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(71) Applicant: BP P.L.C. [GB/GB]; 1 St James's Square, London SW1Y 4PD (GB).

(72) Inventors; and

(71) Applicants (for US only): DOUGLAS, Thomas Mark [GB/GB]; Saltend, Hedon, Hull East Yorkshire HU12 8DS

(GB). THAKAR, Nakul [GB/GB]; Saltend, Hedon, Hull East Yorkshire HU12 8DS (GB).

(74) Agent: PEDLEY, Michael Ewan; BP International Limited, Global Patents & Technology Law, Chertsey Road, Sunbury on Thames Middlesex TW16 7LN (GB).

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(54) Title: REMOVAL OF NITROGEN-CONTAINING IMPURITIES FROM ALCOHOL COMPOSITIONS

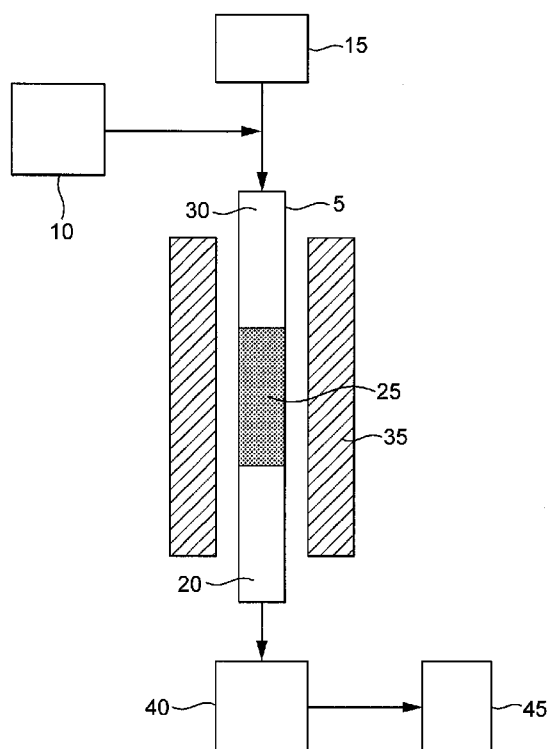


FIG. 1

(57) Abstract: A process for the treatment of an alcohol composition comprising nitrogen-containing contaminants, the process comprising contacting the alcohol composition in the vapour phase with an adsorbent in an adsorption zone.



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REMOVAL OF NITROGEN-CONTAINING IMPURITIES FROM ALCOHOL COMPOSITIONS

This invention provides a process for the treatment of alcohol compositions to remove nitrogen-containing contaminants. Also provided is a process for the preparation of olefins from alcohols by dehydration, the process comprising treating an alcohol composition to remove nitrogen-containing contaminants prior to dehydration of the alcohols. Also provided are alcohol compositions obtainable by the treatment process of the present invention.

Alcohols, such as saturated monohydric alcohols, are important chemical commodities which may be used as fuels or as components of fuels, as solvents, and as feedstocks for the preparation of other important commodity chemicals. Ethanol in particular is widely used commercially as a gasoline additive or as a fuel *per se*, as a solvent, as a germicide, as an antifreeze, as a component in the food and beverage industry, and as a chemical feedstock.

Ethanol, and to a lesser extent propanol and butanol, are of increasing significance as chemical feedstocks, since they are readily obtainable from biological sources, in particular by the fermentation of sugars and/or biomass. Alcohols from biological sources, so-called bio-alcohols, thus provide one way of reducing the dependence on crude oils for fuel uses and as chemical feedstocks.

Bio-alcohols, and bio-ethanol in particular, are typically produced by fermentation processes performed on biomass and/or derivatives thereof. As used herein, the term "biomass" includes sugar sources, for instance sugar beet, sugar cane, molasses and corn syrup, starches and cellulosic materials, such as lignocellulose. Starches and cellulosic materials are generally converted by enzymatic or chemical hydrolysis to produce simple sugars which can then be converted to bio-alcohols by fermentation. Ethanol obtained from cellulosic materials is commonly referred to as cellulosic ethanol or lignocellulosic ethanol.

Alcohols obtained by fermentation contain low levels of nitrogen-containing contaminants. One possible source of nitrogen-containing contaminants may be ammonia which may be introduced during the fermentation stage. Once in the process, the ammonia can react with ethanol and other impurities to form a variety of nitrogen-containing

compounds. Nitrogen-containing contaminants are also often present in alcohols from other sources.

The presence of nitrogen-containing contaminants in alcohol compositions is undesirable since these compounds may interfere with subsequent chemical processing in which the alcohol composition is used as a feedstock. For example, nitrogen-containing contaminants can poison, deactivate or otherwise interfere with a number of catalysts which may be used in the processing of alcohol feedstocks, for example by neutralising acidic sites on heterogeneous acidic catalysts.

An example of the use of heterogeneous acidic catalysts for the processing of alcohols is the dehydration of alcohols to form olefins. Olefins, such as ethylene, have historically been produced by steam or catalytic cracking of hydrocarbons derived from crude oil. However, as crude oil is a finite resource, methods for the preparation of olefins by the dehydration of alcohols have been proposed. For instance, WO 2009/098262 discloses a process for the catalytic dehydration of an alcohol to the corresponding olefin wherein the catalyst is selected from a crystalline silicate, a dealuminated crystalline silicate or a phosphorus modified zeolite; WO 2008/138775 discloses a process for the dehydration of one or more alcohols comprising contacting one or more alcohols with a supported heteropolyacid catalyst in the presence of one or more ethers; and WO 2008/062157 discloses a heteropolyacid catalyst and the use thereof in a process for the production of olefins from oxygenates.

Olefins produced in this way have a range of potential applications, for instance as feedstocks for the production of polymeric materials. In particular, ethylene obtained by the dehydration of ethanol may usefully be processed into polyethylene. Similarly, the dehydration of propanols provides a route to propylene which may subsequently be processed into polypropylene.

It has been observed that catalysts used for the dehydration of alcohols, such as crystalline silicate, dealuminated crystalline silicate, phosphorus modified zeolite or supported heteropolyacid catalysts, are sensitive to the presence of low levels of nitrogen-containing contaminants in alcohol feedstocks. Consequently, in order to ensure commercially acceptable catalyst performance and lifetime, it is highly desirable to treat alcohol feedstocks to remove nitrogen-containing contaminants prior to the dehydration

reaction. As noted above, the presence of low levels of nitrogen-containing contaminants is a feature of alcohol compositions obtained from at least biological sources.

The use of cation exchange resins and sorbents for the removal of nitrogen-containing compounds from hydrocarbon streams is known in the petrochemical industry.

5 However, the sensitivity of many acidic catalysts, such as the supported heteropolyacid catalysts mentioned above, to nitrogen-containing contaminants is such that very stringent removal of these compounds is required, for instance to 1 ppm or less, preferably 0.5 ppm or less, and most preferably 0.2 ppm or less; very low concentrations of nitrogen-containing contaminants are desirable in order to obtain a useful catalyst lifetime. It has
10 been observed that the use of cation exchange resins alone may be inadequate to obtain such stringent removal of nitrogen-containing contaminants from alcohol compositions and that additional treatment of the alcohol composition may be required. It is therefore of significant commercial interest to be able to identify new processes which are able to remove nitrogen-containing contaminants from alcohols, particularly bio-alcohols such as
15 bio-ethanol.

WO 1997/045392 discloses a process for the production of ethers in which deactivation of an acidic ion-exchange resin etherification catalyst is reduced by separating nitriles from an olefin feedstock by aqueous extraction. The nitriles are subsequently separated into an alcohol phase and hydrogenated to form amines which are more easily
20 separable from the alcohol phase by fractionation.

EP 1 176 132 A1 discloses a process for preparing ethers comprising reacting an alcohol and an olefin in the presence of an acidic catalyst. Excess alcohol is recycled to the reaction zone together with nitrile compounds originating from the olefin feed. To avoid accumulation of nitriles in the system and deactivation of the catalyst, the excess
25 alcohol comprising nitrile compounds is contacted in the liquid phase with a solid acid prior to being recycled to the reaction zone. It is reported that this reduces the level of nitriles in the recycled alcohol stream by at least 50 %.

US 6,770,790 discloses a process for removing oxygen-containing impurities from tertiary butyl alcohol comprising contacting the tertiary butyl alcohol in the liquid phase
30 with at least two solid adsorbents, wherein the at least two solid adsorbents comprise aluminium oxide and a large pore zeolite.

WO 2010/060981 discloses a process for the purification of an alcohol in the course of a process for the preparation of olefins by acid-catalysed dehydration of the alcohol, the process comprising contacting the alcohol with one or more adsorbent materials. It is disclosed in WO 2010/060981 that while ammonia and amines can be adsorbed, nitrile
5 impurities such as acetonitriles must be hydrogenated to provide modified impurities which are more readily adsorbed. Thus, according to WO 2010/060981, the alcohol feed is subjected to a hydrogenation step prior to contacting the alcohol with the one or more adsorbent materials. The Examples of WO 2010/060981 teach the removal of basic compounds from bio-ethanol by adsorption on a sulfonic acid resin at ambient temperature
10 and pressure.

There remains a need in the art for processes which are able to remove nitrogen-containing contaminants from alcohols, particularly bio-alcohols such as bio-ethanol. Preferably such a process would provide a further reduction in the residual content of nitrogen-containing compounds of the treated alcohol over what has been reported in the
15 art to date and/or would avoid the need for pre-treatment of the alcohols (e.g. by hydrogenation) to convert nitrogen-containing contaminants into modified contaminants that are more easily removed.

In a first aspect, the present invention provides a process for the treatment of an alcohol composition comprising nitrogen-containing contaminants, the process comprising
20 contacting the alcohol composition in the vapour phase with an adsorbent in an adsorption zone.

Following contact with the adsorbent, a treated alcohol composition may be recovered which has a reduced content of nitrogen-containing contaminants compared with the untreated alcohol composition. This treated alcohol composition is suitable for use in a
25 number of chemical processes, and in particular those types of chemical processes which are sensitive to the presence of nitrogen-containing contaminants in alcohol feedstocks.

Thus, in another aspect (also referred to herein as the 'second aspect' of the present invention), the present invention provides a process for the preparation of olefins from an alcohol composition comprising a dehydratable alcohol and nitrogen-containing
30 contaminants, the process comprising:

(i) contacting the alcohol composition in the vapour phase with an adsorbent in an adsorption zone to produce a treated alcohol composition; and

(ii) contacting the treated alcohol composition with an alcohol dehydration catalyst in an alcohol dehydration zone under conditions effective to dehydrate the alcohol to the corresponding olefin.

In a further aspect, the present invention provides an alcohol composition derived from the fermentation of biomass and/or biomass derivatives and having a total nitrogen concentration of 0.25 ppmw (parts per million by weight) or less, such as 0.1 ppmw or less or 0.05 ppmw or less. Such an alcohol composition is obtainable by the process according to the first aspect of the invention.

In a further aspect, the present invention provides the use of an aluminosilicate such as a zeolite, or a silica-alumina as an adsorbent to remove nitrogen-containing contaminants from an alcohol composition containing said nitrogen-containing contaminants by contacting said alcohol composition in the vapour phase with said aluminosilicate or silica-alumina.

The present inventors have unexpectedly found that the removal of nitrogen-containing contaminants from alcohol compositions is more effective when the alcohol composition is in the vapour phase when it is brought into contact with the adsorbent, whereas it would be expected that the higher temperatures and/or reduced pressures required for the alcohol composition to be in the vapour phase would promote desorption of the nitrogen-containing contaminants from the adsorbent.

Unexpectedly, embodiments of the processes of the present invention may be able to effectively remove nitrogen-containing compounds from alcohol compositions without the need for any pre-treatment steps being performed on the alcohol composition prior to contacting the alcohol composition with an adsorbent, such as a hydrogenation step to reduce compounds such as nitriles. Furthermore, since the dehydration of alcohols is typically carried out in the vapour phase, the process of the present invention can readily be integrated into an overall process for the production of olefins from alcohols, particularly bio-alcohols such as bio-ethanol.

