

POLYMERIZATION PROCESS

PRIORITY CLAIM

[0001] This application claims the benefit of Serial No. 62/158,736, filed May 08, 2015,
5 the disclosure of which is fully incorporated by reference in its entirety.

FIELD OF THE INVENTION

[0002] The disclosure relates to polymerization processes for the production of polyolefin
polymers. In particular, the disclosure relates to gas phase polymerization processes that
employ certain condensing agents.

BACKGROUND

[0003] The condensing mode of operation in gas phase polymerization reactors
significantly increases the production rate or space time yield by providing extra heat-
removal capacity through the evaporation of condensates in the cycle gas. Additional
condensation is often promoted to extend the utility of condensed mode operation by adding
15 an inert condensing agent ("ICA") into the reactor. The most commonly used ICA's in
commercial practice are n-pentane, isopentane, n-butane, isohexane, and isobutane. The
amount of ICA that can be introduced into the reactor, however, must be kept below the
"stickiness limit" beyond which the bed material becomes too sticky to discharge or to
maintain a normal fluidization status. Running in excess of this limit will result in different
20 types of fouling or sheeting in both type of fouling or sheeting and location in the reactor
system. The primary limitation on increasing the reaction rate in a fluidized bed reactor is the
rate at which heat can be removed from the polymerization zone. For example, in the
commercial application of one of the most commons ICA's, isopentane, concentrations are
pushed to the maximum allowable levels but no higher so as to avoid expanded dome section
25 sheeting in a gas phase reactor. Past endeavors have attempted to improve on this technology
by providing higher production rates for longer continuous run times.

[0004] For example, U.S. Patent No. 5,352,749, is directed to a process for polymerizing
alpha-olefin(s) in a gas phase reactor having a fluidized bed and a fluidizing medium wherein
the fluidizing medium serves to control the cooling capacity of said reactor, the improvement
30 comprising employing a level of liquid in the fluidizing medium entering the reactor which is
in the range of from 17.4 to 50 weight percent based on the total weight of the fluidizing
medium and maintaining the ratio of fluidized bulk density to settled bulk density above 0.59.
Additionally, it is directed to a continuous process for increasing reactor productivity of a gas
phase polymerization reactor having a fluidizing medium and a fluidized bed, said process

comprising passing a gaseous stream comprising monomer through a reaction zone in the presence of a catalyst to produce a polymeric product, withdrawing said polymeric product, withdrawing said fluidizing medium comprising unreacted monomer from said reaction zone, mixing said fluidizing medium with hydrocarbon and polymerizable monomer(s) to form a liquid phase and a gas phase, and recycling said fluidizing medium to said reactor, the improvement comprising: a) introducing said hydrocarbon into said fluidizing medium to permit an increase in the cooling capacity of the fluidizing medium to a level in the range of from 42 Btu/lb to 110 Btu/lb; b) increasing the rate of withdrawal of polymer product to above 500 lb/hr-ft²; and c) maintaining the ratio of fluidized bulk density to settled bulk density above 0.59. A description of condensable fluids is provided in Col. 6, lines 31-47.

[0005] U.S. Patent No. 6,063,877 is directed to a process for controlling a continuous gas phase exothermic process in a reactor having (1) a reactor inlet; (2) a reactor bed; (3) a reactor outlet; and (4) a recycle line with (a) a compressor and (b) a heat exchanger; with a pre-selected temperature for the reactor bed or outlet (2 or 3) and with a temperature differential (ΔT) between the temperature of the reactor inlet (1) and the pre-selected temperature of the reactor bed or outlet (2 or 3), comprising: (A) controlling the heat transfer provided by the heat exchanger (4(b)) to maintain the pre-selected reactor bed (2) or outlet (3) temperature, while simultaneously (B) controlling the feed rate to the reactor of a condensable fluid to maintain the temperature differential (ΔT) constant. Examples of condensable fluids are listed in Col. 2, lines 24-34.

[0006] U.S. Patent No. 7,696,289 is directed to a gas phase polymerization process comprising the steps of: passing a recycle stream through a fluidized bed in a gas phase fluidized bed reactor, wherein the recycle stream comprises a low molecular weight dew point increasing component and a high molecular weight dew point increasing component; polymerizing at least one alpha-olefin monomer in the presence of a catalyst; and controlling an amount of the low molecular weight dew point increasing component in the recycle stream such that a dew point approach temperature of the recycle stream is less than the dew point approach temperature when operating with the higher molecular weight dew point increasing component alone. ICA's are described, for example, at Col. 15, lines 34-45, and Claim 5.

[0007] U.S. Patent No. 7,858,719 is directed to a gas phase process for polymerizing one or more hydrocarbon monomer(s) in a reactor in the presence of a catalyst system and a fluorinated hydrocarbon, where the fluorinated hydrocarbon is present at a partial pressure of 6.9 to 3448 kPa in the reactor and the reactor temperature is from 30 to 120°C., wherein the

catalyst system comprises a Group 3 to 12 metal and the molar ratio of the fluorinated hydrocarbon to the metal of the catalyst system is from 2000-3500:1. A number of fluorinated hydrocarbons under the section header, "Condensable Fluids," may be found in Col. 19 to Col. 21.

5 [0008] U.S. Patent Application Publication No. 2005/0182207 is directed to a continuous gas fluidized bed polymerization process for the production of a polymer from a monomer comprising: continuously passing a gaseous stream comprising the monomer through a fluidized bed reactor in the presence of a catalyst under reactive conditions; withdrawing a polymeric product and a stream comprising unreacted monomer gases; cooling said stream
10 comprising unreacted monomer gases to form a mixture comprising a gas phase and a liquid phase and reintroducing said mixture into said reactor with sufficient additional monomer to replace that monomer polymerized and withdrawn as the product, wherein said liquid phase is vaporized, and wherein the stream comprises at least two inert condensing agents selected from the group consisting of alkanes, cycloalkanes, and mixtures thereof, each of the inert
15 condensing agents having a normal boiling point less than 40°C. Table 1 provides a listing of ICA's.

[0009] Other background references include WO 94/28032, WO 2011/147539, and U.S. Patent Nos. 6,262,192 and 7,683,140.

