

Method for producing a polyisobutene

Description

- 5 The invention relates to a process and an apparatus for producing polyisobutene at low temperatures.

Isobutene-containing homo- and copolymers with a number-average molecular weight M_n of 500 to 1 000 000 are produced on an industrial scale under *Lewis* acid catalysis at temperatures that are usually well below room temperature. The reaction temperature can be lowered to
10 down to -90°C .

In general, the higher the desired average molecular weight M_n of the polyisobutene, the lower the reaction temperature. For example, low molecular weight polyisobutene with a number-average molecular weight M_n up to a few thousand can be produced at temperatures around 0°C , or
15 only a little below. For polyisobutene with a number-average molecular weight M_n of a few tens of thousands, temperatures in the range of -10°C to -30°C are usually required. For the production of high molecular weight polyisobutene with a molar mass of more than 100 000, by contrast, reaction temperatures of no more than -50°C are required.

20 EP 322241 A2 discloses a process for producing polybutenes having a molecular weight M_n of 500 to 5000 by reaction of isobutene in the presence of BF_3 under particular reaction conditions.

EP 628575 A1 and WO 2013/62763 describe various reactors and the operation thereof for production of highly reactive polyisobutenes.
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None of the documents cited addresses energy management in the reaction regime.

US 6525149 B1 describes the performance of ionic polymerizations in shell and tube reactors, wherein the reaction mixture is circulated in a particular ratio to the monomer feed. The examples disclose specific flow rates and dimensions of the reaction zone, but heat management is not discussed.
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US 2019/0118158 A1 describes the performance of ionic polymerizations, for example the polymerization of isobutene to polyisobutene, in a circulation heat exchanger reactor system (HERS), wherein this reactor system comprises special channels in the form of parallelepipeds.
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A disadvantage is that such reactor systems are complex in terms of manufacture, since the lateral faces have to be welded. Welds are firstly costly in terms of manufacture, and secondly a source of leakage and corrosion.

- 5 DE 102009019470 A1 discloses the cationic polymerization of monomers, wherein at least the mixing of the streams and preferably also the polymerization take place in microstructures. The microstructures enable high heat exchanger surface areas, which means that polymerization can be conducted virtually isothermally, but the microstructures bring the disadvantage that they quickly become clogged by polymer deposits. Therefore, the reactions, according to DE
- 10 102009019470 A1, are conducted exclusively in a straight pass without circulation, since the reaction mixture conducted within the circuit comprises polymer that would cause deposits or blockage of the microstructures.

- Owing to the low reaction temperatures, these processes for production of polyisobutene are
- 15 very energy-intensive, especially for the generation and maintenance of low temperatures and for the removal of the heat of reaction at a low temperature level.

- As a result of the low reaction temperature, the use of inexpensive cooling media, particularly water, especially river water, for the removal of the heat of reaction in the polymerization to polyisobutene is usually not an option.
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- It was therefore an object to provide a process and an apparatus for production of isobutene homo- and copolymers, with which the energy intensity in the maintenance of low temperatures is reduced and the energy efficiency of the apparatus is optimized. An isothermal reaction regime may be desirable from a chemical point of view, but it is uneconomic.
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- It is customary to insulate cooled apparatuses and pipelines against ambient temperature, but this insulation cannot be complete. In order to assure operability and functionality of plant components that are movable or need to be kept easily accessible, for example pumps or fittings,
- 30 the insulation is penetrated at a multitude of points, creating thermal bridges. Such thermal bridges heat up the contents of the apparatuses, fittings and piping at these sites, firstly reducing energy efficiency. When the contents of the apparatuses and pipelines at these sites are still reactive by virtue of presence of non-deactivated *Lewis* acid, warming above the desired reaction temperature secondly additionally accelerates the reaction, which can lead to formation of
- 35 by-products or generally inhomogeneity of the product, since the reaction temperature, as set out above, has a strong influence on the reaction and particularly on the molar mass distribution, which leads to a high polydispersity of the product.

The object was achieved by a process for producing polyisobutenes having a number-average molecular weight M_n of 500 to 1 000 000 from isobutene or an isobutene-containing monomer mixture, in which the reaction is performed in a reaction system wherein

- the ratio of cooled surface area S_{cool} and reaction volume V is subject to the inequation

- 5 $S_{cool}/V \geq 50 \text{ m}^2/\text{m}^3$, preferably at least 55, more preferably at least 60, even more preferably at least 70 and in particular at least $80 \text{ m}^2/\text{m}^3$, and

- the ratio of cooled surface area S_{cool} and uncooled surface area S_{uncool} is subject to the inequation

- 10 $S_{cool}/S_{uncool} \geq 5 [\text{m}^2/\text{m}^2]$, preferably at least 7, more preferably at least 10, and most preferably at least 12 $[\text{m}^2/\text{m}^2]$.

These measures minimize energy inputs into the reaction mixture via the surface of the reaction system.

- 15 A further advantage is that the reaction temperature does not need to be kept lower than required for the desired result of polymerization. Otherwise, the energy of polymerization released would have to be removed at a lower temperature level, which would reduce the efficiency of the chiller for generation of the cooling medium.

20 Definitions

- The reaction system in the context of this document means the part of the plant in which isobutene or an isobutene-containing monomer mixture reacts with increasing average molecular weight M_n to give polyisobutene. In particular, in the plant, this includes reactors, heat exchangers, conduits, pumps, valves, fittings and flanges, preferably reactors, heat exchangers and conduits. This is preferably the part of the plant in which the isobutene or an isobutene-containing monomer mixture is in contact with at least one Lewis acid. The reaction is generally ended by deactivating the at least one Lewis acid, for example by adding water or alcohols, preferably water. Therefore, the plant parts and apparatuses with which the reaction mixture comes into contact after deactivation of the Lewis acid are no longer included in the reaction system.