As used herein, the term "alcohol composition" refers to a composition which comprises at least 50 wt% alcohol. Preferably, an alcohol composition to be treated according to the process of the present invention comprises at least 90 wt% alcohol, more preferably at least 95 wt% alcohol, such as at least 98 wt% alcohol or at least 99 wt% alcohol.

The alcohol composition may additionally comprise an inert component, wherein said inert component is any component which does not react with alcohols or adversely affect the alcohol treatment step under the conditions used and would not adversely affect a process for the dehydration of alcohols. By way of example, the inert component may be selected from saturated hydrocarbon compounds having from 1 to 10 carbon atoms, naphthenes, water and inert gases such as nitrogen. Advantageously, the alcohol composition may comprise water. For example, the alcohol composition may be a hydrous alcohol composition which has not been subjected to a dewatering step.

The alcohol composition may comprise a single type of alcohol, or it may comprise a mixture of two or more different alcohols. In one particular embodiment the alcohols present in the alcohol composition are substantially a single type of alcohol, that is, at least 95 wt% of the alcohols present in the alcohol composition are alcohols having the same number of carbon atoms, preferably at least 98 wt%, such as at least 99 wt% or at least 99.5 wt%, of the alcohols present in the alcohol composition are alcohols having the same number of carbon atoms. In this embodiment, it is preferably that the alcohols having the same carbon number also are substantially of a single isomeric form of the alcohols having the same carbon number.

The alcohol composition preferably comprises one or more alcohols selected from C_1 to C_6 saturated monohydric alcohols, more preferably C_2 to C_6 saturated monohydric alcohols, and still more preferably C_2 to C_4 saturated monohydric alcohols.

Preferably, the one or more alcohols are selected from dehydratable C_2 to C_6 saturated monohydric alcohols, and more preferably from dehydratable C_2 to C_4 saturated monohydric alcohols. By dehydrateable alcohol, it is meant that the alcohol is capable of being converted into the corresponding olefin through the loss of a water molecule.

In one particular embodiment, the alcohol composition comprises one or more alcohols selected from ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol and isobutanol (2-methyl-propan-1-ol), more preferably an alcohol selected from ethanol, 1-propanol and isobutanol, and most preferably the alcohol composition comprises ethanol.

In one particular embodiment, the alcohol composition comprises one or more alcohols produced from a biological source, for example by fermentation of biomass and/or a derivative thereof. The term "biomass" as used herein refers to any biological source of a carbohydrate which may be converted to an alcohol by fermentation of the

biomass directly or fermentation of a derivative of the biomass; for example biological sources of sugars, starches and cellulose. For instance, bio-alcohols, such as bio-ethanol, may be obtained by the fermentation of sugars from sources such as sugar beet, sugar cane, molasses or corn syrup. Examples of alcohols produced from biological sources include
5 bio-ethanol, bio-propanol and bio-butanol. In one particular embodiment, the alcohol composition comprises bio-ethanol, such as obtained by fermentation of feedstocks derived from sugar cane, such as sugar cane molasses and sugar cane juice; sugar beet, such as sugar beet molasses and sugar beet juice; cereal crops, such as corn or wheat derived feedstocks like corn syrup; and lignocellulosic materials, such as fast growing grasses or
10 "energy grasses".

In one particular embodiment, the alcohol composition comprises at least 50 wt% ethanol, preferably at least 90 wt% ethanol, more preferably at least 95 wt% ethanol, such as at least 98 wt% ethanol or at least 99 wt% ethanol. In one aspect of this embodiment, the ethanol is bio-ethanol.

15 In one embodiment of the present invention, the alcohol composition is a hydrous ethanol composition. Such hydrous ethanol compositions may be the raw or crude ethanol composition which is the resultant from the distillation of an ethanol product which has been obtained by the fermentation of biomass without further subjecting the obtained ethanol to a dewatering step. Such hydrous ethanol compositions may contain an amount
20 of water which is equal to or greater than the amount of water which is determined by the azeotrope of the ethanol water composition produced during the fermentation process.

The concentration of nitrogen-containing contaminants in the alcohol composition to be treated according to the process of the present invention will generally be at a level which is detrimental to the performance of an acidic alcohol dehydration catalyst, such as a
25 supported heteropolyacid catalyst. In this disclosure, the concentration of nitrogen-containing contaminants is reported as parts per million by weight (ppmw) of the total nitrogen content of said nitrogen-containing contaminants. References herein to ppmw of nitrogen shall be interpreted as ppmw of nitrogen in the form of nitrogen-containing contaminants.

30 Thus, the alcohol composition to be treated according to the process of the invention preferably comprises at least 0.2 ppmw (parts per million by weight) of nitrogen, more preferably at least 0.25 ppmw of nitrogen, more preferably at least 0.3 ppmw of nitrogen,

still more preferably at least 0.4 ppmw of nitrogen, and most preferably at least 0.5 ppmw of nitrogen. For instance, the alcohol composition to be treated according to the process of the invention may comprise at least 0.6 ppmw, at least 0.7 ppmw, at least 0.8 ppmw, at least 0.9 ppmw or at least 1.0 ppmw of nitrogen.

5 The upper limit of the nitrogen concentration of the alcohol composition is not critical to the invention. Thus, concentrations of nitrogen-containing contaminants of over 100 ppmw of nitrogen, such as over 200 ppmw of nitrogen, over 500 ppmw of nitrogen, or even over 1000 ppmw of nitrogen, are readily treatable by the process of the present invention. However, to avoid rapid exhaustion of the adsorbent it may be preferable that
10 the alcohol composition comprises 50 ppmw or less of nitrogen, more preferably 25 ppmw or less of nitrogen, more preferably 10 ppmw or less of nitrogen, more preferably 8 ppmw or less of nitrogen, for instance 6 ppmw or less of nitrogen, 4 ppmw or less of nitrogen, or 2 ppmw or less of nitrogen. Thus, depending upon the initial concentration of nitrogen in the alcohol composition to be treated, it may be desirable to subject alcohol compositions
15 comprising very high levels of nitrogen-containing contaminants to a pre-treatment step to reduce the level of nitrogen-containing contaminants. Such a pre-treatment may be carried out by any suitable technique, for instance by contacting the alcohol composition with an adsorbent in the liquid phase, such as an adsorbent may be an adsorbent as listed herein for use in the vapour phase or an acidic ion exchange resin.

20 The concentration of nitrogen-containing contaminants in the alcohol composition to be treated according to the process of the invention may be determined by any suitable analytical technique known to persons of skill in the art. Suitable techniques include gas chromatography in conjunction with a nitrogen/phosphorus detector (GC-NPD), chemiluminescence methods and ion exchange chromatography. It has been found that
25 GC-NPD is a particularly effective technique for observing individual nitrogen-containing species in the alcohol composition. The use of a nitrogen/phosphorus detector provides significantly enhanced signal strength for nitrogen compounds in comparison to carbon species (approximately 10^4 enhancement). As a result, nitrogen compounds are clearly visible in the GC chromatogram along with the signals for the alcohol and in some cases
30 the corresponding dialkyl ether.

A suitable chemiluminescence technique may involve vaporising and oxidizing an alcohol composition, measuring the concentration of nitrogen oxides in the vaporized and

oxidized alcohol composition by chemiluminescence and hence determining the concentration of nitrogen atoms in the alcohol composition from the measured concentration of nitrogen oxides. Such techniques are described in further detail in US 4,018,562 and GB 2373856.

5 The nitrogen-containing contaminants may include a number of different types of nitrogen-containing compounds, for instance nitriles (i.e. compounds containing one or more nitrile moiety, such as acetonitrile), amines (i.e. compounds containing one or more amine moiety, such as ammonia, methylamine, ethylamine, dimethylamine, diethylamine, triethylamine, trimethylamine, ethanolamine), ammonium cations, amides, imides and
10 mixtures thereof; additionally, more complex and heterocyclic nitrogen-containing compounds, such as azines, diazines, pyrroles, diazoles, triazoles and tetrazoles and mixtures thereof, and more complex molecules containing one or more different nitrogen-containing moieties and optional other functional groups, such as amino acids, may also be present in the alcohol composition. Nitriles have low basicity due to the sp hybridization
15 of the nitrogen atom which places the electron density of the nitrogen lone-pair close to the nitrogen nucleus, thus making the lone-pair relatively unreactive. Consequently, nitriles in particular pass through strong acid ion exchange resins with substantially no adsorption. Nonetheless, nitriles are found to be capable of quantitatively deactivating acidic catalysts used for alcohol dehydration processes. It has previously been proposed to carry out a
20 pretreatment step to convert nitriles to amines by hydrogenation, as amines are more readily adsorbed. By employing the process of the present invention, a reduction in the concentration of all nitrogen-containing compounds to very low levels without the need to pretreat the alcohol composition to modify nitrile contaminants is achievable.

 In preferred embodiments of the invention, the treated alcohol composition has a
25 nitrogen content of less than 2 ppmw, more preferably less than 1 ppmw, still more preferably less than 0.5 ppmw, still more preferably less than 0.25 ppmw, such as less than 0.1 ppmw or less than 0.05 ppmw (50 parts per billion by weight, ppbw).

 The adsorbent used for the treatment of the alcohol composition may be any adsorbent capable of adsorbing nitrogen-containing compounds and is stable under the
30 conditions at which the alcohol composition is brought into contact with it. Preferably, the adsorbent used for the treatment of the alcohol composition is a porous solid acidic adsorbent. Examples of suitable adsorbent materials include aluminosilicates such as

zeolites, silica-alumina; silicates; silicas; aluminates; aluminas such as activated aluminas; molecular sieves; carbon-based adsorbent materials such as activated carbons; clays; and, aluminophosphates. The adsorbent used in the treatment of the alcohol composition may optionally be treated or impregnated with an acid, such as phosphoric acid, phosphonic acid, sulfuric acid or a sulphonic acid, and/or may optionally be modified with a transition metal. Preferably, the adsorbent used in the treatment of the alcohol composition is selected from a microporous aluminosilicate, a mesoporous aluminosilicate or a silica-alumina. Most preferably, the adsorbent material used for the treatment of the alcohol composition is selected from the group consisting of zeolites, silica-aluminas and mixtures thereof. The adsorbent material may be used individually or in admixture with other adsorbent materials and/or inert materials.

In one particular embodiment of the present invention, the adsorbent material is a zeolite. The zeolite may be any zeolite which is effective to remove nitrogen-containing contaminants from an alcohol composition. However, in preferred embodiments, the zeolite has at least one channel defined by a 10-membered or 12-membered ring, and more preferably the zeolite has at least one channel defined by a 12-membered ring.

The zeolite is preferably a large-pore zeolite having at least one channel having a diameter of at least 5 Å, preferably at least one channel having a diameter of at least 6 Å, and most preferably at least one channel having a diameter of at least 7 Å.

Preferably the zeolite has the framework type FAU or MOR, and is preferably a faujasite or a mordenite zeolite. Still more preferably the zeolite has the framework type FAU, and is most preferably a faujasite. Examples of faujasites are zeolite Y and zeolite X. Preferably zeolite Y is used.

The zeolite is preferably in the acidic (H) form. Thus, in one particular embodiment, the preferred zeolites include H-faujasites and H-mordenites, more preferably the zeolite is zeolite H-Y or zeolite H-X, and most preferably is zeolite H-Y.

