

INTEGRATED MANUFACTURING PROCESS FOR TERTIARY MERCAPTAN PRODUCTS

FIELD

The disclosure relates to processes and apparatus for manufacturing tertiary mercaptan
5 products that can typically contain some secondary mercaptans.

BACKGROUND

Mercaptans find utility in wide-ranging technical areas, including as biocorrosion
inhibitors, anti-fungal drugs, chain transfer agents in polymerizations, coating agents for metallic
surfaces, and vulcanization accelerators for rubber. The activity of mercaptans in such
10 applications may depend on their structure, especially the substitution of the carbon atom alpha
to the sulfur atom. Published processes to produce mercaptans are summarized as follows.

U.S. Patent No. 2,950,323 relates to preparation of thiols, sulfides, hydropolysulfides or
polysulfides of thiols by replacement of hydroxyl groups or etherified or esterified hydroxyl
groups.

15 U.S. Patent No. 4,102,931 relates to the use of synthetic zeolites as catalysts in the
addition reaction of hydrogen sulfide with branched, unsymmetrical olefins to produce tertiary
mercaptans.

U.S. Patent No. 7,217,843 relates to a process for selectively producing 2-thiols from
alpha olefins.

20 U.S. Patent No. 9,505,011 relates to a process for the recovery of a metal from an ore
using a collector composition.

U.S. Patent No. 9,527,090 relates to a process for the recovery of a metal from an ore
using a collector composition.

25 U.S. Patent No. 9,663,461 relates to a method for synthesizing sec-butyl mercaptan and
n-butyl mercaptan from 1-butene, a terminal olefin, and hydrogen sulfide.

U.S. Patent No. 10,011,564 relates to compositions including branched C10 mercaptans.

U.S. Patent No. 10,040,758 relates to compositions including branched C10 mercaptans selected from 5-methyl-1-mercapto-nonane, 3-propyl-1-mercapto-heptane, 4-ethyl-1-mercapto-octane, 2-butyl-1-mercapto-hexane, 5-methyl-2-mercapto-nonane, 3-propyl-2-mercapto-heptane, 4-ethyl-2-mercapto-octane, 5-methyl-5-mercapto-nonane, and combinations thereof.

5 U.S. Patent No. 10,807,949 relates to systems and processes for obtaining desired mercaptans or thiophenes from a feed stream containing a mixture of mercaptans, thiophenes and other components.

U.S. Patent No. 11,161,810 relates to continuous photochemical production of high purity linear mercaptan and sulfide compositions.

10 US 2010/249366A1 relates to a radical polymerization process in which a tert-dodecyl mercaptan is prepared by reaction of hydrogen sulfide with tri(n-butene) in the presence of a catalyst as chain-transfer agent.

US 2007/0197748A1 relates to a process for the preparation of tert-dodecyl mercaptan by reaction of hydrogen sulfide with tri(n-butene) in the presence of a catalyst.

15 PCT Publication No. WO 05/030710 relates to a low-odor tert-dodecanethiol which is particularly suitable as a molecular weight regulator and which can be obtained by acidic catalytic addition of hydrogen sulfide to a hydrocarbon mixture.

Dietrich *et al.*, "Chain Transfer Constants of Mercaptans in the Emulsion Polymerization of Styrene," Journal of Applied Polymer Science, Vol. 36, 1129-1141 (1988) relates to styrene
20 polymerizations using various mercaptans and discusses amounts of secondary mercaptans in commercial grade tertiary dodecyl mercaptan.

There are at least two problems associated with the production of mercaptans. First, in the catalytic production of tertiary mercaptans, a certain amount of secondary mercaptans may typically also be produced. As such, the product sold as "tertiary mercaptan" may also include
25 secondary mercaptans as a minor component and, in such cases, may be more accurately considered to be a blend of tertiary and secondary mercaptans. As will be described below, the amount of these secondary mercaptans may have an effect of the efficacy of the tertiary and secondary mercaptan blends in certain applications, notably as a chain transfer agent in some

polymerizations. Additionally, the amount of the secondary mercaptans may vary as the catalyst ages. Another problem is in the production of primary linear mercaptans. As in the production of the tertiary mercaptans, a certain amount of secondary mercaptans may be produced as a minor by-product. Primary branched mercaptans may also be produced as a minor byproduct. These
5 secondary mercaptans and primary branched mercaptans are typically removed in a separation process and discarded.

SUMMARY

The present disclosure attempts to solve the above problems by providing processes and integrated manufacturing systems for the consistent, compositionally stable production of tertiary
10 mercaptans, typically in blends with secondary mercaptans. The processes can also provide economic and environmentally responsible options for these secondary and tertiary mercaptan blends. In such processes, at least a portion of the secondary mercaptans in the tertiary mercaptan blend can be comprised of by-products produced from a linear (primary) mercaptan production unit and a tertiary mercaptan production unit. The tertiary mercaptans can be produced from a
15 tertiary mercaptan production unit. The secondary mercaptan byproducts of the linear mercaptan production process can be combined with the product of the tertiary mercaptan process. This integration of the two processes can allow for production of mercaptan mixtures with consistent and/or desired secondary and tertiary mercaptan content. Examples are shown demonstrating how a consistent, targeted blend of secondary and tertiary mercaptans can provide a useful chain
20 transfer agent for certain polymerization processes. In addition, economic and environmental advantages are described and can be associated with blending the byproducts of the linear (primary) mercaptan production unit with an intermediate (product) stream of the tertiary mercaptan production unit.

A continuous or semi-continuous process for producing a product mixture including
25 tertiary and secondary mercaptans is provided. The process can include the following steps. A first olefin stream including an asymmetric branched olefin or oligomer thereof can be reacted with a first sulfhydryl source (*e.g.*, H₂S-containing or capable of forming an *in situ* reactive mercaptan) stream in the presence of a catalyst to provide an intermediate stream comprising tertiary mercaptans and secondary mercaptans. Reacting a second olefin stream including a
30 linear alpha-olefin with a second sulfhydryl source (*e.g.*, H₂S-containing or capable of forming

an *in situ* reactive mercaptan) stream to provide a crude stream including linear and/or branched primary mercaptans, as well as secondary mercaptans. Separating the secondary mercaptans and optionally some or all of the linear and/or branched primary mercaptans from the crude stream to provide a make-up stream including secondary mercaptans and optional linear and/or branched
5 primary mercaptans. Combining at least a portion of the make-up stream with the intermediate stream to produce the product mixture including tertiary mercaptans, secondary mercaptans, and optionally linear and/or branched primary mercaptans.

An apparatus to perform the process is also provided. The apparatus includes a first reactor configured and arranged to react a first olefin stream including an asymmetric branched
10 olefin or oligomer thereof with a first sulfhydryl source (*e.g.*, H₂S-containing) stream in the presence of a catalyst to provide an intermediate stream comprising tertiary mercaptans and secondary mercaptans. The apparatus also includes a second reactor configured and arranged to react a second olefin stream including a linear alpha-olefin with a second sulfhydryl source (*e.g.*, H₂S-containing) stream to provide a crude stream including primary linear mercaptans, branched
15 primary mercaptans, and secondary mercaptans. Also part of the apparatus is a separation apparatus configured and arranged to separate the secondary mercaptans and optionally the linear and/or branched primary mercaptans from the crude stream to provide a make-up stream including secondary mercaptans and optional linear and/or branched primary mercaptans, as well as to combine at least a portion of the make-up stream with the intermediate stream to produce a
20 product mixture including tertiary mercaptans, secondary mercaptans, and optionally linear and/or branched primary mercaptans.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a simplified flow diagram for an embodiment of tertiary mercaptan production.

