

Method and System for Preparing (Alkyl)acrylates

Technical Field

The invention relates to the field of organic synthesis, specifically to a
5 method for preparing (alkyl)acrylates and a system for preparing (alkyl)acrylates.

Background Art

(Meth)acrylates possess active double bonds and are important fine
10 chemical products and polymer monomers, of which the homopolymers or copolymers exhibit characteristics such as water resistance, flexibility, hardness, and impact resistance, are commonly used as oil additives, adsorbent resins, adhesives, and internal plasticizers, and widely applied in fields such as coatings, oil additives, plastics, papermaking, leather, and
15 cosmetics.

(Meth)acrylates are typically prepared via transesterification or direct esterification of (meth)acrylic acid. Compared to transesterification, direct esterification of (meth)acrylic acid with fatty alcohols is more efficient, i.e., (meth)acrylate undergoes an esterification reaction with higher fatty
20 alcohols. To promote the reaction, water needs to be continuously removed; a common approach is to add a low-boiling-point solvent that can form an azeotropic mixture with water to the reaction system; the azeotropic reaction between the low-boiling-point solvent and water increases the water removal rate. CN1733687A discloses a method for preparing
25 (meth)acrylates, in which benzene, toluene, cyclohexane, carbon tetrachloride, chloroform, n-pentane, and n-hexane are added to the reaction system as azeotropic agents to enhance water removal, achieving a product yield of up to 97.8%. The drawback of this method is the addition of a new substance as an azeotropic solvent to the reaction mixture, on one hand this
30 increases the difficulty of distillation and purification of the reaction system, and on the other hand the azeotropic solvent must be purified before it can be recycled upstream for reuse. Although the solvent azeotropic method can

efficiently and rapidly improve the conversion rate of the esterification reaction, problems such as solvent secondary distillation and process losses are prominent, resulting in overall energy consumption and long time, and poor product color. In existing continuous production methods for methacrylates, such as CN113416133A, a solid acid catalyst is packed in a distillation column, and the reaction efficiency is improved by real-time in-situ removal of water, but this method has high energy consumption; although it can promote the forward esterification reaction to some extent, even with the use of a large amount of polymerization inhibitor, the risk of self-polymerization of methacrylates remains high, affecting the yield of methacrylates.

Furthermore, a large amount of acid-containing aqueous solution is produced during the preparation of acrylates. This acid-containing solution, of which primary components include acrylic acid, are characterized by high acid concentration, complex composition, and high toxicity, which poses serious environmental problems. Therefore, post-treatment of the acid-containing solution is necessary. However, post-treatment methods incur additional costs and energy consumption. Moreover, the prepared products also contain impurities such as polymerization inhibitors. Current technologies typically use alkaline washing to remove these inhibitors; however, alkaline washing will generate large amount of alkaline waste solution, which also negatively impacts the environment and increases the burden of post-treatment.

Summary of the Invention

The objective of the invention is to overcome the problems of high energy consumption and high risk of self-polymerization in the preparation of (alkyl)acrylates in the prior art, as well as the problem of generating a large amount of acid-containing aqueous solution and alkaline waste solution during the preparation of acrylates that require post-treatment.

To achieve the above objective, according to a first aspect of the invention, the invention provides a method for preparing (alkyl)acrylates,

the method comprises:

(1) mixing (alkyl)acrylic acid, an alcohol and optionally a polymerization inhibitor to perform the first-stage esterification reaction;

(2) separating the aqueous phase in the product of the first-stage esterification reaction, and adding (alkyl)acrylic acid, optionally an alcohol, and/or a polymerization inhibitor to the remaining organic phase to allow the organic phase to undergo a second-stage esterification reaction; and optionally

(3) separating the aqueous phase in the product of the previous-stage esterification reaction and discharging the remaining organic phase containing esterification product, or continuing to add (alkyl)acrylic acid, optionally an alcohol and/or a polymerization inhibitor to the remaining organic phase to subject the organic phase to a N^{th} -stage esterification reaction, wherein $N \geq 3$, and repeating this cycle multiple times, discharging the remaining organic phase containing esterification product, and optionally,

(4) subjecting the remaining organic phase containing esterification product obtained in step (3) to post-treatment to obtain purified (alkyl)acrylates.

According to a second aspect of the invention, the invention provides a system for preparing (alkyl)acrylates, particularly a system implementing the method according to the first aspect above, comprising: a plurality of esterification reactors connected in series, and one or more phase separators or distillers for separating an organic phase and an aqueous phase which are respectively connected to each reactor; wherein each esterification reactor includes an inlet dedicated for feeding fresh reaction feedstock, or alternatively, an inlet is provided between the esterification reactor and the phase separator or distiller for introducing fresh reaction feedstock into the remaining organic phase from the previous-stage reaction from which the aqueous phase has been separated.

The inventors propose the invention based on the following discovery: when the method for preparing (alkyl)acrylates is carried out by staged

reactions to control the conversion rate of each stage reaction within a certain range, and the aqueous phase is removed after each stage reaction, and an appropriate amount of (alkyl)acrylic acid is supplemented to the remaining organic phase, it is possible to significantly reduce the usage of (alkyl)acrylic acid in the method (thereby reducing the amount of acid-containing aqueous solution requiring post-treatment), while also increasing the conversion rate of alcohol, and the staged reactions can significantly shorten the reaction time.

Through the above-described technical solution of the invention, the invention can realize the continuous preparation of (alkyl)acrylates. Furthermore, the method of the invention has a short reaction cycle, significantly lower process energy consumption, lower waste emissions, and lower (alkyl)acrylate self-polymerization risk, and has significant economic benefits and environmental advantages.

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Brief Description of the Figure

The Figure in the specification is used to illustrate the technical solution of the invention and constitute a part of the specification, but do not constitute a limitation to the invention. Wherein:

20 Figure 1 shows a simplified schematic flowchart of the technical solution according to the invention.

Detailed Description of the Invention

25 The following specific embodiments illustrate the technical solution of the invention. It should be understood that the specific embodiments described herein are only for illustrating preferred embodiments of the invention and are not intended to limit the scope of the invention.

Any specific numerical value (including the endpoints of a numerical range) disclosed in the specification of the invention is not limited to the exact value, but should be understood to also cover values close to the exact value, such as all possible values within $\pm 5\%$ of the exact value. Furthermore, with respect to the disclosed numerical ranges, one or more

new numerical ranges can be obtained by arbitrarily combining the endpoint values of these ranges, the endpoint values with specific point values within the ranges, and the different specific point values, and these new numerical ranges should also be considered to be specifically disclosed herein.

5 Unless otherwise stated, the terms used in the specification of the invention have the same meaning as commonly understood by those skilled in the art, and if a term is defined herein and its definition differs from the common understanding in the art, the definition herein shall prevail.

10 In the specification of the invention, except where expressly stated, any matters or items not mentioned herein are directly applicable to those known in the art without any modification. Furthermore, any embodiments described herein can be freely combined with one or more other embodiments described herein, and the resulting technical solutions or concepts are considered as a part of the original disclosure or original record
15 of the invention, and should not be regarded as new content not disclosed or anticipated herein, unless those skilled in the art consider the combination to be clearly unreasonable.

All patent and non-patent literature mentioned in the specification of the invention, including but not limited to textbooks and journal articles, are
20 incorporated herein by reference in their entirety.

In the specification of the invention, the term "comprise" is synonymous with "include" and "contain" and is inclusive or open-ended, without excluding other elements not described. It should be understood that the term "comprise" covers the exclusive and closed term "consist of...". In
25 the specification of the invention, the term "carrier" has the same meaning as "matrix carrier" and they are used equivalently throughout the invention.

The measurement of the performance parameters disclosed in the specification of the invention, unless otherwise specified, is carried out by the most conventional methods in the art. In the specification of the
30 invention, unless otherwise stated, the term "(alkyl)acrylic acid" refers to acrylic acid and/or alkyl acrylic acid; the term "(alkyl)acrylate" refers to acrylate and/or alkyl acrylate.

According to the first aspect of the invention, the invention provides a method for preparing (alkyl)acrylates, which is characterized in that the method comprises:

(1) mixing (alkyl)acrylic acid, an alcohol and optionally a polymerization inhibitor to perform the first-stage esterification reaction (also known as "primary esterification");

(2) separating the aqueous phase in the product of the first-stage esterification reaction and adding (alkyl)acrylic acid, optionally an alcohol, and/or a polymerization inhibitor to the remaining organic phase to perform the second-stage esterification reaction (also known as "secondary esterification") of the organic phase; and optionally,

(3) separating the aqueous phase in the product of the previous-stage esterification reaction, to obtain and discharge the remaining organic phase containing esterification product, or adding (alkyl)acrylic acid, optionally an alcohol and/or a polymerization inhibitor to the remaining organic phase to continue the N^{th} -stage esterification reaction (also known as " N^{th} esterification") of the organic phase, wherein $N \geq 3$, and repeating this cycle multiple times, and discharging the remaining organic phase containing esterification product, and optionally,

(4) subjecting the remaining organic phase containing esterification product obtained in step (3) to a post-treatment to obtain purified (alkyl)acrylates.