[0010] Despite these past endeavors, there is a need and desire to increase production
20 rates while maintaining the continuity of the reactor system in a continuous process. Additionally, there is also a desire to broaden the polymer grade operating windows to produce polymers with different properties at higher production rates, for example, decreasing the density or raising the melt index of the polymer, which was not previously possible with current commercial practices due to the limitations of process conditions and
25 readily available ICA's.

SUMMARY

[0011] In a class of embodiments, the invention provides for a polymerization process, the process comprising contacting one or more monomers, at least one catalyst system, and a condensing agent comprising a majority of 2,2-dimethylpropane under polymerizable
30 conditions to produce a polyolefin polymer; wherein the production rate of the polyolefin polymer is at least 20% greater than the same process polymerizing with another C₄-C₈ condensing agent.

[0012] In another class of embodiments, the invention provides for a polymerization process, the process comprising contacting one or more monomers, at least one catalyst system, and a condensing agent comprising a mixture of 2,2-dimethylpropane and at least another C₄-C₈ condensing agent under polymerizable conditions to produce a polyolefin polymer.

[0013] In the previous embodiment, the ratio of the 2,2-dimethylpropane to the at least another C₄-C₈ condensing agent may be greater than or equal to 50:50, greater than or equal to 65:35, or greater than or equal to 85:15.

[0014] In any of the previous embodiments, at least another C₄-C₈ condensing agent may comprise propane, n-butane, isobutane, n-pentane, isopentane, n-hexane, isohexane, n-heptane, n-octane, or mixtures thereof.

[0015] In any of the previous embodiments, at least one catalyst system may comprise a Ziegler-Natta, chromium, chromium oxide, AlCl₃, cobalt, iron, palladium, vanadium, metallocene catalyst, or mixtures thereof.

[0016] In any of the previous embodiments, the polyolefin polymer may be a copolymer of ethylene and C₃-C₁₂ alpha-olefin or a copolymer of ethylene and C₄-C₈ alpha-olefin.

[0017] The polyolefin polymer may have a density from 0.905 g/cm³ to 0.918 g/cm³ and/or a melt index (I_{2.16}) (ASTM D1238) from 15 g/10min to 100 g/10min.

[0018] Other embodiments of the invention are described and claimed herein and are apparent by the following disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] Figure 1 is a graph of DSC measurements versus the weight fraction of pentane.

[0020] Figure 2 is a graph of DSC heat flow versus temperature.

[0021] Figure 3 is a graph of the heat removal capacity of various inert condensing agents.

DETAILED DESCRIPTION

[0022] Before the present compounds, components, compositions, and/or methods are disclosed and described, it is to be understood that unless otherwise indicated, this invention is not limited to specific compounds, components, compositions, reactants, reaction conditions, ligands, metallocene structures, or the like, as such may vary, unless otherwise specified. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting.

[0023] It must also be noted that, as used in the specification and the appended claims, the singular forms “a”, “an” and “the” include plural referents unless otherwise specified. Thus, for example, reference to “a leaving group” as in a moiety “substituted with a leaving group” includes more than one leaving group, such that the moiety may be substituted with
5 two or more such groups. Similarly, reference to “a halogen atom” as in a moiety “substituted with a halogen atom” includes more than one halogen atom, such that the moiety may be substituted with two or more halogen atoms, reference to “a substituent” includes one or more substituents, reference to “a ligand” includes one or more ligands, and the like.

[0024] The invention is generally directed toward polymerization processes, particularly,
10 gas phase processes, for polymerizing one or more monomer(s) in the presence of at least one catalyst system. The invention also relates in several classes of embodiments to polymerization processes having increased production rates and/or product capabilities.

[0025] The polymerization processes described herein may be a continuous process. As used herein, “a continuous process” is process that operates (or is intended to operate)
15 without interruption or cessation but of course may be interrupted for customary maintenance or for the occasional disrupting event. For example, a continuous process to produce a polymer would be one in which the reactants are continuously introduced into one or more reactors and polymer product is continually or semi-continually withdrawn.

[0026] In many classes of embodiments of the invention, the invention provides for a gas
20 phase process for polymerizing one or more monomer(s) in the presence of at least one catalyst system and a condensable agent wherein the process is operated in a condensed mode.

[0027] For example, in a class of embodiments, the invention provides for a polymerization process, the process comprising contacting one or more monomers, at least
25 one catalyst system, and a condensing agent comprising a mixture of 2,2-dimethylpropane and at least another C₄-C₈ condensing agent, preferably, at least another C₄-C₆ condensing agent, under polymerizable conditions to produce a polyolefin polymer.

[0028] In another class of embodiments, the process comprises contacting one or more monomers, at least one catalyst system, and a condensing agent comprising a majority of 2,2-
30 dimethylpropane under polymerizable conditions to produce a polyolefin polymer; wherein the production rate of the polyolefin polymer is at least 20% greater than the same process polymerizing with another C₄-C₈ condensing agent. As used herein, “the same process” shall refer to any gas phase process producing similar polymer products using comparable

equipment. However, it shall not exclude the presence of or omission of other variances, steps, elements, equipment, or materials, whether or not, specifically mentioned.

[0029] In other embodiments, the production rate may be at least 25% greater than the same process polymerizing with another C₄-C₈ condensing agent or may be at least 30% greater than the same process polymerizing with another C₄-C₈ condensing agent.

Catalyst Components and Catalyst Systems

[0030] All polymerization catalysts including conventional-type transition metal catalysts are suitable for use in the polymerization processes of the invention. The following is a non-limiting discussion of the various polymerization catalysts useful in the process of the invention. All numbers and references to the Periodic Table of Elements are based on the new notation as set out in Chemical and Engineering News, 63(5), 27 (1985), unless otherwise specified.

[0031] In the description herein, the transition metal compound may be described as a catalyst precursor, a transition metal catalyst, a polymerization catalyst, or a catalyst compound, and these terms are used interchangeably. The term activator is used interchangeably with the term co-catalyst. As used herein, "at least one catalyst system" refers to a combination comprising a catalyst compound and an activator capable of polymerizing monomers.

Conventional Catalysts

[0032] Conventional catalysts generally known in the art refer to Ziegler Natta catalysts or Phillips-type chromium catalysts. Examples of conventional-type transition metal catalysts are discussed in U.S. Patent Nos. 4,115,639, 4,077,904 4,482,687, 4,564,605, 4,721,763, 4,879,359 and 4,960,741. The conventional catalyst compounds that may be used in the present invention include transition metal compounds from Groups 3 to 10, preferably 4 to 6 of the Periodic Table of Elements.

