SLURRY PHASE POLYMERISATION PROCESS

The present invention is concerned with olefin polymerisation in slurry phase loop reactors.

Slurry phase polymerisation of olefins is well known wherein an olefin monomer and optionally olefin comonomer are polymerised in the presence of a catalyst in a diluent in which the solid polymer product is suspended and transported.

This invention is specifically related to polymerisation in a loop reactor where the slurry is circulated in the reactor typically by means of a pump or agitator. Liquid full loop reactors are particularly well known in the art and are described for example in U.S. Patent Numbers 3,152,872, 3,242,150 and 4,613,484.

Polymerisation is typically carried out at temperatures in the range 50-125°C and at pressures in the range 1-100 bara. The catalyst used can be any catalyst typically used for olefin polymerisation such as chromium oxide, Ziegler-Natta or metallocene-type catalysts. The product slurry comprising polymer and diluent, and in most cases catalyst, olefin monomer and comonomer can be discharged intermittently or continuously, optionally using concentrating devices such as hydrocyclones or settling legs to minimise the quantity of fluids withdrawn with the polymer.

The loop reactor is of a continuous tubular construction comprising at least two, for example four, vertical sections and at least two, for example four, horizontal sections. The heat of polymerisation is typically removed using indirect exchange with a cooling medium, preferably water, in jackets surrounding at least part of the tubular loop reactor. The volume of the loop reactor can vary but is typically in the range 20 to 120 m^3; the loop reactors of the present invention are of this generic type.

Maximum commercial scale plant capacities have increased steadily over the years. Growing operating experience over the last few decades has led to operation of increasingly high slurry and monomer concentrations in reaction loops. The increase in slurry concentrations has typically been achieved with increased circulation velocities achieved for example by higher reactor circulation pump head or multiple circulation pumps as illustrated by EP 432555 and EP 891990. The increase in solids loading is desirable to increase reactor residence time for a fixed reactor volume and also to reduce downstream diluent treatment and recycling requirements. The increased velocity and

head requirement of the loop has however led to increasing pump design sizes and complexity, and energy consumptions as slurry concentrations increase. This has both capital and operating cost implications.

Historically the circulation velocity in the reaction loop has typically been maximised to ensure maintenance of good thermal, compositional and particle distribution across the reactor cross-section, particularly the avoidance of solids settling, stable flow characteristics, or excessive solids concentrations at the pipe wall rather than reduced to minimise pressure drop/power in the polymerisation loop.

Inadequate cross-sectional distribution could lead to increased fouling, reduced heat transfer and reduced polymer productivity and homogeneity. Construction and commissioning of new commercial plants is very expensive and therefore new designs seek to avoid or minimise changes to operating parameters that are seen to increase risk to the successful operation of the new unit.

In accordance with the present invention there is provided a process comprising polymerising in a loop reactor an olefin monomer optionally together with an olefin comonomer in the presence of a polymerisation catalyst in a diluent to produce a slurry comprising solid particulate olefin polymer and the diluent wherein the Froude number is maintained at or below 20.

One advantage of the present invention is that the specific energy consumption of the reactor (i.e. the energy consumed per unit weight of polymer produced) is reduced whilst maintaining a given reactor residence time and avoiding unacceptable reactor fouling. The invention is especially advantageous when it is desired to design and operate a plant at high solids loadings when it has previously been considered necessary to use what have now been found to be excessively high loop circulation velocities.

This invention relates to a method and apparatus for continuous polymerization of olefins, preferably alpha mono olefins, in an elongated tubular closed loop reaction zone. The olefin(s) is continuously added to, and contacted with, a catalyst in a hydrocarbon diluent. The monomer(s) polymerise to form a slurry of solid particulate polymer suspended in the polymerisation medium or diluent.

Typically, in the slurry polymerisation process of polyethylene, the slurry in the reactor will comprise the particulate polymer, the hydrocarbon diluent(s), (co) monomer(s), catalyst, chain terminators such as hydrogen and other reactor additives In

particular the slurry will comprise 20-75, preferably 30-70 weight percent based on the total weight of the slurry of particulate polymer and 80-25 , preferably 70-30weight percent based on the total weight of the slurry of suspending medium, where the suspending medium is the sum of all the fluid components in the reactor and will comprise the diluent, olefin monomer and any additives; the diluent can be an inert diluent or it can be a reactive diluent in particular a liquid olefin monomer; where the principal diluent is an inert diluent the olefin monomer will typically comprise 2-20, preferably 4-10 weight percent of the total weight of the slurry.

