B flows to reactor 300C via line 306B. Slurry from flash drum 304C is routed through line 306C for further treatment to separate the liquid suspension medium from polymer particles.

[0066] The Ziegler-type catalyst for the slurry polymerization in reactors 300A, 300B, and 300C is delivered through line 307, catalyst pump 308, and line 309 to reactor 300A. The polymerization in reactors 300B and 300C occurs with the catalyst which is transferred with the slurry, mainly comprised within the polyethylene particles, from reactor 300A to reactor 300B and then from reactor 300B to reactor 300C. No additional catalyst is fed to reactors 300B and 300C.

Ethylene Feed Control

[0067] Ethylene feed control is configured to target constant ethylene flow rates to the ethylene slurry polymerization reactors; however the amount of ethylene fed per time to an individual polymerization reactor may be different for different slurry polymerizations producing different polyethylene grades or may even be different for different polymerizations producing the same polyethylene grades if these different polymerizations producing the same polyethylene grades differ in the targeted production rate because the flow rate of ethylene to an individual polymerization reactor determines the production rate of for this polymerization reactor.

Ethylene for reactors 300A, 300B, and 300C is delivered through lines 311A, 311B, and 311C to control valves 312A, 312B, and 312C. Flow meters 313A, 313B, and 313C produce flow signals 401A, 401B, and 401C, which are representative of the flow rate of ethylene in lines 314A, 314B, and 314C. Flow controllers 402A, 402B, and 402C receive flow signals 401A, 401B, and 401C, and setpoints (SP) which are representative of desired flow rates for ethylene flowing in lines 314A, 314B, and 314C. Flow controllers 402A, 402B, and 402C provide output signals 403A, 403B, and 403C which are responsive of the difference between signals 401A, 401B, and 401C and the setpoints for the respective ethylene flows. Control valves 312A, 312B, and 312C are manipulated in response to signals 403A, 403B, and 403C to adjust the ethylene flows in lines 314A, 314B, and 314C to the desired flow rates for ethylene.

[0068] One skilled in the art would recognize that the controllers could use any of the well-known algorithms employed, such as proportional, proportional-integral, proportional-derivative, or proportional-integral-derivative.

[0069] For controlling the slurry polymerization, reactor vapor is withdrawn from reactor vapor sections 302A, 302B, and 302C and fed, via lines 315A, 315B, and 315C, to heat exchangers 316A, 316B, and 316C in which the reactor vapor is conditioned by being cooled to a temperature of from 3°C to 10°C using chilled hexane. A part of the reactor vapor, mainly diluent, condenses and the obtained liquid flows back down into the reactor through lines 315A, 315B, and 315C. The conditioned reactor vapor is then fed via lines 317A, 317B, and 317C to analysis transducers 318A, 318B, and 318C which are adapted to determine the composition of the conditioned reactor vapor and to deliver signals 404A, 404B, and 404C, representative of the vapor composition, to calculators 400A, 400B, and 400C. Calculators 400A, 400B, and 400C calculate, based on signals 404A, 404B, and 404C, the ratios for the partial pressures of hydrogen and ethylene and of comonomer and ethylene in the reactor vapor sections 302A, 302B, and 302C. When provided with information about the absolute pressure in reactors 300A, 300B, and 300C (not shown for reactors 300B, and 300C) calculators 400A, 400B, and 400C are also able to calculate the absolute partial pressures of ethylene, hydrogen and comonomer in the reactor vapor sections 302A, 302B, and 302C.

Catalyst Feed Control

[0070] Catalyst feed to the reactor 300A is configured to maintain the ethylene partial pressure in the reactor vapor section 302A at a targeted level by adjusting the pumping rate of catalyst pump 308. Pressure transducer 319 produces a pressure signal 405 which is representative of the pressure of reactor 300A. Calculator 400A receives signal 405 and signals 404A representative of the composition of the conditioned reactor vapor, and produces a signal 406 which is representative of the ethylene partial pressure in the reactor vapor section 302A and thus the ethylene concentration in the slurry in reactor 300A. Controller 407 receives signal 406 along with a setpoint (SP) which is representative of the desired ethylene partial pressure in the reactor vapor section 302A. Controller 407 provides output signal 408 which is responsive of the difference between signal 406 and the setpoint for the ethylene partial pressure. Pump speed of catalyst pump 308 is regulated in response to signal 408 to control the catalyst flow through lines 309, to effect that the targeted ethylene partial pressure in the reactor vapor section 302A is maintained.