[0033] These conventional-type transition metal catalysts may be represented by the formula:



where M is a metal from Groups 3 to 10, preferably Group 4, more preferably titanium; R is a halogen or a hydrocarbyloxy group; and x is the valence of the metal M, preferably x is 1, 2, 3 or 4, more preferably x is 4. Non-limiting examples of R include alkoxy, phenoxy, bromide, chloride and fluoride. Non-limiting examples of conventional-type transition metal

catalysts where M is titanium include TiCl_3 , TiCl_4 , TiBr_4 , $\text{Ti}(\text{OC}_2\text{H}_5)_3\text{Cl}$, $\text{Ti}(\text{OC}_2\text{H}_5)\text{Cl}_3$, $\text{Ti}(\text{OC}_4\text{H}_9)_3\text{Cl}$, $\text{Ti}(\text{OC}_3\text{H}_7)_2\text{Cl}_2$, $\text{Ti}(\text{OC}_2\text{H}_5)_2\text{Br}_2$, $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ and $\text{Ti}(\text{OC}_{12}\text{H}_{25})\text{Cl}_3$.

[0034] Conventional chrome catalysts, often referred to as Phillips-type catalysts, may include CrO_3 , chromocene, silyl chromate, chromyl chloride (CrO_2Cl_2), chromium-2-ethyl-
5 hexanoate, chromium acetylacetonate ($\text{Cr}(\text{AcAc})_3$). Non-limiting examples are disclosed in U.S. Patent Nos. 2,285,721, 3,242,099 and 3,231,550.

[0035] For optimization, many conventional catalysts require at least one cocatalyst. A detailed discussion of cocatalysts may be found in U.S. Patent No. 7,858,719, col. 6, line 46, bridging col. 7, line 45.

10 **Metallocene Catalysts**

[0036] Polymerization catalysts useful in embodiments of the invention include one or more metallocene compounds (also referred to herein as metallocenes or metallocene catalysts). Metallocene catalysts are generally described as containing one or more ligand(s) and one or more leaving group(s) bonded to at least one metal atom, optionally with at least
15 one bridging group. The ligands are generally represented by one or more open, acyclic, or fused ring(s) or ring system(s) or a combination thereof. These ligands, preferably the ring(s) or ring system(s) are typically composed of one or more atoms selected from Groups 13 to 16 atoms of the Periodic Table of Elements; preferably, the atoms are selected from the group consisting of carbon, nitrogen, oxygen, silicon, sulfur, phosphorous, germanium, boron and
20 aluminum or a combination thereof. Most preferably, the ring(s) or ring system(s) are composed of carbon atoms such as, but not limited to, those cyclopentadienyl ligands or cyclopentadienyl-type ligand structures or other similar functioning ligand structures such as a pentadiene, a cyclooctatetraendiyl, or an imide ligand. The metal atom is preferably selected from Groups 3 through 15 and the lanthanide or actinide series of the Periodic Table
25 of Elements. Preferably, the metal is a transition metal from Groups 4 through 12, more preferably Groups 4, 5 and 6, and most preferably the transition metal is from Group 4.

[0037] Exemplary metallocene catalysts and catalyst systems are described in for example, U.S. Patent Nos. 4,530,914, 4,871,705, 4,937,299, 5,017,714, 5,055,438, 5,096,867, 5,120,867, 5,124,418, 5,198,401, 5,210,352, 5,229,478, 5,264,405, 5,278,264, 5,278,119,
30 5,304,614, 5,324,800, 5,347,025, 5,350,723, 5,384,299, 5,391,790, 5,391,789, 5,399,636, 5,408,017, 5,491,207, 5,455,366, 5,534,473, 5,539,124, 5,554,775, 5,621,126, 5,684,098, 5,693,730, 5,698,634, 5,710,297, 5,712,354, 5,714,427, 5,714,555, 5,728,641, 5,728,839, 5,753,577, 5,767,209, 5,770,753, 5,770,664; EP-A-0 591 756, EP-A-0 520-732, EP-A-0 420

436, EP-B1 0 485 822, EP-B1 0 485 823, EP-A2-0 743 324, EP-B1 0 518 092; WO 91/04257, WO 92/00333, WO 93/08221, WO 93/08199, WO 94/01471, WO 96/20233, WO 97/15582, WO 97/19959, WO 97/46567, WO 98/01455, WO 98/06759, and WO 98/011144.

Mixed Catalysts

- 5 [0038] In a class of embodiments of the invention, the at least one catalyst system may comprise a mixed catalyst, i.e., two or more of the same or different types of catalysts, such as the ones described above. For example, a metallocene catalyst may be combined with one or more of a conventional catalysts or advanced catalysts known in the art. An example of such catalyst is PRODIGY™ Bimodal Catalyst available from Univation Technologies, LLC,
10 Houston, TX.

Activator and Activation Methods

- [0039] The above described polymerization catalysts, particularly, metallocene catalysts, are typically activated in various ways to yield polymerization catalysts having a vacant coordination site that will coordinate, insert, and polymerize olefin(s).
- 15 [0040] As used herein, the term “activator” refers to any compound that can activate any one of the polymerization catalyst compounds described herein by converting the neutral polymerization catalyst compound to a catalytically active catalyst cation compound. Non-limiting activators, for example, include alumoxanes, aluminum alkyls, ionizing activators, which may be neutral or ionic, and conventional-type cocatalysts. A detailed discussion of
20 activators and activation methods may be found in Patent No. 7,858,719, col. 14, line 21, bridging col. 17, line 30.

Method for Supporting

- [0041] The above described catalysts and catalyst systems may be combined with one or more support materials or carriers using one of the support methods well known in the art. In
25 several classes of embodiments of the invention, the at least one catalyst system is in a supported form.

- [0042] As used herein, the terms “support” or “carrier” are used interchangeably and are any porous or non-porous support material, preferably, a porous support material, for example, talc, inorganic oxides and inorganic chlorides, for example silica or alumina. Other
30 carriers include resinous support materials such as polystyrene, a functionalized or crosslinked organic supports, such as polystyrene divinyl benzene polyolefins or polymeric compounds, or any other organic or inorganic support material and the like, or mixtures thereof.