The slurry is pumped around the relatively smooth path-endless loop reaction system at fluid velocities sufficient to (i) maintain the polymer in suspension in the slurry and (ii) to maintain acceptable cross-sectional concentration and solids loading gradients.

It has now been found that cross-sectional slurry concentration distributions (as evidenced by fouling, flow variations and/or heat transfer) can be maintained within acceptable operating limits whilst maintaining the Froude number in the reactor loop below 20, preferably between 2 and 15, most preferably between 3 and 10. This is contrary to what the man skilled in the art would believe to be the case in the light of conventional process conditions where the Froude number is typically above 20, for example above 30, typically in the range 30-40.

The Froude number will be maintained at or below 20, for example in the range 20 to 1 preferably in the range 15 to 2, more preferably in the range 10 to 3. The Froude number is a dimensionless parameter indicative of the balance between the suspension and settling tendencies of particles in a slurry. It provides a relative measure of the momentum transfer process to the pipe wall from particles compared to the fluid. Lower values of the Froude number indicate stronger particle-wall (relative to fluid-wall) interactions. The Froude number (Fr) is defined as $v^2/(g(s-1)D)$ where v is the average velocity of the slurry, g is the gravitational constant, s is the specific gravity of the solid in the diluent and D is the internal pipe diameter. The specific gravity of the solid polymer which is the ratio of the density of the polymer to the density of water is based on the annealed density of the degassed polymer after being substantially devolatilised and immediately prior to any extrusion as measured using method ISO1183A.

The solids concentration in the slurry in the reactor will typically be above 20

vol%, preferably about 30 volume %, for example 20-40 volume %, preferably 25-35 volume% where volume % is [(total volume of the slurry – volume of the suspending medium)/(total volume of the slurry)]x100. The solids concentration measured as weight percentage which is equivalent to that measured as volume percentage will vary according to the polymer produced but more particularly according to the diluent used. Where the polymer produced is polyethylene and the diluent is an alkane, for example isobutane it is preferred that the solids concentration is above 40 weight % for example in the range 40-60, preferably 45%-55 weight % based on the total weight of the slurry.

It is a particular feature of the present invention that operation of the slurry phase polymerisation at low Froude numbers enables the reactor to be run at high solids loading. A preferred embodiment of the present invention is a process comprising polymerising in a loop reactor an olefin monomer, in particular ethylene, optionally together with an olefin comonomer in the presence of a polymerisation catalyst in a diluent, particularly isobutane, to produce a slurry comprising solid particulate olefin polymer and the diluent wherein the Froude number is maintained at or below 20, particularly in the range 3 to 10 and the solids concentration in the reactor is in the range 25-35% volume .

It is a further feature of the present invention that operation of the process can be carried out in larger diameter reactors than are conventionally used in slurry polymerisation without any significant problems particularly from fouling at the reactor walls. For example, reactors having internal diameters over 500 millimeters, in particular over 600 for example between 600 and 750 millimetres can be used where historically there would have been increased concern. A further advantage of this invention is therefore that high slurry concentrations at relatively low circulation velocities and/or relatively high reactor loop diameters can be achieved. A further embodiment of the present invention is a process comprising polymerising in a loop reactor an olefin monomer optionally together with an olefin comonomer in the presence of a polymerisation catalyst in a diluent to produce a slurry comprising solid particulate olefin polymer and the diluent wherein the Froude number is maintained at or below 20, preferably 3-10 and the internal diameter of the reactor is in the range 600-750 millimeters.

It has been found that reactors can be designed and operated at specific pressure drop both per unit reactor length and per mass of polymer and total pressure drop for the loop less than that taught as being required, particularly at high solids loadings and/or large

reactor diameters. This invention permits total loop pressure drops of less than 1.3bar, particularly less than 1 bar even for polymer production rates of above 25, even above 45 tonnes per hour It is possible to employ one or more than one pump in the loop preferably on one or more horizontal sections ; these can be located on the same horizontal section or on different sections. The pump or pumps can be of the same diameter or larger or smaller diameter preferably of the same diameter as the internal diameter of the section of the reactor where the pump or pumps are located.. It is preferable to employ a single pump and it is a feature of the present invention that requirements for number and power of pump(s) is less onerous than for conventional processes.