According to a preferred embodiment of the first aspect of the invention, as shown in Figure 1, (alkyl)acrylic acid, an alcohol, and optionally a polymerization inhibitor are mixed and fed as reaction feedstock into a first esterification reactor to perform the first-stage esterification reaction (also known as "primary esterification"). After the alcohol conversion reaches a certain value, the reaction is stopped, and the reaction feedstock is cooled to room temperature and then fed into a dehydration device to separate aqueous phase from organic phase. The organic phase, supplemented (alkyl)acrylic acid, and optionally a polymerization inhibitor are then fed into a second esterification reactor to perform the second-stage esterification

reaction (also known as "secondary esterification"), wherein the supplemented (alkyl)acrylic acid and optionally a polymerization inhibitor are fed separately or together with the organic phase into the second esterification reactor; after the conversion rate of alcohol reaches a certain value, the reaction is stopped, and the reaction feedstock is cooled to room temperature, and then enter a dehydration device to separate the aqueous phase from the organic phase. Optionally, the remaining organic phase, supplemented (alkyl)acrylic acid, and optionally a polymerization inhibitor are fed into the Nth-stage esterification reactor to perform a Nth-stage esterification reaction (also known as "Nth esterification"), wherein the supplemented (alkyl)acrylic acid and optionally a polymerization inhibitor are fed into the Nth-stage esterification reactor separately or together with the organic phase. After the secondary esterification or the Nth-stage esterification reaction, the organic phase product obtained after removing the aqueous phase through the dehydration device undergoes post-treatment, including removal of the polymerization inhibitor, dehydration, etc., to obtain purified (alkyl)acrylate product. Wherein the dehydration device used to treat the products obtained from the different stage esterification reactions can be the same one dehydration device or different dehydration devices, such as those selected from distillation columns or centrifugal separator.

The method according to the invention, by controlling the conversion rate of each stage esterification reaction within a suitable range, can more effectively reduce the amount of (alkyl)acrylate used, promote the reaction of alcohol, and reduce the risk of self-polymerization of reaction feedstock and products. Preferably, the conversion rate of the first-stage esterification reaction, calculated as alcohol hydroxyl group, is 40-96%, more preferably 70-94%, for example 75%, 80%, 85%, 86%, 87%, 88%, 89%, 90%, 92%, and 93%, or any value or range between the above values. In the invention, the conversion rate of a certain stage esterification reaction refers only to the conversion rate calculated as alcohol hydroxyl group at that stage. The inventors have found that, for the method of the invention for preparing

(alkyl)acrylates, performing the esterification reaction in multiple stages, controlling the conversion rate of each stage esterification reaction within a certain range, and adding fresh (alkyl)acrylic acid in a certain proportion can actually achieve the desired high conversion rate in a shorter
5 esterification reaction time, and can significantly reduce the amount of (alkyl)acrylate used, and reduce the self-polymerization reaction of unsaturated acids and esters.

Preferably, the conversion rate of the second-stage esterification reaction is 40-100% calculated as alcohol hydroxyl group, more preferably
10 70-99.5%.

Preferably, the conversion rate of the Nth-stage esterification reaction is 40-100% calculated as alcohol hydroxyl group, more preferably 70-99.5%.

Preferably, the total conversion rate of each stage esterification reaction is $\geq 99\%$, more preferably $\geq 99.5\%$.

15 Controlling the conversion rates of the first-, second-, and Nth-stage esterification reactions according to the conversion rates described above allows to further accelerate the esterification reaction (shortening the reaction cycle), significantly reduce the amount of (alkyl)acrylic acid used, and reduce the risk of self-polymerization.

20 According to one embodiment of the first aspect above, step (3) is an optional step, that is, it can or cannot be performed. According to the method of the invention, not performing step (3) can also achieve the objective of the invention effectively and simplify the requirements of equipment while reducing energy consumption. When production conditions permit, step (3)
25 can be performed according to actual circumstances, and the total stage number of the esterification reaction (or the value of N) can be selected, thereby facilitating full utilization of the equipment and further improving production efficiency. Preferably, N is an integer greater than or equal to 2 and less than or equal to 5.

30 According to one embodiment of the first aspect above, the aqueous phase in the reaction feedstock can be separated by using methods commonly used in the art. Preferably, in step (2) and optional step (3), the

method for separating the aqueous phase in the esterification reaction products is distillation and/or liquid-liquid phase separation, for example, at least one selected from distillation, flash evaporation, stripping, sedimentation, decantation, coalescence, and centrifugation, more preferably centrifugal separation. In step (2) and optional step (3), the separation of the aqueous phase in the esterification reaction products can be carried out in the same one separation or dehydration device, such as a distillation column or centrifugal separator, or in different separation or dehydration devices, such as distillation columns or centrifugal separators.

According to a preferred embodiment of the first aspect above, in order to further improve production efficiency and reduce the risk of self-polymerization, each stage esterification reaction is carried out under the condition of a companionship of inactive gas. More specifically, if the esterification reaction is performed in a fixed-bed reactor, the inactive gas is introduced into the reactor together with the liquid reaction feedstock and passes through the fixed bed together to simultaneously contact the catalyst. During each stage esterification reaction, the ratio of the volumetric space velocity of the inactive gas to the liquid hourly space velocity of the liquid reaction feedstock is independently 0-1000:1, more preferably 10-250:1. More preferably, during each stage esterification reaction, the volumetric space velocity of the inactive gas is 3-500 h⁻¹, preferably 4-200 h⁻¹, more preferably 8-80 h⁻¹, and even more preferably 9-15 h⁻¹. The inactive gas can be a gas commonly found in the art that does not react with any of the reaction feedstock in the method of the invention and is gaseous under the esterification reaction conditions, for example, it can be nitrogen and/or rare gases. The preferred embodiment in which each stage esterification reaction is carried out under the companionship of inactive gas is particularly suitable for the processes in which the esterification reaction pressure is positive. The inventors have surprisingly discovered during research that, for the esterification reaction of the invention, contacting the liquid reaction feedstock with the catalyst under a companionship of gas during the esterification reaction can significantly increase the reaction rate and

significantly reduce the reaction time while achieving the same conversion rate. Without being bound by any particular theory, the inventors believe that this advantage arising from the companionship of an inactive gas may be related to the contact state and contact time between the catalyst, especially solid catalyst, and the liquid reaction feedstock, this is because, when the inactive gas contacts the catalyst along with the liquid reaction feedstock, the inactive gas can disturb and accelerate the flow of the liquid reaction feedstock on the catalyst surface, thereby improving mass transfer of the liquid reaction feedstock on the catalyst surface and accelerating the removal of heat generated by the reaction and water produced by the esterification reaction, thus enhancing the esterification reaction kinetics, lowering the reaction temperature, and effectively preventing the self-polymerization reaction of the reaction feedstock and products.

According to a preferred embodiment of the first aspect above, in order to further improve the conversion rate of alcohol, the method further includes: in step (2) and/or step (3), supplementing (alkyl)acrylic acid such that the molar ratio of the supplemented (alkyl)acrylic acid each time (calculated as carboxyl groups) to the alcohol in the remaining organic phase (calculated as hydroxyl groups) is 0.1-2, more preferably 0.1-1.5, more preferably 0.2-1.0, for example 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8. In order to more effectively reduce the risk of self-polymerization of the reaction feedstock and products, the method may further include: in step (2) and/or step (3), supplementing a polymerization inhibitor, wherein the amount of supplemented polymerization inhibitor each time is 0.01-3wt% of the total weight of the (alkyl)acrylic acid and the alcohol, more preferably 0.01-1wt%, further preferably less than 0.08wt%, and particularly preferably less than 0.07wt%. In step (2) and/or step (3), alcohol may be supplemented as needed.

According to one embodiment of the first aspect above, the molar ratio of (alkyl)acrylic acid (calculated as carboxyl group) and alcohol (calculated as hydroxyl group) in step (1) can be 0.1-2, preferably 0.5-1.5, more preferably 0.8-1.1, for example 0.9 or 1.0.

According to one embodiment of the first aspect above, the total molar

ratio of the (alkyl)acrylic acid (calculated as carboxyl group) and the alcohol (calculated as hydroxyl group) during the entire preparation method can be 1-4, preferably 2-3, more preferably 1.05-1.5, for example 1.1, 1.2, 1.3 or 1.4.

5 According to one embodiment of the first aspect above, the (alkyl)acrylic acid can be any of the various (alkyl)acrylic acids commonly used in the art for the preparation of (alkyl)acrylates. Preferably, the alkyl group in the (alkyl)acrylic acid has less than or equal to 8 carbon atoms, more preferably less than or equal to 4 carbon atoms, and more preferably,
10 the alkyl group in the (alkyl)acrylic acid is methyl, ethyl, or propyl. More preferably, the (alkyl)acrylic acid is (meth)acrylic acid.