[0071] Comonomer Feed Control

[0072] Comonomer feed control is configured to target comonomer/ethylene partial pressure ratios in the reactor vapor sections 302A, 302B, and 302C by adjusting the comonomer flow rates to the reactors. Comonomer for reactors 300A, 300B, and 300C is delivered through lines 320A, 320B, and 320C to control valves 321A, 321B, and 321C. Smaller amounts of comonomer are further delivered to reactor 300B by slurry transferred from reactor 300A to reactor 300B if comonomer was fed to reactor 300A and to reactor 300C by slurry transferred from reactor 300B to reactor 300C if comonomer was fed to reactor 300B.

[0073] Calculators 400A, 400B, 400C receive signals 404A, 404B, and 404C representative of the composition of the conditioned reactor vapor, and produce signals 409A, 409B, and 409C which are representative of the comonomer/ethylene partial pressure ratios in the reactor vapor sections 302A, 302B, and 302C. Controllers 410A, 410B, and 410C receive signals 409A, 409B, and 409C along with setpoints (SP) which are representative of the desired comonomer/ethylene partial pressure ratios in the reactor vapor section 302A, 302B, and 302C. Controllers 410A, 410B, and 410C provide output signals 411A, 411B, and 411C which are responsive of the difference between signals 409A, 409B, and 409C and the setpoints for the comonomer/ethylene partial pressure ratios. Control valves 321A, 321B, and 321C are manipulated in response to signals 411A, 411B, and 411C to adjust the comonomer flows in lines 322A, 322B, and 322C, to effect that the targeted comonomer/ethylene partial pressure ratios in the reactor vapor section 302A, 302B, and 302C are maintained.

[0074] Hydrogen Feed Control

[0075] Hydrogen feed control is configured to target hydrogen/ethylene partial pressure ratios in the reactor vapor sections 302A, 302B, and 302C by adjusting the hydrogen flow rates to the reactors. Hydrogen for reactors 300A, 300B, and 300C is delivered through lines 323A, 323B, and 323C to control valves 324A, 324B, and 324C. Amounts of hydrogen comonomer are further delivered to reactor 300B by slurry transferred from reactor 300A to reactor 300B if hydrogen was fed to reactor 300A and to reactor 300C by slurry transferred from reactor 300B to reactor 300C if hydrogen was fed to reactor 300B.

[0076] Calculators 400A, 400B, 400C receive signals 404A, 404B, and 404C representative of the composition of the conditioned reactor vapor, and produce signals 412A, 412B, and 412C which are representative of the hydrogen/ethylene partial pressure ratios in the reactor vapor sections 302A, 302B, and 302C. Controllers 413A, 413B, and 413C receive signals 412A, 412B, and 412C along with setpoints (SP) which are representative of the desired hydrogen/ethylene partial pressure ratios in the reactor vapor section 302A, 302B, and 302C. Controllers 413A, 413B, and 413C provide output signals 414A, 414B, and 414C which are responsive of the difference between signals 412A, 412B, and 412C and the setpoints for the hydrogen/ethylene partial pressure ratios. Control valves 324A, 324B, and 324C are manipulated in response to signals 414A, 414B, and 414C to adjust the hydrogen flows in lines 325A, 325B, and 325C, to effect that the targeted hydrogen/ethylene partial pressure ratios in the reactor vapor section 302A, 302B, and 302C are maintained.

[0077] When polymerizing in reactors 300B and 300C with lower partial pressures of hydrogen than in the previous reactors 300A and 300B, it can occur that more hydrogen may be delivered to reactors 300B and 300C by transfer of slurry from reactors 300A and 300B than is needed to maintain the targeted hydrogen/ethylene partial pressure ratios in reactors 300B and 300C. For such polymerizations, little or no hydrogen is delivered through lines 323B and 323C and the hydrogen flow to reactors 300B and 300C is adjusted by removing hydrogen from the slurry transferred to reactors 300B and 300C. The amount of hydrogen fed to reactors 300B and 300C by slurry transfer via lines 306A and 306B is the lower the more gas is withdrawn from the slurry in flash drums 304A and 304B via lines 305A and 305B, that means the lower the pressure in flash drums 304A and 304B becomes. The pressure in flash drums 304A and 304B, and consequently also the amount of withdrawn hydrogen, can be regulated by control valves 326A and 326B to adjust the gas flow through lines 327A and 327B.

