PROCESS FOR THE PRODUCTION OF EPDM ELASTOMERS IN SOLUTION AND POLYMERISATION REACTOR FOR USE IN SAID PROCESS.

FIG. 2

The present invention relates to a process for the preparation of ethylene-propylene elastomeric copolymers or ethylene-propylene-diene EP(D)M elastomeric terpolymers in solution, and a polymerisation reactor for use in said process. In particular, the process comprises: a monomer polymerisation reaction stage, in which ethylene, propylene, optionally a diene, a catalytic system, hydrogen and a hydrocarbon solvent for said EP(D)M elastomers are fed continuously to a stirred reactor (CSTR) with the formation of a reaction bath in which the EP(D)M elastomer is dissolved in said hydrocarbon solvent; said reaction bath is kept boiling at a temperature in the range of 40°C to 70°C and a pressure in the range of 8 to 15 barg, such that a partial vapourisation of said reaction bath occurs; in a degassing stage, the solution containing the EP(D)M elastomer and unreacted monomers emerging from said CSTR stirred reactor is fed to a distillation column where said unreacted monomers are separated from the solution containing the polymer; said unreacted monomers are drawn from said distillation column, compressed at a pressure in the range of 18 to 22 barg, cooled to a temperature lower than the temperature of said reaction bath, and recycled to said stirred reactor (CSTR). During said process, the vapours formed by the partial vapourisation of said reaction bath in said reaction phase and a liquid stream of said hydrocarbon solvent are sent to an absorption column and placed in countercurrent contact therein, so as to induce an absorption of said vapours in said solvent. Said hydrocarbon in which the vapours have been absorbed as explained above is drawn from said absorption column, submitted to a first cooling stage in a water heat exchanger, then to a second cooling stage in a subcooler, then fed to said stirred reactor (CSTR) at a temperature lower than the temperature of said reaction bath.
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PROCESS FOR THE PRODUCTION OF EPDM ELASTOMERS IN SOLUTION AND POLYMERISATION REACTOR FOR USE IN SAID PROCESS

DESCRIPTION

The present invention relates to a process for the preparation of ethylene-propylene elastomeric copolymers or ethylene-propylene-diene (EPDM) elastomeric terpolymers in solution, and a polymerisation reactor for use in said process. In the present description ethylene-propylene elastomeric copolymers and ethylene-propylene-diene elastomeric terpolymers are collectively designated as EP(D)M.

The polymerisation of ethylene and propylene, optionally with a diene, to produce EP(D)M elastomers is typically obtained in the presence of a Ziegler-Natta catalytic system, either of traditional type or using metallocenes. Conventional Ziegler-Natta (Z/N) systems comprising vanadium compounds, which are soluble in hydrocarbon solvents and consequently form an essentially homogeneous system, have been widely used. Elastomeric polymers obtained with these catalysts contain little or no crystalline homopolymer fraction. The vanadium compounds most commonly used are vanadium oxytrichloride VOCl₃, vanadium tetrachloride VCl₄, and vanadium triacetylacetonate V(ACAC)₃.

The Z/N catalytic system also comprises an aluminium alkyl as a co-catalyst, such as diethyl aluminium chloride, or ethylaluminium sesquichloride.

The molecular weight of the EP(D)M copolymer or terpolymer is controlled by means of the use of chain transfer agents, typically hydrogen or diethyl zinc.

In solution polymerisation processes, the monomers, the catalytic system and the molecular weight regulator, and any other component in the mixture, are fed into a polymerisation reactor. A solvent of the resulting polymer, usually a saturated hydrocarbon such as hexane, is fed into the polymerisation reactor. The polymerisation process usually takes place within a temperature range of 10-70°C and is exothermic, so the heat released by the reaction has to be removed.

The reaction involved in the production of EP(D)M is one of the most complex currently known polymerisation processes. In fact, the production of EP(D)M entails the reaction of three monomers having a very different reactivity, a multi-component catalytic system and molecular weight regulator, such as hydrogen that, being a very lightweight gas, is very difficult to distribute evenly through the reaction solution. In addition, the reaction solution is highly viscous because of the dissolved polymer.

A very broad range of types of EP(D)M can be produced for various applications, including more than twenty different types of polymer, each of which must comply with very strict
specifications in terms of composition, acceptability ranges, molecular weight, and molecular weight distribution. The polymerisation reactions and the related control methods must consequently be such that they ensure a perfect reproducibility of the reaction conditions and their stability in time and space.

In the processes known to date, the polymerisation reaction is obtained with equipment and procedures that make it difficult to ensure that the reaction medium remains homogeneous in time and space, and it is consequently difficult to control the reaction itself. For instance, multiple reactors, connected in series or in parallel, are widely used, into which the raw materials and catalyst are fed from above and/or below, at distinctly lower temperatures than that of the reagent, thus making it difficult to distribute them evenly within the polymeric solution (which is highly viscous) and to achieve uniform temperature conditions in said solution. As a consequence, it is difficult to obtain the same concentrations of the monomers, the molecular weight regulator and the components of the catalytic system throughout the reagent liquid.