According to one embodiment of the first aspect above, the alcohol can be any alcohol commonly used in the art for preparing (alkyl)acrylates. Preferably, the alcohol is a fatty alcohol insoluble or slightly soluble in
15 water having a boiling point above 100°C at normal pressure. A term "a fatty alcohol insoluble or slightly soluble in water" refers to an alcohol of which solubility in 100g of water at 20°C is less than or equal to 1g. More preferably, the alcohol is at least one of monohydric alcohols having 9-22 carbon atoms, and more preferably at least one of n-decanol, n-undecylol,
20 n-dodecanol, n-tetradecylol, n-hexadecylol, and n-octadecylol.

According to a preferred embodiment of the first aspect above, the total amount of the polymerization inhibitor is 0.03-5wt% of the total weight of (alkyl)acrylic acid and alcohol, more preferably less than 0.2wt%, and particularly preferably less than 0.15wt%. The invention can prevent the
25 self-polymerization of (alkyl)acrylates even with a lower amount of polymerization inhibitor, thus allowing for higher production efficiency of (alkyl)acrylates.

According to one embodiment of the first aspect above, the polymerization inhibitor may be selected from polymerization inhibitors
30 commonly used in the art, but preferably, the polymerization inhibitor is at least one selected from phenolic polymerization inhibitors, quinone polymerization inhibitors, aromatic amine polymerization inhibitors, and

inorganic salt polymerization inhibitors. The phenolic polymerization inhibitor may be selected from at least one selected from hydroquinone, pyrogallol, and p-tert-butylcatechol. The quinone polymerization inhibitor may be at least one selected from tetrachlorobenzoquinone and 1,4-naphthoquinone, etc. The aromatic amine polymerization inhibitor may be selected from at least one selected from p-phenylenediamine, benzidine, diphenylamine and p-(methyl)aniline, etc. The inorganic salt polymerization inhibitor may be selected from at least one selected from ferric chloride, cuprous oxide, etc.

10 According to one embodiment of the first aspect above, the conditions for each stage esterification reaction can independently include: a temperature of 80-140°C, preferably 90-130°C. Preferably, the temperature of the previous stage esterification reaction is lower than that of the subsequent stage esterification reaction by 1-10°C, particularly preferably
15 by 1-5°C.

According to one embodiment of the first aspect above, the conditions for each stage esterification reaction may also independently include: a pressure of 0-10 MPaG, preferably 0.002-2 MPaG, more preferably 0.01-1.5 MPaG. More preferably, the pressure of the previous stage esterification
20 reaction is lower than the pressure of the subsequent stage esterification reaction by 0.2-1 MPaG, particularly preferably by 0.35-0.85 MPaG.

According to a preferred embodiment of the first aspect above, steps (1), (2), and (3) are carried out in separate reactors and/or separators, thereby allowing the preparation process to proceed continuously. The reactors may
25 be packed with a solid acid catalyst (e.g., an acidic resin) in a fixed-bed configuration, wherein the total liquid hourly space velocity of the (alkyl)acrylic acid, alcohol, and optionally the polymerization inhibitor may be 0.1-3 h⁻¹, preferably 0.18-1 h⁻¹. More preferably, the liquid hourly space velocity of the subsequent stage esterification reaction (including the liquid
30 hourly space velocity of the supplemented reaction feedstock, such as the supplemented (alkyl)acrylic acid and optionally the polymerization inhibitor) is greater than the liquid hourly space velocity of the previous

stage esterification reaction by $0-0.2\text{ h}^{-1}$, more preferably by $0-0.11\text{ h}^{-1}$.

According to one embodiment of the first aspect above, the conditions for each stage esterification reaction may be the same or different, but controlling the temperature, pressure and liquid hourly space velocity of the
5 previous and subsequent stage esterification reactions in the manner described above can further promote the progress of the reaction and reduce the risk of self-polymerization of (alkyl)acrylates.

According to one embodiment of the first aspect above, in order to promote the progress of the reaction, the esterification reaction can be
10 carried out in the presence of a catalyst commonly used in esterification reactions. The catalyst may be at least one selected from sulfuric acid, sulfonic acid catalysts, heteropolyacid catalysts, and acidic resins. The amount of the catalyst is 0.05-10wt% of the total weight of the (alkyl)acrylic acid and the alcohol, more preferably 0.3-3wt%. The sulfonic acid catalyst
15 may be at least one selected from p-toluenesulfonic acid and methanesulfonic acid. Heteropolyacid catalysts are a class of oxygen-containing polyacids composed of heteroatoms and polycoordinated atoms bridged and coordinated through oxygen atoms. The heteropolyacid catalyst may be at least one selected from phosphotungstic acid,
20 phosphotungmolybdic acid, and silicotungstic acid. The acidic resin is capable of releasing hydrogen ions, wherein the acidic resin may be selected from macroporous acidic resins, etc.

Since the organic phase obtained after the reaction and dehydration steps contains polymerization inhibitors and is colored, the reaction
25 products need to be post-treated to obtain a final product that meets the requirements. The post-treatment of the reaction products includes: sequentially removing polymerization inhibitors from the reaction products and decolorizing the products. Therefore, according to one embodiment of the first aspect above, in order to purify the esterification reaction products,
30 the method of the invention may further include step (4): after removing the aqueous phase of the second-stage esterification reaction product of step (2) or the N^{th} -stage esterification reaction product of step (3), performing their

post-treatment to obtain purified (alkyl)acrylate; preferably, step (4) includes removing the polymerization inhibitors contained in the products obtained in the previous steps; wherein the method for removing the polymerization inhibitors may be alkaline washing or extraction, and the alkaline washing method may be: performing an alkaline washing with an alkali metal hydroxide solution (especially sodium hydroxide solution) with a concentration of 1-20wt%, then treating it with demineralized water until neutral. Preferably, the method for removing the polymerization inhibitors is extraction. More preferably, the extractant used for extraction includes alcohol-based extractants and/or water-based extractants, and more preferably water-based extractants. Most preferably, the water content in the water-based extractant is 10-100wt%, preferably 50-95wt%, more preferably 55-90wt%, with the balance being a hydrophilic monohydric alcohol and/or a hydrophilic polyhydric alcohol, wherein the hydrophilic monohydric alcohol is for example a C1-C6 monohydric alcohol, preferably methanol or ethanol, most preferably methanol, and the hydrophilic polyhydric alcohol is, for example, ethylene glycol. Preferably, the extraction is carried out in a continuous or multi-stage cross-flow manner. According to one embodiment of the first aspect above, the extraction conditions are: an extraction temperature of 25-70°C; a mass ratio of the extractant to the (alkyl)acrylate solution containing hydroquinone of 0.1-5:1, preferably 0.3-1.2:1; and/or the extraction device is one or more combinations of packed columns, plate columns, rotating disc columns, centrifugal extractors, spiral extractors, and mixer-settler.

According to one embodiment of the first aspect above, in order to purify the esterification reaction product, step (4) may also include a decolorization operation on the product, which may be carried out in a manner common in the art, for example, using bleaching clay to perform decolorization, which will not be described in detail here.

The aqueous phase removed during the aforementioned inter-stage dehydration process requires further treatment to meet environmental protection requirements due to its high content of (alkyl)acrylic acid. A

preferred method for removing (alkyl)acrylic acid from the aqueous phase is extraction. Therefore, according to one embodiment of the first aspect above, the method may further include step (5): further recovering (alkyl)acrylic acid from the aqueous phase obtained in step (2) and / or step 5 (3), preferably by extracting the (alkyl)acrylic acid from the aqueous phase with an extractant to obtain an extract containing (alkyl)acrylic acid. The extraction recovery step may specifically include: mixing the extractant and the aqueous phase, performing extraction, and separating the phases to obtain water and an organic phase containing (alkyl)acrylic acid, wherein 10 the extractant is at least one selected from hydrophobic higher fatty alcohols. When (alkyl)acrylic acid is recovered by using the method described above, the operation is relatively simple, the extraction rate of (alkyl)acrylic acid is higher, and no additional polymerization inhibitor is required, and it is environmentally friendly. Preferably, the hydrophobic higher fatty alcohol 15 is at least one selected from monohydric fatty alcohols with 9-26 carbon atoms, and more preferably at least one selected from monohydric fatty alcohols with 9-16 carbon atoms. More preferably, the hydrophobic higher fatty alcohol is at least one selected from (n)decanol, (n)undecylol, (n)dodecanol, (n)tridecylol, and (n)tetradecylol. According to a particularly 20 preferred embodiment of the invention, the extractant is dodecylol, and the volume ratio of dodecylol to the aqueous phase is 2.8-3.2 :1. According to a preferred embodiment, the extraction is carried out in a packed column filled with packing material in a continuous countercurrent extraction manner. Preferably, the mass flow rate ratio of the aqueous phase containing 25 (alkyl)acrylic acid to the extractant is 0.5-10:1, preferably 0.8-5:1, more preferably 1-3:1, and the extraction temperature is 0-90°C, preferably above room temperature (25 °C) to below 60°C, more preferably above 35 °C and below 50°C. According to a preferred embodiment, the extractant is at least one or more of a hydrophobic alcohol that participate in the esterification 30 reaction and a hydrophobic (alkyl)acrylate; the extraction conditions are: an extraction temperature of 0-90°C, preferably 30-60°C, and a mass ratio of the extractant to the aqueous phase of 0.1-5:1, preferably 0.3-1.0:1; the

extraction device is one or more of a packed column, a plate column, a rotating disc column, a centrifugal extractor, a spiral extractor, and a mixer-settler, preferably a packed column, and preferably the packing material is a surface-hydrophilic packing material. According to a preferred
5 embodiment, the extract containing (alkyl)acrylate recovered in step (5) is returned to any of steps (1) to (3) as a reaction feedstock.