- More preferably, the reaction system thus means that part of the plant in which the isobutene or an isobutene-containing monomer mixture is in contact with a non-deactivated Lewis acid, such that the apparatus in which the deactivation takes place is no longer included in the reaction system. Most preferably, the reaction system thus comprises the reactor and the heat exchangers, pumps, and conduits that lead from the reactor to the inlet of the apparatus in which the deactivation takes place. A further means of ending the reaction is to the removal of monomeric

isobutene from the Lewis acid-containing reaction mixture, for example by distillation or extraction, preferably single- or multistage distillation. Also conceivable is complete conversion of the monomeric isobutene. In general, the reaction no longer occurs when there is no more reactive Lewis acid and no more monomeric isobutene that are in contact with one another.

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The reaction system comprises at least one part, for example one to three parts, preferably one or two parts or more preferably one part in which the reaction mixture is in direct contact via a thermally conductive surface with a colder medium than the reaction mixture, and at least one part, for example one to three parts, preferably one or two parts or more preferably one part in which this is not the case.

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The reaction mixture is circulated via at least one cooled heat exchanger. Fresh isobutene-containing feed is fed into this circulated reaction mixture, and the corresponding amount of reaction product is removed in order to keep the total amount of reaction mixture constant.

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For homogenization of both the reaction mixture and of the exothermicity during the reaction, the volume of the circulated reaction mixture should preferably be at least 15 times the fresh isobutene-containing feed, preferably at least 20 times and more preferably at least 25 times.

100 times the volume of the fresh isobutene-containing feed should not be exceeded, since otherwise the energy used for the pump output makes the overall process uneconomic; preferably 80 times, more preferably 70 times, even more preferably 60 times and in particular 50 times should not be exceeded.

25 In addition, energy is introduced into the system via a high pump output, which in turn has to be removed from the reaction mixture by cooling. Therefore, pumped circulation of a high volume counteracts the optimization of energy efficiency.

The fresh isobutene-containing feed is generally mixed with the reaction mixture by energy input by shear energy. This is possible, for example, in dynamic mixing apparatuses, i.e. by mixing by stirrer or by pumped circulation (natural circulation or forced circulation) or pumped circulation with static mixing units such as static mixers or nozzles in the pumped circuit, by static mixing apparatus such as static mixers, nozzles, baffles, Y or T pieces, or by dynamic mixing apparatuses such as mixing pumps. The mixing is preferably effected by means of a mixing zone with static mixers or nozzles, preferably static mixers.

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Heat exchangers are selected from the group consisting of temperature-controllable tubular reactors, shell and tube heat exchangers, plate heat exchangers and temperature-controllable

tubular reactors with internals, preferably shell and tube heat exchangers and plate heat exchangers, more preferably shell and tube heat exchangers.

A conceivable but less preferred option is performance in at least one stirred tank reactor or a cascade of at least two stirred tank reactors, preferably 2 to 5 and more preferably 2 to 3 stirred tank reactors, each of which is cooled by means of a jacket and/or internal heat exchangers.

It is an advantage of the present invention that it can be performed in these conventional reactors and does not require complicated reactor systems according to US 2019/0118158 A1.

10 The cooled surface area S_{cool} is the surface area of all plant parts of the reaction system which is in direct contact with a colder medium than the reaction mixture in the respective plant parts via a thermally conductive surface. The temperature differential between the colder medium and the reaction mixture is, for example, at least 5 K, preferably at least 8 K, more preferably at least 10 K and most preferably at least 12 K.

15 A higher temperature differential between the colder medium and the reaction mixture than 30 K generally brings no benefit; the temperature differential is preferably not more than 25 K, more preferably not more than 20 K, even more preferably not more than 18 K and in particular not more than 15 K. High temperature differentials cause subcooling of the reaction mixture close to the wall, and so polyisobutene with higher molar mass is formed there. Moreover, the reduction in temperature locally increases the viscosity, making mixing more difficult and increasing the dwell time at the reactor wall. As a result, the average molar mass of the polyisobutene becomes more uneven, i.e. polydispersity increases.

25 The colder medium may, for example, be brine, particularly glycol/water mixtures, or ammonia. It is also possible to use organic hydrocarbons, for example propane, butane isomer mixtures or ethene, or partly or fully fluorinated hydrocarbons.

30 The thermally conductive surfaces are, for example, the surfaces of the heat exchanger tubes or plates, or jackets of reactors or pipes that carry the colder medium.

S_{cool} refers to the inside of the surfaces mentioned that is in direct thermal contact with the reaction mixture, and any gas phase above it.

35 In contrast, the uncooled surface area S_{uncool} is the area of all plant parts within the reaction system that is in direct heat-conducting contact with a medium having a higher temperature than the reaction mixture. Here too, the inside of the surfaces mentioned is considered. The medium

having a higher temperature than the reaction mixture is preferably the ambient atmosphere under the respective prevailing conditions. The respective surfaces are generally thermally insulated from the outside, which means that they nevertheless have a higher temperature than the reaction mixture. Typical uncooled surfaces are particularly pumps, fittings, valves and pipes, unless they are provided with a jacket (trace cooling) that carries a colder medium.

Delimitation of S_{cool} and S_{uncool} and calculation of the respective surface areas are accomplished by considering the sites where the temperature of the wall is equal to or higher than the temperature of the reaction mixture.

The reaction volume V is the total volume of the reaction system enclosed by plant components in which isobutene or an isobutene-containing monomer mixture reacts with increasing number-average molar mass M_n . The preferred embodiments described above in the definition of the reaction system are correspondingly applicable here.

The volume refers to the volume enclosed by the surface defined above.

In the case of the reaction volume, it may be useful to distinguish between conduits and vessels:

In this document, conduits are defined as machines and apparatuses that have a surface:volume ratio (S/V) of at least $4 \text{ m}^2/\text{m}^3$, preferably at least 8, more preferably at least 16 and in particular at least $40 \text{ m}^2/\text{m}^3$. These are especially pipelines having a nominal diameter (ND) of 100 mm to 1000 mm, preferably 300 to 500 mm.