A very important factor for proper polymerisation concerns the elimination of the heat of polymerisation, which is commonly dissipated by means of a heat exchange through the metal wall that creates a temperature gradient in the reaction tank between the centre of the reactor and the refrigerated wall. This can cause fouling phenomena on the wails, however, with a consequent loss of productivity of the reactor and an impaired temperature control. The energy consumption for dissipating the heat of the reaction also has an enormous influence on the energy balance of the polymerisation reactor, which is translated into a higher cost in economic terms for the production of EP(D)M elastomers in solution.

US2008/0207852 A1 describes a solution polymerisation process involving several stages for the production of ethylene-α-olefin copolymers in two reactors in series. The heat released by the polymerisation reaction is dissipated using two different methods, with a cooling jacket installed on the reactor, and with a cooling method that relies on the latent heat of evaporation (vaporisation) of the solvent and of the monomers (see paragraph [0035]). The examples provide no information on which cooling method is preferable, or on which the process is mainly based. This type of process has several drawbacks, however, including: the use of several reactors connected in series, which makes it difficult to control the polymerisation reaction in order to guarantee a homogeneous reaction medium; the use of a cooling jacket or wall, which demands a high temperature difference between the reaction bath and the cooling wall or, in other words, a rather low wail temperature. Because the solubility of the EP(D)M produced is lower at lower temperatures, this leads to the formation of elastomer deposits on
the reactor wall, which can reduce the quality of the product and make it necessary to frequently interrupt production to remove them. In addition, the use of these cooling systems is costly both in energy terms and in economic terms in order to obtain a cooling jacket capable of regulating the temperature adequately. Using the latent heat of evaporation of the solvent as the sole cooling method is also a drawback because, in order to avoid problems with liquids entrained in the vapours being released, it would be necessary to use reactors with a low ratio between the height of the liquid and the diameter of the reactor (i.e. very wide reactors with very limited heights), which would be commercially unsuitable and inappropriate for ensuring a good stirring action.

WO 2012/156393 A1 describes a solution process for the production of EPDM in a continuous stirred-tank reactor (CSTR), in which the reaction bath is kept boiling at a temperature between 40°C and 60°C, and a pressure between 6 and 13 bar, and in which from 40% to 80% of the heat of the reaction is dissipated by the boiling of the reaction bath, while the remaining heat is removed by means of the subcooling of the fluids recycled to the reactor. The reactor is equipped with a stirring system with three impellers, a device for distributing the recycled fluids to the bottom of the reactor, and a gamma ray level control device. This type of process requires a considerable quantity of energy to cool the recycled fluids that are fed back into the reactor because, in order to control the reaction temperature (inside the reactor) it is necessary to add the reagents at a temperature much lower than the reaction temperature, and this entails the use of very powerful refrigerating appliances and a considerable energy consumption. In addition, for the recycled gases leaving the reactor that are used to remove heat from the reaction bath by evaporation to be partially condensed and fed back inside the reactor, they must first be compressed using suitable compressors that have a high energy consumption because of the large volumes of gas produced.

It would consequently be desirable to have a solution process for the production of EP(D)M elastomers capable of obtaining a high-quality product while keeping the reaction conditions stable and controllable, and limiting the energy consumption at the same time, in order to be able to reduce the plant management costs without reducing the quality of the polymer produced.

The object of the present invention is a solution process for the production of EP(D)M elastomers that enables the production of the elastomer to be optimised by taking action on the reaction parameters so as to ensure an efficient and reproducible control of the reaction involved and reduce the process management costs.
Another object of the present invention is a solution process for the production of EP(D)M elastomers in which the energy consumption for controlling the temperature and pressure parameters is considerably reduced.

A further object of the present invention is a plant for the production of EP(D)M elastomers in solution that enables the costs of managing said plant to be reduced while maintaining a high quality of the polymer produced, and that enables the use of less extreme compression and refrigeration systems, that are consequently easier to maintain and demand lower investment costs.

The above-mentioned objects are achieved by a solution process for the production of EP(D)M elastomers comprising:

- a monomer polymerisation reaction step in which ethylene, propylene, optionally a diene, the catalytic system, hydrogen and a hydrocarbon solvent for said EP(D)M elastomers, are fed continuously into a stirred reactor (CSTR) with the formation of a reaction bath in which the EP(D)M elastomer is dissolved in said hydrocarbon solvent, and wherein said reaction bath is maintained in a boiling condition at a temperature from 40° to 70°C, and at a pressure from 8 to 15 barg, such that the partial vaporisation of said reaction bath occurs;

- a degassing step, wherein the solution containing the EP(D)M elastomer and the unreacted monomers drawn from said CSTR stirred reactor, is fed to a distillation column in which said unreacted monomers are separated from the solution containing the polymer; said unreacted monomers are removed from said distillation column, compressed to a pressure ranging from 18 to 22 barg, cooled to a temperature lower than the temperature of said reaction bath, and fed to said stirred reactor (CSTR), characterized in that:

  i. the vapours formed by the partial vaporisation of said reaction bath in said reaction step and a liquid stream of said hydrocarbon solvent are fed to an absorption column and placed in contact in a countercurrent therein, whereby said vapours are absorbed in said solvent;

  ii. said hydrocarbon solvent in which the vapours are absorbed according to item (i) is drawn from said absorption column, subjected to a first cooling stage in a water heat exchanger, sent to a second cooling stage in a subcooler and fed to said CSTR stirred reactor at a temperature lower than the temperature of said reaction bath.
According to another aspect of the invention, the unreacted monomers of said degassing step and a liquid stream of said hydrocarbon solvent are fed to an absorption column and placed in contact therein, so as to cause an absorption of said unreacted monomers in said solvent. The hydrocarbon solvent in which the unreacted monomers are absorbed as explained above is drawn from said absorption column, submitted to a first cooling stage in a water heat exchanger, sent to a second cooling stage in a subcooler, and then fed to said stirred reactor (CSTR) at a temperature lower than the temperature of said reaction bath.