According to a second aspect of the invention, the invention provides a reaction system for carrying out the method according to the first aspect above, comprising: a plurality of esterification reactors connected in series,
10 and one or more phase separators or distillers respectively connected to each reactor for separating an organic phase and an aqueous phase; wherein each esterification reactor comprises an inlet dedicated for feeding fresh reaction feedstock, or alternatively, an inlet is provided between the esterification reactor and the phase separator or distiller for introducing fresh reaction
15 feedstock into the remaining organic phase from which the aqueous phase has been separated and which comes from the previous reaction stage.

According to one embodiment of the second aspect above, the phase separator or distiller is selected from a centrifugal phase separator or a distillation column.

20 According to one embodiment of the second aspect above, the reaction system further includes: an extraction device for separating the polymerization inhibitor, connected to the last phase separator. Preferably, the extraction device is one or more selected from a packed column, plate column, rotating disc column, centrifugal extractor, spiral extractor, and
25 mixer-settler.

The invention will be described in detail below through examples. In the following examples, the macroporous acidic resin is a commercially available macroporous sulfonic acid type acidic resin; "room temperature" refers to 25°C; the temperature of the mixed raw materials after preheating
30 is about 100°C;

The calculation method of the conversion rate of alcohol is as follows: the residual alcohol content in the obtained reaction liquid is measured by

gas chromatography, and the amount of alcohol converted is calculated, then the ratio of this amount to the initial amount of alcohol is the conversion rate.

In the examples and comparative examples below, the yield of dodecyl methacrylate = molar yield of dodecyl methacrylate / molar amount of alcohol initially added $\times 100\%$.

In the following examples and comparative examples, all raw materials were commercially available. Measurement methods for the parameters involved are conventional measurement methods, unless otherwise explicitly stated.

Example 1

571.98 g of methacrylic acid, 1179.03 g of 1-dodecanol and 1.22 g of hydroquinone were mixed thoroughly. After the mixed raw materials were preheated to approximately 100°C , they were introduced into a first-stage fixed-bed reactor filled with macroporous acidic resin at a liquid hourly space velocity of 0.1936 h^{-1} . The center temperature of the first-stage fixed-bed reactor was 111°C , and the reaction pressure was 1.6 MPa. During the reaction, the liquid reaction mixture was accompanied by nitrogen flow at a nitrogen space velocity of 9.61 h^{-1} . The conversion rate of dodecanol was monitored by periodic sampling and gas chromatography detection during the first-stage reaction. The reaction was stopped when the conversion rate of dodecanol reached 93.18%. The reaction liquid was then discharged from the reactor, cooled to room temperature, and centrifuged (at a rotational speed of 2000 rpm for 20 min, same below) to obtain an organic phase and an aqueous phase. The aqueous phase was removed and post-treated to recover the methacrylic acid contained therein (see Example 14 below for details). 151.19 g of methacrylic acid and 1.22 g of hydroquinone were added to the organic phase and, after thorough mixing, introduced into a second-stage fixed-bed reactor filled with macroporous acidic resin at a liquid hourly space velocity of 0.2581 h^{-1} . The center temperature of the second-stage fixed-bed reactor was 113°C , and the reaction pressure was

1.3 MPa. During the reaction, the liquid reaction mixture was accompanied by nitrogen flow at a nitrogen space velocity of 11.24 h^{-1} . During the reaction, the conversion rate of dodecanol during the second-stage reaction was monitored by periodic sampling and gas chromatography detection. The reaction was terminated when the conversion rate of dodecanol reached 99.69%. After being discharged from the reactor, the reaction liquid was cooled to room temperature. The organic phase obtained by centrifugation was subjected to a post-treatment to remove polymerization inhibitors contained herein (see Example 10 below for details) and to decolorize the product, yielding purified dodecyl methacrylate. Gas chromatography analysis of the final product showed a yield of dodecyl methacrylate of 98.70%. The total residence time of the reaction liquid in the two-stages fixed-bed reactors was 9.04 h.

Example 2

628.34 g of methacrylic acid, 1301.78 g of 1-dodecanol and 1.3 g of hydroquinone were mixed thoroughly. After the mixed raw materials were preheated to approximately 100°C , they were introduced into a first-stage fixed-bed reactor filled with macroporous acidic resin at a liquid hourly space velocity of 0.2582 h^{-1} . The center temperature of the first-stage fixed-bed reactor was 111°C , and the reaction pressure was 0.68 MPa. During the reaction, the liquid reaction mixture was accompanied by nitrogen flow at a nitrogen space velocity of 14.98 h^{-1} . During the reaction, the conversion rate of dodecanol during the first-stage reaction was monitored by periodic sampling and gas chromatography detection. The reaction was stopped when the conversion rate of dodecanol reached 87.61%. The reaction liquid was discharged from the reactor, cooled to room temperature, and centrifuged to obtain the organic phase and aqueous phase, and the aqueous phase was removed. 30.57 g of methacrylic acid and 1.3 g of hydroquinone were added to the organic phase. After thorough mixing, the mixture was introduced into a second-stage fixed-bed reactor filled with macroporous acidic resin at a liquid hourly space velocity of 0.2582 h^{-1} . The center temperature of the

second-stage fixed-bed reactor was 113°C, and the reaction pressure was 1.04 MPa. During the reaction, the liquid reaction mixture was accompanied by nitrogen flow at a nitrogen hourly space velocity of 12.18 h⁻¹. During the reaction, the conversion rate of dodecanol during the second-stage reaction
5 was monitored by periodic sampling and gas chromatography detection process. The reaction was terminated when the conversion rate of dodecanol reached 98.54%. After being discharged from the reactor, the reaction liquid was cooled to room temperature, and the organic phase obtained by centrifugation was subjected to a post-treatment to remove polymerization
10 inhibitors contained herein and decolorize the product, yielding purified dodecyl methacrylate. Gas chromatography analysis of the final product showed a yield of dodecyl methacrylate of 98.67%. The total residence time of the reaction liquid in the two fixed-bed reactors was 8.15 h.

15 Example 3

628.34 g of methacrylic acid, 1301.78 g of 1-dodecanol and 1.3 g of hydroquinone were mixed thoroughly. After the mixed raw materials was preheated to approximately 100°C, they were introduced into a first-stage fixed-bed reactor filled with macroporous acidic resin at a liquid hourly
20 space velocity of 0.2582 h⁻¹. The center temperature of the first-stage fixed-bed reactor was 111°C, and the reaction pressure was 0.68 MPa. During the reaction, the liquid reaction mixture was accompanied by nitrogen flow at a nitrogen space velocity of 14.98 h⁻¹. The conversion rate of dodecanol during the first-stage reaction was monitored by periodic sampling and gas
25 chromatography detection. The reaction was stopped when the conversion rate of dodecanol reached 87.61%. The reaction liquid was discharged from the reactor, cooled to room temperature, and centrifuged to obtain an organic phase and an aqueous phase. 80.36 g of methacrylic acid and 1.3 g of hydroquinone were added to the organic phase, thoroughly mixed, and then
30 introduced into a second-stage fixed-bed reactor filled with macroporous acidic resin at a liquid hourly space velocity of 0.2582 h⁻¹. The center temperature of the second-stage fixed-bed reactor was 113°C, and the

reaction pressure was 1.2 MPa. During the reaction, the liquid reaction mixture was accompanied by nitrogen flow at a nitrogen space velocity of 10.75 h^{-1} . During the reaction, the conversion rate of dodecanol during the second-stage reaction was monitored by periodic sampling and gas chromatography detection process. The reaction was terminated when the conversion rate of dodecanol reached 99.04%. After being discharged from the reactor, the reaction liquid was cooled to room temperature, and the organic phase obtained by centrifugation was subjected to a post-treatment to remove polymerization inhibitors contained herein and decolorize the product, yielding purified dodecyl methacrylate. Gas chromatography analysis of the final product showed a yield of dodecyl methacrylate of 98.85%. The total residence time of the reaction liquid in the two-stages fixed-bed reactors was 7.55 h.

