

Improved method for the depolymerization of polyethylene terephthalate

The present invention relates to a method of depolymerization of polyethylene terephthalate (= "PET"), in which PET is reacted with sodium ethyleneglycolate or potassium ethyleneglycolate that
 5 has been obtained by a reactive distillation to give a mixture **M₁** comprising bis-2-hydroxyethyl terephthalate (= "**BHET**"; CAS No.: 959-26-2).

It is a feature of the method according to the invention that **BHET** forms a particularly high proportion among the cleavage products in the mixture **M₁**. As a result, the method according to the
 10 invention affords a high yield of **BHET**, which can be used directly for new production of **PET**.

The present invention thus also relates to a method of recycling **PET**, in which the **BHET** obtained in the method of depolymerization of **PET**, optionally after further purification from **M₁**, is polymerized again to give **PET**.
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Background of the invention

Polyethylene terephthalate (= "**PET**") is one of the most important plastics which is used in textile fibres, as films, and as material for plastic bottles. In 2007 alone, the volume used in plastic bottles
 20 was ~ 10⁷ t (W. Caseri, Polyethylenterephthalate, RD-16-03258 (2009) in F. Böckler, B. Dill, G. Eisenbrand, F. Faupel, B. Fugmann, T. Gamse, R. Matissek, G. Pohnert, A. Rühling, S. Schmidt, G. Sprenger, RÖMPP [Online], Stuttgart, Georg Thieme Verlag, January 2022).

On account of its persistence and the volumes of refuse originating from **PET**, it constitutes one of the greatest environmental challenges at present. The solution to this problem lies in the avoidance
 25 and in the efficient reutilization of **PET**.

The prior art proposes multiple methods of cleavage of **PET**.

GB 784,248 A describes the methanolysis of **PET**.

Hydrolytic methods for depolymerization of **PET** are described by JP 2000-309663 A, US 4,355,175 A and T. Yoshioka, N. Okayama, A. Okuwaki, Ind. Eng. Chem. Res. **1998**, 37, 336-340.
 30 The reaction of **PET** with glycol is described in EP 0723951 A1, US 3,222,299 A, WO 2020/002999 A2, by S.R. Shukla, A.M. Harad, Journal of Applied Polymer Science **2005**, 97, 513-517 ("Shukla & Harad" hereinafter) and by N.D. Pingale, S.R. Shukla, European Polymer Journal **2008**, 44, 4151-4156.

35 Shukla & Harad state that PET glycolysis gives rise to bis-2-hydroxyethyl terephthalate (= "**BHET**"). This cleavage product may simultaneously be used as reactant for production of new **PET**.

There is accordingly an interest in methods of depolymerization of **PET** in which a maximum proportion of **BHET** is obtained among the cleavage products.

The problem addressed by the present invention was that of providing such a method.

5 **Brief description of the invention**

A method that solves the problem addressed by the invention has now surprisingly been found.

10 The present invention relates to a method of depolymerization of polyethylene terephthalate **PET**, comprising the following steps:

(a) converting M_AOR and glycol in a reactive distillation to obtain a solution S_{AP} comprising glycol and M_A glycolate, where M_A is an alkali metal selected from sodium, potassium, preferably M_A = sodium, and where R is an alkyl radical having 1 to 4, especially 1 to 3, preferably 1 or 2, carbon
15 atoms, and most preferably R = methyl,

(b) reacting the solution S_{AP} with **PET** to give a mixture M_1 comprising bis-2-hydroxyethyl terephthalate (**BHET**).

20 Preferably, S_{AP} is obtained in step (a) by reacting a reactant stream S_{AE1} comprising glycol with a reactant stream S_{AE2} comprising M_AOR in countercurrent in a reactive rectification column RR_A to give a crude product RP_A comprising M_A glycolate, ROH, glycol, M_AOR ,

wherein S_{AP} is withdrawn as bottom product stream at the lower end of RR_A .
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Optionally, a vapour stream S_{AB} comprising ROH, with or without glycol, is withdrawn at the upper end of RR_A .

In a further aspect, the present invention relates to a method of recycling **PET**, in which **BHET**
30 obtained in the method according to the invention for depolymerization is polymerized in a step (ζ) to give **PET**.

It has been found that, surprisingly, the reaction of the **PET** with the S_{AP} obtained from the alkoxide M_AOR by reactive distillation affords a higher proportion of **BHET** than in conventional methods in
35 which the alkaline alkali metal glycolate solution is obtained by mixing the glycol in the corresponding alkali metal hydroxide.

Detailed description of the invention

It has now been found that, surprisingly, the glycolysis of **PET** proceeds particularly efficiently when sodium glycolate or potassium glycolate that has been obtained by reactive distillation is used. In the reactive distillation according to the invention, the glycolate is obtained by reaction of the corresponding alkali metal alkoxide M_AOR with glycol. It has now been observed that, in the method according to the invention, by comparison with the prior art methods in which glycolate that has been obtained by dissolution of the alkali metal hydroxides in glycol is used, a higher proportion of **BHET** is obtained in the cleavage product.

1. Step (a): Reactive distillation to obtain the solution S_{AP} comprising glycol and M_A glycolate

According to the invention, the solution S_{AP} comprising glycol and M_A glycolate which is used in the method according to the invention is obtained by means of reactive distillation, by conversion of M_AOR and glycol.

M_A is an alkali metal selected from sodium, potassium. M_A is preferably sodium.

R is an alkyl radical having 1 to 4 carbon atoms, preferably an alkyl radical having 1 to 3 carbon atoms, more preferably methyl or ethyl, most preferably methyl.

Alkyl radicals having 1 to 4 carbon atoms are especially selected from methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *sec*-butyl, *tert*-butyl, preferably selected from methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *tert*-butyl, more preferably selected from methyl, ethyl, *iso*-propyl, *tert*-butyl.

Alkyl radicals having 1 to 3 carbon atoms are selected from methyl, ethyl, *n*-propyl, *iso*-propyl, preferably selected from methyl, ethyl, *iso*-propyl.