Reactor size is typically over $20m^3$ in particular over $50m^3$ for example $75\text{-}150m^3$ preferably in the range $100\text{-}125m^3$

The discovery of an operating window at low Froude numbers enables acceptable design bases for larger reactor diameters to be defined. This enables reactor volumes, for example of greater than 80 m^3 to be built with a reactor length to internal diameter ratio of less than 500, preferably less than 400 more preferably less than 250. Reduction in reactor length to internal diameter ratio minimises compositional gradients around the reaction loop and enables production rates of greater than 25 tonnes (per reactor) per hour to be achieved with only a single point of introduction for each reagent around the reaction loop. Alternatively it is possible to have multiple inlets into the loop reactor for reactants (e.g. olefins), catalyst, or other additives.

The pressure employed in the loop will be sufficient to maintain the reaction system 'liquid full' i.e. there is substantially no gas phase. Typical pressures used are between 1-100 bara, preferably between 30 to 50 bara. In ethylene polymerization the ethylene partial pressure will typically be in the range 0.1 to 5 MPa, preferably from 0.2 to 2 MPa, more particularly from 0.4 to 1.5 MPa. The temperatures selected are such that substantially all of the polymer produced is essentially (i) in a non-tacky and non-agglomerative solid particular form and (ii) insoluble in the diluent. The polymerization temperature depends on the hydrocarbon diluent chosen and the polymer being produced. In ethylene polymerisation the temperature is generally below 130C , typically between 50 and 125C, preferably between 75 and 115C. For example in ethylene polymerisation in isobutane diluent, the pressure employed in the loop is preferably in the range 30-50 bara, the ethylene partial pressure is preferably in the range 0.2-2MPa and the polymerisation

temperature is in the range 75-115C. The space time yield which is production rate of polymer per unit of loop reactor volume for the process of the present invention is in the range 0.1-0.4 preferably 0.2-0.35 ton/hour/m^3.

The process according to the invention applies to the preparation of compositions containing olefin (preferably ethylene) polymers which can comprise one or a number of olefin homo-polymers and/or one or a number of copolymers. It is particularly suited to the manufacture of ethylene polymers and propylene polymers. Ethylene copolymers typically comprise an alpha-olefin in a variable amount which can reach 12% by weight, preferably from 0.5 to 6% by weight, for example approximately 1% by weight.

The alpha mono-olefin monomers generally employed in such reactions are one or more 1-olefins having up to 8 carbon atoms per molecule and no branching nearer the double bond than the 4-position. Typical examples include ethylene, propylene, butene-1, pentene-1, hexene-1 and octene-1, and mixtures such as ethylene and butene-1 or ethylene and hexene-1. Butene-1, pentene-1 and hexene-1 are particularly preferred comonomers for ethylene copolymerisation.

Typical diluents employed in such reactions include hydrocarbons having 2 to 12, preferably 3 to 8, carbon atoms per molecule, for example linear alkanes such as propane, n-butane, n-hexane and n-heptane, or branched alkanes such as isobutane, isopentane, toluene, isooctane and 2,2,-dimethylpropane, or cycloalkanes such as cyclopentane and cyclohexane or their mixtures. In the case of ethylene polymerization, the diluent is generally inert with respect to the catalyst, cocatalyst and polymer produced (such as liquid aliphatic, cycloaliphatic and aromatic hydrocarbons), at a temperature such that at least 50% (preferably at least 70%) of the polymer formed is insoluble therein. Isobutane is particularly preferred as the diluent for ethylene polymerisation.

The operating conditions can also be such that the monomers (e.g. ethylene, propylene) act as the diluent as is the case in so called bulk polymerisation processes. The slurry concentration limits in volume percent have been found to be able to be applied independently of molecular weight of the diluent and whether the diluent is inert or reactive, liquid or supercritical. Propylene monomer is particularly preferred as the diluent for propylene polymerisation

Methods of molecular weight regulation are known in the art. When using Ziegler-Natta, metallocene and tridentate late transition metal type catalysts, hydrogen is

preferably used, a higher hydrogen pressure resulting in a lower average molecular weight. When using chromium type catalysts, polymerization temperature is preferably used to regulate molecular weight.