Example 4

633.34 g of methacrylic acid, 1301.78 g of 1-dodecanol and 1.3 g of hydroquinone were mixed thoroughly. After the mixed raw materials were preheated to approximately 100°C , they were introduced into a first-stage fixed-bed reactor filled with macroporous acidic resin at a liquid hourly space velocity of 0.2151 h^{-1} . The center temperature of the first-stage fixed-bed reactor was 111°C , and the reaction pressure was 0.68 MPa. During the reaction, the liquid reaction mixture was accompanied by nitrogen flow at a nitrogen space velocity of 14.61 h^{-1} . During the reaction, the conversion rate of dodecanol during the first-stage reaction was monitored by periodic sampling and gas chromatography detection. The reaction was stopped when the conversion rate of dodecanol reached 89.77%. The reaction liquid was discharged from the reactor, cooled to room temperature, and centrifuged to obtain an organic phase and an aqueous phase, and the aqueous phase was removed. 95.49 g of methacrylic acid and 1.3 g of hydroquinone were added to the organic phase, and after thorough mixing, the mixture was introduced into a second-stage fixed-bed reactor filled with macroporous acidic resin at a liquid hourly space velocity of 0.2797 h^{-1} . The center temperature of the

second-stage fixed-bed reactor was 113°C, and the reaction pressure was 1.49 MPa. During the reaction, the liquid reaction mixture was accompanied by nitrogen flow at a nitrogen space velocity of 10.47 h⁻¹. During the reaction, the conversion rate of dodecanol during the second-stage reaction
5 was monitored by periodic sampling and gas chromatography detection. The reaction was terminated when the conversion rate of dodecanol reached 99.33%. After being discharged from the reactor, the reaction liquid was cooled to room temperature, and the organic phase obtained by centrifugation was subjected to a post-treatment to remove polymerization
10 inhibitors contained herein and decolorize the product, yielding purified dodecyl methacrylate. Gas chromatography analysis of the final product showed a yield of dodecyl methacrylate of 98.92%. The total residence time of the reaction liquid in the two-stages fixed-bed reactors was 8.22 h.

15 Example 5

633.34 g of methacrylic acid, 1301.78 g of 1-dodecanol and 1.3 g of hydroquinone were mixed thoroughly. After the mixed raw materials were preheated to approximately 100°C, they were introduced into a first-stage fixed-bed reactor filled with macroporous acidic resin at a liquid hourly
20 space velocity of 0.2151 h⁻¹. The center temperature of the first-stage fixed-bed reactor was 111 °C, and the reaction pressure was 0.68 MPa. During the reaction, the liquid reaction mixture was accompanied by nitrogen flow at a nitrogen space velocity of 14.61 h⁻¹. During the reaction, the conversion rate of dodecanol during the first-stage reaction was monitored by periodic
25 sampling and gas chromatography detection; the reaction was stopped when the conversion rate of dodecanol reached 89.76%. The reaction liquid was discharged from the reactor, cooled to room temperature, and centrifuged to obtain an organic phase and an aqueous phase, and the aqueous phase was removed. 95.49 g of methacrylic acid and 1.3 g of hydroquinone were added
30 to the organic phase, and after thorough mixing, the mixture was introduced into a second-stage fixed-bed reactor filled with macroporous acidic resin at a liquid hourly space velocity of 0.3227 h⁻¹. The center temperature of the

second-stage fixed-bed reactor was 113°C, and the reaction pressure was 1.2 MPa. During the reaction, the liquid reaction mixture was accompanied by nitrogen flow at a nitrogen space velocity of 10.4 h⁻¹. During the reaction, the conversion rate of dodecanol during the second-stage reaction was monitored by periodic sampling and gas chromatography detection. The reaction was terminated when the conversion rate of dodecanol reached 99.25%. After being discharged from the reactor, the reaction liquid was cooled to room temperature, and the organic phase obtained by centrifugation was subjected to a post-treatment to remove polymerization inhibitors contained herein and decolorize the product, yielding purified dodecyl methacrylate. Gas chromatography analysis of the final product showed a yield of dodecyl methacrylate of 98.8%. The total residence time of the reaction liquid in the two-stages fixed-bed reactors was 7.75 h.

Example 6

485.065 g of methacrylic acid, 1000 g of 1-dodecanol, and 1.0 g of hydroquinone were thoroughly mixed. After the mixed raw materials were preheated to approximately 100°C, they were introduced into a first-stage fixed-bed reactor filled with macroporous acidic resin at a liquid hourly space velocity of 0.3240 h⁻¹. The center temperature of the first-stage fixed-bed reactor was 111 °C, and the reaction pressure was 0.10 MPa. The liquid reaction feedstock was not accompanied by nitrogen flow during the reaction. The conversion rate of dodecanol during the first-stage reaction was monitored by periodic sampling and gas chromatography detection. After 3.09 h of reaction, the conversion rate of dodecanol reached 47.83%.

Example 7

607.08 g of methacrylic acid, 976.56 g of 1-dodecanol, 312.39 g of 1-tetradecanol and 1.3 g of hydroquinone was mixed thoroughly. After the mixed raw materials were preheated to approximately 100°C, they were introduced into a first-stage fixed-bed reactor filled with macroporous acidic resin at a liquid hourly space velocity of 0.323 h⁻¹. The center temperature

of the first-stage fixed-bed reactor was 111 °C, and the reaction pressure was 0.3 MPa. During the reaction, the liquid reaction mixture was accompanied by nitrogen flow at a nitrogen space velocity of 70.41 h⁻¹. During the reaction, the conversion rate of dodecanol during the first-stage
5 reaction was monitored by periodic sampling and gas chromatography detection. The reaction was stopped when the conversion rate of dodecanol reached 92.55%; after the reaction liquid was discharged from the reactor, the organic phase was distilled under reduced pressure to reduce the water content in the organic phase to 870 ppm; at this time the conversion rate of
10 tetradecanol was 90.17%. 148.54 g of methacrylic acid and 1.3 g of hydroquinone were added to the organic phase, and after thorough mixing, the mixture was introduced into a second-stage fixed-bed reactor filled with macroporous acidic resin at a liquid hourly space velocity of 0.387 h⁻¹. The center temperature of the second-stage fixed-bed reactor was 111°C and the
15 reaction pressure was 0.3 MPa. During the reaction, liquid reaction feedstock was accompanied by nitrogen flow at a nitrogen hourly space velocity of 8.4 h⁻¹. During the reaction, the conversion rate of dodecanol during the second-stage reaction was monitored by periodic sampling and gas chromatography detection. The reaction was terminated when the
20 conversion rate of dodecanol reached 99.45%. The reaction liquid was discharged from the reactor and cooled to room temperature. The organic phase obtained by centrifugation was subjected to a post-treatment to remove polymerization inhibitors contained herein and decolorize the product, yielding a purified mixture of dodecyl methacrylate and tetradecyl
25 methacrylate. Gas chromatography analysis of the final product showed a conversion rate of tetradecanol of 99.5%, a yield of dodecyl methacrylate of 98.75%, and a yield of tetradecyl methacrylate of 98.25%. The total residence time of the reaction liquid in the two-stages fixed-bed reactors was 5.68 h.

30

Example 8

607.08 g of methacrylic acid, 976.56 g of 1-dodecanol, 312.39 g of 1-

tetradecanol and 1.3 g of hydroquinone was mixed thoroughly. After the mixed raw materials were preheated to approximately 100°C, they were introduced into a first-stage fixed-bed reactor filled with macroporous acidic resin at a liquid hourly space velocity of 0.323 h⁻¹. The center temperature of the first-stage fixed-bed reactor was 111 °C, and the reaction pressure was 10 kPa. During the reaction, the liquid reaction mixture was not accompanied by nitrogen. The conversion rate of dodecanol was monitored by periodic sampling and gas chromatography detection. The reaction was stopped when the conversion rate of dodecanol reached 96.25%. The reaction liquid was discharged from the reactor and centrifuged to obtain an organic phase and an aqueous phase. At this point, the conversion rate of tetradecanol was 93.57%. 210.36 g of methacrylic acid and 1.3 g of hydroquinone were added to the organic phase, and after thorough mixing, the mixture was introduced into a second-stage fixed-bed reactor filled with macroporous acidic resin at a liquid hourly space velocity of 0.43 h⁻¹. The center temperature of the second-stage fixed-bed reactor was 112 °C, and the reaction pressure was 10 kPa. During the reaction, the liquid reaction mixture was not accompanied by nitrogen. During the reaction, the conversion rate of dodecanol during the reaction was monitored by periodic sampling and gas chromatography detection. The reaction was terminated when the conversion rate of dodecanol reached 99.41%. The reaction liquid was discharged from the reactor and then cooled to room temperature. The organic phase obtained by centrifugation was subjected to a post-treatment to remove polymerization inhibitors contained herein and decolorize the product, yielding a purified mixture of dodecyl methacrylate and tetradecyl methacrylate. Gas chromatography analysis of the final product showed a conversion of tetradecanol of 98.78%, a yield of dodecyl methacrylate of 98.85%, and a yield of tetradecyl methacrylate of 98.45%. The total residence time of the reaction liquid in the two-stages fixed-bed reactors was 5.42 h.

Example 9

607.08 g of methacrylic acid, 976.56 g of 1-dodecanol, 312.39 g of 1-tetradecanol, and 1.3 g of hydroquinone were thoroughly mixed. After the mixed raw materials were preheated to approximately 100°C, they were introduced from the bottom of reactor into a first-stage fixed-bed reactor
5 filled with macroporous acidic resin at a liquid hourly space velocity of 0.323 h⁻¹. The center temperature of the first-stage fixed-bed reactor was 111 °C, and the reaction pressure was 0.1 MPa. During the reaction, the liquid reaction mixture was not accompanied by nitrogen. During the reaction, the conversion rate of dodecanol was monitored by periodic
10 sampling and gas chromatography detection. After 3.10 h of reaction, the conversion rate of dodecanol was measured to be 58.86%, at which point the reaction was stopped. The reaction liquid was discharged from the reactor and centrifuged to obtain an organic phase and an aqueous phase. At this point, the conversion rate of tetradecanol was 54.38%.