Reactive distillation for preparation of alkali metal alkoxides is an important industrial process since alkali metal alkoxides are used as strong bases in the synthesis of numerous chemicals, for example in the production of active pharmaceutical or agrochemical ingredients, and as catalysts in transesterification and amidation reactions.

Alkali metal alkoxides ($MOR^\#$) are prepared by means of reactive distillation, typically in a countercurrent distillation column, from alkali metal hydroxides (MOH) and alcohols ($R^\#OH$), with removal of the water of reaction formed according to the following reaction <1> together with the distillate:



Such a method principle is described, for example, in US 2,877,274 A, wherein aqueous alkali metal hydroxide solution and gaseous methanol are conducted in countercurrent in a rectification column. This method is described again in basically unchanged form in WO 01/42178 A1.

- 5 The most industrially important alkali metal alkoxides are those of sodium and potassium, especially the methoxides and ethoxides. There are many descriptions of the synthesis thereof in the prior art, for example in EP 1 997 794 A1, WO 2021/148174 A1 and WO 2021/148175 A1.

10 Methods that are similar, but in which an introducing agent, for example benzene, is additionally used, are described in GB 377,631 A and US 1,910,331 A.

Correspondingly, DE 96 89 03 C describes a method of continuous preparation of alkali metal alkoxides in a reaction column, wherein the water-alcohol mixture withdrawn at the top of the column is condensed and then subjected to a phase separation. The aqueous phase is discarded
15 and the alcoholic phase is returned to the top of the column together with the fresh alcohol. EP 0 299 577 A2 describes a similar method, wherein the water in the condensate is separated off with the aid of a membrane.

Rather than the alkali metal hydroxide, it is also possible to use a different alkali metal alkoxide
20 MOR* in a "transalcoholisation reaction" by reactive distillation and to react it with the alcohol R[#]OH to give the desired alkali metal alkoxide MOR[#] and the alcohol R*OH. R*OH here is typically an alcohol having a lower boiling point than R[#]OH. Typically, methanol is used as R*OH, and the methoxide as MOR*.

25 Such transalcoholisation reactions are described, for example, in DE 2726491 A1, EP 0776995 or WO 2021/122702 A1.

In a preferred embodiment of the method according to the invention, **S_{AP}** is obtained in step (a) by reacting a reactant stream **S_{AE1}** comprising glycol with a reactant stream **S_{AE2}** comprising M_AOR in
30 countercurrent in a reactive rectification column **RR_A** to give a crude product **RP_A** comprising M_A glycolate, ROH, glycol, M_AOR, wherein **S_{AP}** is withdrawn as bottom product stream at the lower end of **RR_A**.

Even more preferably, a vapour stream **S_{AB}** comprising ROH, with or without glycol, is withdrawn at
35 the upper end of **RR_A**.

According to the invention, a "reactive rectification column" is defined as a rectification column in which the reaction according to step (a) of the method according to the invention proceeds at least in some parts. It may also be referred to as "reaction column" for short.

In the preferred embodiment of the method according to the invention, a bottom product stream S_{AP} comprising glycol and M_A glycolate is withdrawn at the lower end of RR_A . A vapour stream S_{AB} comprising ROH, with or without glycol, is withdrawn at the upper end of RR_A .

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"Glycol" in the context of the invention is understood to mean ethylene-1,2-diol having the chemical formula $HO-CH_2-CH_2-OH$ (CAS No. 107-21-1).

" M_A glycolate" in the context of the invention is understood to mean the salt of the glycol with M_A .

- 10 The term " M_A glycolate" comprises at least one of $M_AO-CH_2-CH_2-OH$ and $M_AO-CH_2-CH_2-OM_A$, preferably at least $M_AO-CH_2-CH_2-OH$, most preferably $M_AO-CH_2-CH_2-OH$ and $M_AO-CH_2-CH_2-OM_A$.

M_A is an alkali metal selected from sodium, potassium, and is preferably sodium.

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The reactant stream S_{AE1} comprises glycol. In a preferred embodiment, the proportion by mass of glycol in S_{AE1} is $\geq 95\%$ by weight, still more preferably $\geq 99.5\%$ by weight, where S_{AE1} otherwise comprises especially water, diethylene glycol.

- 20 The glycol used as reactant stream S_{AE1} in the preferred embodiment of the method according to the invention may also be commercial glycol having a proportion by mass of glycol of more than 99.5% by weight and a proportion by mass of water of up to 0.03% by weight, up to 0.05% by weight, of diethylene glycol.

- 25 In one embodiment of the present invention, the reactant stream S_{AE1} is added in vaporous form to the reactive rectification column RR_A .

- 30 In an alternative, preferred embodiment of the method according to the invention, glycol is initially charged in the bottom of the reactive rectification column RR_A prior to step (a), and then heated to boiling in step (a), which produces a constant reactant stream S_{AE1} in the reactive rectification column RR_A . If necessary, glycol is then replenished in the bottom of the reactive rectification column RR_A during the performance of step (a).

- 35 The reactant stream S_{AE2} comprises M_AOR . In a preferred embodiment, S_{AE2} comprises not only M_AOR but also at least one further compound selected from ROH, glycol. Even more preferably, S_{AE2} comprises not only M_AOR but also ROH, in which case S_{AE2} is an alcoholic solution of M_AOR in ROH.

When the reactant stream **S_{AE2}** comprises M_AOR and ROH, the proportion by mass of M_AOR based on the total weight of the alcoholic solution in ROH that forms **S_{AE2}** is especially in the range from 5% to 75% by weight, preferably from 10% to 40% by weight, more preferably from 15% to 35% by weight and even more preferably from 21% to 30% by weight.

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In the case that R = methyl, the proportion by mass of M_AOR, based on the total weight of the alcoholic solution in ROH that forms **S_{AE2}**, is especially in the range from 25% to 35% by weight, preferably 30% by weight.

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In the case that R = ethyl, the proportion by mass of M_AOR, based on the total weight of the alcoholic solution in ROH that forms **S_{AE2}**, is especially in the range from 15% to 25% by weight, preferably 21% by weight.