In commercial plants, the particulate polymer is separated from the diluent in a manner such that the diluent is not exposed to contamination so as to permit recycle of the diluent to the polymerization zone with minimal if any purification. Separating the particulate polymer produced by the process of the present invention from the diluent typically can be by any method known in the art for example it can involve either (i) the use of discontinuous vertical settling legs such that the flow of slurry across the opening thereof provides a zone where the polymer particles can settle to some extent from the diluent or (ii) continuous product withdrawal via a single or multiple withdrawal ports, the location of which can be anywhere on the loop reactor but is preferably adjacent to the downstream end of a horizontal section of the loop. Any continuous withdrawal ports will typically have an internal diameter in the range 2-25., preferably 4-15, especially 5-10 cm. This invention permits large scale polymerisation reactors to be operated with low diluent recover requirements. The operation of large diameter reactors with high solids concentrations in the slurry minimises the quantity of the principal diluent withdrawn from the polymerisation loop. Use of concentrating devices on the withdrawn polymer slurry, preferably hydrocylones (single or in the case of multiple hydrocyclones in parallel or series), further enhances the recovery of diluent in an energy efficient manner since significant pressure reduction and vaporisation of recovered diluent is avoided.

It has been found that both the slurry concentration and the Froude number in the reactor loop can be optimised by controlling the average particle size and/or the particle size distribution of the powder within the reactor loop. The principal determinant of the average particle size of the powder is the residence time in the reactor. The particle size distribution of the catalyst can be affected by many factors including the particle size distribution of the catalyst fed to the reactor, the initial and average catalyst activity, the robustness of the catalyst support and susceptibility of the powder to fragment under reaction conditions. Solids separating devices (such as hydrocyclones) can be used on the slurry withdrawn from the reactor loop to further assist in control of the average particle size and the particle size distribution of the powder in the reactor. The location of the withdrawal point for the concentrating device and the design and operating conditions of

the concentrating device system, preferably the at least one hydrocyclone recycle loop, also enables the particle size and particle size distribution within the reactor to be controlled. The average particle size is preferably between 100 and 1500 microns, most preferably between 250 and 1000 microns.

The withdrawn, and preferably concentrated, polymer slurry is depressurised, and optionally heated, prior to introduction into a primary flash vessel. The stream is preferably heated after depressurisation.

The diluent and any monomer vapors recovered in the primary flash vessel are typically condensed, preferably without recompression and reused in the polymerization process. The pressure of the primary flash vessel is preferably controlled to enable condensation with a readily available cooling medium (e.g. cooling water) of essentially all of the flash vapour prior to any recompression, typically such pressure in said primary flash vessel will be 4-25, for example 10-20, preferably 15-17 bara. The solids recovered from the primary flash vessel is preferably passed to a secondary flash vessel to remove residual volatiles. Alternatively the slurry may be passed to a flash vessel of lower pressure than in the above mentioned primary vessel such that recompression needed to condense the recovered diluent. Use of a high pressure flash vessel is preferred.

The process according to the invention can be used to produce resins which exhibit specific density in the range 0.890 to 0.930 (low density), 0.930 to 0.940 (medium density) or 0.940 to 0.970 (high density).

The process according to the invention is relevant to all olefin polymerisation catalyst systems, particularly those chosen from the Ziegler-type catalysts, in particular those derived from titanium, zirconium or vanadium and from thermally activated silica or inorganic supported chromium oxide catalysts and from metallocene-type catalysts, metallocene being a cyclopentadienyl derivative of a transition metal, in particular of titanium or zirconium.

Non-limiting examples of Ziegler-type catalysts are the compounds comprising a transition metal chosen from groups IIIB, IVB, VB or VIB of the periodic table, magnesium and a halogen obtained by mixing a magnesium compound with a compound of the transition metal and a halogenated compound. The halogen can optionally form an integral part of the magnesium compound or of the transition metal compound.

Metallocene-type catalysts may be metallocenes activated by either an alumoxane or by an ionising agent as described, for example, in Patent Application EP-500,944-A1 (Mitsui Toatsu Chemicals).