[0078] Accordingly, controllers 413B and 413C provides additional output signals 415B and 415C which are also responsive of the difference between signals 412B and 412C and the setpoints for the hydrogen/ethylene partial pressure ratios. Control valves 326A and 326B are manipulated in response to signals 415B and 415C to adjust the gas flows in lines 327A and 327B, to effect that the targeted hydrogen/ethylene partial pressure ratios in the reactor vapor section 302A, 302B, and 302C are maintained. Detailed configuration of control valves 326A and 326B and 324B and 324C is such that control valves 326A and 326B would open as control valves 324B and 324C close, i.e., when all hydrogen is delivered by transfer from reactor 300A to reactor 300B, or from reactor 300B to reactor 300C.

[0079] The control method of the present disclosure is illustrated in Figure 2 by way of a slurry polymerization employing one comonomer. However, it is evident for a skilled reader that such a scheme is similarly possible with feeding as comonomer a mixture of alpha-olefins or that it is possible to implement one or more additional feeding units with additional control steps for polymerizing in the presence of two or more comonomer. Similarly, it is evident for a skilled reader that the ethylene slurry polymerization illustrated in Figure 2 further includes feeding of diluent and of cocatalyst to all polymerization reactors and may beyond that also include feeding of additives such antistatics to the reactors, although this not shown in Figure 2 to improve the comprehensibility of the drawing.

[0080] Also other features, advantages and embodiments of the subject matter disclosed herein will be readily apparent to those exercising ordinary skill after reading the foregoing disclosure. In this regard, while specific embodiments of the present subject matter have been described in considerable detail, variations and modifications of these embodiments can be effected without departing from the spirit and scope of the present subject matter as described and claimed.

CLAIMS

We claim:

1. A method for controlling a slurry polymerization for the preparation of polyethylene, where the polyethylene is formed in a polymerization reactor comprising, as slurry, a suspension of particulate polyethylene in a suspension medium comprising a diluent by contacting a Ziegler-type catalyst, ethylene, and either hydrogen or, as comonomer(s), one or more C_3 to C_{10} alpha-olefins or hydrogen and one or more C_3 to C_{10} alpha-olefins at a reactor temperature from 60°C to 95°C and a reactor pressure from 0.15 MPa to 3 MPa,

   where a diluent, ethylene, the Ziegler-type catalyst, and either hydrogen or one or more C_3 to C_{10} alpha-olefins or hydrogen and one or more C_3 to C_{10} alpha-olefins are fed to the polymerization reactor and slurry is withdrawn from the polymerization reactor, and

   where the polymerization reactor has a reactor slurry section comprising the slurry and a reactor vapor section comprising a vapor comprising ethylene, diluent, and either hydrogen or one or more C_3 to C_{10} alpha-olefins or hydrogen and one or more C_3 to C_{10} alpha-olefins,

   the method comprising:

   a) withdrawing vapor from the reactor vapor section;
   b) analyzing the vapor to determine its composition; and
   c) calculating thereof, based on the pressure within the polymerization reactor, values for the partial pressure of ethylene, for the partial pressure ratio of hydrogen to ethylene and for the partial pressure ratios of the one or more comonomers to ethylene;
   d) maintaining the flow rate of the ethylene to the polymerization reactor at a constant level;
   e) adjusting the flow rate of the Ziegler-type catalyst to the polymerization reactor to maintain the ethylene partial pressure at a targeted ethylene partial pressure; and
   f) either adjusting the flow rate of hydrogen to the polymerization reactor to maintain the hydrogen/ethylene partial pressure ratio at a targeted hydrogen/ethylene partial pressure ratio;

or adjusting the flow rates of the one or more comonomers to the polymerization reactor to maintain the comonomer/ethylene partial pressure ratios at targeted comonomer/ethylene partial pressure ratios;
or adjusting both the flow rate of hydrogen to the polymerization reactor to maintain the hydrogen/ethylene partial pressure ratio at a targeted hydrogen/ethylene partial pressure ratio and adjusting the flow rates of the one or more comonomers to the polymerization reactor to maintain the comonomer/ethylene partial pressure ratios at targeted comonomer/ethylene partial pressure ratios.

2. The method of claim 1, wherein hydrogen is fed to the polymerization reactor and the flow rate of hydrogen to the polymerization reactor is adjusted to maintain the hydrogen/ethylene partial pressure ratio at a targeted hydrogen/ethylene partial pressure ratio.