25 Figure 2 shows another embodiment of tertiary mercaptan production.

Figure 3 shows a simplified flow diagram for another embodiment of tertiary mercaptan production.

Figure 4 shows a simplified flow diagram for an embodiment of tertiary mercaptan production.

Figure 5 shows a simplified flow diagram for tertiary mercaptan production where the purification flow is configured to separate olefins from mercaptans in two consecutive towers.

Figure 6 shows a simplified flow diagram of an embodiment of a linear primary mercaptan production unit which the by-product from the secondary tower is sent to storage.

5 Figure 7 shows an alternative embodiment process to produce linear primary mercaptans.

Figure 8 shows a simplified integrated tertiary mercaptan production unit including the various feed points options for the make-up stream from the linear primary mercaptan production process. High pressure and low pressure separators have been removed for simplicity.

10 Figure 9 shows an integrated tertiary mercaptan production unit where the make upstream (by-product from linear primary mercaptan production process) is first purified by distillation to remove unwanted olefin, hydrocarbons and lower boiling mercaptans. Also shown are various feed points options from the storage tank to the tertiary mercaptan production unit. High pressure and low-pressure separators shown in Figure 1 have been removed for simplicity.

15 Figure 10 shows a simplified flow diagram of the integrated process in which the make-up stream (by-product) from the secondary tower in the linear primary mercaptan production unit is sent directly to the tertiary mercaptan production unit.

Figure 11 shows an integrated tertiary mercaptan production unit where the make-up stream (by-product) from the linear primary mercaptan production unit is directly fed to the tertiary mercaptan production unit. Also shown are the various feed points options from the
20 linear mercaptan production unit to the tertiary mercaptan production unit. High-pressure and low-pressure separators shown in Figure 1 have been removed for simplicity.

Figure 12 shows number-average molecular weight (M_n) of polystyrene as a function of secondary mercaptan concentration in TDM used as chain transfer agent. Triangle data are commercial grade TDM and circle data are blends of commercial grade TDM and dodecyl
25 mercaptans from a linear mercaptan unit.

Figure 13 shows TGA in air of polystyrene plotted at 10% mass loss temperatures as a function of secondary mercaptan concentration in TDM used as chain transfer agent. Triangle

data are commercial grade TDM and circle are blends of commercial grade TDM and dodecyl mercaptans from a linear mercaptan unit.

DETAILED DESCRIPTION

The following description is merely exemplary in nature and is in no way intended to
5 limit the present disclosure or its application or uses.

As used herein, “TDM” means tertiary dodecyl mercaptan or tert-dodecyl mercaptan; “NDM” means n-dodecyl mercaptan; “SDM” means secondary dodecyl mercaptan; and “TNM” means tertiary nonyl mercaptan. These abbreviations are sometimes used herein to describe product of mixed carbon number where the “target” carbon number of the product can be 12
10 (dodecyl) or 9 (nonyl), even though a range of carbon numbers may be included in said product.

Also as used herein, the terms “minor” and “minority” such as in reference to a component within a composition means that the composition contains less than 50% (in some cases, considerably less) of the “minor” component (constituting a “minority” of the composition), based on the composition, for example less than 40%, less than 30%, less than
15 25%, less than 20%, less than 15%, less than 10%, less than 7.5%, less than 5.0%, less than 2.5%, or less than 1.0% (in particular, less than 50%, less than 30%, less than 20%, less than 10%, or less than 2.5%).

Also as used herein, the terms “predominant” and “predominantly” such as in reference to a component within a composition means that the composition contains more of that
20 component than any other single component and additionally at least 40% of the “predominant” component, based on the composition, for example at least 45%, at least 50%, at least 60%, at least 70%, at least 75%, at least 80%, at least 85%, at least 90%, at least 93%, at least 95%, at least 98%, or at least 99% (in particular, at least 40%, at least 60%, at least 75%, at least 85%, or at least 95%).

Also as used herein, the terms “major” and “majority” such as in reference to a component within a composition means that the composition contains more than 50% of the “majority” component (constituting a “majority” of the composition), based on the composition, for example more than 55%, more than 60%, more than 65%, more than 70%, more than 75%, more than 80% by weight, more than 85% by weight, more than 90% by weight, more than 93%,
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more than 95%, more than 98%, or more than 99% (in particular, more than 50%, more than 65%, more than 75%, more than 85%, or more than 95%).

For each of these aforementioned terms (*i.e.*, “minor[ity]”, “predominant[ly]”, and “major[ity]”), the percentages delineated may be by weight or by mole – with regard to carbon
5 number, for example in describing a hydrocarbon, the relevant percentage(s) is(are) expressed as percent by weight herein, relative to a total weight of the composition; with regard to the substitution level of the carbon alpha to the mercaptan (primary versus secondary versus tertiary mercaptans), the relevant percentage(s) is(are) expressed as mole percent herein, relative to a total number of moles of the composition. Still with respect to each of the aforementioned terms,
10 if relating to neither carbon number nor substitution level, the relevant percentage(s) shall be assumed to be percent by weight, relative to a total weight of the composition, unless otherwise specified differently.

When the term “about” is used herein with respect to a range, it should be understood to modify the lower limit, the upper limit, or both. If there are no overriding contextual bases for
15 interpretation of the numerical bounds of any instances of the term “about” herein, each instance can be independently interpreted as encompassing whatever can round to the stated value(s), based on significant digits. For instance, without context, “about 1.00” can be interpreted to mean from 0.995 to less than 1.005; “about 1.0” can be interpreted to mean from 0.95 to less than 1.05; and “about 1” can be interpreted to mean from 0.5 to less than 1.5.

20 The present disclosure can relate to a process to integrate the linear mercaptan process and tertiary/secondary mercaptan process such that the secondary mercaptan by-product (and optionally linear and/or branched primary mercaptans, in this case less desirable co-products) stream of the linear mercaptan process can be integrated into the tertiary process or product, for example to allow production of tertiary mercaptan blends with additional and/or consistent levels
25 of secondary mercaptans. As discussed above, the present disclosure can additionally or alternatively relate to a process for producing tertiary mercaptans and specifically blends of tertiary and secondary mercaptans. Secondary mercaptans (and optionally also branched primary mercaptans) that are the by-products (co-products) of a primary linear mercaptan production process can be advantageously blended with the product of a process that produces tertiary (or
30 typically a blend of tertiary and secondary) mercaptans. In some cases, such as in which

separation of by-products/co-products in the primary linear mercaptan production process is critical to isolate only a primary linear mercaptan product, some (typically relatively small) amount of linear primary mercaptans may be present in the by-product/co-product stream with the secondary (and optionally also primary branched) mercaptans, which can then be co-blended
5 into the product of the tertiary mercaptan process comprising tertiary (and optionally but typically also secondary) mercaptans.