[0043] The preferred carriers are inorganic oxides that include those Group 2, 3, 4, 5, 13 or 14 metal oxides. The preferred supports include silica, alumina, silica-alumina, magnesium chloride, and mixtures thereof. Other useful supports include magnesia, titania, zirconia, montmorillonite and the like. Also, combinations of these support materials may be used, for example, silica-chromium and silica-titania.

[0044] Examples of supported metallocene catalyst systems are described in U.S. Patent Nos. 4,701,432, 4,808,561, 4,912,075, 4,925,821, 4,937,217, 5,008,228, 5,238,892, 5,240,894, 5,332,706, 5,346,925, 5,422,325, 5,466,649, 5,466,766, 5,468,702, 5,529,965, 5,554,704, 5,629,253, 5,639,835, 5,625,015, 5,643,847, 5,648,310, 5,665,665, 5,698,487, 5,714,424, 5,723,400, 5,723,402, 5,731,261, 5,743,202, 5,759,940, 5,767,032, 5,688,880, 5,770,755 and 5,770,664; WO 95/32995, WO 95/14044, WO 96/06187, WO96/11960, and WO96/00243.

[0045] Examples of supported conventional catalyst systems are described in U.S. Patent Nos. 4,894,424, 4,376,062, 4,395,359, 4,379,759, 4,405,495, 4,540,758 and 5,096,869.

15 **Polymerization Process**

[0046] Embodiments of the at least one catalyst system described above are suitable for use in any gas phase polymerization process, including fluidized bed or stirred bed processes. Particularly preferred is a gas phase polymerization process in which one or more condensable agents as described below is utilized.

20 [0047] Typically in a gas phase polymerization process, a continuous cycle is employed where in one part of the cycle of a reactor system, a cycling gas stream, otherwise known as a recycle stream or fluidizing medium, is heated in the reactor by the heat of polymerization. This heat is removed from the recycle composition in another part of the cycle by a cooling system external to the reactor. Generally, in a gas fluidized bed process for producing
25 polymers, a gaseous stream containing one or more monomers is continuously cycled through a fluidized bed in the presence of at least one catalyst system under polymerizable conditions. As used herein, "polymerizable conditions" refers to any and all process conditions and any and all equipment necessary and suitable to polymerize olefins into polyolefins. In a preferred class of embodiments of the invention, a condensable agent as described below, is
30 introduced to the process for purposes of increasing the cooling capacity of the recycle stream. The purposeful introduction of a condensable agent into a gas phase process is referred to as a "condensed mode process" discussed in greater detail below. The gaseous stream is withdrawn from the fluidized bed and recycled back into the reactor.

Simultaneously, polymer product is withdrawn from the reactor and fresh reactants including monomers are added to the reactor. *See, for example*, U.S. Pat. Nos. 4,543,399, 4,588,790, 5,028,670, 5,317,036, 5,352,749, 5,405,922, 5,436,304, 5,453,471, 5,462,999, 5,616,661 and 5,668,228, and *also* the Background section of this Application.

5 **Condensable Agent(s)**

[0048] Condensable agents or fluids generally include hydrocarbons having little to no solvent power regarding the polymer product(s). Suitable condensing agents include C₄-C₈ hydrocarbons and mixtures thereof, preferably C₄-C₆ hydrocarbons and mixtures thereof, including linear, branched, cyclic, substituted hydrocarbons, as well as their respective
10 isomers. In several classes of embodiments of the invention, the condensing agent comprises 2,2-dimethylpropane. 2,2-dimethylpropane, also called neopentane, is a double-branched-chain alkane with five carbon atoms. 2,2-dimethylpropane is the simplest alkane with a quaternary carbon. It is one of the three structural isomers with the molecular formula C₅H₁₂ (pentanes), the other two being n-pentane and isopentane.

15 [0049] In a class of embodiments of the invention, 2,2-dimethylpropane may be used with other condensing agents, for example, other C₄-C₈ condensing agents or mixtures thereof as described above. In particular, the condensing agent may comprise a mixture of 2,2-dimethylpropane and at least another C₄-C₈ condensing agent, e.g., n-butane, isobutane, n-pentane, isopentane, n-hexane, isohexane, n-heptane, n-octane, or mixtures of two or more
20 thereof. In an embodiment of the invention, the condensing agents comprise or consist essentially of 2,2-dimethylpropane and isopentane.

[0050] In other embodiments, the condensing agent comprises a majority of 2,2-dimethylpropane when used in combination with at least one other condensing agent. The condensing agent may also consist essentially of 2,2-dimethylpropane. As used herein,
25 “consisting essentially of 2,2-dimethylpropane” or using a “majority of 2,2-dimethylpropane” in the condensing agent shall refer to greater than 50 wt%, alternatively, 60 wt% or greater, alternatively, 65 wt% or greater, alternatively, 70 wt% or greater, alternatively, 75 wt% or greater, alternatively, 80 wt% or greater, alternatively, 85 wt% or greater, alternatively, 90 wt% or greater, alternatively, 91 wt% or greater, alternatively, 92 wt% or greater,
30 alternatively, 93 wt% or greater, alternatively, 94 wt% or greater, alternatively, 95 wt% or greater, alternatively, 96 wt% or greater, alternatively, 97 wt% or greater, alternatively, 98 wt% or greater, and alternatively, 99 wt% or greater, based upon the total weight of condensing agent in the reactor.

[0051] In other classes of embodiments of the invention, when a mixture of condensing agents is used, the ratio of the 2,2-dimethylpropane to the at least another C₄-C₈ condensing agent is greater than or equal to 50:50, alternatively, the ratio of the 2,2-dimethylpropane to the at least another C₄-C₈ condensing agent is greater than or equal to 65:35, and
5 alternatively, the ratio of the 2,2-dimethylpropane to the at least another C₄-C₈ condensing agent is greater than or equal to 85:15.

[0052] In a class of embodiments, the production rate of the polyolefin polymer is at least 20% greater, alternatively, at least 25% greater, and alternatively, at least 30% greater, than the same process polymerizing substantially free of 2,2-dimethylpropane. As used herein,
10 "substantially free of 2,2-dimethylpropane" shall mean that no or less than 10% 2,2-dimethylpropane is added or available to the total condensable agent in the reactor by weight.