3. The process of claim 1 or 2, wherein one or more comonomers are fed to the polymerization reactor and the flow rates of the comonomers to the polymerization reactor are adjusted to maintain the comonomer/ethylene partial pressure ratios at targeted comonomer/ethylene partial pressure ratios.

4. The process of claim 3, wherein the comonomers are selected from the group consisting of 1-butene, 1-pentene, 1-hexene, 1-octene or mixtures thereof.

5. The method of any of claims 1 to 4, additionally comprising:
   g) maintaining the flow rate of the diluent to the polymerization reactor at a constant level.

6. The process of any of claims 1 to 5, wherein the diluent is hexane or isobutane.

7. The method of any of claims 1 to 6, wherein the vapor withdrawn from the reactor vapor section is conditioned by being cooled to a temperature of 10°C or below before being analyzed.

8. The method of claim 7, wherein the cooling occurs by means of a heat exchanger located above the polymerization reactor and the liquid, which is obtained by partial condensing of the vapor during cooling, returns to the polymerization reactor by means of gravity.

9. The method of any of claims 1 to 8, wherein the slurry polymerization is carried out in a series of polymerization reactors having a first polymerization reactor and one or more subsequent polymerization reactors and the polymerization reactor of claims 1 to 8 is the first reactor of the series of polymerization reactors and suspension withdrawn from said first reactor is fed to a subsequent reactor, and additional polyethylene is formed in the one or more subsequent reactors at a reactor temperature from 60°C to 95°C and a reactor pressure from 0.15 MPa to 3 MPa,
where additional diluent, ethylene, and either hydrogen or, as comonomer(s), one or more C_3 to C_{10} alpha-olefins or hydrogen and one or more C_3 to C_{10} alpha-olefins are fed to the one or more subsequent polymerization reactors and slurry is withdrawn from the one or more subsequent polymerization reactor, and
where the one or more subsequent polymerization reactors have a reactor slurry section comprising the slurry and a reactor vapor section comprising a vapor comprising ethylene, diluent, and either hydrogen or one or more comonomers or hydrogen and one or more comonomers,
the method for controlling the slurry polymerization comprising the additional steps of:
h) withdrawing vapor from the reactor vapor section of the one or more subsequent polymerization reactors;
i) analyzing the vapor to determine its composition; and
j) calculating thereof, based on the pressure within the subsequent polymerization reactor, values for the partial pressure of ethylene, for the partial pressure ratio of hydrogen to ethylene and for the partial pressure ratios of the one or more comonomers to ethylene;
k) maintaining the flow rate of the ethylene to the one or more subsequent polymerization reactors at a constant level; and
l) either adjusting the flow rate of hydrogen to the one or more subsequent polymerization reactors to maintain the hydrogen/ethylene partial pressure ratio at a targeted hydrogen/ethylene partial pressure ratio;

or adjusting the flow rates of the one or more comonomers to the one or more subsequent polymerization reactors to maintain the comonomer/ethylene partial pressure ratios at targeted comonomer/ethylene partial pressure ratios;

or adjusting both the flow rate of hydrogen to the one or more subsequent polymerization reactors to maintain the hydrogen/ethylene partial pressure ratio at a targeted hydrogen/ethylene partial pressure ratio and adjusting the flow rates of the one or more comonomers to the one or more subsequent polymerization reactors to maintain the comonomer/ethylene partial pressure ratios at targeted comonomer/ethylene partial pressure ratios.

10. The method of claim 9, additionally comprising:
    m) maintaining the flow rates of the diluent to the one or more subsequent polymerization reactors at a constant level.

11. The method of claim 9 or 10, wherein the series of polymerization reactors has two polymerization reactors.

12. The method of claim 9 or 10, wherein the series of polymerization reactors has three polymerization reactors.

13. The method of any of claims 9 to 12, wherein hydrogen is fed to a previous polymerization reactor; the slurry withdrawn from the previous polymerization reactor is subjected to a flashing step in a flashing vessel before being fed to the subsequent reactor; and the flow rate of hydrogen to the subsequent polymerization reactor is adjusted to maintain the hydrogen/ethylene partial pressure ratio at a targeted hydrogen/ethylene partial pressure ratio by adjusting the pressure in the flashing vessel.