The term subcooler is used, according to the present invention, to mean a heat exchanger that uses a fluid coming from a refrigeration cycle as the cooling medium. This makes it possible to reduce the quantity of heat that the subcooler must remove from the vapours being recycled because the absorption column and the subsequent cooling stage in the water heat exchanger contribute to dissipating a part of the heat. With this phase of the process, the consumption of the subcooler is consequently reduced, and also the total cost of managing the polymerisation process.

The vapours formed by the partial vaporisation of the reaction bath are preferably submitted to partial condensation in a water condenser located upstream from the inlet to the absorption column. The vapours thus undergo a first cooling action that contributes to reducing the consumption of the subcooler, further reducing the process management costs.

The vapours formed by the partial vaporisation of the reaction bath are preferably compressed with a compression ratio in the range of 1.3-1.6 before they are fed to said absorption column. This makes it possible to recycle the vapours, which are subsequently condensed, inside the stirred reactor (CSTR) without altering the pressure conditions of the reaction, while maintaining a stable and efficient polymerisation reaction.

The vapours leaving from the top of the absorption column are preferably compressed with a compression ratio in the range of 1.3-1.6, submitted to partial condensation in a water condenser, cooled to a temperature lower than the temperature of said reaction bath and fed into said stirred reactor (CSTR). This makes it possible to recycle the gases leaving the absorption column and feed them back into the stirred reactor (CSTR) without altering the pressure balances involved in the polymerisation reaction.

The hydrocarbon solvent for the EP(D)M in which the vapours are absorbed is preferably fed into the bottom of the reactor. In this way, the balances of the reaction inside the stirred reactor (CSTR) remain unaffected, and the vapours used to remove the reaction heat from the reaction bath can be fully recycled.
Said absorption column preferably contains a packing material. This makes it possible to obtain an optimal absorption of the solvent vapours and enables a significant recycling of the unreacted monomers contained in the vapours formed by the partial vaporisation of the reaction bath.

The flow rate of the vapours formed by the partial vaporisation of the reaction bath is preferably proportional to the productivity of the reactor and it is recorded, processed and used to control the flow rates of the monomers, solvent and catalyst fed into the reactor. This makes it possible to achieve an optimal control of the reaction parameters, while keeping the reaction stable and efficient for the purposes of optimising the polymerisation process.

A further aspect of the present invention concerns a plant for the production of EP(D)M elastomers in solution characterised in that it comprises:

* a polymerisation section comprising:
  i. a subcooler
  ii. a stirred reactor (CSTR) for the polymerization of monomers of ethylene, propylene and optionally a diene, located downstream from said subcooler, with multi-impeller stirring means and a distributor of inlet streams in the proximity of the bottom, said reactor comprising an upper portion and a lower portion, said upper portion having a diameter greater than the diameter of said lower portion, and the height of said upper portion being less than the height of said lower portion;
  iii. an absorption column, for the absorption of said monomers contained in the vapours formed by the partial vaporization of the reaction bath in the stirred reactor (CSTR) in a hydrocarbon solvent for said EP(D)M elastomers, equipped with a packing material and located downstream from said reactor;
  iv. a water heat exchanger placed downstream from said absorption column;

* a degassing section comprising:
  i. a distillation column for separating the unreacted monomers from the solution containing the EP(D)M elastomer.
  ii. a water heat exchanger located downstream from said distillation column;
  iii. a compressor located downstream from said distillation column.

In the degassing section, the plant for the production of EP(D)M elastomers in solution preferably comprises an absorption column located downstream from said distillation column for the absorption of said unreacted monomers in the hydrocarbon solvent, and a water heat exchanger located downstream from said absorption column. This makes it possible to have a
plant in which the vapours leaving the degassing column are also recycled, and the energy needed to compress the unabsorbed vapours is reduced at the same time.

In the polymerisation section, the plant for the production of EP(D)M elastomers in solution preferably comprises a water condenser located downstream from the stirred reactor (CSTR) and upstream from the absorption column. This makes it possible to reduce the load on the subcooler located upstream from the stirred reactor, and to obtain an energy saving and a consequent economic saving.

In the polymerisation section, the plant for the production of EP(D)M elastomers in solution preferably comprises a compressor located downstream from the stirred reactor (CSTR) and upstream from the absorption column. This makes it possible to feed the recycled fluids directly back into the reactor, reducing the energy consumption for the compression stage without reducing the output of the polymerisation process or modifying the reaction parameters.