It is not relevant for this purpose whether the surface is cooled or uncooled.

A pipeline of ND 100 mm, for example, has an S/V ratio of about $40 \text{ m}^2/\text{m}^3$, ND 250 mm an S/V of $16 \text{ m}^2/\text{m}^3$, and ND 1000 mm an S/V of $4 \text{ m}^2/\text{m}^3$. The S/V ratio depends solely on the radius r of the pipe: $S/V=2/r$.

Vessels in this document are those machines and apparatuses that have a smaller surface:volume ratio than the conduits defined above.

If a container is assumed to be an ideal cylinder with a circular flat base and top, typical S/V ratios at a radius r of 0.5 m and a height $h = 1 \text{ m}$ are $S/V = 6 \text{ m}^2/\text{m}^3$, at $r = 1 \text{ m}$ and $h = 1 \text{ m}$ $S/V = 4$, at $r = 0.5 \text{ m}$ and $h = 0.5 \text{ m}$ $S/V = 8$, and at $r = 1 \text{ m}$ and $h = 5 \text{ m}$ $S/V = 2.4 \text{ m}^2/\text{m}^3$. It is generally the case for such an ideal cylinder that $S/V = (2 \times h + 2 \times r)/(r \times h)$.

It is apparent from these S/V ratios that, for achievement of the inventive ratio of $S_{cool}/V \geq 50 \text{ m}^2/\text{m}^3$, the cooling, particularly of the conduits, has a strong influence since these, according to the above definition, have a high S/V ratio, i.e. a high surface area via which heat exchange can take place in relation to their volume. Preferably, the ratio of S_{cool}/V is at least 55, more preferably at least 60, even more preferably at least 70 and in particular at least $80 \text{ m}^2/\text{m}^3$.

A ratio of S_{cool}/V of $250 \text{ m}^2/\text{m}^3$ is preferably not exceeded; more preferably, the ratio of S_{cool}/V is not more than 200, most preferably not more than 175, in particular not more than $150 \text{ m}^2/\text{m}^3$.

High ratios S_{cool}/V are essential for the achievement of an isothermal reaction, which is not required for an inventive optimization of energy efficiency.

According to the invention, the ratio of uncooled surface area to cooled surface area has to be at least 5 [m^2/m^2], preferably at least 7, more preferably at least 10 and most preferably at least 12 [m^2/m^2].

This makes it possible to limit the temperature rise in the uncooled reaction system to not more than 2.5 K, preferably not more than 2.2 K, more preferably not more than 2.0 K and most preferably not more than 1.8 K compared to the inlet temperature in the uncooled reaction system.

This limitation in the temperature rise means that the reaction mixture is subject to smaller fluctuations in temperature, which would result in an inhomogeneous product mixture.

On the other hand, it is unnecessary to conduct the reaction isothermally, i.e. without a temperature rise. However, an isothermal reaction would require a high cooled area. It has been found that a temperature rise in the uncooled reaction system of 0.3 K or more is acceptable without the product mixture becoming excessively inhomogeneous, preferably 0.5 K or more, more preferably 0.75 K or more, even more preferably 1.0 K or more, and in particular 1.5 K or more.

The present invention further provides a production plant for production of polyisobutene, comprising at least the following plant parts:

- at least one apparatus for provision of the isobutene-containing monomer mixture, selected from the group consisting of conduit, tank and buffer vessel,
- at least two reservoir vessels for at least one Lewis acid and at least one cocatalyst,
- metering apparatus for the at least one Lewis acid and at least one cocatalyst into the isobutene-containing monomer mixture
- cooling system
- at least one reaction system for conversion of the isobutene-containing monomer mixture, comprising at least one reactor, heat exchanger and conduits,

- at least one vessel for ending the reaction by injecting water or alcohol, and
- at least one distillation apparatus for working up the reaction mixture,

in which,

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in the reaction system, the ratio of cooled surface area S_{cool} and reaction volume V is subject to the inequation

$S_{cool}/V \geq 50 \text{ m}^2/\text{m}^3$, preferably at least 55, more preferably at least 60, even more preferably at least 70 and in particular at least $80 \text{ m}^2/\text{m}^3$, and

- 10 - the ratio of cooled surface area S_{cool} and uncooled surface area S_{uncool} is subject to the inequation

$S_{cool}/S_{uncool} \geq 5 [\text{m}^2/\text{m}^2]$, preferably at least 7, more preferably at least 10 and most preferably at least $12 [\text{m}^2/\text{m}^2]$.

- 15 The remarks made in respect of the process are also applicable to the production plant of the invention.

The present invention further provides for the use of such a production plant for production of polyisobutene having a number-average molecular mass M_n of 500 to 1 000 000 from isobutene or an isobutene-containing monomer mixture.

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The present invention further provides a process for producing polyisobutene from an isobutene-containing monomer mixture in the presence of at least one Lewis acid in such a production plant.

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Polyisobutene in the context of this document means homopolymers and copolymers comprising isobutene in polymerized form.

- 30 For the preparation of such homo- or copolymers comprising isobutene in copolymerized form, suitable isobutene sources in a preferred embodiment are either pure isobutene or, in another preferred embodiment, isobutene-containing C4 hydrocarbon streams, for example C4 raffinates, especially "raffinate 1", C4 cuts from isobutane dehydrogenation, C4 cuts from steamcrackers and from FCC crackers (fluid catalyzed cracking), provided that they have substantially been freed
- 35 of 1,3-butadiene present therein. A C4 hydrocarbon stream from an FCC refinery unit is also known as a "b/b" stream. Further suitable isobutene-containing C4 hydrocarbon streams are, for example, the product stream of a propylene-isobutane cooxidation or the product stream from a

metathesis unit, which are generally used after customary purification and/or concentration. Suitable C4 hydrocarbon streams comprise generally less than 500 ppm, preferably less than 200 ppm, of butadiene. The presence of 1-butene and of cis- and trans-2-butene is largely non-critical. Typically, the isobutene concentration in said C4 hydrocarbon streams is in the range from 40% to 60% by weight. For instance, raffinate 1 generally consists essentially of 30% to 50% by weight of isobutene, 10% to 50% by weight of 1-butene, 10% to 40% by weight of cis- and trans-2-butene and 2% to 35% by weight of butanes; in the polymerization process of the invention, the unbranched butenes in the raffinate 1 are generally virtually inert, and only the isobutene is polymerized. In a preferred embodiment, the monomer source used for polymerization is a C4 hydrocarbon stream having an isobutene content of 1% to 100% by weight, especially of 1% to 99% by weight, in particular of 1% to 90% by weight, more preferably of 30% to 60% by weight, especially a raffinate 1 stream, a b/b stream from an FCC refinery unit, a product stream from a propylene-isobutane cooxidation or a product stream from a metathesis unit.