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The reactant stream **S_{AE2}** preferably comprises little water, i.e. the portion of water in the reactant stream **S_{AE2}** is preferably < 1% by weight, more preferably < 0.2% by weight, even more preferably < 0.1% by weight, even more preferably < 0.01% by weight, based in each case on the total weight of the reactant stream **S_{AE2}**.

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Step (a) of the method according to the invention is preferably performed in a reactive rectification column (or "reaction column") **RR_A**.

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The reaction column **RR_A** preferably contains internals. Suitable internals are, for example, trays, structured packings or unstructured packings. When the reaction column **RR_A** contains trays, suitable trays are bubble-cap trays, valve trays, tunnel-cap trays, Thormann trays, cross-slit bubble-cap trays or sieve trays. When the reaction column **RR_A** contains trays, it is preferable to choose trays where not more than 5% by weight, more preferably less than 1% by weight, of the liquid trickles through the respective trays. The construction measures required to minimize trickle-through of the liquid are familiar to those skilled in the art. In the case of valve trays, particularly tightly closing valve designs are selected for example. Reducing the number of valves also makes it possible to increase the vapour velocity in the tray openings to twice the value typically established. When using sieve trays it is particularly advantageous to reduce the diameter of the tray openings while maintaining or even increasing the number of openings.

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When using structured or unstructured packings, structured packings are preferred in terms of uniform distribution of the liquid.

Step (a) of the method according to the invention may be carried out either continuously or batchwise. It is preferably effected continuously.

“Reaction of a reactant stream S_{AE1} comprising glycol with a reactant stream S_{AE2} comprising M_{AOR} in countercurrent in a reactive rectification column RR_A ” is achieved in one embodiment of the invention, in particular, by virtue of the feed point for at least a portion of the reactant stream S_{AE1} comprising glycol being located in the reaction column RR_A below the feed point for the
 5 reactant stream S_{AE2} comprising M_{AOR} .

In an alternative preferred embodiment, the “reaction of a reactant stream S_{AE1} comprising glycol with a reactant stream S_{AE2} comprising M_{AOR} in countercurrent in a reactive rectification column RR_A ” can also be achieved by virtue of the feed point for at least a portion of the reactant stream
 10 S_{AE1} comprising glycol being located in the reaction column RR_A above the feed point for the reactant stream S_{AE2} comprising M_{AOR} .

In this embodiment, the reaction column RR_A preferably comprises at least 2, in particular 15 to 40, theoretical plates between the feed point for the reactant stream S_{AE1} and the feed point for the
 15 reactant stream S_{AE2} .

The reaction column RR_A may be operated as a pure stripping column. In that case, the reactant stream S_{AE1} comprising glycol is introduced in vaporous form in the lower region of the reaction column RR_A .
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Optionally, a portion of the reactant stream S_{AE1} comprising glycol is added in vaporous form below the feed point for the reactant stream S_{AE2} comprising M_{AOR} , but nevertheless at the upper end or in the region of the upper end of the reaction column RR_A . This makes it possible to reduce the dimensions of the lower region of the reaction column RR_A . When a portion of the reactant stream
 25 S_{AE1} comprising glycol is added, especially in vaporous form, at the upper end or in the region of the upper end of the reaction column RR_A , preferably only a portion of 10% to 70% by weight, preferably of 30% to 50% by weight, (based in each case on the total amount of glycol used) is fed in at the lower end of the reaction column RR_A , and the remaining portion is added, in vaporous form in a single stream or divided into a plurality of substreams, preferably 1 to 10 theoretical
 30 plates, more preferably 1 to 3 theoretical plates, below the feed point for the reactant stream S_{AE2} comprising M_{AOR} .

In an alternative embodiment of step (a) of the method according to the invention, “reaction of a reactant stream S_{AE1} comprising glycol with a reactant stream S_{AE2} comprising M_{AOR} in
 35 countercurrent in a reactive rectification column RR_A ” is achieved, in particular, by virtue of glycol being present in the bottom of the reactive rectification column RR_A and the feed point for the reactant stream S_{AE2} comprising M_{AOR} being located above the bottom. During step (a) of the method according to the invention, glycol is then heated to boiling in the bottom of RR_A and a

reactant stream S_{AE1} comprising glycol is produced. S_{AE1} and S_{AE2} are then directed in countercurrent to one another.

In the reaction column RR_A , the reactant stream S_{AE1} comprising glycol then reacts with the reactant stream S_{AE2} comprising M_AOR to give M_A glycolate and ROH, with these products being present in a mixture with the glycol and M_AOR reactants since the reaction is an equilibrium reaction. Accordingly, step (a) affords a crude product RP_A in the reaction column RR_A that comprises not only the M_A glycolate and ROH products but also glycol and M_AOR .

At the lower end of RR_A , the bottom product stream S_{AP} comprising glycol and M_A glycolate is then obtained and withdrawn.

At the upper end of RR_A , preferably at the top of the column of RR_A , in a preferred embodiment of the method according to the invention, a stream of ROH that may or may not still contain glycol, referred to above as "vapour stream S_{AB} comprising ROH, with or without glycol" is withdrawn.

If the vapour stream S_{AB} contains not only ROH but also glycol, glycol is obtained, preferably by distillation, for example in a rectification column. In this embodiment, at least a portion of the glycol obtained in the distillation can be fed back to the reaction column RR_A as reactant stream S_{AE1} .

In a preferred embodiment, S_{AB} , when it comprises not only ROH but also glycol, is directed into a rectification column RD_A and is separated in RD_A into at least one vapour stream S_{OA} comprising ROH which is withdrawn at the upper end of RD_A , and at least one stream S_{UA} comprising glycol which is withdrawn at the lower end of RD_A .

The amount of glycol encompassed by the reactant stream S_{AE1} is preferably chosen such that said glycol simultaneously serves as a solvent for the M_A glycolate obtained in the bottom product stream S_{AP} . The amount of glycol in the reactant stream S_{AE1} is preferably chosen such that the desired concentration of the M_A glycolate solution which is withdrawn as bottom product stream S_{AP} comprising glycol and M_A glycolate is present in the bottom of the reaction column.