As mentioned previously, the stirred reactor (CSTR) of the polymerisation section of the plant for the production of EP(D)M elastomers has an upper portion with a larger diameter than the diameter of the lower portion, and the height of said upper portion is lower than the height of said lower portion. Preferably, the ratio between said diameter of the upper portion and said diameter of the lower portion is between 1 and 2.

Using this type of reactor makes it possible to prevent any reaction bath entrainment phenomena, thus avoiding any loss of reactor efficiency or fouling phenomena in the vapour recycling circuit.

Further characteristics and advantages of the present invention will emerge clearly from the description of preferred embodiments, illustrated as a non-limiting example in the attached figures, wherein:

- Figure 1 shows a simplified layout of the process according to the known state of the art.
- Figure 2 shows a simplified layout of the process according to the present invention in a first embodiment.
- Figure 3 shows a simplified layout of the process according to the present invention in a second embodiment.
- Figure 4 shows a simplified layout of the process according to the present invention in a third embodiment.
- Figure 5 shows a simplified layout of the process according to the present invention in a fourth embodiment.
- Figure 6 shows a simplified layout of the process according to the present invention in a fifth embodiment.
- Figure 7 shows a schematic cross-sectional view of the CSTR reactor in a particular embodiment according to the present invention.
- Figure 8 is a diagram illustrating the energy consumption of the process in the various embodiments compared with the consumption of the process according to the known state of the art.

The diene used in the process for the production of EP(D)M elastomers according to the invention is a non-conjugated diene chosen from the group comprising: ethylidene norbornene (ENB), vinyl norbornene (VNB), dicyclopentadiene (DCPD) and 1,4-hexadiene (HD).

The diene is typically contained in the EPDM polymer in a quantity below 12% by weight. Ethylidene norbornene (ENB) is the preferred diene.

The process according to the invention comprises a polymerisation reaction stage conducted in a CSTR stirred reactor, where the monomers are polymerised to produce the EP(D)M elastomer, and a degassing stage, where the unreacted monomers are separated from the polymer solution emerging from the bottom of the polymerisation reactor.

The process according to the invention is characterised in the polymerisation reaction stage by an innovative method for removing the heat of the polymerisation reaction achieved by means of a combination of partial vaporisation of the bath and the use of subcooled fluids recycled to the reactor.

The partial vaporisation is obtained by keeping the bath in a boiling condition at a temperature in the range of 40° to 70°C and a pressure in the range of 8 to 15 barg. The quantity of heat dissipated with the vaporisation is in the range of 30% to 80% of the total heat of the reaction. The heat dissipated with the vaporisation is preferably in the range of 35% to 60% of the total heat of the reaction.

The term 'subcooling' is used here to mean the operation of cooling each of the fluids to be recycled in the reactor to a temperature lower than the temperature of the reaction bath, i.e. below 40-70°C. The fluids recycled at said temperature are called 'subcooled fluids'. The quantity of heat dissipated by feeding the subcooled fluids to the reactor is between 70% and 20% of the total heat released by the reaction. The heat dissipated by this method is preferably in the range of 65% to 40% of the total heat of the reaction.
The recycled fluids, like the fresh reagents used in the reaction, are subcooled by means of a subcooler. As mentioned previously, the subcooler has a high energy consumption that considerably influences the polymerisation process management costs.

In the process according to the invention, the polymerisation reaction is completed in a boiling liquid so that the temperature is the same in every part of the reactor. By establishing the composition of the bath, i.e. the concentration of the monomers and of the molecular weight regulator in the solvent, the pressure at which the liquid boils and the composition of the gaseous phase produced by the partial vaporisation of the solution are also established.

The heat released by the polymerisation reaction varies according to the type of EP(D)M elastomer being produced, but averages approximately 700 kcal/kg. Exact values of the heat of the reaction are known to a person skilled in the art. The latent heat of vaporisation depends on the composition of the liquid phase, and averages approximately 70 kcal/kg. Here again, the exact values of the latent heat of vaporisation can be calculated by a person skilled in the art. Since the ratio between the heat of polymerisation and the heat of vaporisation is approximately 10 to 1, if all the heat of polymerisation were to be removed by boiling the reaction bath, 1 kg of elastomer produced would cause the vaporisation of approximately 10 kg of liquid from the reaction bath.

If the proportion between the heat dissipated by vaporisation and the heat removed by subcooling is 50%-50%, each kilogram of elastomer produced generates 700 kcal, 350 of which are removed by subcooling, and 350 are dissipated by the vaporisation of 5 kg of liquid.

If the proportions are 60% in vaporisation and 40% in subcooling, the heat removed by subcooling is 700 x 0.4 = 280 kcal and the heat dissipated by vaporisation is 700 x 0.6 = 420 kcal, which causes the vaporisation of 6 kg of liquid.