Preferably, the content of isobutene in the C4 hydrocarbon stream is at least 40% and especially preferably at least 45% by weight.

Especially when a raffinate 1 stream is used as the isobutene source, it has been found to be useful to use water as the sole initiator or as a further initiator, especially when polymerization is effected at temperatures of -20°C to +30°C, particularly of 0°C to +20°C. However, at temperatures of -20°C to +30°C, in particular of 0°C to +20°C, it is possible to dispense with the use of an initiator when a raffinate 1 stream is used as the isobutene source.

The isobutene-containing monomer mixture mentioned may comprise small amounts of contaminants such as water, carboxylic acids or mineral acids without causing any critical yield or selectivity losses. It is useful to avoid accumulation of these impurities by removing such harmful substances from the isobutene-containing monomer mixture, for example, by adsorption on solid adsorbents such as activated carbon, molecular sieves or ion exchangers.

The proportion of comonomers other than isobutene in polyisobutene is generally not more than 10% by weight, preferably not more than 7.5% by weight, more preferably not more than 5% by weight, even more preferably not more than 2.5% by weight and in particular not more than 1% by weight.

The process of the invention can be used to produce polyisobutenes with a number-average molecular weight M_n of 500 to 1 000 000, preferably 500 to 250 000, more preferably 550 to 200 000, even more preferably 650 to 100 000 and in particular 750 to 50 000 g/mol.

The polydispersity, i.e. the quotient of weight-average MW and number-average molar mass M_n ($PDI = M_w/M_n$) is from 1.05 up to 3.5, preferably from 1.05 to 2.5, especially from 1.05 to 2.0 and in particular from 1.1 to 1.85. Typical PDI values for optimal processing are 1.2 to 1.7.

- 5 Molar mass is determined by gel permeation chromatography with polystyrene as the standard.

Among these polyisobutenes, preference is given to those having a high content of terminal ethylenic double bonds (α double bonds), particularly those having a content of α double bonds of at least 50 mol%, preferably at least 60 mol%, more preferably at least 70 mol%, even more preferably at least 80 mol% and in particular at least 90 mol%. These are referred to as highly reactive polyisobutenes, and the formation of the terminal ethylenically unsaturated double bonds is particularly sensitive to any variation in the reaction temperature.

15 The process of the invention is run at different reaction temperatures depending on the desired molar mass of the polyisobutene:

In a preferred embodiment of the present invention, when the aim is a polyisobutene with a number-average molar mass M_n of 500 to 5000, the reaction temperature in the reaction mixture is preferably from minus 5 (-5) to 25°C.

20 More preferably, this homo- or copolymer is a highly reactive polyisobutene having a content of terminal vinylidene groups of at least 70 mol%, preferably at least 80 mol%, more preferably at least 90 mol%.

25 In an alternative preferred embodiment of the present invention, when a number average molar mass M_n of 10 000 to 100 000 is the aim, the reaction temperature in the reaction mixture is preferably from -10 to -30°C.

30 In an alternative preferred embodiment of the present invention, when a number average molar mass M_n of at least 150 000 to 1 000 000 is the aim, the reaction temperature in the reaction mixture is preferably from -50 to -90°C.

The average dwell time in the reaction system without mixing, for example by recirculation, stirring or backmixing, should generally be less than 2 hours, preferably less than 90 minutes and 35 more preferably less than 60 minutes.

The polymerization is generally conducted at a pressure of 700 mbar to 20 bar, especially at a pressure of 1 bar to 10 bar, in particular at a pressure of 1.2 bar to 7 bar. An elevated pressure

normally brings benefits for the C₄ hydrocarbon mixture used and for some inert diluents that may be used.

The polymerization reactors used for the process according to the invention may in principle be all batchwise or continuous reactor types suitable for such liquid phase polymerizations, for example stirred tanks, stirred tank cascades, tubular reactors or loop reactors. If the polymerization by the process of the invention is effected at or above the boiling temperature of any inert diluents used or of the monomer to be polymerized, it is preferably conducted in pressure vessels, for example in autoclaves or in pressure reactors.

It is also important that polymerizable compounds in containers are agitated, for example by stirring, natural circulation or pumped (forced) circulation.

The polymerization by the process of the invention can be conducted in the presence of an inert diluent. The inert diluent used should be capable of reducing the increase in viscosity of the reaction solution that generally occurs during the polymerization reaction, such that dissipation of the heat of reaction that arises can be assured. Suitable diluents are solvents or mixtures of solvents that are inert with respect to the reagents used. Suitable diluents are, for example, aliphatic hydrocarbons such as n-butane, n-pentane, n-hexane, n-heptane, n-octane and isooctane, cycloaliphatic hydrocarbons such as cyclopentane and cyclohexane, aromatic hydrocarbons such as benzene, toluene and the xylenes, and halogenated hydrocarbons, in particular halogenated aliphatic hydrocarbons such as methyl chloride, dichloromethane, trichloromethane (chloroform), 1,1-dichloroethane, 1,2-dichloroethane, trichloroethane and 1-chlorobutane, halogenated aromatic hydrocarbons and alkylaromatics halogenated in the alkyl side chains, such as chlorobenzene, monofluoromethylbenzene, difluoromethylbenzene and trifluoromethylbenzene, and mixtures of the above diluents. The diluents should appropriately be freed of impurities such as water or mineral acids prior to use, for example by adsorption onto solid adsorbents such as activated carbon, molecular sieves or ion exchangers. It is of course also possible for the inert portions of the isobutene-containing C₄ hydrocarbon mixture used as starting material to act as diluents or as components of the solvent mixtures mentioned.