The density of acid sites in zeolites is dependent on the silica to alumina ratio (SAR) of the zeolite. The lower the SAR value the greater the proportion of aluminium atoms and the greater the density of acidic sites. It has been found that the removal of nitrogen-containing contaminants from alcohol compositions quantitatively deactivates the acid sites of the zeolite adsorbent. Thus, for optimum adsorption capacity it is preferred to use zeolites having low SAR values. Thus, in preferred embodiments, the zeolite has an SAR

of at most 100, for example in the range of from 1 to 100, more preferably has an SAR of at most 50, for example in the range of from 1 to 50, more preferably has an SAR of at most 20, for example in the range of from 1 to 20, still more preferably has an SAR of at most 15, for example in the range of from 1 to 15, and most preferably has an SAR of at most 10, for example in the range of from 1 to 10.

In one particular embodiment, the zeolite adsorbent is zeolite H-Y having an SAR value in the range of from about 2 to about 10, for instance about 4 to about 8.

The temperature at which the alcohol composition contacts the adsorbent is preferably at least 0 °C, more preferably at least 25 °C, even more preferably at least 50 °C, such as at least 75 °C or at least 100 °C. Preferably, the temperature at which the alcohol composition contacts the adsorbent is at most 300 °C, more preferably at most 275 °C, even more preferably at most 250 °C, such as at most 225 °C or at most 200 °C; lower maximum temperatures may be employed such as the use of a maximum temperature of at most 175 °C or at most 150 °C. Preferred temperature ranges for contacting the alcohol composition with the adsorbent may be selected from the combinations of the above identified preferred minimum temperatures with the above identified maximum temperatures. Examples of suitable temperature ranges at which the alcohol composition may contact the adsorbent include temperature ranges of from 0 °C to 300 °C, from 25 °C to 300 °C, from 50 °C to 300 °C, from 75 °C to 300 °C, from 100 °C to 300 °C, 0 °C to 275 °C, from 25 °C to 275 °C, from 50 °C to 275 °C, from 75 °C to 275 °C, from 100 °C to 275 °C, 0 °C to 250 °C, from 25 °C to 250 °C, from 50 °C to 250 °C, from 75 °C to 250 °C, from 100 °C to 250 °C, 0 °C to 225 °C, from 25 °C to 225 °C, from 50 °C to 225 °C, from 75 °C to 225 °C, from 100 °C to 225 °C, 0 °C to 200 °C, from 25 °C to 200 °C, from 50 °C to 200 °C, from 75 °C to 200 °C, from 100 °C to 200 °C, 0 °C to 175 °C, from 25 °C to 175 °C, from 50 °C to 175 °C, from 75 °C to 175 °C, from 100 °C to 175 °C, 0 °C to 150 °C, from 25 °C to 150 °C, from 50 °C to 150 °C, from 75 °C to 150 °C, from 100 °C to 150 °C. It has been found that while the removal of nitrogen-containing contaminants is effective throughout these temperatures ranges, some adsorbents may catalyse dehydration of the alcohols at higher temperatures. If it is desired to avoid any dehydration of the alcohol composition, appropriate temperatures may readily be selected to minimize any unwanted dehydration of the alcohol.

In one particular embodiment, the alcohol composition is contacted with the adsorbent at a temperature which is at least 5 °C, preferably at least 10 °C, above the dew point temperature of the alcohol composition at the operating pressure of the adsorption zone.

- 5 The pressure is selected such that the alcohol composition is in the vapour phase as it is brought into contact with the adsorbent. The skilled person is readily capable of selecting suitable operating pressures depending on the alcohol composition. In general, however, the pressure at which the alcohol composition contacts the adsorbent is preferably at least 0.1 bara (bar absolute), more preferably at least 0.25 bara, even more preferably at least 0.5 bara, even more preferably at least 0.75 bara and most preferably at least 1.0 bara (i.e. ambient pressure). Preferably, the pressure at which the alcohol composition contacts the adsorbent is at most 25 bara, more preferably at most 20 bara, even more preferably at most 15 bara, lower maximum pressures may be beneficially employed such as the use of a maximum pressure of at most 10 bara or even 5 bara.
- 10 Preferred pressure ranges for contacting the alcohol composition with the adsorbent may be selected from the combinations of the above identified preferred minimum pressures with the above identified maximum pressures. Examples of suitable pressure ranges at which the alcohol composition may contact the adsorbent include pressure ranges of from 0.1 to 25 bara, from 0.25 to 25 bara, from 0.5 to 25 bara, from 0.75 to 25 bara, from 1.0 to 25 bara, 0.1 to 20 bara, from 0.25 to 20 bara, from 0.5 to 20 bara, from 0.75 to 20 bara, from 1.0 to 20 bara, 0.1 to 15 bara, from 0.25 to 15 bara, from 0.5 to 15 bara, from 0.75 to 15 bara, from 1.0 to 15 bara, 0.1 to 10 bara, from 0.25 to 10 bara, from 0.5 to 10 bara, from 0.75 to 10 bara, from 1.0 to 10 bara, 0.1 to 5 bara, from 0.25 to 5 bara, from 0.5 to 5 bara, from 0.75 to 5 bara, from 1.0 to 5 bara.

- 25 In one particular embodiment, the alcohol composition is contacted with the adsorbent at a pressure which is at least 0.1 bar, preferably at least 0.2 bar, below the dew point pressure of the alcohol composition at the operating temperature of the adsorption zone.

- 30 As used herein, the dew point temperature of the alcohol composition is the temperature, at a given pressure, at which the alcohol component(s) of the vapour-phase alcohol composition will start to condense out of the gaseous phase. Likewise, as used herein, the dew point pressure of the alcohol composition is the pressure, at a given

temperature, at which the alcohol component(s) of the vapour-phase alcohol composition will start to condense out of the gaseous phase.

The alcohol composition is preferably contacted with the adsorbent at a liquid hourly space velocity relative to the volume of adsorbent of from 0.01 to 100 h⁻¹, more preferably from 0.1 to 10 h⁻¹, such as from 0.5 to 2 h⁻¹, based on the volume of alcohol composition at 25 °C and 1 bar. It will be appreciated that although the flow rate is defined herein in terms of a liquid hourly space velocity, the alcohol composition will be in the vapour phase when it is contacted with the adsorbent.

The processes of the present invention may be operated as continuous or batch process, preferably as continuous processes. Preferably, the processes of the invention are carried out by passing the alcohol composition in the vapour phase through a fixed bed, fluidised bed or moving bed of the adsorbent. Multiple adsorption zones may also be used in the process of the present invention, wherein each adsorption zone may contain the same or different adsorbents and may be operated at the same or different conditions. One particular example of the use of multiple adsorption zones comprises treating the alcohol in a system comprising at least two adsorption zones, wherein at least one adsorption zone is operating under conditions such that the alcohol composition is contacted with an adsorbent in the liquid phase and at least one adsorption zone is operating under conditions such that the alcohol composition is contacted with an adsorbent in the vapour phase.

The alcohol composition may optionally be contacted with the adsorbent in the presence of an inert carrier gas. Examples of suitable inert carrier gases include nitrogen (N₂) and argon.

In a further embodiment of the process of the present invention, prior to the alcohol being contact with the adsorbent in the vapour phase, it is contact with a solid acid adsorbent in the liquid phase in a liquid phase adsorption zone. In this embodiment of the invention, the adsorbent used in the liquid phase adsorption zone may be any adsorbent as described herein above. Conveniently, the adsorbent used in such a liquid phase adsorption zone may be the same as the adsorbent used in the adsorption zone wherein the alcohol composition is contacted with the adsorbent in the vapour phase. Preferably, the adsorbent used in such a liquid phase adsorption zone is selected from a microporous aluminosilicate, a mesoporous aluminosilicate, a silica-alumina or an acidic ion exchange resin; more preferably, the adsorbent used in such a liquid phase adsorption zone is

selected from the group consisting of zeolites, silica-aluminas and mixtures thereof, or an acidic ion exchange resin.

In the case where there alcohol composition comprises a dehydratable alcohol, the process for treating an alcohol composition according to the first aspect of the present invention may be integrated with a process for the dehydration of alcohols to form olefins. Therefore, according to a second aspect of the present invention there is provided a process for the preparation of olefins from an alcohol composition comprising a dehydratable alcohol and nitrogen-containing contaminants, the process comprising:

(i) contacting the alcohol composition in the vapour phase with an adsorbent in an adsorption zone to form a treated alcohol composition; and

(ii) contacting the treated alcohol composition with an alcohol dehydration catalyst in an alcohol dehydration zone under conditions effective to dehydrate the alcohol to the corresponding olefin.

As step (i) of the second aspect of the present invention corresponds to the first aspect of the present invention, all of the preferences and embodiments expressed in relation to the first aspect of the present invention are equally applicable in the second aspect of the present invention.

The treated alcohol composition from step (i) may be fully or partially condensed prior to feeding to the alcohol dehydration zone in step (ii) of the process of the second aspect of the invention. Typically, alcohol dehydration processes are performed in the vapour phase, therefore the treated alcohol composition may conveniently pass from the adsorption zone of step (i) to the alcohol dehydration zone of step (ii) with the alcohol remaining in the vapour phase.

Preferably, in step (ii) of the process according to the second aspect of the invention, the treated alcohol composition is contacted with the alcohol dehydration catalyst in the vapour phase. In this way, vaporisation of the alcohol for the removal of nitrogen-containing contaminants may be integrated with vapour phase alcohol dehydration. The temperature and pressure of the alcohol dehydration step (ii) may be greater or lower than the temperature and pressure of the treated alcohol composition resulting from step (i) of the process according to the second aspect of the invention, thus the temperature and pressure of the treated alcohol composition may need to be adjusted prior to contacting the treated alcohol composition with the alcohol dehydration catalyst; alternatively, the

temperature and pressure of the alcohol treatment step (i) in the second aspect of the present invention may be selected such that the treated alcohol composition resultant from the adsorption zone is at the same temperature and pressure as the alcohol dehydration zone.

5 The alcohol dehydration catalyst may be any of the alcohol dehydration catalysts that are known in the art. For example, the alcohol dehydration catalyst may be a crystalline silicate, a dealuminated crystalline silicate or a phosphorus modified zeolite as described in WO 2009/098262, the contents of which are incorporated herein by reference.

10 Alternatively, the alcohol dehydration catalyst may be a heteropolyacid catalyst, for instance as described by WO 2008/138775 and WO 2008/062157, the contents of which are incorporated herein by reference. In preferred embodiments, the alcohol dehydration catalyst is a heteropolyacid catalyst. The heteropolyacid catalyst is preferably supported on a suitable inert support, such as silica or alumina.

15 Suitable conditions for dehydrating alcohols are well-known in the art and to the skilled person, for instance with reference to the prior art documents cited herein.

20 However, in the case of a crystalline silicate or zeolite alcohol dehydration catalyst, typical reaction conditions include a temperature of from 280 to 500 °C, a total pressure of from 0.5 to 30 bara, and a partial pressure of alcohol that is preferably from 1.2 to 4 bara. In the case of a heteropolyacid catalyst, typical reaction conditions include a temperature of from 180 to 270 °C and a pressure of from 1 to 45 bara.

 An olefin product may be recovered from the alcohol dehydration zone and may subsequently be used in a wide range of industrial applications, for instance in the preparation of polymers and oligomers, as components of fuels and lubricants and in the preparation of surfactants.

25 In further embodiments, the present invention provides a polymeric product obtained by polymerisation of olefins produced according to the second aspect of the invention, an oligomeric product obtained by oligomerisation of olefins produced according to the second aspect of the invention, fuel and lubricant compositions comprising said olefins and/or said oligomeric or polymeric products, and surfactant compositions comprising said
30 olefins and/or said oligomeric or polymeric products.

 The present invention will now be illustrated, without limiting the scope thereof, with reference to the following Examples and the accompanying Figures, in which:

Figure 1 shows a schematic of an experimental apparatus for testing the removal of nitrogen compounds from alcohol compositions in the vapour phase.