The benefits of the overall integrated production can encompass either or both of the following. First, the composition of the tertiary (and secondary) mercaptans emerging from the process that produces them may vary over time, such as due to changes in the feedstock, effects
10 of catalyst aging, or the like. Blending the byproduct secondary mercaptans (and optionally but not preferably linear and/or branched primary mercaptan co-products) from the primary linear mercaptan production process can provide a compositionally more consistent blend of tertiary and secondary (and optionally but not preferably linear and/or branched primary) mercaptan product. Second, the integrated process may additionally or alternatively provide economic
15 and/or environmental benefits, because the byproduct secondary mercaptans (and/or some portion of other co-products) from the primary linear mercaptan production process can be at least partially recycled instead of needing to be disposed of as waste and/or can be repurposed in a more expensive manner (*e.g.*, requiring additional chemical modification and/or purification, *inter alia*).

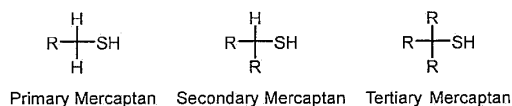
20 First Reaction/Reactor – Production of Intermediate Stream Including Tertiary Mercaptans from a First Olefin Stream and a First Sulfhydryl source Stream

According to an embodiment, a step of the process is reacting a first olefin stream comprising an asymmetric branched olefin or oligomer thereof with a first sulfhydryl source stream in the presence of a catalyst to provide an intermediate stream including tertiary
25 mercaptans and secondary mercaptans.

Sulfhydryl sources can typically contain hydrogen sulfide (H_2S), and are occasionally described herein as being H_2S , for brevity only – they may include any compound capable of forming an *in situ* reactive sulfhydryl group, in this case in the presence of one or more olefins. Sulfhydryl sources may thus include, but are not necessarily limited to, sulfhydryl donors such as
30 hydrogen sulfide, thioacetic acid, branched hydrocarbon mercaptans with relatively stable

leaving groups (typically having from 3 to 14 carbon atoms, *e.g.*, t-butyl mercaptan or the like), salts (*e.g.*, Group I such as sodium, potassium, lithium, or the like or combinations thereof; Group II such as magnesium, calcium, or the like or combinations thereof; mono- and/or di-valent transition metals such as copper, silver, yttrium, iron, nickel, zinc, or the like or combinations thereof; quaternary ammonium salts; or combinations thereof) thereof, and/or combinations thereof.

The reaction of trisubstituted olefins with a sulfhydryl source such as H₂S, catalyzed by an acid catalyst, can produce tertiary mercaptans as a predominant or major product. The reaction of tetrasubstituted olefins with a sulfhydryl source such as H₂S, catalyzed by an acid catalyst, can also produce tertiary mercaptans.

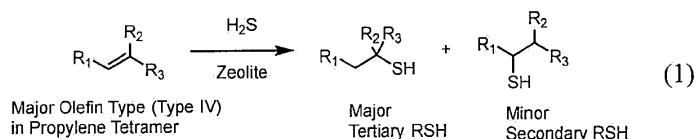


Tertiary dodecyl mercaptan (TDM) may be produced by reacting propylene tetramer, a C₁₂ enriched branched mono-olefin, and a sulfhydryl source such as hydrogen sulfide (H₂S) over an acid catalyst. Additionally or alternatively, tertiary dodecyl mercaptan (TDM) may be produced by reacting tri-n-butene with a sulfhydryl source such as H₂S. Tertiary nonyl mercaptan (TNM) may be produced with the same catalyst and reactor configuration, using a C₉ enriched propylene trimer (nonene) as the feed stock. The catalyst may include at least one of a zeolite, an acid compound, a metal oxide, a sulfonic acid resin, or a combination thereof. Additionally or alternatively, the catalyst may include a synthetic zeolite comprising an alkali metal content (expressed as the corresponding oxide, for sodium as Na₂O) of less than 10% by weight. Additionally or alternatively, the catalyst may be a Lewis and/or Brønsted acid which is solid or liquid and which is miscible or immiscible in the reaction medium, for example chosen from an organic or inorganic acid, an alumina, a clay, a silica or a silica-alumina, a zeolite, a heteropolyacid or a weakly or strongly acidic cation-exchange resin. Mention may be made, among the metals having an oxide which can be used as catalyst, of chromium, cobalt, molybdenum, tungsten, zirconium, niobium, nickel, or combinations thereof. Additionally or alternatively, the catalyst may include at least one of synthetic zeolite type X, synthetic zeolite type Y, sulfonic acid resin, a cation exchange resin, a copolymer of sulfonated styrene with

divinylbenzene, or combination thereof. Additionally or alternatively, the catalyst may include a Type Y acid zeolite catalyst.

Further additionally or alternatively, various polymers and copolymers including acid functional groups known to a person skilled in the art as cation exchangers may be suitable as catalysts. For example, use may be made of resins based on sulfonated polystyrenes which may be crosslinked (in particular with divinylbenzene), acrylic or phenylacrylic resins including free carboxyl groups, resins of phenol-formaldehyde type such as derived from phenolsulfonic acids, lignosulfonic exchangers, or the like, or combinations thereof. Resins of this type may be sold under various names. One example of a commercially available catalyst is a sulfonated styrene/divinylbenzene copolymer resin called AmberLyst™ 15 commercially available from DuPont.

The reaction scheme for production of the intermediate stream including tertiary mercaptans can be described as shown in reaction (1) below. Under most commercially relevant conditions, a minor product of this reaction can be secondary mercaptans and therefore a mixture or blend of tertiary mercaptans and secondary mercaptans may typically be produced.



In the above reaction scheme, each R₁ may be a C1-C16 (in particular C3-C10) linear or branched alkyl group and each R₂ and R₃ may independently be C1-C16 (in particular C1-C10) linear or branched alkyl groups, such that the sum of R₁ + R₂ + R₃ averaged over the total (major + minor + any thiol-containing hydrocarbonaceous product) product can have 5 to 20 carbons, 6 to 17 carbons, 6 to 15 carbons, 7 to 15 carbons, 8 to 14 carbons, 10 to 13 carbons, or 9 to 11 carbons (in particular, 6 to 15 carbons, 8 to 14 carbons, or 10 to 13 carbons).

In various embodiments, the intermediate stream containing a mixture of tertiary and secondary mercaptans can be produced from a first olefin stream containing propylene tetramer that includes a Type IV asymmetric olefin as the predominant or major olefin component. As known in the art, there are five major olefin types: Type I (R-CH=CH₂); Type II (R-CH=CH-R); Type III (R₂C=CH₂); Type IV (R₂C=CH-R); and Type V (R₂C=CR₂). In regards to the

propylene tetramer olefin structure in the first olefin stream, it can advantageously comprise or be a C12-rich mixture, such as produced by the oligomerization of propylene, with trisubstituted (Type IV) and tetrasubstituted (Type V) collectively constituting the majority of olefin types in propylene tetramer. If the first olefin feed stream includes linear alpha-olefins, the linear alpha-olefins may be reacted with a sulfhydryl source such as hydrogen sulfide in the presence of an acid catalyst under conditions so as to produce secondary mercaptans as predominant or major products, where the mercaptan functionality is typically installed on the most substituted carbon. This reaction may also provide a source of secondary mercaptans in the intermediate stream, *e.g.*, as a result of the composition of the first olefin feed stream. Additionally or alternatively, if the first olefin stream includes tetrapropylene oligomer, it may include a C12-rich mixture of alkenes comprising from 10 to 14 carbon atoms in which the content of alkene including 12 carbon atoms (also referred to as dodecene or C12 olefin) can advantageously range from 55% to 85% by weight, such as from 60% to 80% by weight, in which each of said types of alkenes can be present in the mixture/stream in the form of positional isomers of the double bond and of geometric isomers. As such, dodecene in such first olefin stream can correspond to an oligomerized propylene tetramer and the presence of a C12-rich product also containing C10, C11, C13 and C14 olefins, typically resulting from side reactions.