In a preferred embodiment, no further diluents which increase the heat capacity of the reaction mixture and have to be cooled down as well are added to the reaction mixture.

The reaction mixture may be mono- or polyphasic, preferably monophasic. Typically, gaseous, liquid and solid components are present alongside one another; the reaction mixture is preferably kept in liquid form, and the liquid reaction mixture may also include solid constituents, for example polymer or Lewis acid.

Preferably, the polymerization by the process of the invention is conducted under largely aprotic and in particular under largely anhydrous reaction conditions. What is meant by largely aprotic or largely anhydrous reaction conditions is that the water content (or the content of protic impurities) in the reaction mixture is less than 50 ppm by weight and in particular less than 5 ppm by weight. In general, the feedstock is therefore dried before use by physical and/or chemical measures. In particular, it has been found to be useful to add an organometallic compound, for example, an organolithium, organomagnesium or organoaluminum compound, to aliphatic or cycloaliphatic hydrocarbons used as diluent, after customary prepurification and predrying, in an amount sufficient to largely remove the traces of water from the solvent. The solvent thus treated is then preferably condensed directly into the reaction vessel. A similar procedure may also be followed for the isobutene-containing C₄ hydrocarbon mixture. Also suitable is drying with other customary desiccants such as molecular sieves or predried oxides such as aluminum oxide, silicon dioxide, calcium oxide or barium oxide. The halogenated solvents, for which drying with metals such as sodium or potassium or with metal alkyls is not an option, are freed of water or traces of water with desiccants suitable for the purpose, for example with calcium chloride, phosphorus pentoxide or molecular sieve.

In order to stop the reaction, the reaction mixture is preferably deactivated, for example by adding sufficient amounts of a protic compound, in particular by adding water, alcohols such as methanol, ethanol, n-propanol and isopropanol or mixtures thereof with water, or by adding an aqueous base, for example an aqueous solution of an alkali metal or alkaline earth hydroxide such as sodium hydroxide, potassium hydroxide, magnesium hydroxide or calcium hydroxide, an alkali metal or alkaline earth carbonate such as sodium carbonate, potassium carbonate, magnesium carbonate or calcium carbonate, or an alkali metal or alkaline earth hydrogencarbonate such as sodium hydrogencarbonate, potassium hydrogencarbonate, magnesium hydrogencarbonate or calcium hydrogencarbonate.

The workup of the reaction mixture comprises at least one phase separation in which the water, alcohol or aqueous solution added to stop the reaction is separated from the organic phase of the reaction mixture. This can optionally be assisted by adding further water or aqueous solutions in order to wash the reaction mixture.

The low boilers present in the reaction mixture are then removed by distillation.

The low boilers may be unconverted isobutene, nonreacting constituents of the C₄ hydrocarbon stream used as starting material, and solvents. Also separated off are lower oligomers, such as diisobutene, triisobutene, etc.

Unconverted isobutene and the lower oligomers are preferably at least partly returned to the reaction.

- 5 The distillative removal of these low boilers may be effected discontinuously or preferably continuously and in one or more stages, preferably one or two stages, more preferably two stages. A continuous and at least two-stage distillative separation is preferred, wherein the last stage in each case is effected under reduced pressure, for example from 10 mbar to standard pressure, preferably from 20 to 900 mbar and more preferably from 30 to 800 mbar, and a temperature of
10 60 to 250°C, preferably 80 to 200°C and more preferably 100 to 190°C.

It will be apparent that the distillation can also be effected in a falling-film or thin-film evaporator. For this purpose, the mixture is run through the apparatus preferably repeatedly in circulation, under reduced or standard pressure, for example from 10 mbar to standard pressure, preferably
15 20 to 900 mbar and more preferably 30 to 800 mbar, and a temperature of 60 to 250°C, preferably 80 to 200°C and more preferably 100 to 190°C.

It is advantageously possible to introduce an inert gas, preferably argon or a nitrogen-containing gas, more preferably argon, nitrogen or a mixture of air and nitrogen (lean air), most preferably
20 nitrogen, into the distillation apparatus, for example 0.1-1, preferably 0.2-0.8 and more preferably 0.3-0.7 m³/m³h, based on the volume of the liquid mixture.

In a particularly preferred variant, degassing can also be effected in a vessel with internals that promote degassing.
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Possible apparatuses for degassing are also paddle driers with or preferably without a cooling zone, optionally with forced discharge devices.

Such usable paddle driers preferably have no separation in the heating and cooling zone, in order not to cause any abrupt drop in temperature. Instead, the temperature of the residue rises as the residue passes through the apparatus, preferably by a temperature gradient that varies over the course of the passage of the residue through the apparatus by not more than 50°C, and there is more preferably no significant temperature change in the course of the passage of the residue through the apparatus, i.e. less than 20°C and in particular less than 10°C.
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35 Such paddle driers are of essentially horizontal construction, and the residue is generally conveyed via one or two mixing and kneading shafts in the interior of the apparatus. In the technical

literature, these apparatuses are also referred to as particle bed reactors, kneader-driers or kneader-reactors.

5 It is preferable when the paddle drier has forced conveying in axial direction. Forced conveying is achieved, for example, by an oblique position of the surfaces of the conveying elements.

Axial transport through the apparatus can preferably be effected by arrangement of conveying, kneading and/or mixing elements, for example disk elements, shafts, screws, blades, wipers or rotors.

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It is particularly preferable when the residence time distribution in the paddle drier is narrowed by separating the product-conducting interior into various segments with baffle-like plates. More preferably, at least two plates are used.