In a preferred embodiment of the method according to the invention, and especially in the cases in which S_{AE2} comprises not only M_AOR but also ROH, the ratio of the total weight (mass; unit: kg) of glycol used as reactant stream S_{AE1} to the total weight (mass; unit: kg) of M_AOR used as reactant stream S_{AE2} is 1:1 to 50:1, more preferably 2:1 to 40:1, even more preferably 3:1 to 30:1, yet more preferably 5:1 to 13.5 :1.

The reaction column RR_A in the preferred embodiment of the method according to the invention is operated with or without, preferably with, reflux.

- What is meant by “with reflux” is that the vapour stream S_{AB} comprising ROH, with or without glycol, that is withdrawn at the upper end of the respective column, especially the reaction column RR_A , is not removed completely. The relevant vapour stream S_{AB} is thus fed at least partly,
- 5 preferably partly, back to the respective column as reflux, especially to the reaction column RR_A . In the cases where such a reflux is established, the reflux ratio is preferably 0.01 to 1, more preferably 0.02 to 0.9, yet more preferably 0.03 to 0.34, especially preferably 0.04 to 0.27 and very especially preferably 0.05 to 0.24, most preferably 0.2.
- 10 A reflux ratio is understood generally and in the context of this invention to mean the ratio of the proportion of the mass flow rate withdrawn from the column (kg/h) which is removed from the respective column in liquid form or gaseous form to the proportion of this mass flow rate (kg/h) which is returned back to the column in liquid form (reflux).
- 15 A reflux can be established by mounting a condenser at the top of the respective column. For this purpose, in particular, a condenser K_{RRA} is mounted on the reaction column RR_A . In the condenser K_{RRA} , the vapour stream S_{AB} is at least partly condensed and fed back to the respective column, especially to the reaction column RR_A .
- 20 In the embodiment in which a reflux is established in the reaction column RR_A , the M_{AOR} used as reactant stream S_{AE2} in the preferred embodiment of the method according to the invention may also be at least partly mixed with the reflux stream, and the resulting mixture may thus be supplied to the reaction column RR_A .
- 25 In a preferred embodiment of the method according to the invention, step (a) is especially conducted under distillative conditions under which glycol is refluxed.

Step (a) is performed especially at a temperature in the range from 80°C to 197°C, preferably 100°C to 197°C, more preferably 120°C to 140°C, and at a pressure of 0.01 bar abs. to 1 bar abs.,

30 preferably in the range from 0.05 bar abs. to 1 bar abs., more preferably in the range from 0.05 bar abs. to 0.15 bar abs., more preferably in the range from 0.05 bar abs. to 0.10 bar abs.

In a more preferred embodiment, the reaction column RR_A comprises at least one evaporator which is especially selected from intermediate evaporators V_{ZA} and bottom evaporators V_{SA} . The reaction column RR_A more preferably comprises at least one bottom evaporator V_{SA} .

35 According to the invention, “intermediate evaporators” V_Z refer to evaporators above the bottom of the respective column, especially above the bottom of the reaction column RR_A (in which case they are referred to as “ V_{ZA} ”) or of the rectification column RD_A which is used in the preferred embodiment and is described in detail further down (in which case they are referred to as “ V_{ZRD} ”).

In the case of **RR_A**, said evaporators especially evaporate crude product **RP_A** which is withdrawn from the column as side stream **S_{ZAA}**.

According to the invention, "bottom evaporators" **V_S** refer to evaporators that heat the bottom of the respective column, especially the bottom of the reaction column **RR_A** or the bottom of the rectification column **RD_A** which is used in the preferred embodiment and is described in detail further down (in which case they are referred to as "**V_{SRD}**" or "**V_{SRD}**"). In the case of **RR_A**, said evaporators especially evaporate at least a portion of the bottom product stream **S_{AP}**. In the case of **RD_A**, said evaporators especially evaporate bottom product stream **S_{UA}** or a portion of **S_{UA}**, **S_{UA1}**.

An evaporator is typically arranged outside the respective reaction column or rectification column.

Suitable evaporators employable as intermediate evaporators and bottom evaporators include for example natural circulation evaporators, forced circulation evaporators, forced circulation flash evaporators, kettle evaporators, falling-film evaporators or thin-film evaporators. Heat exchangers for the evaporator typically employed in the case of natural circulation evaporators and forced circulation evaporators are shell and tube or plate apparatuses. When using a shell and tube exchanger the heat carrier may flow through the tubes with the mixture to be evaporated flowing around the tubes or else the heat carrier may flow around the tubes with the mixture to be evaporated flowing through the tubes. In the case of a falling-film evaporator, the mixture to be evaporated is typically introduced as a thin film on the inside of a tube and the tube is heated externally. In contrast to a falling-film evaporator, a thin-film evaporator additionally comprises a rotor with wipers which distributes the liquid to be evaporated on the inner wall of the tube to form a thin film.

In addition to the recited evaporator types it is also possible to employ any desired further evaporator type known to those skilled in the art and suitable for use on a rectification column.

In the preferred embodiment of the method according to the invention, **S_{AP}** comprising glycol and **M_A** glycolate is withdrawn as bottom product stream at the lower end of the reaction column **RR_A**.

It is preferable that the reaction column **RR_A** comprises at least one bottom evaporator **V_{SA}** through which some of the bottom product stream **S_{AP}** is then passed and glycol is partly removed therefrom, which affords a bottom product stream **S_{AP*}** having an elevated proportion by mass of **M_A** glycolate compared to **S_{AP}**.

In particular, in the method according to the invention, **S_{AP}**, or **S_{AP*}** if at least one bottom evaporator **V_{SA}** through which at least some of the bottom product stream **S_{AP}** is passed is used and glycol is removed at least partly therefrom, has a proportion by mass of **M_A** glycolate in glycol in the range

from 1% to 50% by weight, preferably 5% to 35% by weight, more preferably 15% to 35% by weight, most preferably 20% to 35% by weight, in each case based on the total mass of S_{AP} .