Condensed Mode Process

[0053] The condensing agent may be used in a gas phase polymerization process or simply a gas phase process. The gas phase process is operated in a condensed mode where a
15 condensing agent as described above is introduced to the process to increase the cooling capacity of the recycle stream. The gas phase process is particularly well-suited for polymerizing one or more olefin(s), preferably at least one of which is ethylene or propylene, in a fluidized bed reactor, the process operating in a condensed mode in which a liquid and a gas are introduced to the fluidized bed reactor having a fluidizing medium or a stirred bed
20 reactor having a medium, wherein the level of condensable fluid, is greater than 5 weight percent, preferably, greater than 10 weight percent, or greater than 15 weight percent or greater than 20 weight percent, more preferably greater than 25 weight percent, even more preferably greater than 30 weight percent, still even more preferably greater than 35 weight percent, and most preferably greater than 30 weight percent up to 60 weight percent,
25 preferably 50 weight percent or alternatively, 55 weight percent, 60 weight percent, 65 weight percent, 70 weight percent, 75 weight percent, 80 weight percent, 85 weight percent, 90 weight percent, 91 weight percent, 92 weight percent, 95 weight percent, 96 weight percent, 97 weight percent, 98 weight percent, or 99 weight percent, based on the total weight of the liquid and gas entering the reactor. For further details of a condensed mode process
30 *see, for example*, U.S. Pat. Nos. 5,342,749 and 5,436,304.

[0054] In one preferred embodiment of the invention, the invention is directed to a process, preferably a continuous process, for polymerizing monomer(s) in a reactor, said process comprising the steps of: (a) introducing a recycle stream into the reactor, the recycle

Reactor Conditions

[0056] The reactor temperature in any of the gas phase processes described in the above embodiments vary from about 30°C to about 120°C, preferably from about 60°C to about 115°C, more preferably in the range of from about 70°C. to 110°C, and most preferably in the range of from about 70°C to about 100°C. In another embodiment, the polymerization temperature is above ambient temperature (23°C), preferably above 30°C, preferably above 50°C, preferably above 70°C.

Monomers and Polymers

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and preferably at least 99 mole %. Hydrocarbon monomers are monomers made up of only carbon and hydrogen. For example, the monomers to be polymerized are aliphatic or alicyclic hydrocarbons. (as defined under "Hydrocarbon" in Hawley's Condensed Chemical Dictionary, 13th edition, R. J. Lewis ed., John Wiley and Sons, New York, 1997). In another embodiment of the invention, the monomers to be polymerized are linear or branched alpha-olefins, preferably C₂ to C₄₀ linear or branched alpha-olefins, preferably C₂ to C₂₀ linear or branched alpha-olefins, e.g., ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, or mixtures thereof. Well-suited monomers include two or more olefin monomers of ethylene, propylene, butene-1, pentene-1, 4-methyl-pentene-1, hexene-1, octene-1, decene-1, and mixtures thereof.

[0059] Other monomers useful in the process of the invention include ethylenically unsaturated monomers, diolefins having 4 to 18 carbon atoms, conjugated or nonconjugated dienes, polyenes, vinyl monomers and cyclic olefins. Non-limiting monomers useful in the invention include butadiene, norbornene, norbornadiene, isobutylene, vinylbenzocyclobutane, ethylidene norbornene, isoprene, dicyclopentadiene and cyclopentene.

[0060] In another embodiment of the invention, ethylene or propylene is polymerized with at least two different comonomers, optionally, one of which may be a diene, to form a terpolymer.

[0061] The polymers produced by the process of the invention are useful in making a wide variety of products and useful in many end-use applications. The polymers produced by the process of the invention include low density polyethylenes, linear low density polyethylenes, medium density polyethylene, and high density polyethylenes.

[0062] The polymers produced, typically polyethylene polymers, may have a density in the range of from 0.860 g/cc to 0.970 g/cc, preferably in the range of from 0.880 g/cc to 0.965 g/cc, more preferably in the range of from 0.900 g/cc to 0.960 g/cc, even more preferably in the range of from 0.905 g/cc to 0.950 g/cc, yet even more preferably in the range from 0.910 g/cc to 0.940 g/cc, and most preferably greater than 0.912 g/cc.

[0063] In one embodiment, the polymers produced by the process of the invention typically have a molecular weight distribution, a weight average molecular weight to number average molecular weight (Mw/Mn) of about 1.5 to about 30, particularly about 2 to about 15, more preferably about 2 to about 10, even more preferably about 2.2 to less than about 8, and most preferably from about 2.5 to about 8. The ratio of Mw/Mn is measured by gel permeation chromatography techniques well known in the art.

[0064] In several classes of embodiments of the invention, the polyethylene polymers typically have a narrow or broad composition distribution as measured by Composition Distribution Breadth Index (CDBI). Further details of determining the CDBI of a copolymer are known to those skilled in the art. *See, for example*, WO 93/03093. CDBI's may be
5 generally in the range of greater than 50% to 99%, preferably in the range of 55% to 85%, and more preferably 60% to 80%, even more preferably greater than 60%, still even more preferably greater than 65%. Alternatively, CDBI's may be generally less than 50%, more preferably less than 40%, and most preferably less than 30%.

[0065] Polyethylene polymers may have a melt index (MI) or (I_2) as measured by ASTM-
10 D-1238-E in the range from 0.01 dg/min to 1000 dg/min, more preferably from about 0.01 dg/min to about 100 dg/min, even more preferably from about 0.1 dg/min to about 50 dg/min, and most preferably from about 0.1 dg/min to about 10 dg/min. The polyethylene polymers may have a melt index ratio ($I_{21.6}/I_{2.16}$ or for a shorthand " I_{21}/I_2 ") (measured by ASTM-D-1238-F) of from 10 to less than 25, more preferably from about 15 to less than 25. Further, in
15 another embodiment, the polymers have a melt index ratio (I_{21}/I_2) of from preferably greater than 25, more preferably greater than 30, even more preferably greater than 40, still even more preferably greater than 50 and most preferably greater than 65. Alternatively, the polyethylene polymers may have a melt index ratio (I_{21}/I_2) in the range of from 15 to 40, preferably in the range of from about 20 to about 35, more preferably in the range of from
20 about 22 to about 30, and most preferably in the range of from 24 to 27.