Figure 2 shows a GC-NPD chromatogram for Bioethanol A prior to treatment for the removal of nitrogen containing compounds. The portion of the chromatogram from ca. 0 to 5 min is shown enlarged in the inset.

Figure 3 shows a GC-NPD chromatogram for Bioethanol B prior to treatment for the removal of nitrogen containing compounds.

Figure 4 shows a GC-NPD chromatogram for Bioethanol A following contacting with zeolite HY (SAR = 5.2) at 25 °C in the liquid phase.

Figure 5 shows a GC-NPD chromatogram for Bioethanol A following contacting with zeolite HY (SAR = 5.2) at 130 °C in the liquid phase. The portion of the chromatogram from ca. 1 to 3 min is shown enlarged in the inset.

Figure 6 shows a GC-NPD chromatogram for Bioethanol A following contacting with zeolite HY (SAR = 5.2) at 200 °C in the vapour phase.

Figure 7 shows a GC-NPD chromatogram for Bioethanol A following contacting with zeolite HY (SAR = 5.2) at 150 °C in the vapour phase. The portion of the chromatogram from ca. 1 to 3 min is shown enlarged in the inset.

Figure 8 shows a GC-NPD chromatogram for Bioethanol A following contacting with zeolite HY (SAR = 5.2) at 130 °C in the vapour phase. The portion of the chromatogram from ca. 1 to 3 min is shown enlarged in the inset.

Figure 9 shows a GC-NPD chromatogram for Bioethanol B following contacting with zeolite HY (SAR = 5.2) at 150 °C in the vapour phase. The portion of the chromatogram from ca. 1 to 3 min is shown enlarged in the inset.

Figure 10 shows a GC-NPD chromatogram for Bioethanol B following contacting with zeolite H-Mordenite (SAR = 20) at 25 °C in the liquid phase. The portion of the chromatogram from ca. 1 to 3 min is shown enlarged in the inset.

Figure 11 shows a GC-NPD chromatogram for Bioethanol B following contacting with zeolite H-Mordenite (SAR = 20) at 100 °C in the liquid phase. The portion of the chromatogram from ca. 1 to 3 min is shown enlarged in the inset.

Figure 12 shows a GC-NPD chromatogram for Bioethanol B following contacting with zeolite H-Mordenite (SAR = 20) at 150 °C in the vapour phase. The portion of the chromatogram from ca. 1 to 3 min is shown enlarged in the inset.

Examples

In the following Examples, the removal of nitrogen containing contaminants using zeolite adsorbents was examined in the liquid and vapour phases.

Liquid phase experiments were carried out using a Vapourtec (TM) reactor unit. The apparatus comprises a feed reservoir, an HPLC pump, a pre-heater, a reactor tube, a cool-down section and a product reservoir. In each experiment the reactor tube was loaded with 20 mL of adsorbent. The adsorbent bed was flushed with approximately 150 mL of pure synthetic ethanol using flow rates up to 7.5 mL/min. This process removed trapped air bubbles from the adsorbent bed thus preventing channelling. Reactions were all carried out with a LHSV of 1 h^{-1} relative to the volume of adsorbent (0.333 mL/min). The process was carried out over four consecutive days and stopped overnight (~24 hours total run time). The first day of each new experiment used a pure synthetic ethanol feed to ensure a reliable baseline. Bio-ethanol was fed on the subsequent 3 days. When restarting the process each day, the adsorbent bed was washed with ~40 mL of the bio-ethanol feed prior to sample collection to avoid results being distorted by possible leaching of nitrogen-containing contaminants from the adsorbent bed into the stationary liquid alcohol phase overnight. Samples collected on each of the four consecutive days were analysed by chemiluminescence, ion-chromatography, GC and GC-NPD techniques.

The experimental set-up for vapour phase reactions is shown in Figure 1. The apparatus comprises a quartz reactor tube (5) fitted with a porosity 1 quartz frit (not shown) and connected to a syringe pump (10) to supply the alcohol composition and to a source of nitrogen carrier gas (15). The reactor tube was loaded with 12 mL carborundum (20), 5 mL of the active zeolite material (25) and a further 12 mL of carborundum (30) to act as a vaporiser. In order to ensure effective gas flow through the zeolite bed all zeolites were pressed (12 tonnes, 32 mm die set) and sieved (250-500 μm) prior to use. The reactor tube was secured in a CarboliteTM tube furnace (35) and heated to the desired temperature. A cooled liquid trap (40) was provided to collect the treated alcohol and a gas collection vessel (45) was supplied to collect non-condensable components.

In each vapour phase experiment, the N_2 flow rate was 50 mL/min and the liquid flow rate was 5 mL/hour (LHSV = 1). Vapour phase reactions were conducted at ambient pressure unless stated otherwise. Liquid and gaseous samples were analysed by GC and GC-NPD.

Alcohol Compositions

In the following Examples, the clean up of two bioethanol compositions from two different sources is examined. Details of the amounts of contaminants present in the two bioethanol compositions are provided in Table 1.

5

Table 1

Contaminant	Bioethanol A	Bioethanol B
Other alcohols	720 ppmw	425 ppmw
Non-alcohol oxygenates	431 ppmw	1245 ppmw
Water	0.54 wt%	0.15 wt%
Total nitrogen	1.0 ppmw	6.1 ppmw
Nitrogen as acetonitrile	60 ppbw	240 ppbw
Total acetonitrile	180 ppbw	700 ppbw

GC-NPD chromatograms for Bioethanol A and Bioethanol B prior to treatment to remove nitrogen-containing contaminants are shown in Figures 2 and 3, respectively. The peak at ca. 2.4 min is ethanol, and the remaining peaks are attributed to nitrogen-containing compounds.

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Comparative Examples A and B - Liquid Phase Testing

In these Examples, the removal of nitrogen-containing contaminants from Bioethanol A was examined in the liquid phase using zeolite HY (SAR = 5.2) as the adsorbent at 25 °C (Example A) and at 130 °C (Example B).

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The GC-NPD chromatogram for the test at 25 °C is shown in Figure 4, with the bottom trace on the chromatograph corresponds to a synthetic ethanol composition which contained no discernable amounts of nitrogen-containing contaminants; the remaining three traces on the chromatographs correspond, from bottom to top, to the first, second and third day.. The GC-NPD chromatogram of the liquid collected from the 25°C test showed a number of signals consistent with the presence of nitrogen-containing contaminants from the bio-ethanol. The residual nitrogen content was found to be 0.4 ppm by chemiluminescence.

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The GC-NPD chromatogram for the test at 130 °C is shown in Figure 5, with results from the 1st to 4th days shown in order from bottom to top. The chromatogram showed a

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reduced number of signals that are consistent with the presence of nitrogen-containing compounds. The residual nitrogen content was found to be 0.3 ppm by chemiluminescence.

Examples 1 to 3 - Vapour Phase Testing

5 In these Examples, the removal of nitrogen-containing contaminants from Bioethanol A was examined in the vapour phase using zeolite HY (SAR = 5.2) as the adsorbent at 200 °C (Example 1), 150 °C (Example 2) and 130 °C (Example 3) and at ambient pressure.

Nitrogen-containing contaminants were completely removed from Bioethanol B at 200°C. However, this temperature also resulted in the ethanol undergoing both
10 etherification and dehydration reactions to give a mixture of water and the following carbon containing products; ethanol (11.9%), diethylether (38.3 %), ethylene (49.1 %) and ethane (0.15 %).

Reducing the reaction temperature to 150°C resulted in lower conversion of the ethanol to diethyl ether (18.9 %) and almost no conversion to ethylene (0.05%). No ethane
15 was observed at 150°C. The GC-NPD chromatogram of the liquid fraction shows that almost all nitrogen compounds were effectively removed, the only exception was acetonitrile which was observed at 130 ppbw (40 ppbw of nitrogen).

At 130 °C conversion of ethanol to diethyl ether was lower still (3.6%) with no observable formation of ethylene or ethane.

20 It can clearly be seen from the comparison of the GC-NPD results of comparative Examples A and B and Examples 1 to 3, presented in Figures 4-5 and 6-8 respectively, that contacting the alcohol composition with the adsorbent in the vapour phase leads to an unexpected improvement in the removal of nitrogen containing impurities from the alcohol composition compared to when the alcohol composition is contacted with the adsorbent in
25 the liquid phase.

Example 4 - Vapour Phase Testing

In this Example, the removal of nitrogen-containing contaminants from Bioethanol B was examined in the vapour phase using zeolite HY (SAR = 5.2) as the adsorbent at 150 °C and at ambient pressure. The GC-NPD chromatogram is shown in Figure 9.

30 Nitrogen-containing contaminants were almost completely removed at 150°C, with the only exception being a small amount of acetonitrile (290 ppbw, corresponding to 100 ppbw of nitrogen). This result shows that, although the acetonitrile was not fully

removed, the concentration is significantly reduced and the large amounts of other nitrogen-containing contaminants in Bioethanol B were completely removed.

Comparative Examples C and D – Liquid Phase Testing

In these Examples, the removal of nitrogen-containing contaminants from Bioethanol B was examined in the liquid phase using H-Mordenite (H-MOR; SAR = 20) as the adsorbent at 25 °C (comparative example C) and at 100 °C (comparative example D); the GC-NPD chromatograms are shown in Figures 10 and 11 respectively. In each of Figures 10 and 11, the bottom trace on the chromatograph corresponds to a synthetic ethanol composition which contained no discernable amounts of nitrogen-containing contaminants; the remaining three traces on the chromatographs correspond, from bottom to top, to the first, second and third day.

The experiment using H-MOR (SAR 20) at 25°C with Bioethanol B showed an unusual result in that less than 100 ppbw acetonitrile was detected. However, the concentrations of significant number of other organic nitrogen compounds remained unchanged.

At 100°C the H-MOR (SAR 20) showed enhanced removal of organic nitrogen compounds (compared to the 25°C experiment) but significant levels remained (see Figure 11). Acetonitrile was initially removed to below 100 ppbw (see 2nd chromatogram in Figure 11), but at this temperature the effect was short lived with breakthrough observed on only the second day of the test (see the 3rd and 4th chromatograms in Figure 11).

Example 5 – Vapour Phase Testing

In this Example, the removal of nitrogen-containing contaminants from Bioethanol B was examined in the vapour phase using H-MOR (SAR = 20) as the adsorbent at 150 °C. The GC-NPD chromatogram for this test is shown in Figure 12.

Nitrogen-containing contaminants were almost completely removed at 150°C, with the only exception being a small amount of MeCN (250 ppbw, corresponding to 85 ppbw of nitrogen).

Claims

1. A process for the treatment of an alcohol composition comprising nitrogen-containing contaminants, the process comprising contacting the alcohol composition
5 in the vapour phase with an adsorbent in an adsorption zone.
2. A process according to Claim 1, wherein the alcohol composition comprises one or more alcohols selected from C₁ to C₆ saturated monohydric alcohols, preferably C₂ to C₆ saturated monohydric alcohols, and more preferably C₂ to C₄ saturated monohydric alcohols.
- 10 3. A process according to Claim 2, wherein the alcohol composition comprises one or more alcohols selected from ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol and isobutanol (2-methyl-propan-1-ol), more preferably one or more alcohols selected from ethanol, 1-propanol and isobutanol, and most preferably the alcohol composition comprises ethanol.
- 15 4. A process according to any one of the preceding claims, wherein the alcohol composition comprises one or more alcohols produced from a biological source.
5. A process according to Claim 4, wherein the alcohol composition comprises bio-ethanol.
6. A process according to any one of the preceding claims, wherein the nitrogen-
20 containing contaminants comprise one or more nitrogen-containing compounds from the group consisting of nitriles, amines, ammonium cations, amides, imides and mixtures thereof.
7. A process according to any one of the preceding claims, wherein the treated
25 alcohol composition has a nitrogen content of less than 2 ppmw, more preferably less than 1 ppmw, still more preferably less than 0.5 ppmw, still more preferably less than 0.25 ppmw, such as less than 0.1 ppmw or less than 0.05 ppmw.
8. A process according to any one of the preceding claims, wherein the adsorbent is selected from a microporous aluminosilicate, a mesoporous aluminosilicate or a silica-alumina.
- 30 9. A process according to any one of the preceding claims, wherein the adsorbent is a zeolite.