Further additionally or alternatively, the intermediate stream containing a mixture of tertiary and secondary mercaptans can be produced from oligomerization (particularly trimerization) of *n*-butene. With regard to butylene trimer/tri-*n*-butene, the alkenes present can generally contain from 11 to 13 carbon atoms with dodecene (C12 isomers) being present in amounts of at least 90% or at least 95% by weight.

Dietrich et al. (Journal of Applied Polymer Science, Vol. 36, 1129-1141 (1988)) discloses that technical tert-dodecyl mercaptan is the H₂S adduct with the C12 cut from a propylene oligomerization. It discloses a propylene tetramer product being a mixture of C9 to C14 mercaptans with ~55-60% being C12 mercaptan. According to this reference, approximately 80% of the resulting mercaptan is tertiary, with the remainder being secondary.

In the present disclosure, the secondary mercaptan content in the intermediate stream and/or the mercaptan-containing product therefrom (sometimes abbreviated herein as "TDM" for convenience) can often decrease as the catalyst used for its production ages. When H₂S is used as

the sulfhydryl source and the catalyst is fresh (more active), the secondary mercaptan content of the intermediate stream may be about 20 mol% (with about 80 mol% being tertiary mercaptan and with no detectable primary mercaptan). However, as the catalyst ages and activity loss progresses, the secondary mercaptan content in the intermediate stream may decrease to about 8 mol% (about 92 mol% tertiary and still no detectable primary). Importantly, significant change in secondary mercaptan content in the ultimate product of/from the intermediate stream may impact performance as a chain transfer agent. Therefore it can be desirable to maintain a constant level of secondary mercaptan in the intermediate stream (mercaptan-containing product).

According to some embodiments, the intermediate stream may include from 0.1 to 30 mol%, from 0.1 to 29 mol%, from 0.1 to 28 mol%, from 0.1 to 27 mol%, from 0.1 to 26 mol%, from 0.1 to 25 mol%, from 0.1 to 24 mol%, from 0.1 to 23 mol%, from 0.1 to 22 mol%, from 0.1 to 21 mol%, from 0.1 to 20 mol%, from 0.1 to 19 mol%, from 0.1 to 18 mol%, from 0.1 to 17 mol%, from 0.1 to 16 mol%, from 0.1 to 15 mol%, from 0.1 to 14 mol%, from 0.1 to 13 mol%, from 0.1 to 12 mol%, from 0.1 to 11 mol%, from 0.1 to 10 mol%, from 0.1 to 9 mol%, from 0.1 to 8 mol%, from 0.1 to 7 mol%, from 0.1 to 6 mol%, from 0.1 to 5 mol%, from 0.1 to 4 mol%, from 0.1 to 3 mol%, from 0.1 to 2 mol%, from 0.1 to 1 mol%, from 0.1 to 0.5 mol%, from 0.5 to 30 mol%, from 0.5 to 29 mol%, from 0.5 to 28 mol%, from 0.5 to 27 mol%, from 0.5 to 26 mol%, from 0.5 to 25 mol%, from 0.5 to 24 mol%, from 0.5 to 23 mol%, from 0.5 to 22 mol%, from 0.5 to 21 mol%, from 0.5 to 20 mol%, from 0.5 to 19 mol%, from 0.5 to 18 mol%, from 0.5 to 17 mol%, from 0.5 to 16 mol%, from 0.5 to 15 mol%, from 0.5 to 14 mol%, from 0.5 to 13 mol%, from 0.5 to 12 mol%, from 0.5 to 11 mol%, from 0.5 to 10 mol%, from 0.5 to 9 mol%, from 0.5 to 8 mol%, from 0.5 to 7 mol%, from 0.5 to 6 mol%, from 0.5 to 5 mol%, from 0.5 to 4 mol%, from 0.5 to 3 mol%, from 0.5 to 2 mol%, from 0.5 to 1 mol%, from 1 to 30 mol%, from 1 to 29 mol%, from 1 to 28 mol%, from 1 to 27 mol%, from 1 to 26 mol%, from 1 to 25 mol%, from 1 to 24 mol%, from 1 to 23 mol%, from 1 to 22 mol%, from 1 to 21 mol%, from 1 to 20 mol%, from 1 to 19 mol%, from 1 to 18 mol%, from 1 to 17 mol%, from 1 to 16 mol%, from 1 to 15 mol%, from 1 to 14 mol%, from 1 to 13 mol%, from 1 to 12 mol%, from 1 to 11 mol%, from 1 to 10 mol%, from 1 to 9 mol%, from 1 to 8 mol%, from 1 to 7 mol%, from 1 to 6 mol%, from 1 to 5 mol%, from 1 to 4 mol%, from 1 to 3 mol%, from 1 to 2 mol%, from 2 to 30 mol%, from 2 to 29 mol%, from 2 to 28 mol%, from 2 to 27 mol%, from 2 to 26 mol%, from 2 to 25 mol%, from 2 to 24 mol%, from 2 to 23 mol%, from 2 to 22 mol%, from 2 to 21 mol%, from 2

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25 mercaptans.

Additionally or alternatively, the intermediate stream may include from 70 to 99 mol%, from 70 to 98 mol%, from 70 to 96 mol%, from 70 to 94 mol%, from 70 to 92 mol%, from 70 to 90 mol%, from 70 to 88 mol%, from 70 to 86 mol%, from 70 to 84 mol%, from 70 to 82 mol%, from 70 to 80 mol%, from 70 to 78 mol%, from 70 to 76 mol%, from 70 to 74 mol%, from 70 to
30 72 mol%, from 72 to 99 mol%, from 72 to 98 mol%, from 72 to 96 mol%, from 72 to 94 mol%, from 72 to 92 mol%, from 72 to 90 mol%, from 72 to 88 mol%, from 72 to 86 mol%, from 72 to

84 mol%, from 72 to 82 mol%, from 72 to 80 mol%, from 72 to 78 mol%, from 72 to 76 mol%,
from 72 to 74 mol%, from 74 to 99 mol%, from 74 to 98 mol%, from 74 to 96 mol%, from 74 to
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94 mol%, from 94 to 99 mol%, from 94 to 98 mol%, from 94 to 96 mol%, from 96 to 99 mol%,
from 96 to 98 mol%, or from 98 to 99 mol% of tertiary mercaptans.