It is consequently clear that, by measuring the flow rate of the vapours leaving the reactor, it is possible to know the flow rate of the elastomer being produced at any given time when the reactor is in operation. This gives rise to a production control system that processes the data generated by the recording instruments used to detect and measure the process parameters, so that the exact composition of the elastomer being produced can be known and kept constant at all times while the process is underway. The key components of this system for controlling production are:

a) the analyser of the composition of the gaseous phase formed by the reactor;

b) the instrument for measuring the flow rate of the gaseous phase formed by the reactor;
c) the instrument for measuring the flow rate of the liquid condensed from the gaseous phase formed by the reactor and recycled to the reactor;
d) the analyser of the composition of the liquid in the above-mentioned item (c);
e) the instrument for measuring the temperature of the liquid in the above-mentioned item (c);
f) the instrument for measuring the temperature and flow rate of each raw material fed to the reactor, e.g. ethylene, propylene, diene, solvent, hydrogen, catalyst;
g) means for regulating the ratios between the monomer flow rates;
h) means for regulating the ratios of the catalytic system components he, and
i) means for regulating the temperature of the fluids fed to the reactor.

With reference to the polymerisation reaction phase of the process illustrated schematically in Figure 2, the monomers, solvents, catalyst and molecular weight regulator, e.g. hydrogen, are fed continuously to the CSTR stirred reactor after being purified and measured. All the flows being fed to the reactor, except for the recycled flows, take place under controlled flow conditions. The flows fed to the reactor - monomers, hydrogen and recycled fluids, are mixed together and cooled to a temperature lower than that of the reaction bath, in a subcooler 20, before they are fed to the reactor 10. The catalyst is fed to one side of the reactor 10, diluted in additional solvent, and therefore bypasses the subcooler 20.
The polymerisation process takes place inside the reactor 10, stirred by variable-speed, multiple-impeller stirring means, and the reactor contains means for controlling the level, pressure and composition of the vapours that develop from the partial vaporisation of the reaction bath.
The working pressure is in the range of 8 to 15 barg, while the temperature range is preferably between 50° and 60°C, depending on the degree of polymerisation to be obtained.
The reaction takes place in a liquid phase, approximately in equilibrium with the vapour phase. In fact, the stirring action and the arrangement of the reactor inlets are designed to ensure a temperature as evenly distributed as possible and an equilibrium between the liquid and the gaseous phases.
The heat of the exothermic polymerisation reaction generates a partial evaporation of the reaction bath, which contributes to dissipating the heat released and to keeping the reaction stable and homogeneous.
The vapours formed by the partial vaporisation of the reaction bath emerge from the top of the reactor and are partially condensed in a condenser 11 that uses water as a refrigerant. The
condensed liquid, consisting of solvent and unreacted monomers, is sent to the subcooler 20, cooled to a temperature lower than that of the reaction bath and recycled to the reactor 10. The uncondensed flow is sent to the intake of a compressor 12, e.g. an oil-free single-stage screw compressor. This compression has the dual purpose of compensating for the pressure drops in the flow consisting of solvents and unreacted monomers being recycled to the reactor, and also of facilitating heat dissipation and improving the absorption of monomers in the solvent, as explained below.

The flow of compressed vapours is sent to an absorption column 30, and fed into the bottom thereof, while a flow of solvent is fed into the top of said column. The countercurrent contact between the flow of vapours and the flow of solvent causes the absorption of the vapours into the solvent. The fluid leaving the bottom of the absorption column 30 thus contains the solvent and a part of the unreacted monomers previously contained in the flow of compressed vapours.

According to one aspect of the present invention, the absorption column 30 contains a packing material that increases its contact surface area, thereby increasing the absorption efficiency of the column.

The vapours not absorbed in the absorption column 30 emerge from the top of the column and undergo partial condensation in a condenser 32 that uses water as a cooling fluid. The resulting condensate is sent to the subcooler 20, cooled to a temperature lower than that of the reaction bath and recycled to the reactor 10 after being mixed with other recycled fluids and with fresh reagents. Part of the uncondensed vapours are drained off, while the majority is recycled to the reactor 10 together with the condensate.

The liquid leaving the absorption column is thus submitted to a first cooling stage in a heat exchanger 31 that uses water as a refrigerant. The cooled liquid gas, consisting of solvent and unreacted monomers, is partly recirculated to the top of the same column, and partly mixed with other recycled fluids and sent to the subcooler 20, where it is cooled to a temperature lower than that of the reaction bath and recycled to the reactor 10.

This phase in which the vapours are absorbed by the solvent inside the absorption column 30, combined with the cooling stage in the water heat exchanger 31, makes it possible not only to reduce the energy consumption of the subcooler 20 used to cool the fluids that are recycled to the reactor 10, but also to size the compressor 12 for a lower final compression pressure by comparison with the standard case.

The second phase of the process for the production of EP(D)M elastomers, i.e. the degassing phase, has the purpose of separating the lightweight unreacted monomers (ethylene,
propylene) that are dissolved in fairly high quantities (of the order of 10,000 kg/h) in the polymer solution emerging from the bottom of the polymerisation reactor. These monomers are recovered by distillation and then compressed and recycled to the reactor. The degassing operation takes place as explained below.

The polymer solution collected from the reactor is fed continuously to a distillation column 40, in which the lightweight unreacted monomers are separated at the top of the column. The heat required is provided by a reboiler 42.