The proportion by mass of ROH in S_{AP}/S_{AP^*} is preferably $< 1\%$ by weight, preferably $< 0.8\%$ by weight, more preferably $< 0.5\%$ by weight, based on the total mass of S_{AP} .

The proportion by mass of water in S_{AP}/S_{AP^*} is preferably $< 1\%$ by weight, preferably $< 0.8\%$ by weight, more preferably $< 0.5\%$ by weight, based on the total mass of S_{AP} .

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The proportion by mass of reactant M_{AOR} in S_{AP}/S_{AP^*} is preferably $< 1\%$ by weight, preferably $< 0.8\%$ by weight, more preferably $< 0.5\%$ by weight, more preferably $< 0.005\%$ by weight, based on the total mass of S_{AP} .

15 The proportion by mass of water in S_{AE1} is preferably $< 1\%$ by weight, preferably $< 0.8\%$ by weight, more preferably $< 0.1\%$ by weight, more preferably $< 0.005\%$ by weight, based on the total mass of S_{AE1} .

20 The proportion by mass of water in S_{AE2} is preferably $< 1\%$ by weight, preferably $< 0.8\%$ by weight, more preferably $< 0.1\%$ by weight, more preferably $< 0.005\%$ by weight, based on the total mass of S_{AE2} .

25 In an even more preferred embodiment of the method according to the invention, a vapour stream S_{AB} comprising ROH, with or without glycol, is withdrawn at the upper end of RD_A .

2. Rectification of the vapour stream S_{AB} in a rectification column RD_A (preferred)

30 In a further preferred embodiment, the vapour stream S_{AB} , when it comprises ROH and glycol, is directed into a rectification column RD_A and is separated in RD_A into at least one vapour stream S_{OA} comprising ROH which is withdrawn at the upper end of RD_A , and at least one stream S_{UA} comprising glycol which is withdrawn at the lower end of RD_A .

35 "At least one vapour stream S_{OA} comprising ROH which is withdrawn at the upper end of RD_A " shall be understood to mean that the vapour obtained at the upper end of RD_A may be withdrawn there as one or more vapour streams.

"At least one stream S_{UA} comprising glycol which is withdrawn at the lower end of RD_A " shall be understood to mean that glycol obtained at the lower end of RD_A may be withdrawn there as one or more streams.

The vapour stream S_{AB} may be directed into the rectification column RD_A via one or more feed points. In the embodiments of the present invention in which the vapour stream S_{AB} is directed into the rectification column RD_A as two or more separate streams, it is advantageous when the feed
 5 points for the individual streams are at substantially the same height on the rectification column RD_A .

In a preferred embodiment of the method according to the invention, the vapour stream S_{AB} , when it comprises ROH and glycol, is separated in a rectification column RD_A into a vapour stream S_{OA}
 10 comprising ROH which is withdrawn at the upper end of RD_A and a stream S_{UA} comprising glycol which is withdrawn at the lower end of RD_A .

Another term for "upper end of a rectification column" is "head".

Another term for "lower end of a rectification column" is "bottom" or "foot".
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The rectification column RD_A used may be any rectification column known to those skilled in the art.

The rectification column RD_A preferably contains internals. Suitable internals are, for example,
 20 trays, unstructured packings or structured packings. Trays used are typically bubble-cap trays, sieve trays, valve trays, tunnel-cap trays or slotted trays. Unstructured packings are generally beds of random packing elements. Random packing elements used are typically Raschig rings, Pall rings, Berl saddles or Intalox® saddles. Structured packings are for example sold under the Sulzer Mellapak® trade name. Apart from the internals mentioned, further suitable internals are known to
 25 a person skilled in the art and can likewise be used.

Preferred internals have a low specific pressure drop per theoretical plate. Structured packings and random packing elements have, for example, a significantly lower pressure drop per theoretical plate than trays. This has the advantage that the pressure drop in the rectification column RD_A
 30 remains as low as possible and the mechanical power of the compressor and the temperature of the glycol/ROH mixture to be evaporated therefore remain low.

When the rectification column RD_A contains structured packings or unstructured packings, these may be divided or in the form of an uninterrupted packing. Typically, however, at least two packings
 35 are provided, one packing above the feed point for the vapour stream S_{AB} and one packing below the feed point for the vapour stream S_{AB} . It is also possible to provide one packing above the feed point for the vapour stream S_{AB} and two or more trays below the feed point for the vapour stream S_{AB} . If an unstructured packing is used, for example a random packing, the random packing elements are typically disposed on a suitable support grid (for example sieve tray or mesh tray).

In this preferred embodiment, the at least one vapour stream S_{OA} comprising ROH is then withdrawn at the upper end of the rectification column RD_A . The preferred mass fraction of ROH in this vapour stream S_{OA} is $\geq 99\%$ by weight, more preferably $\geq 99.6\%$ by weight, yet more preferably $\geq 99.9\%$ by weight, with the remainder being especially glycol.

Withdrawn at the lower end of RD_A in this preferred embodiment is at least one stream S_{UA} comprising glycol which may preferably include $< 1\%$ by weight, more preferably ≤ 5000 ppm by weight, yet more preferably ≤ 1000 ppm by weight of ROH, more preferably ≤ 100 ppm by weight of ROH.

The withdrawal of at least one vapour stream S_{OA} comprising ROH at the top of the rectification column RD_A shall in particular be understood in the context of the present invention to mean that the at least one vapour stream S_{OA} is withdrawn above the internals in the rectification column RD_A as a top stream or as a side stream.

The withdrawal of the at least one stream S_{UA} comprising glycol at the bottom of the rectification column RD_A shall in particular be understood in the context of the present invention to mean that the at least one stream S_{UA} is withdrawn as bottom stream or at the lower tray of the rectification column RD_A .

The rectification column RD_A is operated with or without, preferably with, reflux.