15 Heating is effected via the wall and may be effected in any desired manner. Heating is preferably effected not only via the outer wall of the apparatus but also via the internals such as cleaning hooks, segmenting plates and kneading shafts.

The thermal energy input into the reactor contents via the walls is typically more than 120 kJ/kg of reactor contents and less than 2400 kJ/kg of reactor contents, preferably more than
20 220 kJ/kg of reactor contents and less than 1800 kJ/kg of reactor contents, more preferably more than 300 kJ/kg of reactor contents and less than 1400 kJ/kg of reactor contents, and most preferably more than 360 kJ/kg of residue and less than 900 kJ/kg of reactor contents.

25 The distance over which the reaction mixture applied to the paddle drier is heated is preferably more than 10% and less than 70% of the total length of the paddle drier, preferably more than 20% and less than 60%, more preferably more than 30% and less than 50% of the total length of the paddle drier.

30 A mechanical energy input of 5 W/kg or more in the apparatus is generally sufficient, preferably 10 or more W/kg, more preferably 20 or more, even more preferably 40 or more, in particular 80 or more and especially 100 W/kg or more. An energy input of more than 200 W/kg generally brings no benefits. The reported specific power input here is the power input per amount of reaction mixture in the apparatus.

35 It is further advantageous that the paddle drier has forced cleaning of the inner surfaces that come into contact with product of at least 50%, preferably at least 60%, even more preferably of at least 70% and especially at least 80% of these inner surfaces that come into contact with

product. Forced cleaning is accomplished by the proximity of the conveying elements to the outer wall/by the proximity of cleaning hooks to the conveying elements.

Such apparatuses are available, for example, from List AG, Arisdorf, Switzerland, under the Dis-
 5 cotherm® B or List-CRP or AP trade name, and also from Buss-SMS-Canzler GmbH, Butzbach, Germany under the Reasol® or Reactotherm® trade name.

It is optionally possible for there to be discharge means for the forced discharge of the reaction output, for example screws, preferably twin screws.

10

However, the mechanical conveying means of the apparatus are usually sufficient to discharge the product from the apparatus.

Preferred Lewis acids are boron halides, for example boron trichloride, boron trifluoride or boron
 15 tribromide, preferably boron trifluoride.

The reactivity of the boron halides is moderated with the aid of one or more cocatalysts that form a complex together with the boron halide.

20 Cocatalysts used are preferably:

C₁- to C₅-alkanols, for example methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-buta-
 nol, iso-butanol, tert-butanol. These alkanols are preferably also used as a mixture of two alka-
 nols, preferably as a mixture of a primary and a secondary alcohol.

25

Aldehydes or ketones having 1 to 20 and preferably 2 to 10 carbon atoms, for example formal-
 dehyde, acetaldehyde, propionaldehyde, n-butyraldehyde, isobutyraldehyde, acetone, methyl
 ethyl ketone or diethyl ketone.

30 Ethers having 2 to 10 carbon atoms, for example dialkyl ethers or cyclic ethers. Examples are dimethyl ether, diethyl ether, diisopropyl ether, di-n-butyl ether, tert-butyl methyl ether, bis(chlo-
 roethyl) ether, chloroethyl ethyl ether, tetrahydrofuran or dioxane.

Carboxylic esters having 2 to 20 carbon atoms, for example C₁-C₄-alkyl formates, C₁-C₄-alkyl
 35 acetates or C₁-C₄-alkyl butyrates.

The molar ratio of boron trihalide to the sum total of all cocatalysts is usually 2:1 to 1:10, prefer-
 ably from 1.5:1 to 1:5, especially from 1.25:1 to 1:2, in particular from 1:1 to 1:1.5. The amount

of cocatalyst can influence the establishment of the molecular weight of the isobutene homopolymer to be achieved and hence serve for controlled adjustment of its molecular weight.

The amount of polymerization catalyst to be used is guided essentially by the type of cocatalyst and by the reaction conditions, especially the reaction temperature and the desired molecular weight of the polymer. This can be determined on the basis of a few test runs for the respective reaction system. In general, the polymerization catalyst is used in amounts of 0.0001% to 1% by weight, especially 0.0005% to 0.5% by weight, in particular 0.001% to 0.1% by weight, based in each case on the boron trihalide content in the catalyst complex and on isobutene used.

As an alternative to the preferred boron trihalides, Lewis acids used may also be aluminum halides, C₁- to C₄-alkylaluminum halides, C₁- to C₄-alkoxyaluminum halides, C₁- to C₄-alkoxy-C₁- to C₄-alkylaluminum halides, iron halides, gallium halides, titanium halides, zinc halides, tin dihalides and tin tetrahalides. Among these, preference is given to aluminum halides, C₁- to C₄-alkylaluminum halides, iron halides and titanium halides, particular preference to aluminum halides and C₁- to C₄-alkylaluminum halides and very particular preference to aluminum halides.

Among the halides in the case of these latter Lewis acids, preference is given to chlorides and bromides, particular preference to the chlorides.

The latter Lewis acids are also used together with the abovementioned cocatalysts; the type and amount of the cocatalysts are also applicable to these Lewis acids.

It is an advantage of the process of the invention that the energy efficiency of the production process is improved since the heat input into the reaction mixture from the outside is reduced, the heat of reaction released can be removed at a higher temperature level, which improves the efficiency of the chillers and/or allows smaller amounts of solvents or diluents to be used.

Increasing energy efficiency accordingly reduces the energy consumption of the process, which indirectly reduces emissions associated with energy supply.

Accordingly, the present invention further provides a process for reducing emissions, in particular carbon dioxide emissions, preferably determined as carbon footprint or life cycle assessment, more preferably according to DIN EN ISO 14021, DIN EN ISO 14067, here in particular the 2019-02 version, DIN EN ISO 14044, here in particular the 2006 + A1:2018 version, and/or DIN EN ISO 14040, here in particular the 2009-11 version, in which polyisobutene is produced by the process of the invention.