In one aspect of the present invention, the column 40 contains segmental perforated plates (or other types of special plate, e.g. 'disc & doughnut') that enable a highly viscous fluid such as the polymer solution to be treated. In one embodiment of the process according to the invention, the working conditions of the column 40 are as follows:

**Top:**

- \( P = 0.4 \) barg
- \( T = 36-38 \) °C

**Bottom:**

- \( P = 0.5 \) barg
- \( T = 80-81 \) °C

The product at the top, containing the lightweight monomers (ethylene, propylene) and part of the solvent, undergoes partial condensation in a condenser 41 that uses water as a refrigerant, and recycled to the reactor that operates at a pressure below 15 barg. A three-stage compressor 43 is used for this purpose, fitted with intermediate partial water condensers (not shown in the figure) and a final partial condenser (E-DEGFIN), that uses water as a refrigerant. The final compression pressure is approximately 20 barg. Both the condensed fluid and the uncondensed fluid have sufficient pressure to be sent to the subcooler 20, cooled to a temperature below that of the reaction bath, and recycled to the reactor 10, after being mixed with fresh monomers and fluids coming from the recycling of the previous stages.

The polymer solution emerging from the bottom of the degassing column 40, and containing polymer, most of the solvent and the unreacted heavy monomer (diene), is sent for subsequent processing by means of a pump. The content of lightweight monomers in the solution is minimal (of the order of 10 kg/h) and consequently allowable without any need for further recovery.

In one aspect of the present invention, the degassing stage of the process for the production of EP(D)M elastomers as illustrated schematically in Figure 3, comprises an absorption column 50 located between the first and second compression stages 43. After undergoing a first cycle of condensation and compression, the fluid emerging from the top of the distillation column is fed to the bottom of an absorption column 50, while a flow of solvent is fed to the top of said column. The countercurrent contact causes the absorption of the lightweight monomers in the solvent. The liquid emerging from the bottom of the absorption column 50 thus contains
solvent and a part of the lightweight unreacted monomers previously contained in the fluid emerging from the distillation column.

According to one aspect of the present invention, the absorption column 50 contains a packing material.

The liquid leaving the absorption column is submitted to a first cooling stage in a heat exchanger 51, that uses water as a refrigerant. A part of the cooled liquid, consisting of solvent and lightweight unreacted monomers, is recirculated to the top of the same column 50, and a part is sent to the top of the absorption column 30 in the first stage of the process, where it may be mixed with fresh solvent before being added to the column. Said liquid thus becomes the liquid in which the unreacted monomers contained in the vapours formed by the partial vaporisation of the reaction bath are absorbed. The inclusion of the absorption column 50 in the degassing phase thus achieves a reduction in the load on the second and third compression stages 43.

In one aspect of the present invention, the polymerisation reaction phase of the process for the production of EP(D)M elastomers illustrated schematically in Figure 4 differs from the layout shown in Figure 2 as regards the relative positions of the temperature-regulating compressor 12 in relation to the absorption column 30, and the omission of the condenser 11 at the outlet for the vapours at the top of the reactor 10. In fact, the compressor C-TH is positioned downstream from the absorption column 30 and upstream from the condenser 32. This enables a reduction in the energy consumption for cooling the vapours and, at the same time, it enables the pressure conditions inside the system to be kept stable so that the recycled fluids can be fed back into the reactor. This solution also enables a reduction in the flow rate to the compressor 12 by comparison with the standard situation.

In one aspect of the present invention, the polymerisation reaction phase of the process for the production of EP(D)M elastomers as shown schematically in Figure 5 differs from the layout illustrated in Figure 2 as regards the relative position of the temperature-regulating compressor 12 in relation to the absorption column 30, which is downstream from the absorption column 30 and upstream from the condenser 32. Here again, there is a reduction in the energy consumption for cooling the vapours, while an adequate pressure of the recycled fluid is nonetheless maintained. This solution also enables a reduction in the flow rate to the compressor 12 by comparison with the standard situation.

In one aspect of the present invention, the polymerisation reaction phase in the process for the production of EP(D)M elastomers as illustrated schematically in Figure 6 differs from the layout shown in Figure 2 as regards the omission of the condenser 11 at the outlet for the
vapours at the top of the reactor 10. Here again, there is a reduction in the energy consumption for cooling the vapours, while an adequate pressure of the recycled fluids is maintained.

The diagram in Figure 8 shows the energy consumptions (shown on the x-axis) as a function of the hourly output of polymer (on the y-axis) of different configurations of the process according to the present invention by comparison with the energy consumptions of a process according to the known state of the art.

Clearly, the energy consumptions of the process according to the known state of the art (schematically illustrated in Figure 1) are higher than the energy consumptions achieved with a process according to the present invention. In particular, the energy consumption in a process where there is an absorption column, with a corresponding water condenser, only in the polymerisation reaction phase (the layout shown in Figure 2) is clearly significantly lower than the energy consumption involved in a process according to the known state of the art. In the configuration of the process in which there is an absorption column in both the reaction stage and the degassing stage (the layout shown in Figure 3), there is a further reduction in the total energy consumption needed to produce the same amount of EP(D)M elastomer.