"With reflux" shall be understood to mean that the vapour stream S_{OA} withdrawn at the upper end of the rectification column RD_A is not completely discharged but rather partly condensed and returned to the respective rectification column RD_A . In the cases where such a reflux is established, the reflux ratio is preferably 0.01 to 1, more preferably 0.02 to 0.9, yet more preferably 0.03 to 0.34, especially preferably 0.04 to 0.27 and very especially preferably 0.05 to 0.24, most preferably 0.2.

A reflux may be established by mounting a condenser K_{RD} at the top of the rectification column RD_A . The respective vapour stream S_{OA} is partly condensed in the condenser K_{RD} and returned to the rectification column RD_A .

3. Step (b): Reaction of PET with the solution S_{AP}

35

In step (b) of the method according to the invention, the solution S_{AP} obtained in step (a), comprising glycol and M_A glycolate, is reacted with PET to give a mixture M_1 comprising BHET.

3.1 PET starting material

The **PET** which is used in step (b) of the method according to the invention may be any **PET** which has to be depolymerized. Typically, such **PET** occurs as waste, especially in the home, in industry
5 or in agriculture.

In one embodiment of the method according to the invention, the **PET** to be depolymerized is thus in a mixture with other plastics, especially at least one plastic selected from polyethylene ("PE"), polyvinylchloride ("PVC"). This is typically the case when **PET** from plastic wastes is to be
10 depolymerized in the method according to the invention. In this embodiment, the **PET** is at least partly separated from the other plastics, preferably by sorting, before being subjected to step (b) of the method according to the invention.

In one embodiment of the method according to the invention, the **PET** is subjected to at least one
15 pretreatment step.

Such pretreatment steps are described, for example, in DE 10032899 C2.

According to the invention, the **PET** is subjected to at least one pretreatment step selected from
20 chemical pretreatment step, comminution step, before being used in step (b).

In the cases in which the **PET** is in a mixture with other plastics, the **PET** is preferably subjected to at least one pretreatment step selected from at least partial separation from other plastics, preferably by sorting, chemical pretreatment step, comminution step, before being used in step (b).
25

In the cases in which the **PET** is in a mixture with other plastics, the **PET** is more preferably first separated at least partly from other plastics, then subjected to at least one chemical pretreatment and finally comminuted.

30 The chemical pretreatment step is especially a wash step. Such a wash step has the advantage that any impurities, especially food residues, residues of cosmetics and/or bodily secretions (e.g. blood, sperm, faeces), are removed prior to the performance of step (b). Such impurities can lower the efficiency of the reaction in step (b) and/or worsen the purity of the **BHET** thus obtained.

35 In the chemical pretreatment step, especially the wash step, the waste is especially heated in a wash solution at a temperature of 30°C to 99°C, preferably 50°C to 90°C, more preferably 70°C to 85°C.

Typical wash solutions are familiar to the person skilled in the art and are preferably selected from:
40

- aqueous solution of a surfactant, preferably a nonionic surfactant;
- aqueous solution of an alkali metal hydroxide or alkaline earth metal hydroxide, preferably aqueous NaOH.

5 The treatment time in the chemical pretreatment step, especially the wash step, is especially 1 min to 12 h, preferably 10 min to 6 h, more preferably 30 min to 2 h, even more preferably 45 to 90 min, most preferably 60 min.

10 After the treatment of the **PET** by the chemical pretreatment step, especially the wash step, the aqueous solution is separated off, for example by filtration, and the cleaned **PET** is preferably washed at least once with water in order to remove residues of the wash solution.

The **PET** waste thus obtained is then dried, especially in a drying cabinet.

15 The temperature used for drying here is especially in the range of 30 to 120°C, preferably 50°C to 100°C, more preferably 60°C to 90°C, most preferably 80°C.

20 The comminution step has the advantage that the surface area of the **PET** available for the reaction in step (b) is increased. This increases the reaction rate of the reaction in step (b). The comminution can be effected in apparatuses known to the person skilled in the art, for example a shredder or a cutting mill.

25 In a further embodiment of the method according to the invention, the **PET** is decolorized or coloured in a controlled manner before being subjected to step (b). This can be conducted by methods known to the person skilled in the art, for example decolorization with hydrogen peroxide or dyeing with a dye.

3.2 Reaction conditions

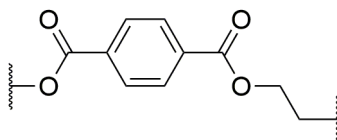
30 The reaction of the **PET** with a solution **S_{AP}** comprising glycol and **M_A** glycolate to give a mixture **M₁** can then be effected under the conditions that are familiar to the person skilled in the art.

35 Preferably, the reaction in step (b) is conducted until, i.e. up to a juncture **t_b** at which, at least **P** = 10%, preferably at least **P** = 20%, more preferably at least **P** = 25%, more preferably at least **P** = 30%, more preferably at least **P** = 40%, more preferably at least **P** = 50%, more preferably at least **P** = 60%, more preferably at least **P** = 70%, more preferably at least **P** = 80%, more preferably at least **P** = 90%, more preferably at least **P** = 95%, even more preferably at least **P** = 99%, of the **PET** used in step (b) has been converted.

This percentage **P** is calculated by the following formula:

$$P = (\eta_{TA} + \eta_{MHET} + \eta_{BHET}) / \eta_{PET}.$$

η_{PET} here is the molar amount of repeat units of the following structure (Ξ) in the **PET** used in step (b):



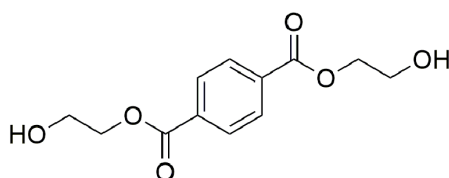
(Ξ)

η_{TA} is the molar amount of **TA** formed in step (b) from commencement of step (b) up to the juncture t_b .