In alternative embodiments, there may be less than 0.5 mol%, less than 0.3 mol%, less
than 0.1 mol%, or no detectable secondary mercaptans in the intermediate stream, in which case
25 there may be approximately 100 mol% of tertiary mercaptans (being that, in most cases, there
can typically be less than 1 mol%, less than 0.5 mol%, less than 0.2 mol%, less than 0.1 mol%,
or no detectable primary mercaptans in the intermediate stream).

In addition to the aging of the catalyst, for reactions of olefins and hydrogen sulfides, the
structure of the olefin and the reaction conditions affect the structure of the resulting mercaptan.

U.S. Patent Nos. 10,011,564 and 10,040,758 describe how the reaction conditions may affect the content of the intermediate stream and are incorporated by reference herein.

The conditions in the first reactor may depend on the catalyst, and the feed rate, and the exact composition of the feed stream. For example, the reaction conditions in the first reactor may be as follows. According to some embodiments, the first olefin stream and the first sulfhydryl source (H_2S) stream may be continuously or semi-continuously passed over the catalyst at a rate of from about 5 to about 250 gram-moles, from about 5 to about 150 gram-moles, or from about 15 to about 100 gram-moles of the first olefin stream per 24 hours per kilogram of catalyst. According to some embodiments, the first sulfhydryl source (H_2S) stream can be present in a molar excess with respect to the first olefin stream and the reaction between the first olefin stream and the first sulfhydryl source (H_2S) stream are carried out at above atmospheric pressures (*e.g.*, from about 100 to about 400 psig, from about 150 to about 300 psig, from about 190 to about 270 psig, or from about 200 to about 240 psig; alternatively, from about 5 to about 80 barg, from about 10 to about 50 barg, or from about 10 to about 20 barg) and at temperatures from about 10°C to about 250°C (*e.g.*, from about 20°C to about 200°C , from about 50°C to about 150°C , or from about 70°C to about 120°C). The hourly space velocity, defined as the ratio of the hourly flow rate by volume of olefin to the volume of catalyst, can depend strongly on the activity of the catalyst used, but can generally range from about 0.01 to about 100 h^{-1} , from about 0.1 to about 10 h^{-1} , or from about 0.2 to about 2 h^{-1} .

As known in the art, propylene tetramer has 5 types of olefins. These are: Type I: $\text{R}_1\text{CH}=\text{CH}_2$; Type II: $\text{R}_1\text{CH}=\text{CHR}_3$; Type III: $\text{R}_1\text{R}_2\text{C}=\text{CH}_2$; Type IV: $\text{R}_1\text{R}_2\text{C}=\text{CHR}_3$; and Type V: $\text{R}_1\text{R}_2\text{C}=\text{CR}_3\text{R}_4$. Type IV is most common in the propylene tetramer stream that feeds the acid-catalyzed reactor.

According to some embodiments, the first olefin stream may include a branched, asymmetric olefin or oligomer thereof having the formula $\text{R}_1\text{R}_2\text{C}=\text{CR}_3\text{R}_4$ where R_1 and R_2 are the same or different alkyl radicals, and R_3 and R_4 are independently either H or the same or different alkyl radicals (*i.e.*, from Type IV and/or Type V categories above). The total number of carbons in $\text{R}_1 + \text{R}_2 + \text{R}_3 + \text{R}_4$ may be from 5 to 30 carbons, 6 to 24 carbons, 7 to 20 carbons, 9 to 15 carbons, 10 to 13 carbons, 7 to 13 carbons, 8 to 12 carbons, or 9 to 11 carbons (in particular, 6 to 24 carbons, 7 to 13 carbons, or 8 to 12 carbons).

Additionally or alternatively in such embodiments, the active ingredients in the first sulfhydryl source stream may be in molar excess (on H₂S molar equivalent basis) with respect to the active ingredients in the first olefin stream (olefinic hydrocarbons), *e.g.*, with the molar ratio of sulfhydryl source (H₂S or H₂S equivalent) to olefinic hydrocarbons (on a carbon-carbon double bond equivalent basis) being from about 100:1 to more than 1:1, such as from about 50:1 to more than 1:1, from about 25:1 to more than 1:1, from about 20:1 to more than 1:1, from about 10:1 to more than 1:1, from about 5:1 to more than 1:1, or from about 2:1 to about 1.05:1. Alternatively, the active ingredients in the first olefin stream (olefinic hydrocarbons, on a carbon-carbon double bond equivalent basis) may be in molar excess with respect to the active ingredients in the first sulfhydryl source stream are in molar excess (on an H₂S molar equivalent basis), *e.g.*, with the molar ratio of olefinic hydrocarbons to sulfhydryl source (H₂S or H₂S equivalent) being from about 100:1 to more than 1:1, such as from about 50:1 to more than 1:1, from about 25:1 to more than 1:1, from about 20:1 to more than 1:1, from about 10:1 to more than 1:1, from about 5:1 to more than 1:1, or from about 2:1 to about 1.05:1.

Types of Reactors

The first reactor may desirably be a continuous reactor or alternatively a semi-continuous reactor. Its type is not particularly limited and may be a tubular reactor, a continuous-stirred tank reactor (CSTR), a plug flow reactor (PFR), and a fixed bed (packed-bed) reactor (PBR). If a PBR/fixed bed reactor is used, it may include one or more than one such bed (for example, 3-7 beds; in particular 4-6 beds) packed with the catalyst(s). The beds may be changed out as needed. They may be connected in series or in parallel (in particular, at least partially in series) and taken on and off line as necessary.

Exemplary TDM Process Descriptions (First Reactor) that Produces an Intermediate Stream of a Blend of Tertiary and Secondary Mercaptans:

As shown in Figure 1, a mixture of fresh olefin (first olefin stream), optionally recycled olefin, and a sulfhydryl source (which may include recycled and/or fresh mercaptans, unreacted/recycled and/or fresh hydrogen sulfide and/or an alternative sulfhydryl source, or a combination thereof, but which recycled and/or fresh mercaptans are typically combined with the first olefin stream) may be passed through a dryer and fed through a preheater to a reactor.

According to the embodiment in Figure 1, the reactor may comprise or be a trickle bed reactor,

which may have five catalyst beds. The catalyst present may be a Type-Y zeolite, such as LZY-64, which is commercially available from UOP (Honeywell), *inter alia*. The liquid feed can be introduced at any one or more bed input locations depending on desired conversion and/or production rates. The sulfhydryl source can be recycled at temperature and/or fed through a preheater (in the case of hydrogen sulfide, perhaps in gaseous form), for instance to the top of the reactor flowing downwards. The reactor/bed(s) may be operated at a pressure of about 100-300 psig, in particular from about 150 to 250 psig, and at a temperature from about 150 to 250°F. Total typical flow rates may get as high as ~15,000 – 20,000 lb/h through the reactor/bed(s). The flow rate may additionally or alternatively be expressed as being from 5 to about 250 gram-moles, or from about 5 to about 150 gram-moles, or from about 15 to about 100 gram-moles of the first olefin stream per 24 hours (day) per kilogram of catalyst.