Ziegler-type catalysts are most preferred. Among these, particular examples include at least one transition metal chosen from groups IIIB, IVB, VB and VIB, magnesium and at least one halogen. Good results are obtained with those comprising:

from 10 to 30% by weight of transition metal, preferably from 15 to 20% by weight, ,

from 20 to 60% by weight of halogen, the values from 30 to 50% by weight being preferred,

from 0.5 to 20% by weight of magnesium, usually from 1 to 10% by weight,

from 0.1 to 10% by weight of aluminium, generally from 0.5 to 5% by weight,

the balance generally consists of elements arising from the products used for their manufacture, such as carbon, hydrogen and oxygen. The transition metal and the halogen are preferably titanium and chlorine.

Polymerisations, particularly Ziegler catalysed ones, are typically carried out in the presence of a cocatalyst. It is possible to use any cocatalyst known in the art, especially compounds comprising at least one aluminium-carbon chemical bond, such as optionally halogenated organoaluminium compounds, which can comprise oxygen or an element from group I of the periodic table, and aluminoxanes. Particular examples would be organoaluminium compounds, of trialkylaluminiums such as triethylaluminium, trialkenylaluminiums such as triisopropenylaluminium, aluminium mono- and dialkoxides such as diethylaluminium ethoxide, mono- and dihalogenated alkylaluminiums such as diethylaluminium chloride, alkylaluminium mono- and dihydrides such as dibutylaluminium hydride and organoaluminium compounds comprising lithium such as $LiAl(C_2H_5)_4$. Organoaluminium compounds, especially those which are not halogenated, are well suited. Triethylaluminium and triisobutylaluminium are especially advantageous.

The chromium-based catalyst is preferred to comprise a supported chromium oxide catalyst having a titania-containing support, for example a composite silica and titania support. A particularly preferred chromium-based catalyst may comprise from 0.5 to 5 wt % chromium, preferably around 1 wt % chromium, such as 0.9 wt % chromium based on the weight of the chromium-containing catalyst. The support comprises at least 2 wt %

titanium, preferably around 2 to 3 wt % titanium, more preferably around 2.3 wt % titanium based on the weight of the chromium containing catalyst. The chromium-based catalyst may have a specific surface area of from 200 to 700 m.sup.2 /g, preferably from 400 to 550 m.sup.2 /g and a volume porosity of greater than 2 cc/g preferably from 2 to 3 cc/g.

Silica supported chromium catalysts are typically subjected to an initial activation step in air at an elevated activation temperature. The activation temperature preferably ranges from 500 to 850.degree. C., more preferably 600 to 750.degree. C.

The reactor loop can be used to make monomodal or multimodal, for example bimodal, polymers. The multi-modal polymers can be made in a single reactor or in multiple reactors. The reactor system can comprise one or more loop reactors connected in series or in parallel. The reactor loop may also be preceded or followed by a polymerisation reactor that is not a loop reactor.

In the case of series reactors, a first reactor of the series is supplied with catalyst and the cocatalyst in addition to the diluent and monomer, and each subsequent reactor is supplied with, at least, monomer, in particular ethylene and with the slurry arising from a preceding reactor of the series, this mixture comprising the catalyst, the cocatalyst and a mixture of the polymers produced in a preceding reactor of the series. It is optionally possible to supply a second reactor and/or, if appropriate, at least one of the following reactors with fresh catalyst and/or cocatalyst. However, it is preferable to introduce the catalyst and the cocatalyst exclusively into a first reactor.

In the case where the plant comprises more than two reactors in series, the polymer of highest melt index and the polymer of lowest melt index can be produced in two adjacent or non-adjacent reactors in the series. Hydrogen is maintained at (i) a low (or zero) concentration in the reactor(s) manufacturing the high molecular weight components, e.g. hydrogen percentages including between 0-0.1 vol % and at (ii) a very high concentration in the reactor(s) manufacturing the low molecular weight components e.g. hydrogen percentages between 0.5-2.4 vol %. The reactors can equally be operated to produce essentially the same polymer melt index in successive reactors.