15

Example 10

607.08 g of methacrylic acid, 976.56 g of 1-dodecanol, 312.39 g of 1-tetradecanol and 1.3 g of hydroquinone were mixed thoroughly. After the mixed raw materials were preheated to approximately 100°C, they were
20 introduced into a first-stage fixed-bed reactor filled with macroporous acidic resin at a liquid hourly space velocity of 0.323 h⁻¹. The center temperature of the first-stage fixed-bed reactor was 111 °C, and the reaction pressure was 0.3 MPa. During the reaction, the liquid reaction mixture was accompanied by nitrogen flow at a nitrogen space velocity of 70.41 h⁻¹. The
25 conversion rate of dodecanol during the first-stage reaction was monitored by periodic sampling and gas chromatography detection. The reaction was stopped when the conversion rate of dodecanol reached 92.55%. After the reaction liquid was discharged from the reactor, the organic phase was distilled under reduced pressure to reduce the water content in the organic
30 phase to 870 ppm, at which point the conversion rate of tetradecanol was 90.17%. 148.54 g of methacrylic acid and 1.3 g of hydroquinone were added to the organic phase, and after thorough mixing, the mixture was introduced

into a second-stage fixed-bed reactor filled with macroporous acidic resin at a liquid hourly space velocity of 0.387 h^{-1} . The center temperature of the second-stage fixed-bed reactor was 111°C , the reaction pressure was 0.3 MPa. During the reaction, the liquid reaction mixture was accompanied by
5 nitrogen flow at a nitrogen space velocity of 8.4 h^{-1} . During the reaction, the conversion rate of dodecanol during the second-stage reaction was monitored by periodic sampling and gas chromatography detection. The reaction was terminated when the conversion rate of dodecanol reached 99.45%. The reaction liquid was discharged from the reactor and cooled to
10 room temperature. The organic phase obtained by centrifugation was subjected to a post-treatment to remove polymerization inhibitors contained herein and decolorize the product, yielding a purified mixture of dodecyl methacrylate and tetradecyl methacrylate. Gas chromatography analysis of the final product showed a conversion rate of tetradecanol of 99.5%, a yield
15 of dodecyl methacrylate of 98.75%, and a yield of tetradecyl methacrylate of 98.25%. The total residence time of the reaction liquid in the two-stages fixed-bed reactors was 5.68 h.

Comparative Example 1

20 905.62 g of methacrylic acid, 1305.8 g of 1-dodecanol and 1.3 g of hydroquinone were thoroughly mixed. After the mixed raw materials were preheated to approximately 100°C , they were introduced into a first-stage fixed-bed reactor filled with macroporous acidic resin at a liquid hourly space velocity of 0.172 h^{-1} . The center temperature of the first-stage fixed-
25 bed reactor was 115°C , and the reaction pressure was 0.3 MPa. During the reaction, the liquid reaction mixture was accompanied by nitrogen flow at a nitrogen space velocity of 10.71 h^{-1} . After the reaction liquid was discharged from the reactor, it was cooled to room temperature and centrifuged to obtain an organic phase and an aqueous phase. At this point, the conversion
30 rate of dodecanol was 94.92%. 1.3 g of hydroquinone was added to the organic phase, and after thorough mixing, it was introduced into a second-stage fixed-bed reactor filled with macroporous acidic resin at a liquid

hourly space velocity of 0.172 h^{-1} . The center temperature of the second-stage fixed-bed reactor was 115°C , and the reaction pressure was 0.3 MPa . During the reaction, the liquid reaction mixture was accompanied by nitrogen flow at a nitrogen space velocity of 11.13 h^{-1} . The reaction liquid
5 was discharged from the reactor and cooled to room temperature. The organic phase obtained by centrifugation was subjected to a post-treatment to remove polymerization inhibitors contained herein and decolorize the product, yielding purified dodecyl methacrylate. Gas chromatography analysis of the final product showed a conversion rate of dodecanol of
10 97.26% and a yield of dodecyl methacrylate of 93.11% . The total residence time of the reaction liquid in the two-stages fixed-bed reactors was 11.63 h .

Comparative Example 2

Methacrylic acid, dodecanol, and hydroquinone were thoroughly mixed
15 in the following proportions: 766.55 g methacrylic acid, 1102.05 g 1-dodecanol, and 2.65 g hydroquinone. After the mixture was preheated to approximately 100°C , it was introduced into a fixed-bed reactor filled with macroporous acidic resin at a liquid hourly space velocity of 0.1 h^{-1} . The center temperature of the fixed-bed reactor was 111°C , and the reaction
20 pressure was 0.95 MPa . During the reaction, the liquid reaction mixture was accompanied by nitrogen flow at a nitrogen space velocity of 33.63 h^{-1} . After the reaction liquid was discharged from the reactor, it was cooled to room temperature and centrifuged to obtain an organic phase and an aqueous phase, wherein the amount of water in the aqueous phase represented 86%
25 of the generated water. The organic phase underwent post-treatment to remove polymerization inhibitors contained herein and decolorize the product, yielding purified dodecyl methacrylate. Gas chromatography analysis of the final product showed a conversion rate of dodecanol of
30 98.99% and a yield of dodecyl methacrylate of 94.75% . The residence time of the reaction liquid in the fixed-bed reactor is 10 h .

Comparative Example 3

77.48 g of methacrylic acid, 111.81 g of 1-dodecanol, and 0.28 g of hydroquinone were added to a reaction flask and mixed thoroughly. 5 g of macroporous acidic resin catalyst was added, and N₂ was introduced into the reaction liquid and the temperature was raised. Distillation was carried out at atmospheric pressure. The esterification reaction time was calculated starting from the reaction solution is heated to 100°C, and the reaction temperature was controlled at 113°C. Water generated during the esterification reaction was continuously distilled off along with the methacrylic acid using a water separator. After 14.0 h of reaction, unreacted methacrylic acid was distilled off under reduced pressure. The catalyst was removed by filtration, and the liquid phase was washed with a 5wt% sodium hydroxide solution at 30°C, then treated with demineralized water until neutral, subjected to a vacuum distillation under a vacuum of 10 kPa, and was decolorized with bleaching clay to obtain dodecyl methacrylate. Gas chromatography analysis of the reaction liquid showed a conversion rate of dodecanol of 98.01%.

The implementation schemes and the obtained technical effects of the above examples and comparative examples are shown in Table 1 below.

Table 1

Exam ple	Methacryl ic acid/ total alcohol (mol/mol)	Stage number of reaction	Space velocity (h ⁻¹) of two nitrogen flows	Inter-stage water removal mode	First-stage conversion rate alcohol (%)	Supple mented methac rylic acid (g)	Total conversion rate of alcohol (%)	yield of methacrylate (%)	Total residen ce time (h)
Ex. 1	6.65/6.34	2	9.61/11.24	Centrifugation	93.18	151.19	99.69	98.70	9.04
Ex. 2	7.31/7	2	14.98/12.18	Centrifugation	87.61	30.57	98.54	98.67	8.15
Ex. 3	7.31/7	2	14.98/10.75	Centrifugation	87.61	80.36	99.04	98.85	7.55
Ex. 4	7.36/7	2	14.61/10.47	Centrifugation	89.77	95.49	99.33	98.92	8.22
Ex. 5	7.36/7	2	14.61/10.4	Centrifugation	89.76	95.49	99.25	98.80	7.75
Ex. 6	7.36/7	1	No nitrogen flow	/	47.83	/	47.83	/	3.09
Ex. 7	7.05/6.71	2	70.41/8.4	Distillation	92.55/90.17 (dodecanol/t etradecanol)	148.54	99.45/99.5 (dodecanol/tet radecanol)	98.75/98.25 (dodecyl methacrylate /tetradecyl methacrylate)	5.68
Ex. 8	7.05/6.71	2	No nitrogen flow, negative pressure	Centrifugation	96.25/93.57 (dodecanol/t etradecanol)	210.36	99.41/98.78 (dodecanol/tet radecanol)	98.85/98.45 (dodecyl methacrylate /tetradecyl methacrylate)	5.42
Ex. 9	7.05/6.71	1	No nitrogen flow	/	58.86/54.38 (dodecanol/t etradecanol)	/	58.86/54.38 (dodecanol/tet radecanol)	/	3.10
Ex. 10	7.05/6.71	2	70.41/8.40	Distillation	92.55/90.17 (dodecanol/t etradecanol)	148.54	99.65/99.50 (dodecanol/tet radecanol)	98.75/98.25 (dodecyl methacrylate /tetradecyl methacrylate)	5.68
Comp .Ex. 1	10.54/7.0 2	2	10.71/11.13	Centrifugation	94.92	none	97.26	93.11	11.63
Comp .Ex. 2	8.9/5.9	1	33.63	No water removal	98.99	none	98.99	94.75	10
Comp .Ex. 3	9/6	1	No nitrogen flow	Continuous water removal during the reaction	-	none	98.01	-	14.0