The outlet stream of the reactor, including tertiary and secondary mercaptans and unreacted sulfhydryl source (*e.g.*, H₂S) and unreacted olefin, alkyl sulfides and other reaction byproducts may be sent to a high-pressure separator where the sulfhydryl source (if H₂S, then typically as vapor) may be separated and optionally but preferably recycled to the reactor. The (liquid) outlet of the high-pressure separator may then be sent to an input of a low-pressure separator, for example to remove residual sulfhydryl source (*e.g.*, H₂S) from the outlet stream. An outlet of the low-pressure separator may be sent to a distillation tower (typically called a residue tower) where alkyl sulfides and other heavies can be separated from the mercaptans and (unreacted) olefins. Distillation (Residue) tower operating conditions may include one, some, or all of the following: a bottoms temperature from about 200°F to about 450°F, or from about 240°F to about 375°F, or from about 250°F to about 350°F; an overhead temperature from about 150°F to about 300°F, or from about 190°F to about 290°F, or from about 200°F to about 290°F; and an overhead pressure from about 30 to about 90 millimeters of mercury absolute (mmHg), from about 40 to about 80 mmHg, or from about 45 to about 75 mmHg. The distillation (residue) tower bottoms containing mostly sulfides and some relatively high boiling mercaptans (C12-C15 mercaptans) may be disposed of, or may be recycled within this or another process. The distillation (residue) tower overhead stream containing mercaptan product and optionally residual (unreacted) olefins may be used as is (if residual olefins are not prevalent) or may be sent to another distillation (product) tower (where the residual olefins can be separated from the product mercaptans). The “product” of this process is the intermediate stream containing tertiary

mercaptans and optionally but preferably secondary mercaptans. The product (intermediate stream) tower operating conditions may include one, some, or all of the following: a bottoms temperature from about 200°F to about 400°F, or from about 220 to about 360°F, or from about 240°F to about 340°F; an overhead pressure from about 20 to about 120 mmHg, or from about 40 to about 110 mmHg, or from about 45 to about 105 mmHg; and a bottoms pressure from about 50 to about 150 mmHg, or from about 70 to about 130 mmHg, or from about 80 to about 120 mmHg. The bottom effluent of the product (intermediate stream) tower can be sent to a product (intermediate stream) storage tank, or forwarded immediately for further use, and the overhead effluent may be recycled, for example back to the front of the unit to be mixed with fresh olefin flow rates (3000-5000 lb/h). The recycle line may be equipped with a purge line, for example to allow a purge of unreactive olefins and hydrocarbons and/or to prevent accumulation in the process loop. The intermediate stream product, as discussed above, can contain tertiary mercaptans and optionally but preferably also secondary mercaptans, the composition of which may vary depending any one or more of a number of factors, such as the composition of the feed stream and the age of the catalyst, *inter alia*.

According to the embodiment shown in Figure 2, the process may be run using a single bed reactor. In such process(es), the first olefin (olefin feed) stream may comprise a C9-C15 propylene tetramer, a C10-C14 propylene tetramer, a C7-C11 propylene trimer, a C8-C10 propylene trimer, and/or a C11-C13 butene trimer, all of which being predominantly Type IV asymmetric olefins. In embodiments containing recycle streams, as noted above, the first olefin stream may be comprised of a mixed stream additionally including up to 10 wt% (e.g., from about 1 wt% to about 10 wt%) of mercaptans, based on a total weight of the stream.

Yet another embodiment of the process that produces a blend of tertiary and secondary mercaptans as the intermediate stream is shown in Figure 3. In this embodiment, a mixture of sulfhydryl source (in this case, H₂S gas) and liquid propylene tetramer, which, as in the above process, includes predominantly type IV asymmetric olefin, can be mixed and preheated before being fed to the reactor. The propylene tetramer may be passed through a dryer and stored into a buffer tank before being fed to the reactor. The reactor can be a fixed bed reactor containing an acidic catalyst. A non-limiting example of a suitable fixed bed catalyst includes a cation exchange resin, such as AmberLyst™ A15 commercially available from DuPont. The reaction

can be either done in one reactor as shown in Figure 3, or in multiple reactors. In the reactor(s), a typical target pressure can be ~200-240 psig. The temperature of feed stream into the reactors may be about 165°F-185°F. The flowrates through the reactor(s) may be from ~1500 lb/h up to ~4000 lb/h. The reactor temperature can be controlled to a range from about 210°F to about 230°F. The reaction conversion rate can vary, for example between 80% and 50%, and can be affected by the catalyst activity and run life (age) of the catalyst. As shown in Figure 3, the liquid outlet of the reaction may be flashed in two drums in series. The first drum may be at ~100 psig, and the second drum may be at ~30 psig. All (or virtually all) the excess sulfhydryl source (H_2S) can be recovered, all or part of which may advantageously be recycled back to the reactor feed.

Residual overhead propylene tetramer and tertiary and secondary mercaptan blend can be recovered through cooling and flash separation and may then be fed to the stripping column. The reaction outlet mixture can be sent to the inlet of the stripper and with gas (*e.g.*, nitrogen) injection at the bottom of the stripping column, *e.g.*, to substantially/fully eliminate residual sulfhydryl source (H_2S). The stripping column may be operated at around 175°F (bottom) and ~4.4 psig. The conversion rate of the residue may be followed by monitoring of the density of the residue.

The bottom of the stripping column may feed the final distillation column, which could also be a stripper column operating under vacuum. The overhead of this distillation/stripper column can be composed mainly of propylene tetramer and may be recycled back to the feed to the reactor. The finished blended tertiary and secondary mercaptan product (abbreviated as TDM/SDM, because of the target carbon number of the mercaptans being about 12, even though the product can contain mercaptans of other carbon numbers as well) is typically recovered at the bottom. Pressure can be about 30 mmHg and bottom temperature can be ~270°F. Both quality of the overhead and bottom product (the intermediate stream) may be continuously (or semi-continuously) monitored and/or controlled using densimeters.

Figure 4 shows an embodiment of a mercaptan blend production unit that can produce the intermediate stream including tertiary mercaptans and secondary mercaptans. As shown in Figure 4, the olefin tower can be designed to remove the unreacted olefins from the mercaptan intermediate product stream by separating and sending the olefins in the olefin tower overhead, while keeping the mercaptan (and any sulfides) at the bottoms. The bottoms of the olefin tower

can be sent to the intermediate stream tower, where the mercaptan intermediate stream can be separated from the heavies (sulfides, considered impurities in this situation) and sent overhead to a product (intermediate stream) storage tank.

In another embodiment, as shown in the configuration in Figure 5, the tertiary mercaptan process can be configured such that both separation towers are designed to separate unreacted olefins from the mercaptan intermediate stream product. The first olefin tower can be configured to remove a majority of the unreacted olefins, sending its overhead back to upstream of the reactor unit. The next tower, the intermediate stream tower can represent a finishing column designed to remove the remaining unreacted olefins from the mercaptan intermediate stream product, which can be sent to storage via the bottom of the tower. This particular arrangement is useful in cases where relatively low amounts of heavies/impurities (sulfides) are formed in the reaction.

Use of Trickle Bed Reactors with Multiple Beds for Mercaptan Production

As demonstrated in Table 3 (in the Examples), the tertiary mercaptan catalyst bed usage can have an impact on the secondary mercaptan content in tertiary mercaptan (TDM) product, and, accordingly, controlling secondary mercaptan content may be accomplished by changing the reactor feed point.

There can be certain technical advantages of using a trickle bed reactor instead of a liquid filled reactor.