[0066] In yet other embodiments of the invention, propylene based polymers may be produced. These polymers include without limitation atactic polypropylene, isotactic polypropylene, and syndiotactic polypropylene. Other propylene polymers include propylene random, block or impact copolymers.

25 [0067] Polymers produced by the processes of the invention are useful in forming a variety of articles. Such articles include without limitation films, sheets, and fibers. The articles may be produced by extrusion and co-extrusion as well as blow molding, injection molding, and rotational molding. Films include blown or cast films formed by coextrusion or by lamination, shrink film, cling film, stretch film, sealing films, and oriented films. The
30 films are useful in packaging, heavy duty bags, grocery sacks, food packaging, medical packaging, industrial liners, geo-membranes, etc. Fibers include melt spinning, solution spinning and melt blown fiber operations for use in woven or non-woven form to make filters, diaper fabrics, medical garments, geotextiles, etc. Extruded articles include medical

tubing, wire and cable coatings, geomembranes, and pond liners. Molded articles include single and multi-layered constructions in the form of bottles, tanks, large hollow articles, rigid food containers, playground equipment, toys, etc.

EXAMPLES

5 **[0068]** It is to be understood that while the invention has been described in conjunction with the specific embodiments thereof, the foregoing description is intended to illustrate and not limit the scope of the invention. Other aspects, advantages and modifications will be apparent to those skilled in the art to which the invention pertains.

10 **[0069]** Therefore, the following examples are put forth so as to provide those skilled in the art with a complete disclosure and description and are not intended to limit the scope of that which the inventors regard as their invention.

EXAMPLE 1

[0070] Differential Scanning Calorimetry (DSC) was run for PE granules in contact with either isopentane or 2,2-dimethylpropane.

15 **[0071]** For each polymer evaluated, only the first-melt DSC was used because this is believed to be more representative of the polymer as it exists in the reactor than the more conventional second-melt DSC curves. The second melt DSC curves may be significantly different than first melt DSC curves, typically showing lower peak melting temperatures and a sharper melt peak.

20 **[0072]** In the data of Table 1 below, the DSC curves were generated with a temperature ramp rate of 10°C/minute. The DSC instrument was TA Instruments Q200. The PE granules were hexene-ethylene copolymers with original MI_{2.1} of 1.0 dg/min (ASTM D-1238) (190°C/2.16 kg), MI_{2.1} of 34 dg/min (ASTM D-1238) (190°C/21.6) and 0.920 g/cc (ASTM D-4703) density. To reduce experimental scatter, the granules were then sieved, with granules
25 remaining on a 35 mesh retained for DSC testing with isopentane, and granules remaining on 60 mesh and through 35 mesh retained for DSC testing with 2,2-dimethylpropane.

[0073] Isopentane was metered to the high-pressure pans, by transferring it from a chilled, septum bottle into the glovebox using a microliter syringe. The pans were then sealed in the glovebox, removed, and the DSC test data was obtained. 2,2-dimethylpropane,
30 being a gas at ambient conditions, was thermosiphoned from a pressurized cylinder into a sealed vessel containing the polymer. The sealed vessel was maintained at 0°C during the transfer by means of an ice bath to induce condensation of the gaseous 2,2-dimethylpropane. After enough 2,2-dimethylpropane was transferred, the sealed vessel was closed,

disconnected from the 2,2-dimethylpropane source, and placed in a freezer operated below -15°C for at least four hours. The amount of 2,2-dimethylpropane in the sample was varied by changing the time that it was allowed to transfer. After ensuring that the entire sample was frozen, some of it was transferred to tared DSC pans in the glovebox which were then quickly sealed. The sealed pans were removed from the glovebox and the DSC test data was obtained. The amount of 2,2-methylpropane in sealed pan was measured by venting the pans after obtaining the thermal analysis, and comparing the final weight to sealed pan weight.

[0074] Results are shown in Table 1 and Figure 1. The results show higher melting points when adding 2,2-dimethylpropane. The overlapping result for one isopentane datapoint (0.106wt fraction) is believed to be caused by experimental variability.

Table 1

Table 1. DSC Results			
2,2-dimethylpropane		isopentane	
wt fraction C5 (g C5/(g C5 + PE))	DSC peak melting point (°C)	wt fraction C5 (g C5/(g C5 + PE))	DSC peak melting point (°C)
0.054	113.11	0.162	107.12
0.093	112.52	0.328	99.89
0.111	110.62	0.454	95.31
0.006	113.83	0.451	95.17
0.016	113.68	0.867	88.99
0.092	110.92	0.929	88.88
0.002	116.67	0.930	89.41
0.023	114.49	0.918	88.91
0.006	117.61	0.102	112.21
0.034	113.32		
0.149	109.81		
0.256	106.04		
0.105	113.17		
0.149	109.8		
0.565	103.38		
0.565	101.13		
0.047	111.57		
0.892	96.84		
0.002	113.68		
0.594	102.12		
0.516	100.64		
0.684	102.76		
0.610	104.57		
0.790	101.27		
0.703	103.47		
0.776	100.28		
0.002	115.21		
0.444	103.85		
0.631	102.38		

EXAMPLE 2

[0075] This example compares DSC first-melt data for samples with similar amounts of ICA. These data are shown as two data points that are included in Table 1. Materials, equipment, and procedure were the same as in Example 1. 2,2-dimethylpropane corresponds to a 0.444 wt fraction that demonstrates a significantly higher melting point and MIT compared to 0.451 wt fraction of isopentane, as shown in Figure 2.

EXAMPLE 3

[0076] These examples model reactor operation that will use a variety of ICAs. Modelling was done using methods shown in U.S. Patent No 7,683,140, column 62, row 48 bridging column 69, row 51. These examples use the same physical property sources as the aforementioned patent. These examples also employ the same exemplary calculation as used in U.S. Patent No. 7,683,140 (see Table 3 in Column 69). The examples demonstrate the Δ MIT. Table 2 shows the full set of solubility parameters used in these examples.