14. A process for the preparation of polyethylene in a slurry polymerization by contacting, in a suspension medium comprising a diluent, ethylene, a Ziegler-type catalyst and either hydrogen or, as comonomer(s), one or more C_3 to C_{10} alpha-olefins or hydrogen and one or more C_3 to C_{10} alpha-olefins at a reactor temperature from 60°C to 95°C and a reactor pressure from 0.15 MPa to 3 MPa, wherein the polymerization is controlled by the method of any of claims 1 to 13.

15. The process of claim 14, wherein the polymerization is carried out in a series of polymerization reactors.

Figure 1a

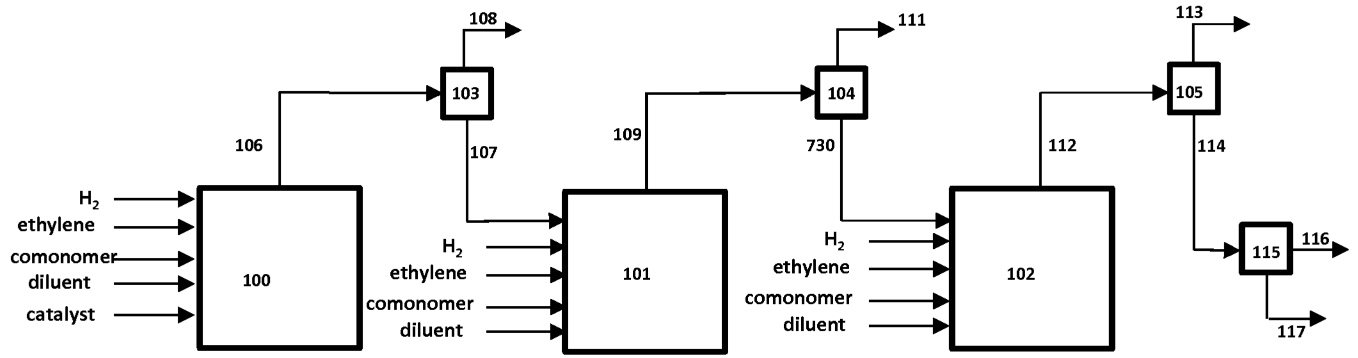


Figure 1b

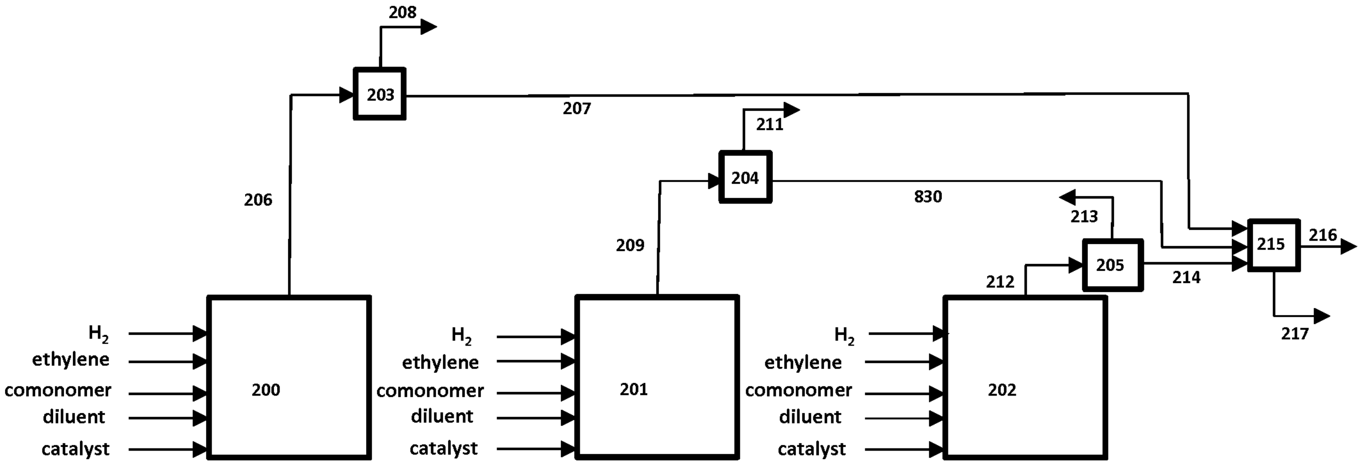
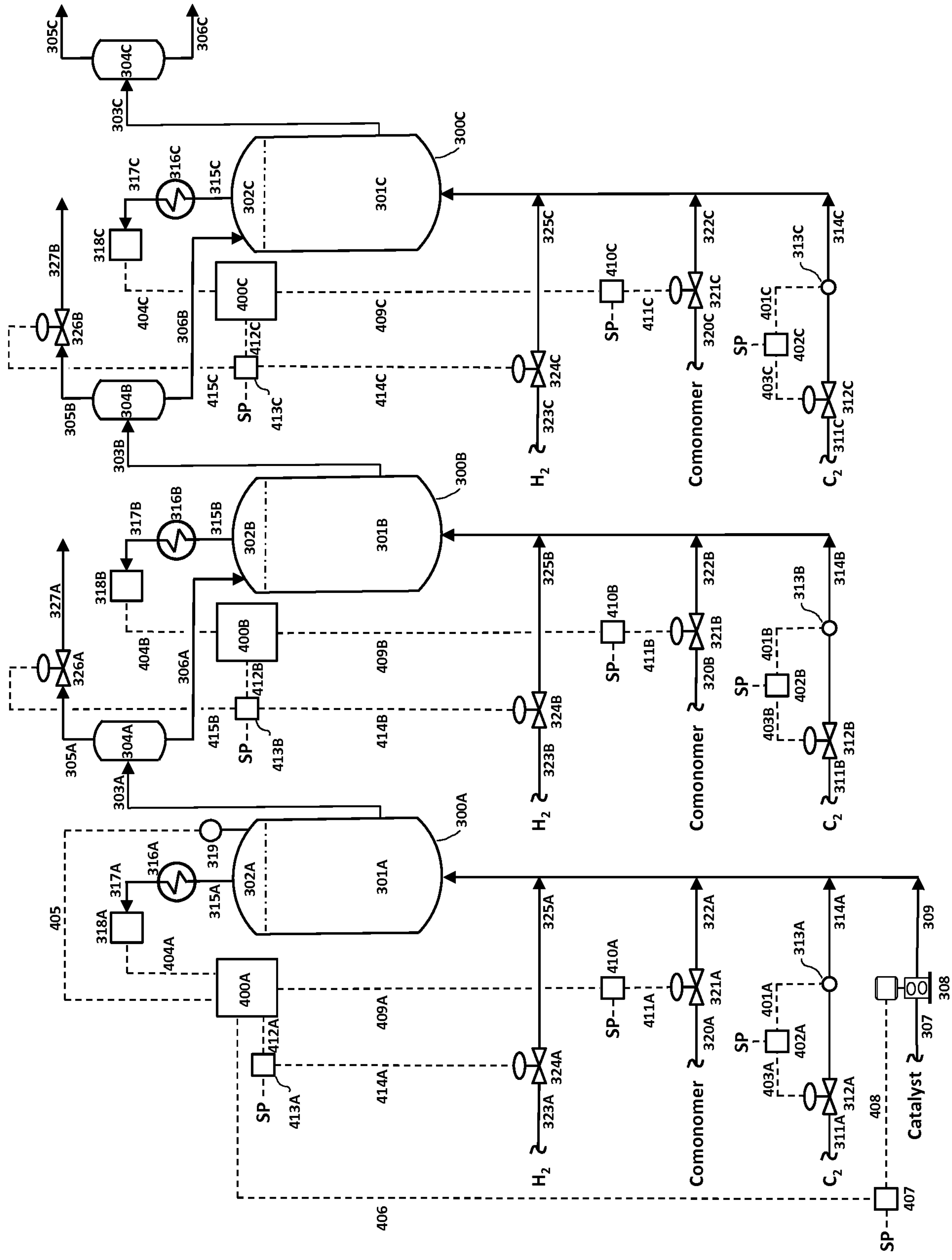


Figure 2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414C

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/063990

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F2/01 C08F2/12 C08F2/18
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)
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 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.
A	EP 2 336 200 A1 (INEOS USA LLC [US]) 22 June 2011 (2011-06-22) cited in the application the whole document -----	1-15
A	WO 2005/040226 A2 (UNIVATION TECH LLC [US]; SANDELL DAVID J [US]; MCBRIDE MARJORIE E [US]) 6 May 2005 (2005-05-06) the whole document -----	1-15
A	US 2005/267267 A1 (SANDELL DAVID J [US] ET AL) 1 December 2005 (2005-12-01) the whole document -----	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 September 2015	11/09/2015

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2015/063990

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