Furthermore, the measures of the invention keep the reaction temperature more constant than without. Without these measures, a greater rise in reaction temperature arises in the reaction mixture, and this, because of the dependence in particular of the molecular weight of the polyisobutene formed on temperature, leads to increased formation of higher molecular weight polyisobutene, i.e. to an increase in inhomogeneity of the molar mass of the polyisobutene, which is expressed in elevated polydispersity. The measures of the invention can thus reduce the polydispersity of the polyisobutene in the process.

Examples

The reaction system for production of polyisobutene with a molar mass of 1000 g/mol consists of a loop reactor that can be divided into 2 subregions: The heat exchanger (cooled reaction volume) (reaction temperature -15°C as starting temperature of the heat exchanger), which consists of a shell and tube heat exchanger with the data and dimensions specified below, in which the reacting medium (raffinate 1, isobutene content 46% by weight, feed temperature 4°C) in the interior of the pipes is pumped through a loop and with the aid of a pumping device. Outside the pipes, but inside the shell and tube heat exchanger, the cooling medium (liquid ammonia at boiling point) removes the heat of reaction. The inner surface of these heat exchanger tubes constitutes the cooled surface.

The second part of the reaction system consists essentially of the loop which is required to keep the reaction medium in motion by means of a pumped circulation device and hence to ensure maximum uniformity of distribution of isobutene, polymer formed and diluent. At the same time, the pumped circulation of the reaction medium in the desired manner facilitates heat transfer in the heat exchanger. Although the surface of the loop is usually insulated, it is generally not cooled owing to its design. The inner surface of all pipelines and apparatuses in the loop (e.g. the pumped circulation device) therefore constitutes the uncooled surface.

A measure used for the efficiency of the shell and tube heat exchanger is the temperature drop across the heat exchanger, i.e. the difference between the temperature at the outlet and the temperature at the inlet of the cooler. This is a measure of the heat to be removed from the uncooled reaction volume. The smaller the temperature drop, the more uniform the reaction temperature of the polymerization.

Example 1

In the energy-efficient inventive example, the reactor, a cooled shell and tube heat exchanger, is characterized by the following data:

Number of tubes:	1356
Diameter of tubes:	0.016 m
Length of tubes:	3.00 m
Shell area per tube:	0.15 m ²
Volume per tube:	0.0006 m ³
Total cooled area:	204.5 m ²
Tube volume (cooled reactor volume):	0.82 m ³

5 The uncooled loop of the reaction system is characterized by the following data:

Suction side length:	7.00 m
Pressure side length:	8.00 m
Diameter:	0.40 m
Loop area:	18.85 m ²
Loop volume:	1.88 m ³
+ volume of each of 2 domed ends	0.4 m ³
+ area of each of 2 domed ends	0.7 m ²
Outer area of reactor (diameter 0.9 m, length 3 m)	8.5 m ²
Total uncooled area	28.75 m ²
S_{cool}/S_{uncool}	7.11 [m ² /m ²]
Total area of reaction system:	223.3 m ²
Total volume of cooled reaction system:	0.82 m ³
Total volume of uncooled reaction system:	2.68 m ³
Total volume	3.50 m ³

Ratio of cooled surface area to total volume: $204.5 \text{ m}^2 / 3.50 \text{ m}^3 = 58.4 \text{ m}^2/\text{m}^3$

Ratio of cooled to uncooled surface area: $204.5 \text{ m}^2 / 28.75 \text{ m}^2 = 7.11 [\text{m}^2/\text{m}^2]$

Temperature drop across the cooler: -1.9 K

5

Example 2

10 In the energy-efficient inventive example, the reactor, a cooled shell and tube heat exchanger, is characterized by the following data:

Number of tubes:	1356
Diameter of tubes:	0.016 m
Length of tubes:	8.00 m
Shell area per tube:	0.40212 m^2
Volume per tube:	0.0016 m^3
Total cooled area:	545.28 m^2
Tube volume (cooled reactor volume):	2.18 m^3

15 The uncooled loop of the reaction system is characterized by the following data:

Suction side length:	7.00 m
Pressure side length:	8.00 m
Diameter:	0.40 m
Loop area:	18.85 m^2
Loop volume:	1.88 m^3
+ volume of each of 2 domed ends	0.4 m^3
+ area of each of 2 domed ends	0.7 m^2
Outer area of reactor (diameter 0.9 m, length 8 m)	22.6 m^2
Total uncooled area	42.85 m^2

$S_{\text{cool}}/S_{\text{uncool}}$	12.73 [m ² /m ²]
Total area of reaction system:	588.1 m ²
Total volume of cooled reaction system:	2.18 m ³
Total volume of uncooled reaction system:	2.68 m ³
Total volume (cooled + uncooled)	4.86 m ³

Ratio of cooled surface area to total volume: $588.1 \text{ m}^2 / 4.86 \text{ m}^3 = 121.0 \text{ [m}^2/\text{m}^3\text{]}$

Ratio of cooled to uncooled surface area: $588.1 \text{ m}^2 / 42.85 \text{ m}^2 = 13.7 \text{ [m}^2/\text{m}^2\text{]}$

5 Temperature drop across the cooler: -1.3 K

The temperature drop in the cooler is balanced by an equally high increase in temperature by virtue of the heat of reaction released in the uncooled part of the reaction system, which is removed in the cooler.

- 10 It can be seen that, with increasing quotients S_{cool}/V or $S_{\text{cool}}/S_{\text{uncool}}$, this increase in temperature in the reaction system is smaller, and so the reaction system is subject to smaller temperature fluctuations.