10. A process according to Claim 9, wherein the zeolite has at least one channel defined by a 10-membered or 12-membered ring.
11. A process according to Claim 10, wherein the zeolite is in the acidic (H) form.
12. A process according to any one of the preceding claims, wherein the alcohol composition is contacted with the adsorbent at a temperature in the range of from 0 °C to 300 °C, or from 25 °C to 275 °C, or from 50 °C to 250 °C, or from 75 °C to 225 °C, or from 100 °C to 200 °C.
13. A process according to any one of the preceding claims, wherein the alcohol compositions is contacted with the adsorbent at a pressure of from 0.1 to 25 bara, or from 0.5 to 20 bara, or from 0.75 to 15 bara, or from 1 to 15 bara.
14. A process for the preparation of olefins from an alcohol composition comprising a dehydratable alcohol and nitrogen-containing contaminants, the process comprising:
 - (i) contacting the alcohol composition in the vapour phase with an adsorbent in an adsorption zone to form a treated alcohol composition; and
 - (ii) contacting the treated alcohol composition with an alcohol dehydration catalyst in an alcohol dehydration zone under conditions effective to dehydrate the alcohol to the corresponding olefin.
15. A process according to Claim 14, wherein the treated alcohol composition is contacted with the alcohol dehydration catalyst in the vapour phase.
16. A process according to Claim 14 or Claim 15, wherein the alcohol dehydration catalyst is selected from crystalline silicates, dealuminated crystalline silicates, phosphorus modified zeolites and supported heteropolyacids.
17. An alcohol composition derived from the fermentation of biomass and/or a derivative thereof, wherein said alcohol composition has a total nitrogen concentration of 0.25 ppmw or less.
18. An alcohol composition according to Claim 17, wherein said alcohol composition has a total nitrogen concentration of 0.1 ppmw or less.
19. An alcohol composition according to Claim 17, wherein said alcohol composition has a total nitrogen concentration of 0.05 ppmw or less.
20. An alcohol composition obtained by a process as defined in any one of Claims 1 to 13.

21. Use of an aluminosilicate or a silica-alumina as an adsorbent to remove nitrogen-containing contaminants from an alcohol composition containing said nitrogen-containing contaminants by contacting said alcohol composition in the vapour phase with said aluminosilicate or silica-alumina.

5 22. Use of a zeolite as an adsorbent to remove nitrogen-containing contaminants from an alcohol composition containing said nitrogen-containing contaminants by contacting said alcohol composition in the vapour phase with said zeolite.

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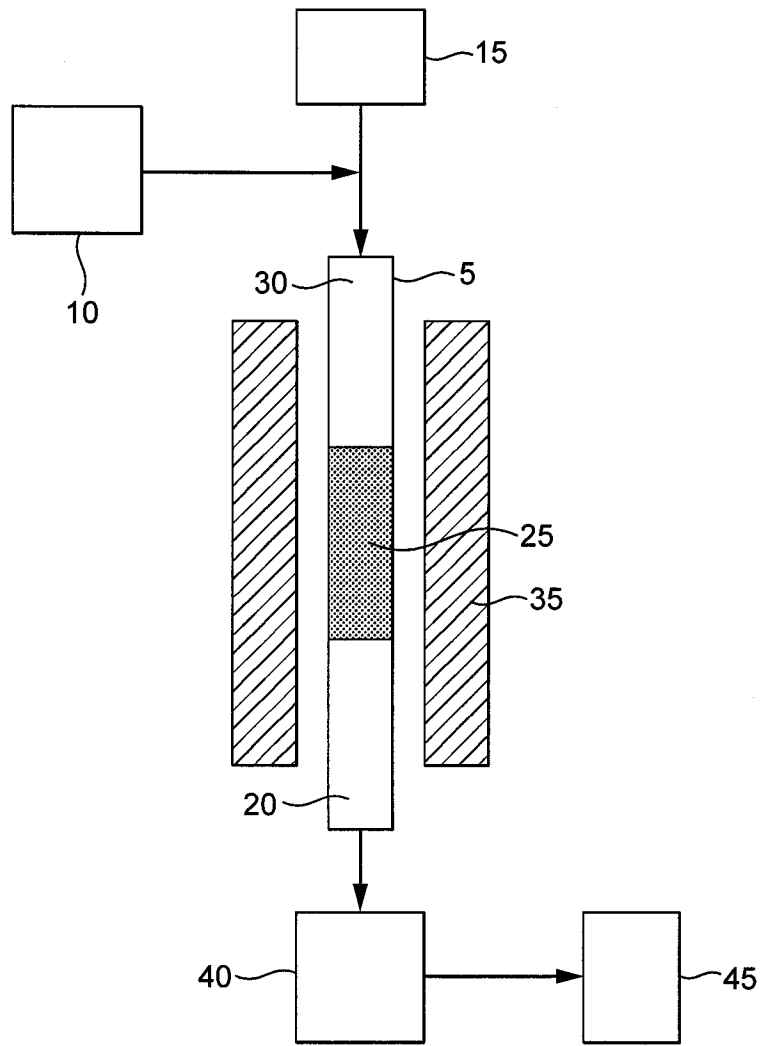