According to the above examples and comparative examples, it can be seen that in Comparative Example 1, after separating the aqueous phase between stages, no methacrylic acid was supplemented to the organic phase; compared to Examples 1-9 of the invention, a significantly longer reaction time was required in Comparative Example 1; no staged reactions method was employed in Comparative Example 2; and compared to Examples 1-9 of the invention, a significantly longer reaction time was required in Comparative Example 2, and both the conversion rate of alcohol and the yield of product are significantly lower; the reaction was carried out in a reaction vessel in Comparative Example 3 instead of a fixed-bed reactor, wherein a water separator was used to continuously distill off the water generated in the esterification reaction along with the methacrylic acid; compared to Examples 1-9 of the invention, a significantly longer reaction time was required in Comparative Example 3, and both the conversion rate and the yield were significantly lower. In Examples 1-5 and 7, the esterification reaction was carried out under nitrogen flow conditions, which can achieve results similar to those of the esterification reaction in Example 8 under negative pressure conditions. However, the nitrogen flow method provides better control of the reaction conditions and reduces energy consumption compared to the negative pressure conditions. By comparing Examples 5 and 6 with Comparative Examples 7 and 9, it can be seen that the nitrogen flow accompanied with the reaction liquid during the esterification reaction can further improve the kinetics of the esterification reaction, increase the reaction rate, and thus further reduce the reaction time. Moreover, the nitrogen flow accompanied with the reaction liquid can also carry away some of the water generated by the reaction. According to the above examples and comparative examples, it can also be seen that controlling the liquid hourly space velocity, the esterification reaction temperature difference, and the amount of supplemented (alkyl)acrylic acid within

the preferred range can produce better reaction results.

The following examples further illustrate the technical solution for removing polymerization inhibitors according to the invention and the produced effect of removing polymerization inhibitors.

5

Example 10

In Example 1, after the reaction was terminated, the organic phase solution containing dodecyl methacrylate and obtained by centrifugation for removing the aqueous phase was analyzed by spectrophotometry to contain 0.14 wt% hydroquinone. This organic phase solution was subjected to a two-stages cross-flow extraction in a centrifugal extractor at 30°C using a water-based extraction solvent containing 60 wt% water (a mixture of 60 wt% water and 40 wt% methanol) as the extractant. The amount of extractant used in each stage was 60 wt% of the mass of the hydroquinone and dodecyl methacrylate solution. After extraction, the hydroquinone content in the dodecyl methacrylate solution was 0.0008 wt%, and the removal rate of hydroquinone was as high as 99.43%.

20 Example 11

The same organic phase solution from Example 1 containing 0.14wt% hydroquinone as in Example 10 above was used. However, in this example, a water-based extraction solvent containing 80% water (a mixture of 80% water and 20% methanol) was used as the extractant for continuous countercurrent extraction in a packed column at 30°C. The flow rate of the organic phase solution containing hydroquinone and dodecyl methacrylate was 265.83 g/h, and the flow rate of the extractant was 159.50 g/h. After extraction, the hydroquinone content in the dodecyl methacrylate solution was 0.0010 wt%, and the removal rate of hydroquinone was as high as 99.29%.

Example 12

The same organic phase solution from Example 1 containing 0.14wt% hydroquinone as in Example 10 above was used. However, in this example, a water-based extraction solvent containing 100wt% water was used as the extractant for continuous countercurrent extraction in a packed column. The flow rate of the organic phase solution containing hydroquinone and dodecyl methacrylate was 265.83 g/h, the flow rate of the extractant was 159.50 g/h, and the extraction temperature was 61.14 °C. After continuous countercurrent extraction, the hydroquinone content in the dodecyl methacrylate solution was 0.0015wt%, and the removal rate of hydroquinone was as high as 98.93%.

Example 13

The same organic phase solution from Example 1 containing 0.14wt% hydroquinone as in Example 10 above was used. However, in this example, water with a water content of 100wt% was used as the extractant for two-stages cross-flow extraction in a centrifugal extractor at 60 °C. The amount of extractant used in each stage was 100wt% of the mass of the hydroquinone and dodecyl methacrylate solution. After extraction, the hydroquinone content in the dodecyl methacrylate solution was 0.0019wt%, and the removal rate of hydroquinone was as high as 98.64%.

The technical solutions and technical effects of the above examples 10-13 are shown in Table 2 below.

Table 2.

	Extractant	Extraction method	Extractant amount relative to the mass of the product solution	Hydroquinone content after extraction	Removal rate of Hydroquinone
Ex. 10	60wt% water + 40wt% methanol	Two-stages cross-flow extraction	60wt%	0.0008wt%	99.43%
Ex. 11	80wt% water + 20wt% methanol	Continuous countercurrent extraction	56wt%	0.0010wt%	99.29%
Ex. 12	100wt% water	Continuous	56wt%	0.0015wt%	98.93%

		countercurrent extraction			
Ex. 13	100wt% water	Two-stages cross-flow extraction	100wt%	0.0019wt%	98.64%

As shown in Table 2 above, the extraction of an organic solution containing hydroquinone and dodecyl methacrylate by a water-based solvent can almost completely extract hydroquinone, yielding high-
5 purity dodecyl methacrylate. The extract can be distilled to recover the alcohol, and since the water-based solvent does not contain alkali, this method does not produce secondary pollution. By comparing Example 10 with Example 13 or by comparing Example 11 with Example 12, it can be seen that including a small amount of alcohol
10 in the water-based extractant can further significantly improve the extraction efficiency.

Examples 14-15 and Comparative Example 4 are used to illustrate the technical solution for separating (alkyl)acrylic acid in the aqueous phase of the invention and the technical effect of recovering
15 (alkyl)acrylic acid. The packed columns used in Examples 14 and 15 differed only in the type of packing material; the packing quantity and packing method were identical.

Example 14

20 After the first-stage reaction in Example 1 was terminated, the aqueous phase obtained through phase separation was analyzed by gas chromatography to contain 18wt% methacrylic acid. By using dodecanol as the extractant, a continuous countercurrent extraction was performed in a packed column filled with hydrophilic packing
25 material. The flow rate of the aqueous solution of methacrylic acid was 141.45 g/h, the extractant flow rate was 132.96 g/h, and the extraction temperature was 45.87°C. After 1 hour of continuous countercurrent extraction, the methacrylic acid content in the extracted aqueous solution of methacrylic acid was 0.0010wt%, and

the mass of the extracted aqueous solution was 116.0 g. Therefore, the removal rate of methacrylic acid was 99.99%.

Example 15

5 This example was implemented according to the operation method of Example 14, except that: a mixed n-dodecanol/n-tetradecanol was used as the extractant, and continuous countercurrent extraction was carried out in a packed column filled with hydrophilic packing materials. The flow rate of the aqueous solution of methacrylic acid
10 was 141.45 g/h, the flow rate of the extractant was 152.15 g/h, the extraction temperature was 47.87 °C; and after 1 hour of continuous countercurrent extraction, the methacrylic acid content in the extracted aqueous solution of methacrylic acid was 0.0017wt%, and the mass of the extracted aqueous solution was 116.0 g; therefore, the
15 removal rate of methacrylic acid was 99.98%.

Comparative Example 4

 This comparative example was carried out according to the operating method of Example 14, except that: continuous
20 countercurrent extraction was carried out in a packed column filled with lipophilic packing material. The flow rate of the aqueous solution of methacrylic acid was 141.09 g/h, the flow rate of the extractant was 141.10 g/h, the extraction temperature was 45.96°C, and after 1 hour of continuous countercurrent extraction, the content of methacrylic
25 acid in the aqueous solution of methacrylic acid was 0.45wt%, and the mass of the extracted aqueous solution was 118.9 g; the removal rate of methacrylic acid was 97.94wt%.

Comparative Example 5

30 The same aqueous solution containing 18wt% of methacrylic acid and extractant as in Example 15, except that: the extraction was carried out in a separatory funnel, wherein the amount of the added

aqueous solution of methacrylic acid was 50 g, the amount of the added extractant was 140 g, and the extraction temperature was 40 °C. The mixed solution was thoroughly mixed in the separatory funnel, left to stand and separate into phases, and after separation, a heavy component aqueous phase and a light component organic phase were obtained; the methacrylic acid content in the aqueous phase was 0.6 wt%, the mass of the aqueous phase was 32.75 g, and the removal rate of methacrylic acid was 97.82%.

The extraction schemes and extraction effects of Examples 14-15 and Comparative Example 4 are shown in Table 3 below.

Table 3.