Claims

1. A process for producing polyisobutenes having a number-average molecular weight M_n of 500 to 1 000 000 from isobutene or an isobutene-containing monomer mixture,
 5 which comprises performing the reaction in a reaction system wherein
 - the ratio of cooled surface area S_{cool} and reaction volume V is subject to the inequation

$$S_{cool}/V \geq 50 \text{ m}^2/\text{m}^3$$
, preferably at least 55, more preferably at least 60, even more preferably at least 70 and in particular at least $80 \text{ m}^2/\text{m}^3$, and
 10 - the ratio of cooled surface area S_{cool} and uncooled surface area S_{uncool} is subject to the inequation

$$S_{cool}/S_{uncool} \geq 5 [\text{m}^2/\text{m}^2]$$
, preferably at least 7 and more preferably at least 10 $[\text{m}^2/\text{m}^2]$, most preferably at least 12,
 where the reaction mixture is circulated through at least one cooled heat exchanger
 15 and isobutene-containing feed is fed into this circulated reaction mixture and the corresponding amount is taken from the circuit,
 where the heat exchanger is selected from the group consisting of temperature-controllable tubular reactors, shell and tube heat exchangers, plate heat exchangers and temperature-controllable tubular reactors with internals.
 20
2. The process according to claim 1, wherein the ratio of cooled surface area S_{cool} and reaction volume V , S_{cool}/V does not exceed the value of $250 \text{ m}^2/\text{m}^3$.
3. The process according to claim 1 or 2, wherein the isobutene-containing monomer mixture is pure isobutene.
 25
4. The process according to claim 1 or 2, wherein the isobutene-containing monomer mixture is a C4 hydrocarbon stream comprising not only isobutene but also 1-butene and cis- and trans-2-butene.
 30
5. The process according to any of the preceding claims, wherein the reaction is performed in the presence of at least one Lewis acid selected from the group consisting of boron halides, aluminum halides, C₁- to C₄-alkylaluminum halides, C₁- to C₄-alkoxyaluminum halides, C₁- to C₄-alkoxy-C₁- to C₄-alkylaluminum halides, iron halides, gallium halides, titanium halides, zinc halides, tin dihalides and tin tetrahalides.
 35

6. The process according to claim 5, wherein, in addition to the Lewis acid, at least one cocatalyst selected from the group consisting of C₁- to C₅-alkanols, aldehydes or ketones having 1 to 20 carbon atoms, ethers having 2 to 10 carbon atoms and carboxylic esters having 2 to 20 carbon atoms is used.
- 5
7. The process according to any of the preceding claims, wherein the cooled surface area S_{cool} is in contact with a cooling medium having a temperature differential from the reaction mixture of at least 5 K.
- 10
8. The process according to any of the preceding claims, wherein the cooled surface area S_{cool} is in contact with a cooling medium having a temperature differential from the reaction mixture of not more than 30 K.
- 15
9. The process according to any of the preceding claims, wherein the volume of the circulated reaction mixture is preferably at least 15 times and not more than 100 times the fresh isobutene-containing feed.
- 20
10. The process according to any of the preceding claims, wherein the temperature rise in the uncooled reaction volume is not more than 2.5 K compared to the inlet temperature into the uncooled reaction volume, preferably not more than 2.2 K, more preferably not more than 2.0 K and most preferably not more than 1.8 K.
- 25
11. The process according to any of the preceding claims, wherein the temperature rise in the uncooled reaction volume is 0.3 K or more.
- 30
12. The process for producing polyisobutenes having a number-average molecular weight Mn of 500 to 5000 according to any of the preceding claims, wherein the reaction temperature in the reaction mixture is from -5 to 25°C.
- 35
13. The process for producing polyisobutenes with a number-average molecular weight Mn of 10 000 to 100 000 according to any of claims 1 to 9, wherein the reaction temperature in the reaction mixture is from -10 to -30°C.
14. The process for producing polyisobutenes with a number-average molecular weight Mn of 150 000 to 1 000 000 according to any of claims 1 to 9, wherein the reaction temperature in the reaction mixture is from -50 to -90°C.

15. A process for reducing emissions in the production of polyisobutenes with a number-average molecular weight M_n of 500 to 1 000 000 from isobutene or an isobutene-containing monomer mixture, in particular carbon dioxide emissions, preferably determined as carbon footprint or life cycle assessment, more preferably according to DIN EN ISO 14021, DIN EN ISO 14067, here in particular the 2019-02 version, DIN EN ISO 14044, here in particular the 2006 + A1:2018 version, and/or DIN EN ISO 14040, here in particular the 2009-11 version, which comprises producing the polyisobutene by a process according to any of claims 1 to 11.

16. The use of a production plant for production of polyisobutenes having a number-average molecular weight M_n of 500 to 1 000 000 from isobutene or an isobutene-containing monomer mixture, comprising at least the following plant components:

- at least one apparatus for provision of the isobutene-containing monomer mixture, selected from the group consisting of conduit, tank and buffer vessel,
- at least two reservoir vessels for at least one Lewis acid and at least one cocatalyst,
- metering apparatus for the at least one Lewis acid and at least one cocatalyst into the isobutene-containing monomer mixture
- cooling system
- at least one reaction system for conversion of the isobutene-containing monomer mixture, comprising at least one reactor, heat exchanger and conduits, where the heat exchanger is selected from the group consisting of temperature-controllable tubular reactors, shell and tube heat exchangers, plate heat exchangers and temperature-controllable tubular reactors with internals, and wherein the reaction mixture can be circulated via at least one cooled heat exchanger,
- at least one vessel for ending the reaction by injecting water or alcohol, and
- at least one distillation apparatus for working up the reaction mixture,

in which,

in the reaction system, the ratio of cooled surface area S_{cool} and reaction volume V is subject to the inequation

$S_{cool}/V \geq 50 \text{ m}^2/\text{m}^3$, preferably at least 55, more preferably at least 60, even more preferably at least 70 and in particular at least $80 \text{ m}^2/\text{m}^3$, and

- the ratio of cooled surface area S_{cool} and uncooled surface area S_{uncool} is subject to the inequation

$S_{cool}/S_{uncool} \geq 5 [\text{m}^2/\text{m}^2]$, preferably at least 7, more preferably at least 10 and most preferably at least $12 [\text{m}^2/\text{m}^2]$.