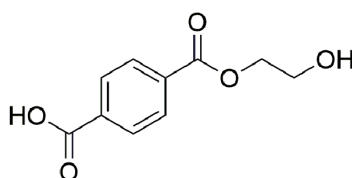
η_{MHET} is the molar amount of **MHET** formed in step (b) from commencement of step (b) up to the juncture t_b .

η_{BHET} is the molar amount of **BHET** formed in step (b) from commencement of step (b) up to the juncture t_b .

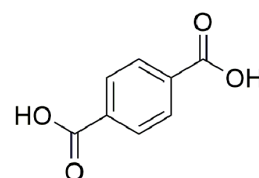
The structures of compounds **BHET**, **MHET**, **TA** are as follows:



BHET



MHET



TA

"**MHET**" also encompasses the corresponding carboxylate of the structure shown.

"**TA**" also encompasses the corresponding mono- and dicarboxylate of the structure shown.

The reaction in step (b) is especially conducted at a temperature of at least 100°C, preferably at a temperature in the range from $\geq 100^\circ\text{C}$ to $\leq 197^\circ\text{C}$, more preferably at a temperature in the range from $\geq 130^\circ\text{C}$ to $\leq 197^\circ\text{C}$, more preferably at a temperature in the range from $\geq 150^\circ\text{C}$ to $\leq 197^\circ\text{C}$, more preferably at a temperature in the range from $\geq 175^\circ\text{C}$ to $\leq 197^\circ\text{C}$.

The reaction in step (b) is preferably conducted at the boiling temperature of the glycol. Even more preferably, glycol is refluxed, meaning that glycol is evaporated out of the reaction, condenses and is then returned to the reaction. This refluxing can be established by means familiar to the person skilled in the art, for example in a distillation apparatus.

The total weight of the M_A glycolate used in the method based on the total weight of the **PET** used in the method is especially in the range from 0.1% to 100% by weight, preferably in the range from 0.5% to 80% by weight, more preferably in the range from 1.0% to 50% by weight, more preferably
 5 in the range from 1.5% to 25% by weight, more preferably in the range from 2.0% to 10% by weight, more preferably in the range from 2.5% to 6.0% by weight, more preferably 3.5% to 5.0% by weight, most preferably 3.9% by weight.

The reaction in step (b) can be effected with devices familiar to the person skilled in the art.
 10

After step (b) of the method according to the invention has ended, a mixture M_1 is obtained, in which the molar ratio η of the molar amount of **BHET** (n_{BHET}) to the sum total of the molar amounts of **MHET** and **TA** ($n_{MHET} + n_{TA}$) is in the range of 1:1 to 1000:1, preferably 2:1 to 500:100, more preferably 4:1 to 300:1, even more preferably 10:1 to 100:1, yet more preferably 13:1 to 60:1, yet
 15 more preferably 13:1 to 24:1.

$$\eta = n_{BHET} / (n_{MHET} + n_{TA})$$

3.3 Preferred step (c)

20 In a preferred further step (c), **BHET** is at least partly separated from M_1 . This is even more preferably effected by crystallization and/or distillation. Even more preferably, **BHET** in step (c) is filtered out of M_1 and then crystallized.

4. Process for recycling of **PET** 25

The **BHET** obtained in the mixture M_1 in the method according to the invention is preferably polymerized to **PET** in a method of recycling of polyethylene terephthalate in a step (ζ).

This polymerization is known to the person skilled in the art as "polycondensation" and is
 30 described, for example, in EP 0 723 951 A1 and by Th. Rieckmann and S. Völker in chapter 2 "Poly(Ethylene Terephthalate) Polymerization – Mechanism, Catalysis, Kinetics, Mass Transfer and Reactor Design" on page 92 of the book "Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters. Edited by J. Scheirs and T. E. Long, 2003, John Wiley & Sons, Ltd ISBN: 0-471-49856-4".

35 In particular, for this purpose, **BHET** is polymerized back to **PET** in step (ζ) in the presence of catalysts, which are especially catalysts selected from the group consisting of antimony compounds, preferably Sb_2O_3 .

Preferably, the polymerization of **BHET** to **PET** in step (ζ) is conducted at least at the boiling temperature of the glycol. In particular, during the polymerization in step (ζ), glycol is removed from the reaction mixture in order to shift the reaction equilibrium to the side of the polymer **PET**.

5

More preferably, the polymerization of **BHET** to **PET** in step (ζ) is conducted at the boiling temperature of the glycol. Even more preferably, in that case, during the polymerization in step (ζ), glycol is removed from the reaction mixture in order to shift the reaction equilibrium to the side of the polymer **PET**.

10

This is especially achieved by distillation at a pressure of < 1 bar, preferably 0.1 mbar, at the simultaneous boiling temperature of the glycol at the respective pressure.

Examples

1. Inventive Example I1:

1.1 Preparation of the glycolic sodium glycolate solution by reactive distillation

5

The following apparatus is utilized as distillation apparatus:

The reservoir vessel or bottom used in the distillation apparatus is a heatable 2.5 l jacketed vessel with temperature sensor and vacuum-tight stirrer. Above that is a 25 cm column with Multifill packing and silver mirror (stripping section). Sodium methoxide ("NaOMe") is metered in above the column by means of a dropping funnel. Above the metering point is a further column that serves to separate off ethylene glycol and methanol vapour (rectifying section). A reflux ratio can be established with the aid of a vapour divider in the upper part of the column, with collection of the distillate in a round-bottomed flask. The round-bottomed flask may be separated from the distillation system via a pressure-equalizing dropping funnel and exchanged. In the rectifying section, a reflux condenser with vacuum connections is attached, by means of which the entire apparatus can be evacuated. The vacuum is generated by means of a rotary vane pump which is connected to the distillation apparatus by two cold traps and a safeguard bottle. The pressure in the distillation apparatus is measured in the safeguard bottle (Büchi vacuum controller), where ventilation is also possible. The bottom reservoir and the column with the Multifill packing are completely surrounded by aluminium foil for insulation in order to assure a uniform temperature in the reactor/column.