The process for the production of EP(D)M elastomers according to the present invention can be implemented in a plant comprising a first polymerisation section comprising a subcooler 20, i.e. a heat exchanger that uses as a refrigerant a flow coming from a cooling cycle in which the previously purified reagents coming from supply lines are cooled to CSTR a temperature below that of the reaction bath. Downstream from the subcooler there is a stirred reactor 10, with stirring means 103 comprising multiple impellers 104, and a distributor of the incoming streams 105 located in the vicinity of the bottom of said reactor. A condenser 11 that uses water as a refrigerant is positioned downstream from the stirred reactor 10 for the purpose of recovering and condensing the vapours formed by the partial evaporation of the reaction bath. The condensate coming from the condenser 11 downstream from the reactor is fed back through recycling lines 21 into the reactor 10, after cooling in the subcooler 20 located upstream from the reactor 10.

A compressor 12, preferably a single-stage screw dry compressor (oil-free), compresses the uncondensed vapours in the condenser located downstream from the reactor 10 and feeds them into the bottom of an absorption column 30. A flow of reaction solvent is fed into the top of the absorption column 30, generating a countercurrent flow between the vapours and the solvent. The absorption column 30 preferably contains a packing material.
A heat exchanger 31 that uses water as a refrigerant and is located downstream from the absorption column 30, is fed with the liquid emerging from the bottom of the absorption column 30 and contributes to reducing the temperature of said liquid by dissipating the heat of absorption. The cooled liquid is partly recirculated to the top of the absorption column 30 and partly recycled through lines 31 to the reactor 10, after cooling in the subcooler 20 located upstream from the reactor 10.

A condenser 32 that uses water as a refrigerant is located downstream from the absorption column 30 for the purpose of recovering and condensing the unabsorbed vapours emerging from the top of the absorption column 30. The condensed vapours are sent back through recycling lines 21 to the reactor 10 after cooling in the subcooler 20 located upstream from the reactor 10. The uncondensed vapours are partly recycled together with the condensate and partly drained off through a drainage line 33.

The plant according to the present invention also comprises a degassing section located downstream from the CSTR stirred reactor 10, in which a distillation column 40, preferably with segmental perforated plates (or other types of special plate, e.g. disc & doughnut) is fed with the liquid coming from the reactor 10. The liquid is fed into the top of the distillation column 40, and the heat needed to achieve the separation inside the column is provided by a reboiler 42.

The liquid leaving the bottom of the distillation column 40 is sent to subsequent processing stages, while the vapours coming from the top of the column 40 are compressed by a three-stage compressor 43 with intermediate condensers 41 and a final water condenser 44.

The liquid obtained from the condensation and compression of the gases coming from the top of the column 40 is sent back through recycling lines 22 to the reactor 10 after cooling in the subcooler 20 located upstream from the reactor 10.

The uncondensed gases are partly recycled and partly drained off through a drainage line 45.

In one aspect of the present invention, the degassing section of the plant for the production of EP(D)M elastomers is complete with an absorption column 50 located downstream from the first condensing and compression cycle performed on the gases emerging from the top of the distillation column 40. The flow coming from the first compression stage is fed to the bottom of the absorption column 50, while a flow of reaction solvent is fed into the top of the absorption column, thus generating a countercurrent flow. The absorption column 50 preferably contains a packing material.

The liquid emerging from the bottom of the absorption column is fed to a heat exchanger 51 that uses water as a refrigerant, and then partly recycled to the top of the column 40 and partly...
sent to the top of the absorption column in the polymerisation section by means of supply lines.

A condenser 44 that uses water as a refrigerant is provided downstream from the absorption column 40 in order to recover and condense the unabsorbed gases coming from the top of the absorption column 40. The condensed gases are fed back through recycling lines 22 into the reactor 10, after cooling in the subcooler 20 located upstream from the reactor 10. The uncondensed gases are partly recycled to the reactor together with the condensed fraction and partly drained off through a drainage line 45.

In one aspect of the present invention, the CSTR stirred reactor 10 is shaped such that the upper portion 101 of the reactor 10 is wider, as shown in Figure 7. More precisely, the upper portion 101 has a larger diameter than the diameter of the lower portion 102. The height of the upper portion 101 is lower than the height of the lower portion 102. In particular, the ratio between the diameter of the upper portion and the diameter of the lower portion is in the range of 1 to 2.

The reactor is complete with stirring means 103 with multiple impellers 104 and a toroidal distributor 105 of the incoming streams. The shape of the reactor 10, combined with the stirring means 103 and the toroidal distributor 105, enables a better mixing of the incoming fluids, particularly thanks to the narrower diameter of the lower portion of the reactor.

The wider top of the reactor reduces the entrainment of reaction fluid by the vapours that emerge from the top of the reactor thanks to a reduction in the flow rate of the vapour induced by said wider diameter. This avoids fouling phenomena in the circuit at the outlet from the top of the reactor, and consequently reduces the plant servicing and management costs.
CLAIMS