Assuming a large excess of sulfhydryl source (H_2S) and that the reaction occurs in the liquid phase (on catalyst surface), a liquid-filled reactor can operate at much higher pressures and concentration of sulfhydryl source (H_2S). In contrast, a trickle bed reactor can provide good mass transfer and can allow rapid replenishment of consumed dissolved sulfhydryl source (H_2S) in the liquid, while preserving the ability to operate and feed the sulfhydryl source in the gas phase (when H_2S). There may also be safety improvements in operating a trickle bed reactor.

Another advantage to a staged bed approach that is typically used in trickle bed reactors can be tighter temperature control. In some situations, one of the reactants may be introduced cold ("cold shots"), for example at each stage. The temperature of these so-called "cold shots" may be from about 40°F to 200°F, from about 70°F to 150°F, or from about 100°F to 200°F. This

approach can be advantageous in providing a cost-effective method to control the reaction temperature (*e.g.*, by offsetting some of the exothermicity of reaction, which can in turn affect solubility of the sulfhydryl source in the other reactants/products, as well as overall mass transfer rates) and to reduce and/or eliminate undesirable side reactions. Accordingly, it can be beneficial to control reaction temperature/range while balancing overall reaction rate with selectivity.

Therefore staging the beds in a trickle bed reactor, and in particularly moving the feed points higher (closer to the reactor entrance) as the catalyst deactivates, can offer an unexpected advantage if the mercaptan product tends toward further reaction to undesired byproducts with excessive contact and/or residence time with active catalyst.

10 Second Reaction and Reactor: Production of Crude Stream Including Primary Linear Mercaptans, Branched Primary Mercaptans, and Secondary Mercaptans; and Separation of Secondary Mercaptans from the Crude Stream to Provide a Make-Up Stream

In this second process step, a second olefin stream including a linear alpha-olefin can be reacted with a second sulfhydryl source (*e.g.*, H₂S-containing) stream to provide a crude stream including linear primary mercaptans, branched primary mercaptans, and secondary mercaptans. The third process step can also be described where the secondary mercaptans and optionally some or all of the linear and/or branched primary mercaptans can be separated from the crude stream to provide the make-up stream.

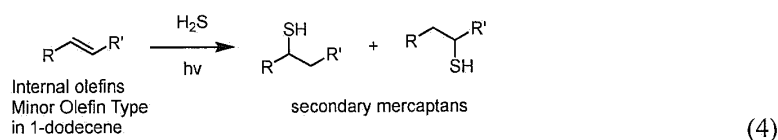
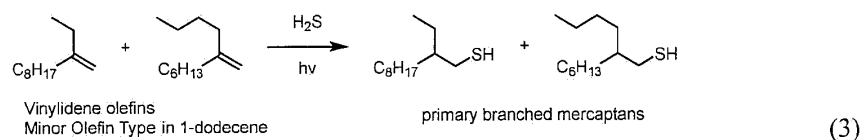
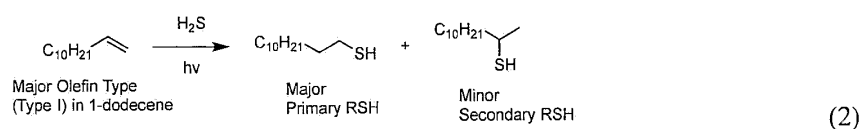
When a free radical initiator is used in this second reactor system, it can include at least one of peroxides, benzophenones, azo-initiators, and electromagnetic radiation having a wavelength from about 10 to 600 nm (such as from about 100 to 300 or from about 140 to 350 nm).

The reaction of linear alpha-olefins (R-CH₂-CH=CH₂) with the second sulfhydryl source (H₂S) stream via a radical pathway (inverse addition) can produce linear primary mercaptans as major products, where the mercaptan functionality is installed on the terminal, least substituted, carbon of the olefin.

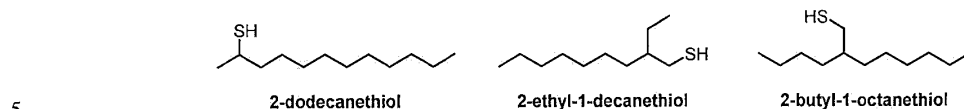
For example, a linear primary mercaptan such as n-dodecyl mercaptan (NDM) may be produced from 1-dodecene (a C₁₂ linear olefin) and H₂S through a photochemical process. The reaction scheme can be described as shown in (2) below. A minor product of this reaction can be

secondary mercaptans. Internal olefins and vinylidene olefins may also be found as impurities in linear alpha-olefin feeds. Under photochemical conditions in the presence of a sulfhydryl source, these reactive impurities can yield branched primary (3) and secondary (4) mercaptan by-products. When linear primary olefins are the desired products, these by-products can be seen as impurities/unwanted products and may often be wholly or partially removed in a linear mercaptan purification process, such as through a distillation tower. This process is described in U.S. Patent No. 11,161,810, which is incorporated by reference herein for its relevant description. Specifically, the secondary mercaptan by-products (impurities) can be removed from the crude stream by a secondary tower of the linear primary mercaptan process. Some of the branched primary mercaptans, and even some tagalong linear primary mercaptans, may be removed from the crude stream along with the secondary mercaptans (although normally only the smallest amounts, or as little as none, of the primary linear mercaptans are co-separated with the secondary mercaptans in linear primary mercaptan processes). This separated stream may be referred to herein as the secondary tower overhead (STO) stream and it can advantageously comprise or be the make-up stream that can be combined with the intermediate product stream of the above acid-catalyzed process to produce the final product stream of the blend of tertiary and secondary mercaptans. The STO stream is typically enriched in secondary mercaptans (product from (3) below) and may or may not also be enriched in primary branched mercaptans (product from (4) below).

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The predominant secondary mercaptan produced can typically be 2-dodecyl mercaptan. The predominant primary branched mercaptans can typically be 2-ethyl-1-decyl mercaptan and 2-butyl-1-octyl mercaptan. Minor products can include 3-dodecanethiol, 4-dodecanethiol, 5-dodecanethiol and 6-dodecanethiol.



In some embodiments when the STO stream is enriched in both secondary and branched primary mercaptans, some or all of the branched primary mercaptans may be removed from the make-up stream before combining it with the intermediate stream from the acid-catalyzed process. In some embodiments when the STO stream is enriched in both secondary and branched primary mercaptans, no additional separation is performed, and the primary branched mercaptans in the STO are co-fed to the intermediate stream along with the secondary mercaptans.

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Figure 6 is a simplified flow diagram of a free-radical catalyzed linear mercaptan production unit in which the by-product from the secondary tower (the make-up stream) can be sent to a storage tank. Figure 6 shows an embodiment of a process to produce a high purity primary thiol. As shown in Figure 6, another (a second) sulfhydryl source stream (not the same sulfhydryl source stream that feeds the above acid catalyzed process) and a linear alpha-olefin stream (a second olefin stream, different from the first olefin stream that feeds the acid-catalyst process above) can be fed to a second reaction system. In this embodiment, the (second) sulfhydryl source stream can be an H₂S stream. The second olefin stream can advantageously comprise linear C₄-C₁₈ alpha-olefins, such as comprising linear C₈-C₁₈ alpha-olefins, in particular comprising n-dodec-1-ene. The second H₂S stream can be present in a molar excess with respect to the second olefin stream.