The bottom is initially charged with the ethylene glycol and the entire apparatus is evacuated to 50 mbar. Subsequently, the bottoms are heated to boiling temperature, such that a reflux from the rectifying section is established. Subsequently, NaOMe (30% by weight in methanol) is metered in with the aid of a dropping funnel. The metering rate is chosen such that the methanolic NaOMe solution does not reach the bottom (about 2 ml/min).

The methanol added/formed is separated by distillation from ethylene glycol in the rectifying section and collected in the round-bottomed flask. The reflux ratio is 5:1 (5 parts as reflux, 1 part as distillate). The amount distilled off must correspond at least to the amount of methanol added. After the distillative removal, the sodium ethyleneglycolate in the bottoms is subjected to continued distillation for about another 2 hours (the methanol present in the rectifying section is removed at constant vacuum and temperature in order to prevent backflow into the bottom).

35

After the experiment has ended and been cooled down, the bottom is opened by means of an outlet valve and about 20% by weight solution of sodium glycolate in ethylene glycol is removed.

1.2 *PET depolymerization with glycolic sodium glycolate solution from the reactive distillation*

In the method according to the invention, an autoclave is initially charged with 100 g of **PET** together with 800 g of ethylene glycol. The solution is then heated to 150°C while stirring. As soon
 5 as the temperature of 150°C has been attained, 19.5 g of 20% sodium glycolate solution in ethylene glycol (corresponding to 0.046 mol) from the reactive distillation is added. The reaction is conducted over the course of five hours, and the reactor output is analysed after cooling. The resultant conversion of **BHET** (1) and 2-hydroxyethyl terephthalate (= "**MHET**") (2) and of terephthalic acid (= "**TA**") (3) is determined by gas chromatography.

10 2. Comparative Example V1:

In a comparative experiment, an autoclave is initially charged with 100 g of **PET** together with 800 g of ethylene glycol. The solution is then heated to 150°C while stirring. The reaction is conducted over the course of five hours, and the reactor output is analysed after cooling. The
 15 resultant conversion of **BHET** (1) and **MHET** (2) and of **TA** (3) is determined by gas chromatography.

3. Comparative Example V2:

In a comparative experiment, an autoclave is initially charged with 100 g of **PET** together with 800 g of ethylene glycol. The solution is then heated to 150°C while stirring. As soon as the temperature of 150°C has been attained, 3.7 g of 50% by weight NaOH solution in water (corresponding to 0.046 mol) is added. The reaction is conducted over the course of five hours, and the reactor output is analysed after cooling. The resultant conversion of **BHET** (1) and **MHET**
 20 (2) and of **TA** (3) is determined by gas chromatography.

4. Result

Comparison of the content of **BHET**, **MHET** and **TA** in the depolymerized product in Inventive
 30 Example **E1** and Comparative Examples **V1**, **V2** shows that the depolymerization using the glycolic sodium glycolate solution obtained by reactive distillation affords a higher proportion of **BHET**. This is advantageous since more product is available as a result, which can be converted directly in a polycondensation to new **PET** product.

Claims

1. Method of depolymerization of polyethylene terephthalate **PET**, comprising the following steps:
 - 5 (a) converting M_AOR and glycol in a reactive distillation to obtain a solution S_{AP} comprising glycol and M_A glycolate, where M_A is an alkali metal selected from sodium, potassium, and where R is an alkyl radical having 1 to 4 carbon atoms,
 - (b) reacting the solution S_{AP} with **PET** to give a mixture M_1 comprising bis-2-hydroxyethyl
 10 terephthalate **BHET**.
2. Method according to Claim 1, wherein S_{AP} is obtained in step (a) by reacting a reactant stream S_{AE1} comprising glycol with a reactant stream S_{AE2} comprising M_AOR in countercurrent in a reactive rectification column RR_A to give a crude product RP_A comprising M_A glycolate, ROH, glycol, M_AOR ,
 15 wherein S_{AP} is withdrawn as bottom product stream at the lower end of RR_A .
3. Method according to Claim 2, wherein a vapour stream S_{AB} comprising ROH, with or without glycol, is withdrawn at the upper end of RR_A .
 20
4. Method according to Claim 3, wherein S_{AB} comprises ROH and glycol, is directed into a rectification column RD_A and is separated in RD_A into at least one vapour stream S_{OA} comprising ROH which is withdrawn at the upper end of RD_A , and at least one stream S_{UA} comprising glycol which is withdrawn at the lower end of RD_A .
 25
5. Method according to any of Claims 1 to 4, wherein step (b) is conducted until at least $P = 10\%$ of the **PET** used in step (b) has been converted.
6. Method according to any of Claims 1 to 5, wherein the content of ROH in S_{AP} is $< 1\%$ by weight.
 30
7. Method according to any of Claims 1 to 6, wherein step (b) is performed at the boiling temperature of the glycol.
8. Method according to any of Claims 1 to 7, wherein a sufficient amount of S_{AP} is used in step (b) that the total weight of the M_A glycolate used in step (b), based on the total weight of the **PET** used in step (b), is in the range from 0.1% to 100% by weight.
 35
9. Method according to any of Claims 1 to 8, wherein **BHET** is at least partly separated from M_1 in a further step (c).
 40

10. Method according to Claim 9, wherein the at least partial separation of **BHET** from **M₁** in step (c) is effected by crystallization and/or distillation.
- 5 11. Method according to any of Claims 1 to 10, wherein the **PET** is subjected to at least one pretreatment step selected from chemical pretreatment step, comminution step, before being used in step (b).
- 10 12. Method of recycling polyethylene terephthalate **PET**, in which **BHET** is obtained by a method according to any of Claims 1 to 11 and the **BHET** thus obtained is polymerized to **PET** in a step (ζ).
13. Method according to Claim 12, wherein the polymerization of **BHET** to **PET** in step (ζ) is conducted at at least the boiling temperature of the glycol.
- 15 14. Method according to Claim 12 or 13, wherein the polymerization in step (ζ) is performed in the presence of a catalyst.
15. Method according to Claim 14, wherein the catalyst is selected from the group consisting of antimony compounds.