FIG. 1

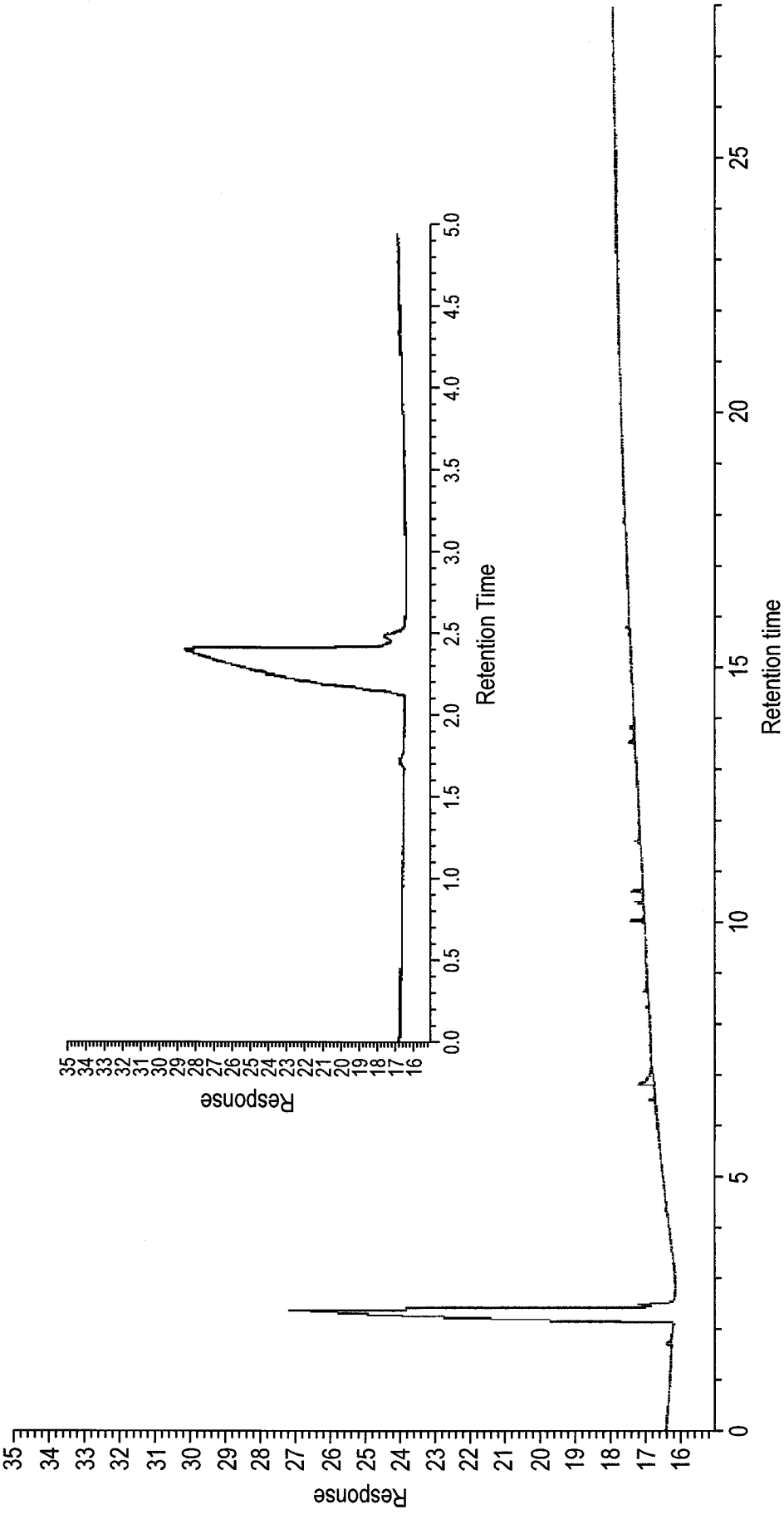


FIG. 2

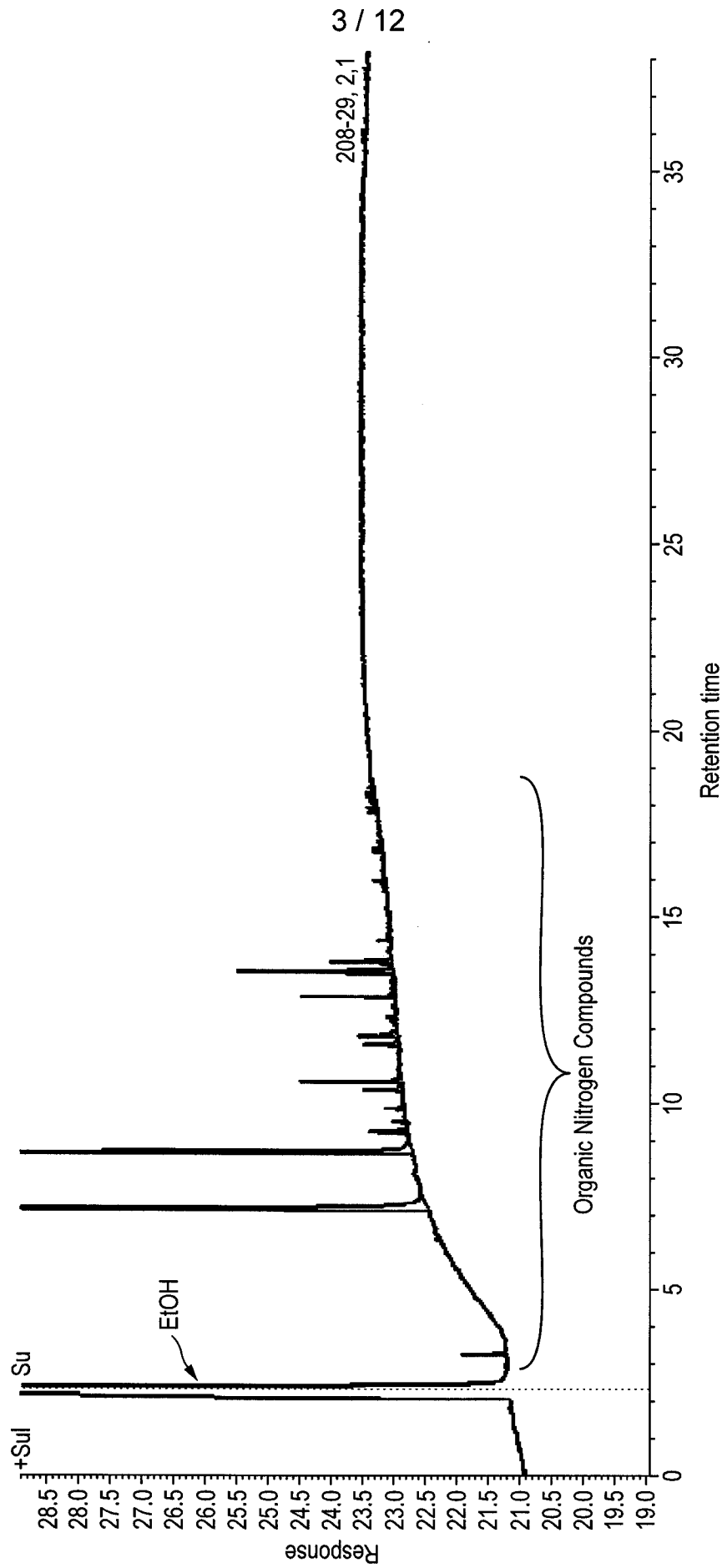


FIG. 3

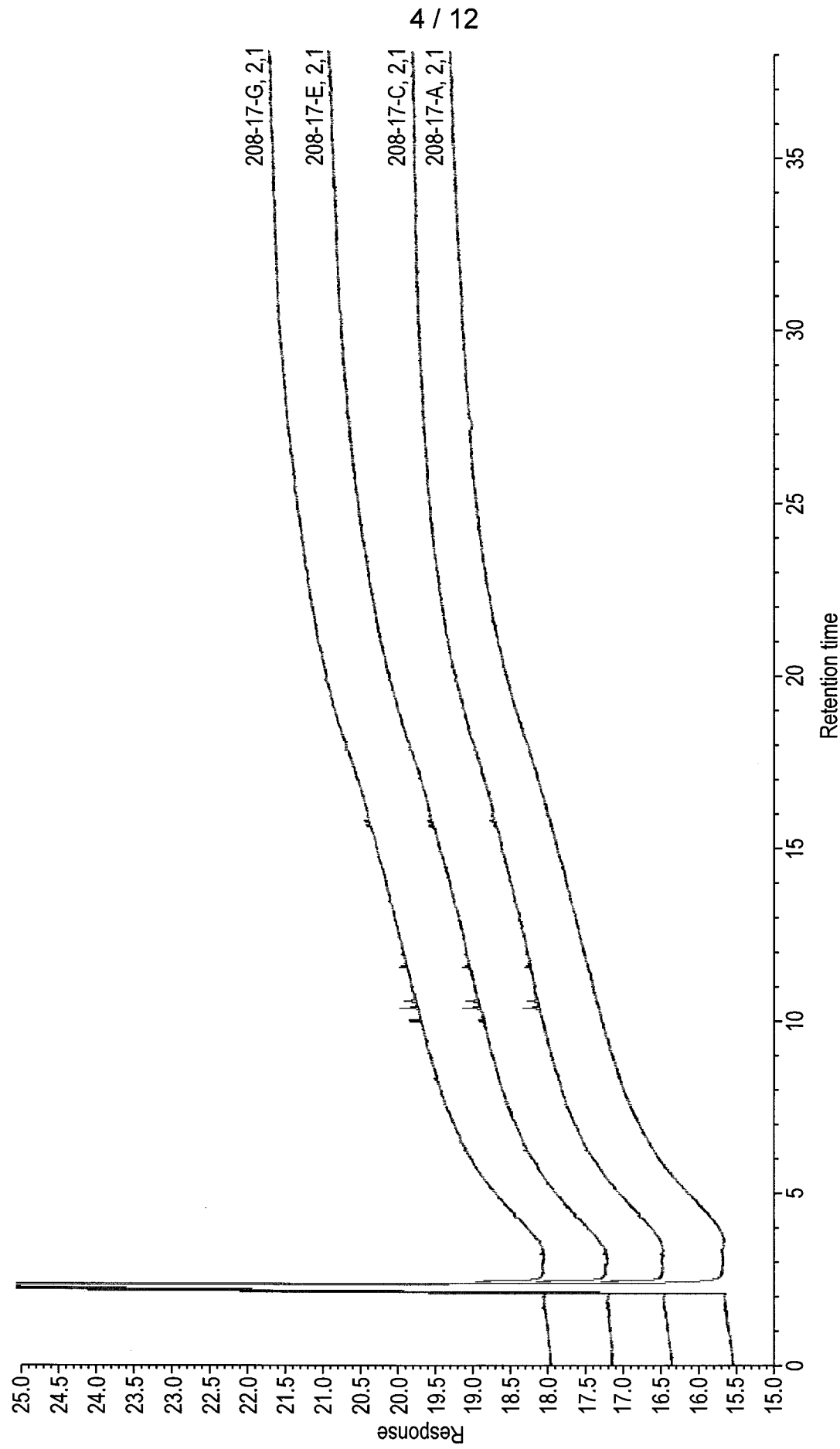
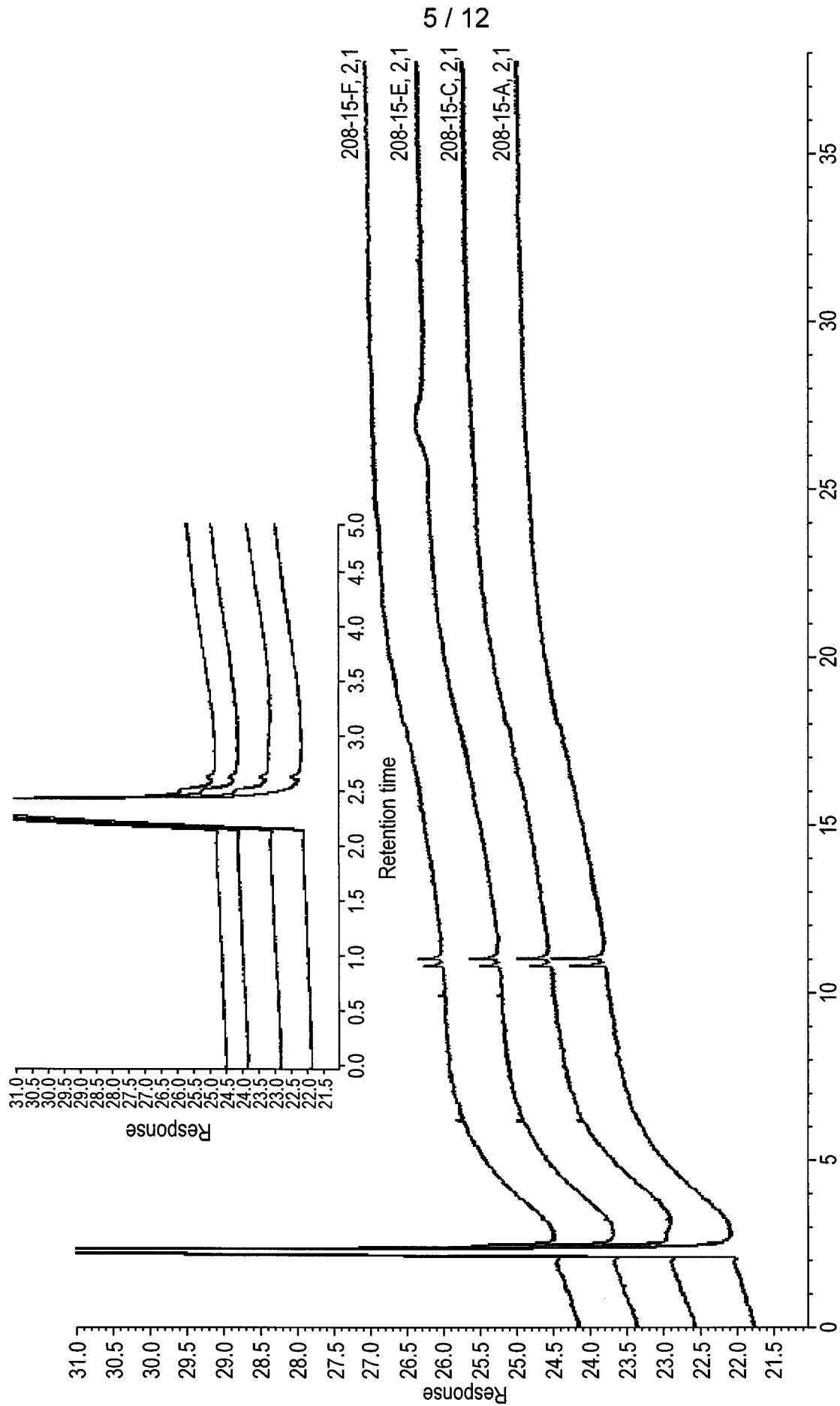