TABLE 2: Solubility Parameters ((cal/cm³)^{1/2})

n-Butane	7.062
Iso-Butane	6.853
n-Pentane	7.055
Iso-Pentane	6.771
2,2-dimethylbutane	6.382
1-Hexene	7.352
Polyethylene	7.95

[0077] Once cycle gas concentrations are fixed, often based on reaching a target value for Δ MIT, the heat removal capacity of the cycle gas loop is calculated. For illustrative purposes, the reactor temperature remains fixed at 85°C and the cycle gas temperature entering the reactor is fixed at a constant value of 40°C. These are typical values for a commercial plant, which uses cooling water to remove heat of polymerization. Calculations are based upon Soave-Redlich-Kwong thermodynamic properties. Example calculations are done based on fixed volumetric flowrate at reactor temperature, because commercial reactors are operated with this method to control particle carryover.

TABLE 3

Product Melt Index (dg/min)	1.00	1.00	1.00	1.00
Product Density (g/cc)	0.918	0.918	0.918	0.918
ICA Type	Isopentane	C4/C5 mixture *	2,2-dimethylpropane	2,2-dimethylpropane
ICA Partial Pressure (kPa)	345	445	345	540.0
1-Hexene Partial Pressure (kPa)	21.7	21.7	21.7	21.7
Ethylene partial Pressure (kPa)	1300	1300	1300	1300
Reactor temperature (°C)	85	85	85	85
Reactor pressure (kPa)	2170	2170	2170	2170
Dry polymer melt initiation temperature (°C)	94.71	94.71	94.71	94.71
Melting point depression (°C)	13.09	13.09	9.03	13.09
Δ MIT, at Trx (°C)	3.38	3.38	-0.68	3.38
Rx inlet temperature (°C)	40	40	40	40
Reactor heat removal (mW / (10,000 actual m3 circulation/hr))	12.7	14.5	9.5	20
Heat removal relative to pure isopentane (ratio)	1.00	1.14	0.75	1.57

*copying US 7,696,289 example 5, with mixed ICA concentration. Relative ICA concentration is 27% isobutane, 27% n-butane, 27.4% isopentane, 18.6% n-Pentane

[0078] These examples show that the same concentration or partial pressure of 2,2-dimethylpentane gives a much lower Δ MIT than isopentane. As the Δ MIT is held constant (as is typical for reactor operation), there is 1.57 times more heat removal capacity with 2,2-dimethylpropane.

EXAMPLE 4

[0079] This example uses the same models and calculation methods used in Example 3. It examines the impact of 2,2-dimethylpropane on production rates of lower density polymers.

TABLE 4

Product Melt Index (dg/min)	1.00	1.00
Product Density (g/cc)	0.912	0.912
ICA Type	Isopentane	2,2-dimethylpropane
ICA Partial Pressure (kPa)	294.3	531.8
1-Hexene Partial Pressure (kPa)	32	32
Ethylene partial Pressure (kPa)	1300	1300
Reactor temperature (°C)	80	80
Reactor pressure (kPa)	2170	2170
Dry polymer melt initiation temperature (°C)	90.13	90.13
Melting point depression (°C)	13.51	13.11
Δ MIT, at Trx (°C)	3.38	2.98
Rx inlet temperature (°C)	40	40
Reactor heat removal (mW / (10,000 actual m3 circulation/hr))	10.6	19.9
Heat removal relative to pure isopentane (ratio)	1.00	1.88

- [0080] Comparing the ICAs, the heat removal increases by a factor of 1.88 with 2,2-dimethylpropane. The use of 2,2-dimethylpropane on 0.912 g/cc density production can still deliver more reactor heat removal than isopentane on 0.918 g/cc density production.

EXAMPLE 5

[0081] This example uses the same models and calculation as the previous examples. It examines the impact of 2,2-dimethylpropane on the production rate of higher MI (lower molecular weight) polymers.

TABLE 5

Product Melt Index (dg/min)	20.00	20.00
Product Density (g/cc)	0.918	0.918
ICA Type	Isopentane	2,2-dimethylpropane
ICA Partial Pressure (kPa)	222.0	406.3
1-Hexene Partial Pressure (kPa)	30	30
Ethylene partial Pressure (kPa)	1300	1300
Reactor temperature (°C)	82	82
Reactor pressure (kPa)	2170	2170
Dry polymer melt initiation temperature (°C)	89.46	89.46
Melting point depression (°C)	10.84	10.84
Δ MIT, at Trx (°C)	3.38	3.38
Rx inlet temperature (°C)	40	40
Reactor heat removal (mW / (10,000 actual m3 circulation/hr))	7.9	12.6
Heat removal relative to pure isopentane (ratio)	1.00	1.59

[0082] These examples show that heat removal increases by a factor of 1.59 with 2,2-dimethylpropane. Therefore, using of 2,2-dimethylpropane on 20 dg/min MI production can deliver reactor heat removal more than isopentane on 1 dg/min MI production.

EXAMPLE 6

[0083] These examples model reactor operation that will use all possible saturated hydrocarbon isomers with 4, 5, or 6 carbons. Calculations used the methods of the previous examples. For all cases, reactor Other Inert Partial Pressure is held greater than or equal to 305 kPa, to give consistent vent rates. Other Inerts were modeled as pure nitrogen. Table 6 and Figure 3 show results of this calculation.

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Product Melt Index (dg/min)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Product Density (g/cc)	0.918	0.918	0.918	0.918	0.918	0.918	0.918	0.918	0.918	0.918	0.918	0.918
ICA Type	Iso Butane	n-Butane	Cyclo Pentane	Iso pentane	2,2-dimethyl propane	nPentane	methylcyclo-Pentane	2-methyl Pentane	3-methyl Pentane	2,2-dimethyl butane	2,3-dimethyl butane	nHexane
ICA Partial Pressure (kPa)	543	543	130	345	543	266	79	153	133	218	159	114
1-Hexene Partial Pressure (kPa)	21.7	21.7	21.7	21.7	21.7	21.7	21.7	21.7	21.7	21.7	21.7	21.7
Ethylene partial Pressure (kPa)	1300	1300	1300	1300	1300	1300	1300	1300	1300	1300	1300	1300
Other inerts partial pressure (kPa)	305	305	718	503	305	582	769	695	715	630	689	734
Reactor temperature (°C)	85	85	85	85	85	85	85	85	85	85	85	85
Reactor pressure (kPa)	2170	2170	2170	2170	2170	2170	2170	2170	2170	2170	2170	2170
Dry polymer melt initiation temperature (°C)	94.71	94.71	94.71	94.71	94.71	94.71	94.71	94.71	94.71	94.71	94.71	94.71
Melting point depression (°C)	9.66	11.99	13.09	13.09	11.77	13.09	13.09	13.09	13.09	13.09	13.09	13.09
ΔMIT, at Trx (°C)	-0.05	2.28	3.38	3.38	2.06	3.38	3.38	3.38	3.38	3.38	3.38	3.38
Rx inlet temperature (°C)	40	40	40	40	40	40	40	40	40	40	40	40
Reactor heat removal (mW / (10,000 actual m3 circulation/hr))	10.4	15.8	6.2	12.7	20.1	10.3	5.7	7.8	7.3	9.7	7.9	6.8
Heat removal relative to pure isopentane (ratio)	0.82	1.24	0.49	1.00	1.58	0.81	0.45	0.61	0.57	0.76	0.62	0.54