	Extractant	Extraction method	Packing material type	Residual methacrylic acid content after extraction	Removal rate of methacrylic acid
Ex. 14	dodecanol	Continuous countercurrent extraction	Hydrophilic packing materials	0.0010wt%	99.99wt%
Ex. 15	mixed dodecanol/tetradecanol mixture	Continuous countercurrent extraction	Hydrophilic packing materials	0.0017wt%	99.98wt%
Comp. Ex. 4	dodecanol	Continuous countercurrent extraction	Lipophilic packing materials	0.45wt%	97.94wt%
Comp. Ex. 5	dodecanol	Separating funnel	No packing material	0.6 wt%	97.82wt%

As can be seen from the data in Table 3 above, the extraction effect of methacrylic acid of Examples 14-15 using hydrophilic packing materials is significantly better than the extraction effect of methacrylic acid of Comparative Example 4 using lipophilic packing materials. Furthermore, the extraction effect of methacrylic acid obtained by continuous countercurrent extraction using a packed column is significantly better than the extraction effect of methacrylic acid of Comparative Example 5 using a separatory funnel. The aqueous phases treated according to Examples 14-15 meet environmental protection requirements. The extract phase obtained in the above examples can be returned as raw materials to the esterification reaction.

The preferred embodiments of the invention have been described in detail above; however, the invention is not limited thereto. Within the scope of the inventive concept, various simple modifications can be made to the technical solutions of the invention, including
5 combinations of various technical features in any other suitable manner. These simple modifications and combinations should also be considered as the content disclosed in the invention and are all within the protection scope of the invention.

Claims

1. A method for preparing (alkyl)acrylates, characterized in that the method comprises the following steps:

5 (1) mixing (alkyl)acrylic acid, an alcohol and optionally a polymerization inhibitor to perform a first-stage esterification reaction;

 (2) separating the aqueous phase in the product of the first-stage esterification reaction, and adding (alkyl)acrylic acid, optionally an
10 alcohol, and/or a polymerization inhibitor to the remaining organic phase to subject the organic phase to a second-stage esterification reaction; and optionally

 (3) separating the aqueous phase in the product of the previous-stage esterification reaction, to obtain and discharge the remaining
15 organic phase containing esterification product, or adding (alkyl)acrylic acid, optionally an alcohol and/or a polymerization inhibitor to the remaining organic phase to subject the organic phase to a N^{th} -stage esterification reaction, wherein $N \geq 3$, repeating this cycle multiple times, to obtain and discharge the remaining organic
20 phase containing esterification product.

2. The method according to claim 1, characterized in that the method further comprises the following steps:

 (4) subjecting the remaining organic phase containing esterification product obtained in step (3) to a post-treatment to obtain
25 purified (alkyl)acrylates, preferably the post-treatment includes: removing the polymerization inhibitor and/or decolorizing the product.

3. The method according to claim 1 or 2, characterized in that, the esterification reaction is carried out in the presence of a solid acid catalyst, preferably the esterification reaction is carried out in a fixed-
30 bed reactor.

4. The method according to any one of claims 1-3, characterized in that, calculated as alcohol hydroxyl group, the conversion rate of

the first-stage esterification reaction is 40-95%, preferably 70-94%;
and/or, calculated as alcohol hydroxyl group, the conversion rate
of the second-stage esterification reaction is 40-100%, preferably 70-
99.5%;

5 and/or, calculated as alcohol hydroxyl group, the conversion rate
of the Nth-stage esterification reaction is 40-100%, preferably 70-
99.5%;

and/or, calculated as alcohol hydroxyl group, the total conversion
rate of each stage esterification reaction is $\geq 99\%$, preferably $\geq 99.5\%$.

10 5. The method according to any one of claims 1-4, characterized
in that, in step (2) and/or step (3), the separation method of aqueous
phase in the product of the esterification reaction is distillation and/or
liquid-liquid phase separation, preferably at least one of distillation,
flash evaporation, stripping, sedimentation, decantation, coalescence
15 and centrifugation.

6. The method according to any one of claims 1-5, characterized
in that each stage esterification reaction is carried out under a flowing
inactive gas atmosphere, preferably, the ratio of the volumetric space
velocity of the inactive gas to the liquid hourly space velocity of the
20 liquid feedstock is 0-1000:1, more preferably 10-250:1; and/or, the
volumetric space velocity of the inactive gas is 3-500 h⁻¹, more
preferably 8-80 h⁻¹, more preferably 8-40 h⁻¹.

7. The method according to any one of claims 1-6, characterized
in that the method further comprises: in step (2) and/or step (3), the
25 amount of (alkyl)acrylic acid supplemented is such that the molar ratio
of (alkyl)acrylic acid in each addition, calculated as carboxyl group,
to all alcohols, calculated as hydroxyl group, is 0.05-2:1, preferably
0.05-0.5:1, and the amount of polymerization inhibitor supplemented
at each time is 0.01-3wt% of the total weight of (alkyl)acrylic acid and
30 alcohols, preferably 0.01-1wt%.

8. The method according to any one of claims 1-7, characterized
in that the molar ratio of the (alkyl)acrylic acid calculated as carboxyl

group to the alcohol calculated as hydroxyl group in step (1) is 0.1-2:1, preferably 0.8-1.1:1;

and/or, the molar ratio of the (alkyl)acrylic acid calculated as carboxyl group to the alcohol calculated as hydroxyl group in the entire preparation process is 1-4:1, preferably 1.05-1.5:1.

9. The method according to any one of claims 1-8, characterized in that the alkyl group in the (alkyl)acrylic acid has less than or equal to 8 carbon atoms, preferably less than or equal to 4 carbon atoms, and more preferably, the alkyl group in the (alkyl)acrylic acid is methyl, ethyl, or propyl;

and/or, the alcohol is a fatty alcohol with a normal boiling point above 100°C, which is insoluble or slightly soluble in water, preferably at least one of monohydric alcohols having 9-22 carbon atoms, more preferably at least one of n-decanol, n-undecanol, n-dodecanol, n-tetradecanol, n-hexadecanol, and n-octadecanol.

10. The method according to any one of claims 1-9, characterized in that the total amount of the polymerization inhibitor used is 0.03-5wt% of the total weight of (alkyl)acrylic acid and alcohol;

and/or, the polymerization inhibitor is at least one of phenolic polymerization inhibitors, quinone polymerization inhibitors, aromatic amine polymerization inhibitors, and inorganic salt polymerization inhibitors.

11. The method according to any one of claims 1-10, characterized in that the conditions for each stage esterification reaction independently include: a temperature of 80-140°C, preferably 90-130°C; a pressure of 0-10 MPa A, preferably 0.002-2 MPa A; and a liquid hourly space velocity of the reaction feedstock of 0.1-3 h⁻¹, preferably 0.18-1 h⁻¹; and/or, the temperature of the previous stage esterification reaction is lower than that of the subsequent stage esterification reaction by 1-10°C, preferably 1-5°C.

12. The method according to claim 2, characterized in that, in step (4), the method for removing the polymerization inhibitor is alkaline

washing or extraction, preferably extraction, wherein the conditions for extraction are: an extraction temperature of 0-90°C, preferably 25-70 °C; the ratio of the mass of the extractant to the mass of the (alkyl)acrylate solution containing the polymerization inhibitor of 5 0.1-5:1, preferably 0.3-1.2:1; and/or the extraction device is one or more combinations of packed column, plate column, rotating disc column, centrifugal extractor, spiral extractor and mixer-settler; and/or the extractant includes alcohol-based extractant and/or water-based extractant, preferably water-based extractant; more preferably, 10 the water content in the mixture of water and alcohol is 10-100wt%, preferably 60-90wt%.

13. The method according to any one of claims 1-12, characterized in that the method further comprises step (5): further extracting the aqueous phase obtained in step (2) and/or step (3) with an extractant 15 to recover (alkyl)acrylic acid to obtain an extract containing (alkyl)acrylic acid; preferably, the extractant is at least one or more of the hydrophobic alcohols that participate in the esterification reaction and the hydrophobic (alkyl)acrylate; extraction conditions: an extraction temperature of 0-90°C, preferably 25-60°C; a mass ratio 20 of the extractant to the aqueous phase of 0.1-5:1, preferably 0.3-1.0:1; the extraction device is one or more selected from packed columns, plate columns, rotating disc columns, centrifugal extractors, spiral extractors and mixer-settler, preferably packed extraction columns, and preferably the packing materials are surface hydrophilic packing 25 materials.

14. The method according to claim 13, characterized in that the extract containing (alkyl)acrylic acid recovered in step (5) is returned to any of steps (1) to (3) as a reaction feedstock.

15. A reaction system for carrying out the method according to 30 any one of claims 1-14, comprising: a plurality of esterification reactors connected in series, and one or more phase separators or distillers for separating an organic phase and an aqueous phase which

are respectively connected to each reactor; wherein each esterification reactor includes an inlet dedicated for feeding fresh reaction feedstock or alternatively, an inlet is provided between the esterification reactor and the phase separator or distiller for introducing fresh reaction
5 feedstock into the remaining organic phase from the previous stage reaction.

16. The reaction system according to claim 15, characterized in that the phase separator or distiller is selected from a centrifugal phase separator or a distillation column.

10 17. The reaction system according to claim 16, characterized in that it further comprises: an extraction device for separating the polymerization inhibitor connected to the last phase separator or distillation column, preferably, said extraction device is one or more selected from packed columns, plate columns, rotating disc columns,
15 centrifugal extractors, spiral extractors, and mixer-settler.