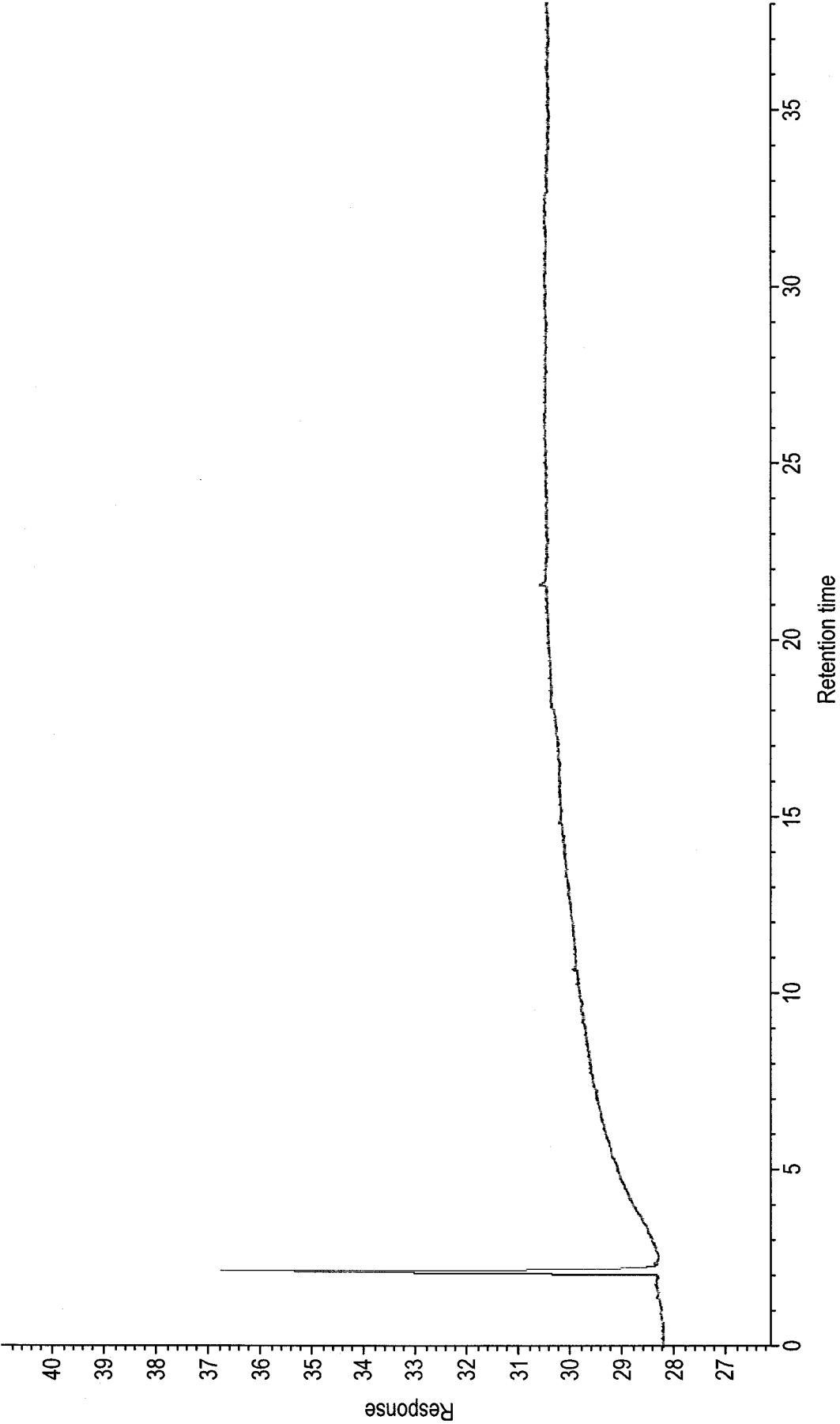
FIG. 4



Retention time

FIG. 5

6 / 12



Retention time

FIG. 6

7 / 12

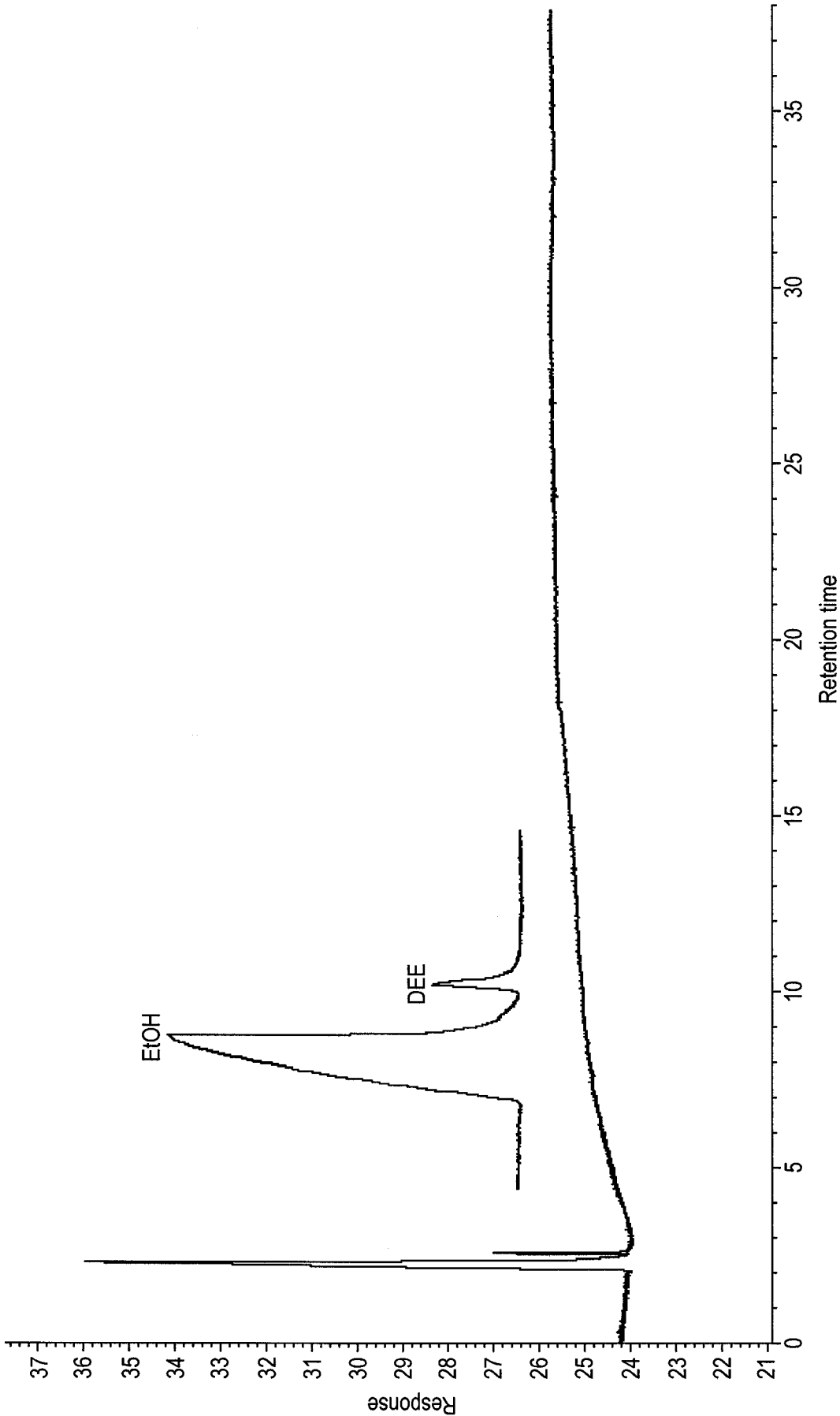


FIG. 7

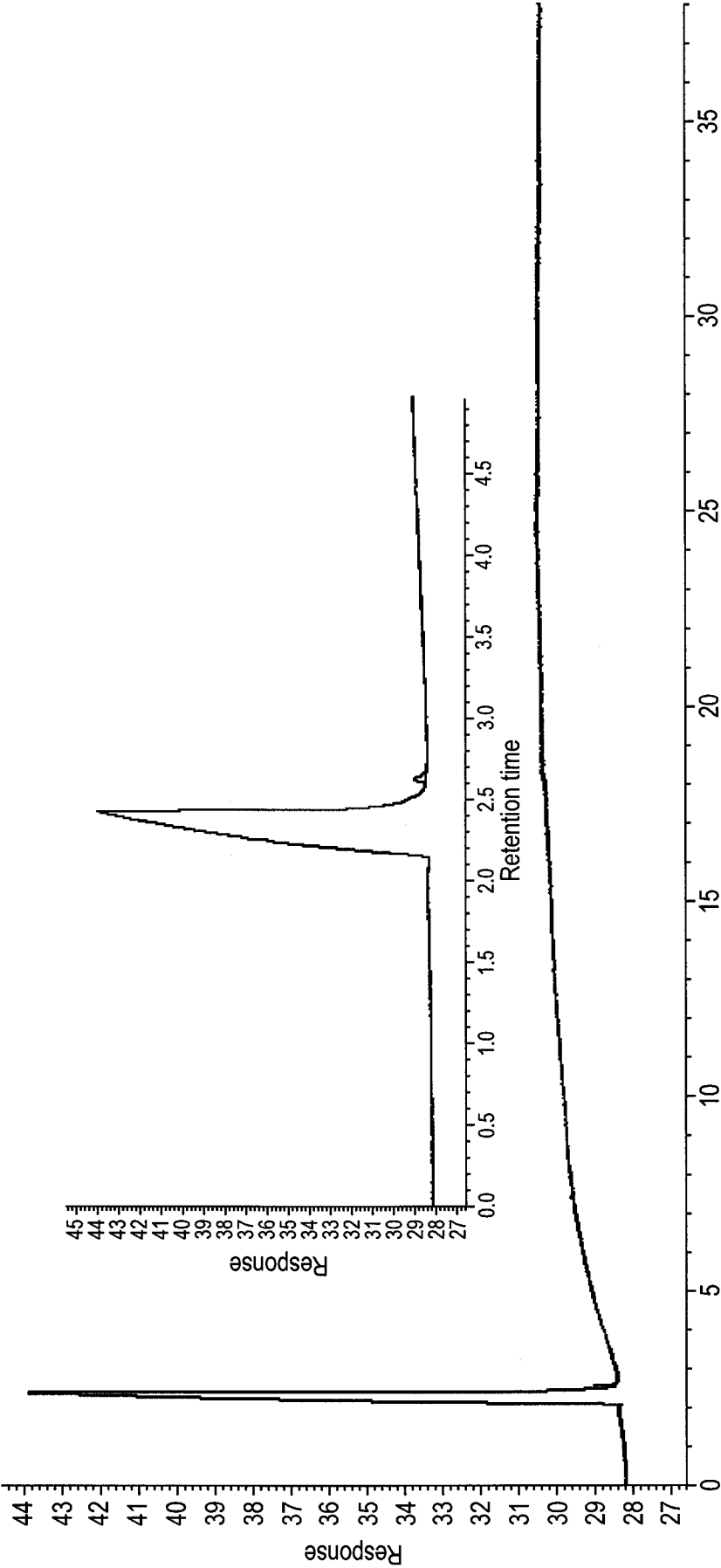


FIG. 8

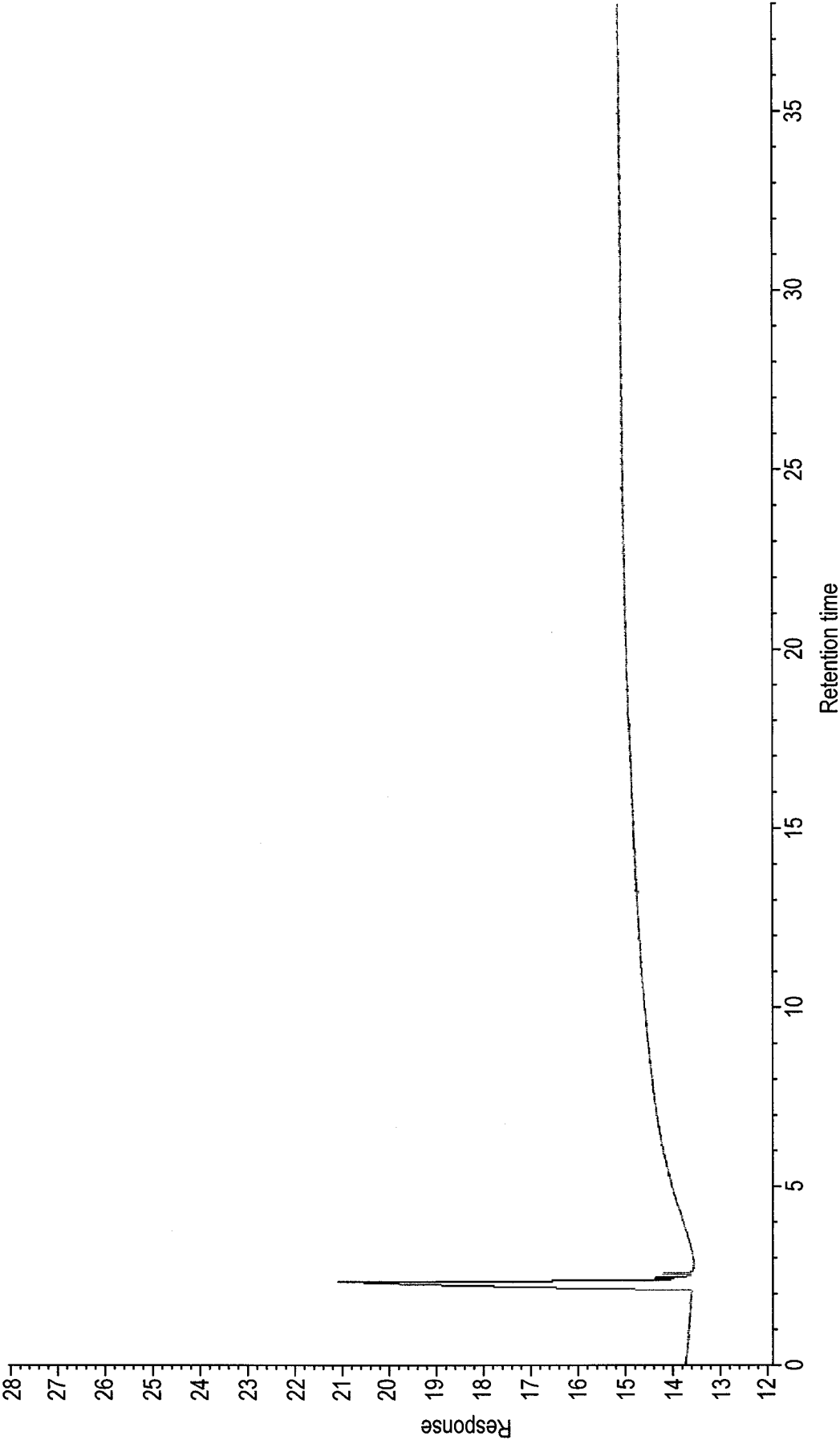


FIG. 9

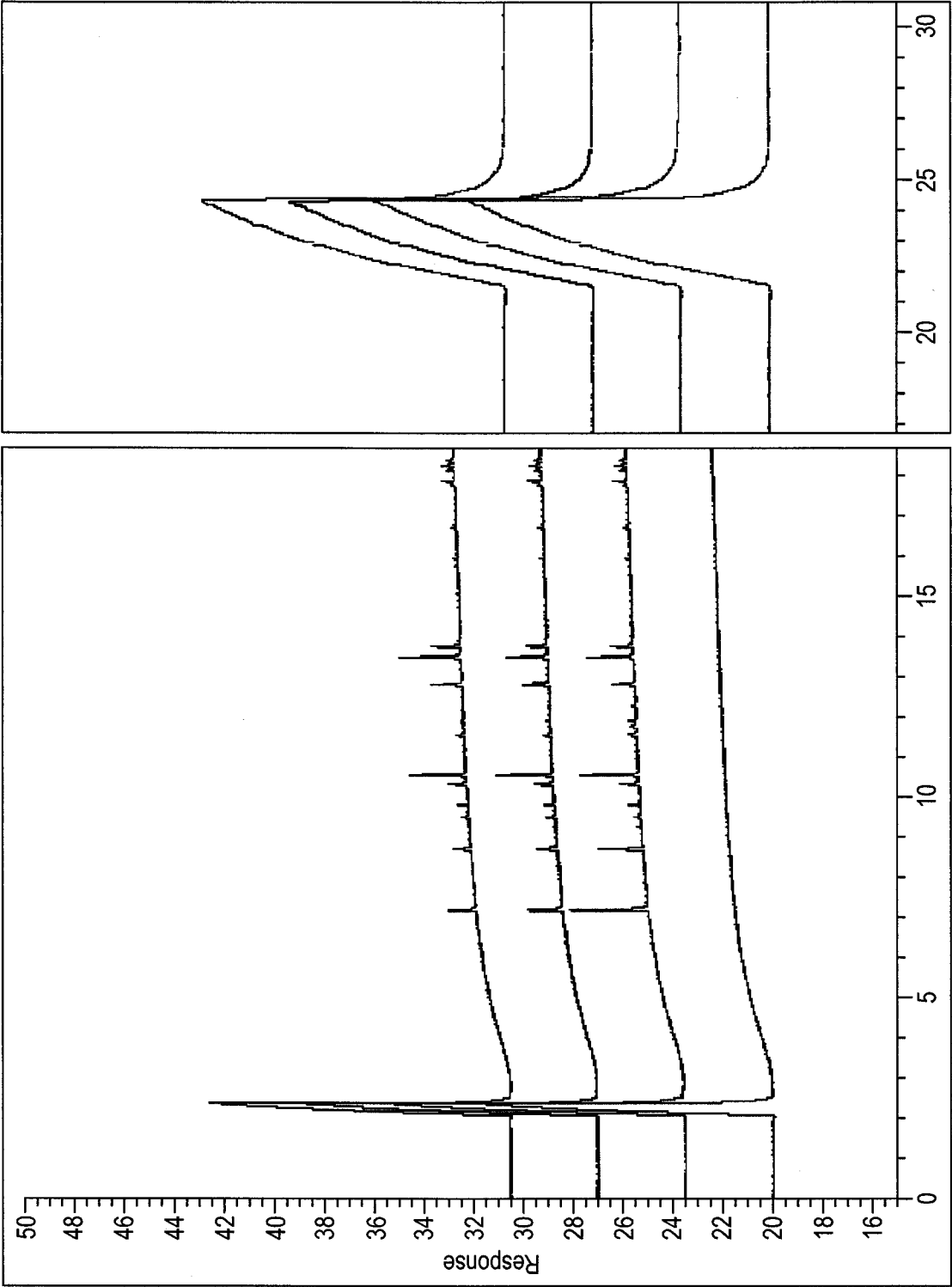


FIG. 10

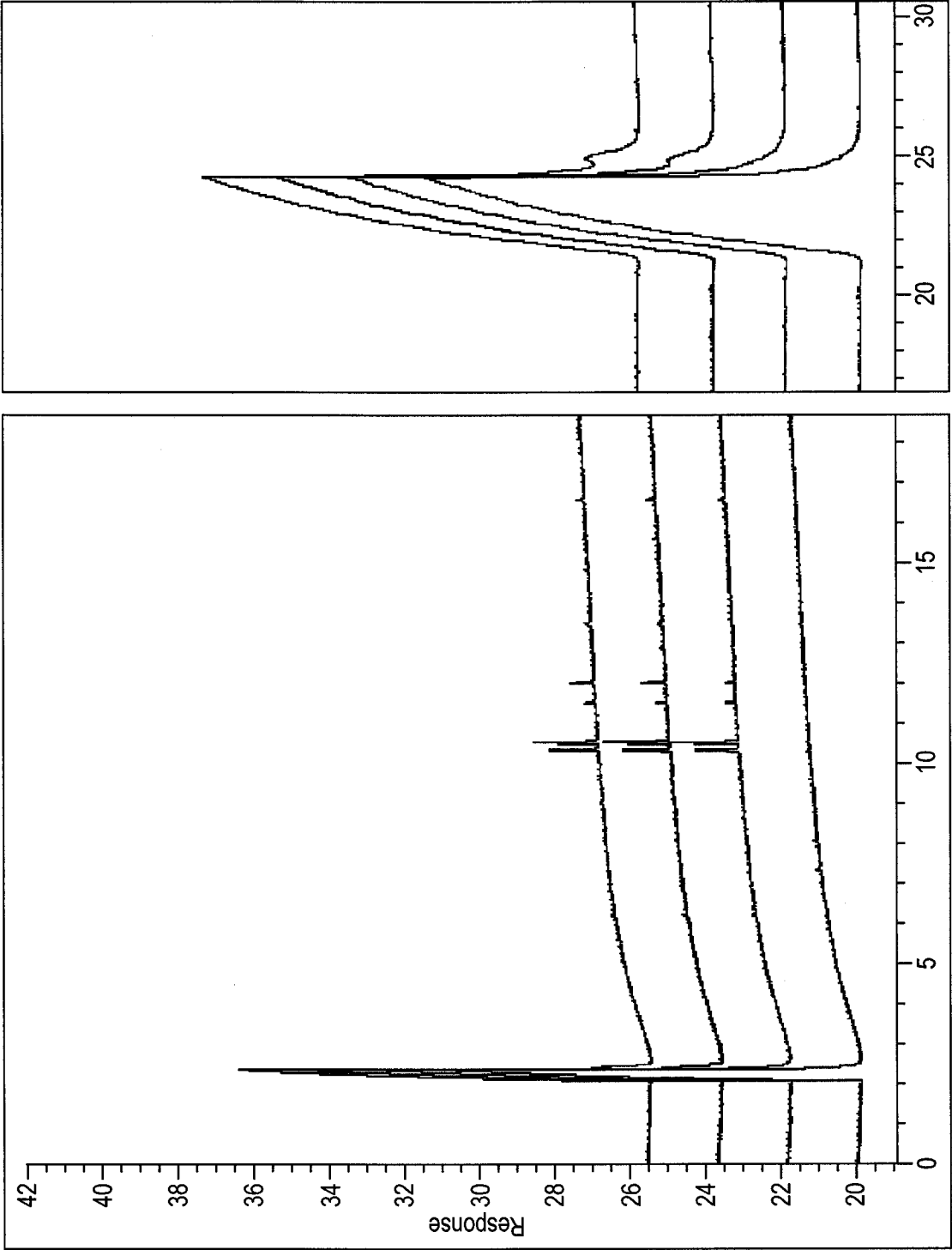


FIG. 11

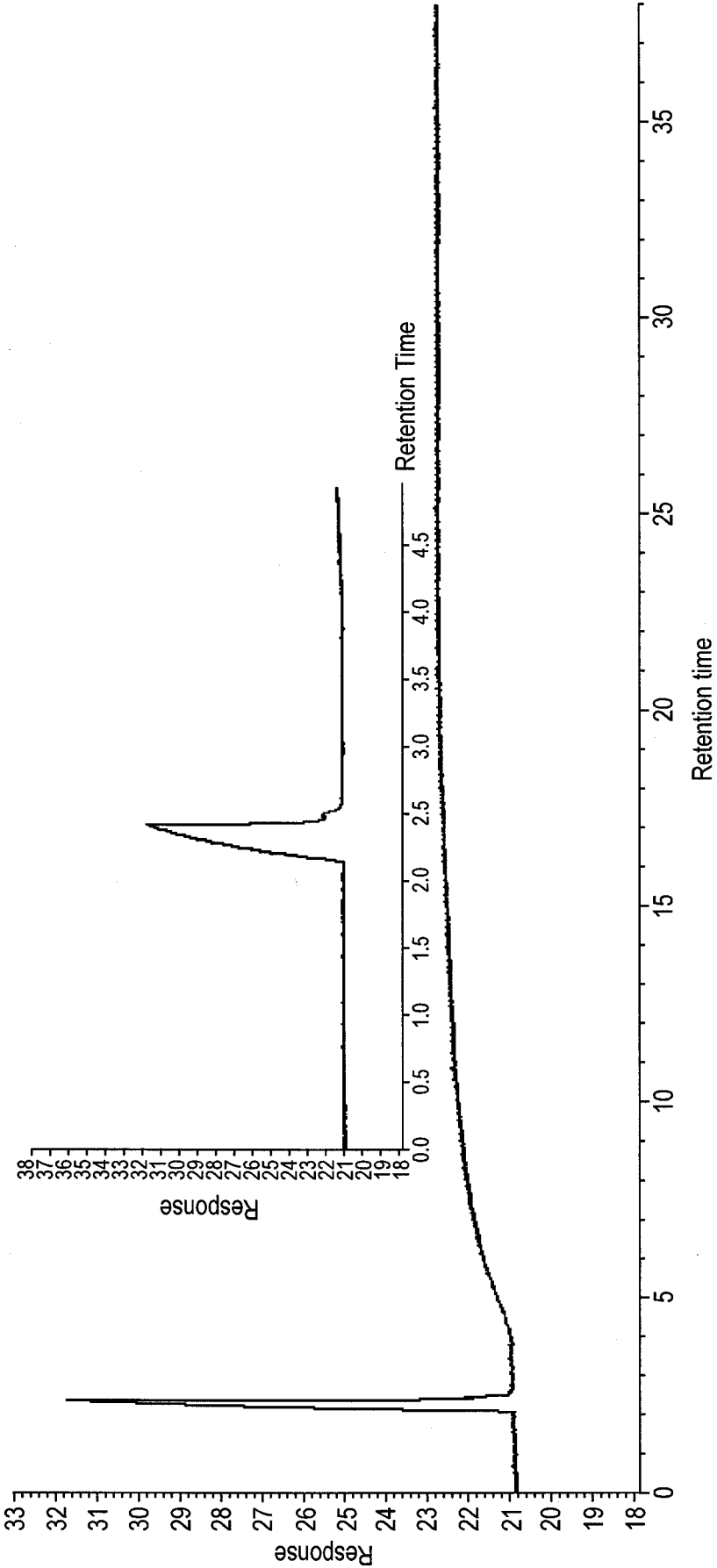


FIG. 12

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/068944

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C1/24 C07C29/76 C07C31/08 C07C11/04
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2010/060981 A1 (TOTAL PETROCHEMICALS RES FELUY [BE]; MINOUX DELPHINE [BE]; VERMEIREN W) 3 June 2010 (2010-06-03) cited in the application	17-20
A	example 2 -----	1-16,21, 22



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

3 February 2014

Date of mailing of the international search report

10/02/2014

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Fritz, Martin

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/068944

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