1. Process for the production of EP(D)M elastomers in solution, comprising:
   • a polymerization reaction step of monomers in which ethylene, propylene,
     optionally a diene, the catalytic system, hydrogen and a hydrocarbon solvent
     for said elastomeric EP(D)M, are continuously fed to a stirred reactor (CSTR)
     with formation of a reaction bath in which the elastomer EP(D)M is dissolved
     in said hydrocarbon solvent, and wherein said reaction bath is maintained at a
     boiling condition at a temperature from 40 to 70 °C and at a pressure from 8 to
     15 barg, such that the partial vaporization of said reaction bath occurs;
   * a degassing step, wherein the solution containing the EP(D)M elastomer and
     unreacted monomers, withdrawn from said CSTR stirred reactor, is fed to a
     distillation column which the separation of said unreacted monomers from the
     solution containing the polymer occurs, said unreacted monomers are removed
     from said distillation column, compressed to a pressure ranging from 18 to 22
     barg, cooled to a temperature lower than the temperature of said reaction bath,
     and fed to said stirred reactor (CSTR),

characterized in that:
   i. the vapours formed by the partial vaporization of said reaction bath in said
      reaction step and a liquid stream of said hydrocarbon solvent are fed to an
      absorption column and contacted in countercurrent, whereby causes an
      absorption of said vapours in said solvent occurs;
   ii. said hydrocarbon solvent in which the vapours are absorbed according to the
      point i. is withdrawn from said absorption column, subjected to a first stage of
      cooling in a water heat exchanger, sent to a second stage of cooling in a
      subcooler and fed to said CSTR stirred reactor at a temperature lower than the
      temperature of said reaction bath.

2. Process according to claim 1, characterized in that:
   a. the unreacted monomers of said degassing step and a liquid stream of said
      hydrocarbon solvent are fed to an absorption column and contacted in
      countercurrent, whereby causes an absorption of said unreacted monomers in
      said solvent occurs;
   b. said hydrocarbon solvent in which the unreacted monomers are absorbed
      according to point a. is withdrawn from said absorption column, subjected to a
      first stage of cooling in a water heat exchanger, sent to a second stage of
cooling in a subcooler and fed to said CSTR stirred reactor at a temperature lower than the temperature of said reaction bath.

3. Process according to one or more of the preceding claims, characterized in that the vapours formed by the partial vaporization of the reaction bath are subjected to a partial condensation in a water condenser located upstream of the introduction into said absorption column.

4. Process according to one or more of the preceding claims, characterized in that the vapours formed by the partial vaporization of the reaction bath are compressed with a compression ratio from 1.3 to 1.6 before introduction into said absorption column.

5. Process according to one or more of claims from 1 to 3, characterized in that the outlet vapour from the head of the absorption column is compressed with a compression ratio from 1.3 to 1.6, subjected to a partial condensation in a water condenser, cooled a temperature lower than the temperature of said reaction bath and fed to said CSTR stirred reactor.

6. Process according to one or more of the preceding claims, characterized in that said hydrocarbon solvent for the EP(D)M is fed to the bottom of the reactor.

7. Process according to one or more of the preceding claims, characterized in that in said absorption column contains a packing material.

8. Process according to one or more of the preceding claims, characterized in that the flow rate of the vapours formed by the partial vaporization of the reaction bath is proportional to the productivity of the reactor and is detected, processed and used to control the flow rates of the monomers, solvents and catalyst fed to the reactor.

9. Plant for the production of EP(D)M elastomers in solution comprising:
   
   * a polymerization section comprising:
     
     i. a subcooler;
     
     ii. a stirred reactor (CSTR) for the polymerization of monomers of ethylene, propylene, optionally a diene, located downstream of said subcooler, provided with a paddles axial agitator and a distributor of inlet streams in the proximity of the bottom, said reactor being formed with an upper portion and a lower portion, said upper portion having a diameter greater than the diameter of said lower portion, the height of said upper portion being less than the height of said lower portion;
     
     iii. an absorption column, for absorption of monomers contained in the vapors formed by the partial vaporization of the reaction bath in the
stirred reactor (CSTR) into the hydrocarbon solvent for said elastomeric EP(D)M, provided with packing material and placed downstream said reactor;

iv. a water heat exchanger placed downstream of said absorption column;

* a degassing section comprising:

iv. a distillation column for the separation of the unreacted monomers from the solution containing the elastomer EP(D)M.

v. a water heat exchanger placed downstream of said distillation column;

vi. a compressor placed downstream of said distillation column.

10. Plant according to claim 9 characterized in that it comprises in the degassing section:

i. an absorption column placed downstream said distillation column, for the absorption of said unreacted monomers in the hydrocarbon solvent;

ii. a water heat exchanger placed downstream said absorption column.

11. Plant according to one or more of claims 9 or 10, characterized by comprising in the polymerization section a water condenser placed downstream the stirred reactor (CSTR) and upstream of the absorption column.

12. Plant according to one or more of claims from 9 to 11, characterized by comprising in the polymerization section a compressor located downstream the stirred reactor (CSTR) and upstream the absorption column.

13. Plant according to claim 9 characterized in that the ratio of said diameter of the upper portion and said diameter of the lower portion of the reactor is from 1 to 2.
Total Consumption (Polymerization + Degassing)

FIG. 8
**INTERNATIONAL SEARCH REPORT**

**International application No**

PCT/EP2014/062934

A. CLASSIFICATION OF SUBJECT MATTER

INV. CQ8F210/18 C08F2/06 B01J8/22

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

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X Further documents are listed in the continuation of Box C. X See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

1 September 2014

Date of mailing of the international search report

08/09/2014

Name and mailing address of the ISA/

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Fax: (+31-70) 340-3016

Authorized officer

Kaumann, Edgar

Form PCT/ISA/210 (second sheet) (April 2005)
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