Particular sensitivity to operating at reduced Froude numbers (and associated cross-sectional compositional, thermal or particulate gradients) has however been related to production of polymer resins where polymer of either high or low molecular weight resins

has been known to lead to increased fouling concerns. Particularly when producing polymers of molecular weights less than 50 kDaltons or greater than 150 kDaltons. These concerns have particularly been confirmed to be accentuated at low polymer solids concentrations in the reactor loop. When producing polymers of molecular weights less than 50 kDaltons or greater than 200 kDa (or melt index below 0.1 and above 50) in large diameter reactors it has however surprisingly been discovered that fouling is decreased when solids loadings are increased to above 20 vol%, particularly above 30 vol%.

The invention will now be illustrated by reference to the following example.

Example 1

In an elongated closed loop tubular reactor having an internal diameter of 711 millimetres and a volumetric capacity of 62 m^3, ethylene was copolymerised with hexene-1 at a temperature of 85°C and a pressure of 30 bara in isobutane as diluent and using a Ziegler-Natta catalyst to produce a copolymer The Froude Number was maintained below 10 for a period of six days, with a essentially constant solids loading of about 44.5 wt%. The reactor circulation pump power as measured by the amp transducer on the pump motor control system (see Table 1) and readings of voltage at the motor control system and heat transfer coefficient as measured by monitoring coolant water flow and coolant water temperature change compared to reactor temperature remained stable to within +/- 0.6% and +/- 0.6% respectively, indicating that there was no detectable fouling of the reactor as evidenced by a build up of polymer on the walls of the reactor, and that flow was stable and well distributed as evidenced by the stable pump power readings.

Table 1

Date	Day 1 21:00:00	Day 6 09:00:00	5.5 days
amps	32.18	32	-0.6%
solids, wt%	44.5	44.5	0

This provides evidence of heat transfer coefficient stability and pump power stability at low Froude numbers.

Claims

1. A process comprising polymerizing in a loop reactor an olefin monomer optionally together with an olefin comonomer in the presence of a polymerization catalyst in a diluent to produce a slurry comprising solid particulate olefin polymer and the diluent wherein the Froude number is maintained at or below 20.

2. A process as claimed in claim 1 wherein the Froude number is in the range 2 to 15.

3. A process as claimed in claim 2 wherein the Froude number is in the rage 3 to 10.

4. A process as claimed in any one of the preceding claims wherein the solids concentration of the slurry in the loop reactor is in the range 40-60% weight based on the total weight of the slurry.

5. A process as claimed in any one of claims 1 to 3 wherein the solids concentration of the slurry in the loop reactor is in the range 25-35% by volume.

6. A process as claimed in any one of the preceding clams wherein the loop reactor has an internal diameter of over 500 millimeters.

7. A process as claimed in claim 6 wherein the internal diameter is in the range 600 to 750 millimeters.

8. A process as claimed in any one of the preceding claims wherein total pressure drop in the loop rector is less than 1.3 bar.

9. A process as claimed in any one of the preceding claims wherein the reactor size is greater than 50 m^3.

10. A process as claimed in claim 9 wherein the reactor size is in the range 75-150m^3.

11. A process as claimed in any one of the preceding claims wherein the reactor length to internal diameter ratio is less than 400.

12. A process as claimed in claim 11 wherein the ratio is less than 250.

13. A process as claimed in any one of the preceding claims wherein the space time yield is in the range 0.2-0.35 ton/hour/m^3.

14. A process as claimed in any one of the preceding claims wherein the olefin is ethylene.

15. A process as claimed in claim 14 wherein the comonomer is at least one of butene-1, pentene-1, or hexane-1.

16. A process as claimed in any one of claims 14 or 15 wherein the diluent is isobutane.

17. A process as claimed in any one of claims 1 to 13 wherein the olefin is propylene.

18. A process as claimed in any one of the preceding claims wherein the particulate polymer is withdrawn from the reactor in a continuous fashion.

19. A process as claimed in any one of the preceding claims wherein the catalyst is chosen for Ziegler - type catalysts, inorganic supported chromium oxide catalysts and metallocene - type catalysts.

20. A process as claimed in any one of the preceding claims wherein the loop reactor is one of two or more loop reactors connected in series.

21. A loop reactor of a continuous tubular construction comprising at least two horizontal sections and at least two vertical sections for carrying out a process as claimed in any one of claims 1 to 20