[0084] These examples show 2,2-dimethylpropane has a high ability to remove heat from the exothermic polymerization reactor.

5 [0085] The phrases, unless otherwise specified, “consists essentially of” and “consisting essentially of” do not exclude the presence of other steps, elements, or materials, whether or not, specifically mentioned in this specification, so long as such steps, elements, or materials, do not affect the basic and novel characteristics of the invention, additionally, they do not exclude impurities and variances normally associated with the elements and materials used.

10 [0086] For the sake of brevity, only certain ranges are explicitly disclosed herein. However, ranges from any lower limit may be combined with any upper limit to recite a range not explicitly recited, as well as, ranges from any lower limit may be combined with any other lower limit to recite a range not explicitly recited, in the same way, ranges from any upper limit may be combined with any other upper limit to recite a range not explicitly recited. Additionally, within a range includes every point or individual value between its end
15 points even though not explicitly recited. Thus, every point or individual value may serve as its own lower or upper limit combined with any other point or individual value or any other lower or upper limit, to recite a range not explicitly recited.

[0087] All priority documents are herein fully incorporated by reference for all jurisdictions in which such incorporation is permitted and to the extent such disclosure is
20 consistent with the description of the present invention. Further, all documents and references cited herein, including testing procedures, publications, patents, journal articles, etc. are herein fully incorporated by reference for all jurisdictions in which such incorporation is permitted and to the extent such disclosure is consistent with the description of the present invention.

25 [0088] While the invention has been described with respect to a number of embodiments and examples, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope and spirit of the invention as disclosed herein.

What is claimed is:

1. A polymerization process, the process comprising contacting one or more monomers, at least one catalyst system, and a condensing agent comprising a majority of 2,2-dimethylpropane under polymerizable conditions in a fluidized bed reactor operating in a condensed mode to produce a polyolefin polymer; wherein the production rate of the polyolefin polymer is at least 20% greater than the same process polymerizing with another C₄-C₈ condensing agent.
2. A polymerization process, the process comprising contacting one or more monomers, at least one catalyst system, and a condensing agent comprising a mixture of 2,2-dimethylpropane and at least another C₄-C₈ condensing agent under polymerizable conditions in a fluidized bed reactor operating in a condensed mode to produce a polyolefin polymer.
3. The process of claim 2, wherein the production rate of the polyolefin polymer is at least 20% greater than the same process polymerizing substantially free of 2,2-dimethylpropane.
4. The process of claim 1, wherein the production rate of the polyolefin polymer is at least 25% greater than the same process polymerizing with another C₄-C₈ condensing agent.
5. The process of claim 1, wherein the production rate of the polyolefin polymer is at least 30% greater than the same process polymerizing with another C₄-C₈ condensing agent.
6. The process of claim 2, wherein the C₄-C₈ condensing agent comprises n-butane, isobutane, n-pentane, isopentane, n-hexane, isohexane, n-heptane, n-octane, or mixtures thereof.
7. The process of claim 2, wherein the C₄-C₈ condensing agent is isopentane.

8. The process of claim 2, wherein the ratio of the 2,2-dimethylpropane to the C₄-C₈ condensing agent is greater than or equal to 50:50.
9. The process of claim 2, wherein the ratio of the 2,2-dimethylpropane to the C₄-C₈ condensing agent is greater than or equal to 65:35.
10. The process of claim 2, wherein the ratio of the 2,2-dimethylpropane to the C₄-C₈ condensing agent is greater than or equal to 85:15.
11. The process of claim 1, wherein the condensing agent consists essentially of 2,2-dimethylpropane.
12. A polymerization process comprising, contacting one or more monomers, at least one catalyst system, and a condensing agent comprising a majority of 2,2-dimethylpropane under polymerizable conditions to produce a polyolefin polymer, wherein the polyolefin polymer is a copolymer of ethylene and one or more C₃-C₁₂ alpha-olefins, and wherein the production rate of the polyolefin polymer is at least 20% greater than the same process polymerizing with another C₄-C₈ condensing agent.
13. The process of claim 1, wherein the polyolefin polymer is a copolymer of ethylene and C₄-C₈ alpha-olefin.
14. The process of claim 1, wherein the polyolefin polymer has a density from 0.905 g/cm³ to 0.918 g/cm³.
15. The process of claim 1, wherein the polyolefin polymer has a melt index (I_{2.16}) (ASTM D1238) from 15 g/10 min to 100 g/10 min.
16. The process of claim 1, wherein the at least one catalyst system comprises a Ziegler-Natta, chromium, chromium oxide, AlCl₃, cobalt, iron, palladium, vanadium, metallocene catalyst, or mixtures thereof.

17. The process of claim 1, wherein the polyolefin polymer has a density from 0.910 g/cm³ to 0.915 g/cm³.
18. The process of claim 1, wherein operating in the condensed mode comprises introducing at least a portion of the condensing agent into the fluidized bed reactor in a liquid phase.
19. The process of claim 1, wherein a level of condensable fluid in a liquid and a gas entering the fluidized bed reactor is greater than 5 weight percent based on a total weight of the liquid and the gas entering the reactor.
20. The process of claim 3, wherein operating in the condensed mode comprises introducing at least a portion of the condensing agent into the fluidized bed reactor in a liquid phase.