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The second reaction system may include an absorber and at least one reactor. The absorber can be configured to dissolve the gaseous hydrogen sulfide (sulfhydryl source) in the liquid olefin and then to feed the hydrogen sulfide dissolved in the olefin into the second reactor(s), as shown in Figure 6. The second reactor system can be configured to enable reaction to form a reactor effluent stream including the linear primary mercaptan, unreacted hydrogen sulfide, optionally but typically unreacted olefin, and optionally other components.

25

Advantageously, the second olefin stream can be reacted with the second H₂S stream at a temperature from about -10 to 120°C and a pressure from about 10 to 1,000 psig. Non-limiting examples of the other components can include secondary mercaptans, unreacted olefin, and impurities from the incoming olefin feed stream, as well as sulfides. Impurities (or undesired co-products) may include, for example, branched primary mercaptans (such as vinylidene mercaptans, 2-ethyl-1-decyl mercaptan, 2-butyl-1-octyl mercaptan, and the like), sulfides (*e.g.*, (C₁₂H₂₅)-S-(C₁₂H₂₅) and the like); disulfides (*e.g.*, (C₁₂H₂₅)-S-S-(C₁₂H₂₅) and the like), secondary mercaptans (*e.g.*, 2-dodecanethiol, and the like), saturated hydrocarbons or paraffins (*e.g.*, octane, decane, dodecane, tetradecane, and the like), internal (isomerized) olefins, and combinations and reaction products thereof.

As shown in Figure 6, a portion of the reactor effluent stream can be immediately recycled back to the second reactor system. As desired, the reactor recycle stream can be fed back to the absorber, *e.g.*, via a recirculating tank that is in communication with the absorber. The remaining portion of the reactor effluent can then be fed to a flash evaporator. The flash evaporator can be configured to flash off hydrogen sulfide (or other sulfhydryl source) from the reactor effluent to produce a hydrogen sulfide (sulfhydryl source) recycle stream and a crude stream. The hydrogen sulfide (sulfhydryl source) recycle stream can be recycled back to the reactor system. As desired, the hydrogen sulfide recycle stream may be fed to the absorber to be dissolved into the fresh and/or recycled olefin stream(s). The crude mercaptan stream may then be fed to a crude mercaptan separation system. As shown in Figure 6, the crude separation system may include a series of separation units, which are represented by the olefin separation unit and the secondary separation unit in Figure 6. These separation units can be distillation columns, also called “towers”, as labelled in Figure 6. The olefin separation unit can be configured to produce an olefin recycle stream as overhead from the column and a secondary stream, out the bottom. The secondary stream may include the secondary mercaptans as an undesirable co-product of primary linear mercaptan production (because the -SH group is not in the terminal/most reactive position on the hydrocarbon group). The olefin recycle stream can include unreacted olefin and can be fed back to the second reactor system. As shown in Figure 6, a purge stream may be taken off the olefin recycle stream. When utilized, the purge stream can be intended to remove inerts and undesired heavy olefins, for example. The secondary stream can be fed to a secondary separation unit. The secondary stream in this embodiment can include

the desired primary linear mercaptan product as well as secondary mercaptans. The secondary separation unit is configured to separate the secondary stream to produce a first by-product stream (*i.e.*, the make-up stream to be fed to the tertiary mercaptan/secondary mercaptan acid catalyzed process) as overhead, which includes the secondary mercaptans. The secondary
5 separation unit can produce a crude linear primary mercaptan product stream as bottoms. This crude product linear primary mercaptan stream can be fed to a product linear primary mercaptan purification unit. The product linear primary mercaptan purification unit can be a distillation column (labelled “product tower” in Figure 6) and can be configured to produce a linear primary mercaptan product stream as overhead, which is the purified linear primary mercaptan product.
10 The product linear primary mercaptan purification unit can also produce a second by-product stream as bottoms that contains other by-product components such as sulfides. This second by-product stream may be fed to a sulfide cracking and stripping unit, which can be configured to recover any thiol in the second by-product stream, convert at least a portion of the sulfides into thiols and optionally but preferably also olefins, and typically also to produce a third by-product
15 stream comprising any remaining sulfides and other impurities. Sulfhydrolysis of sulfides to mercaptans (thiols) and olefins is well known and can be effected by an acid catalyst (*e.g.*, zeolites) at high temperatures. Exemplary complete details can be found in U.S. Patent Nos. 4,313,006 and 4,396,778, which are incorporated by reference herein in their entireties for all purposes, but particularly for their relevant description. The mercaptans and olefins (if present)
20 thus recovered can then be fed back to the crude mercaptan separation system.

Alternatively to the flow diagram for the linear mercaptan production unit presented in Figure 6, the following process configurations are non-limiting examples of other linear mercaptan processes.

Sulfhydryl source (*e.g.*, H₂S-containing stream) and olefin can be pressurized in the
25 absorber recirculation tank prior to being passed into the photochemical reactor, where the catalytic addition of hydrogen sulfide to a terminal olefin can occur via UV light catalysis. Olefin conversion through the reactor can be maintained at approximately 40-50%, for example to limit the formation of sulfides (heavies) as by-products inside the reactor. The majority (in this case, typically 80-90%) of the reactor effluent can be recycled back to the absorber recirculation tank
30 via a reactor recycle line. This recycle line can be equipped with an outlet allowing for a constant

controllable purge of the recycle stream. The purge (split) from the reactor effluent can be sent to the flash vaporizer to remove the majority of the sulfhydryl source (H_2S) from the liquid stream. The crude liquid, essentially free of sulfhydryl source/ H_2S , can be cooled and then introduced into the olefin distillation tower (OT), which can enable separation of unreacted olefins from mercaptans and sulfide products. The olefins removed from the top of this tower can be sent back to the absorber recirculation tank via the fresh olefin supply line. The effluent from the bottom of the olefin tower can be introduced to a secondary mercaptan distillation tower (ST) via a tank, to remove the secondary mercaptans produced as a byproduct of the UV catalyzed reaction. The overhead effluent of this distillation tower may be discarded as waste and the tower bottom effluent may be introduced into a product distillation tower (PT), equipped with structured packing as internals. It is here where the final NDM product (*e.g.*, having less than 1000 ppm of tetradecyl mercaptan and less than 1000 ppm dodecyl sulfide) can be withdrawn as an overhead product and stored in dedicated tanks (or immediately transported for use in one or more downstream processes).

Some examples of suitable conditions in the distillation towers:

Olefin Tower: Overhead $P = 50$ to 200 mmHg (*e.g.*, 60 to 160 mmHg or 80 to 120 mmHg), Bottoms $T = 350$ to 450°F (*e.g.*, 375 to 440°F or 380 to 430°F).

Secondary Tower: Overhead $P = 20$ to 220 mmHg (*e.g.*, 30 to 200 mmHg or 40 to 200 mmHg), Bottoms $T = 400$ to 500°F (*e.g.*, 415 to 500°F or 425 to 490°F).

Product Tower: Overhead $P = 5$ to 80 mmHg (*e.g.*, 15 to 65 mmHg or 15 to 50 mmHg), Bottoms $T = 300$ to 450°F (*e.g.*, 320 to 440°F or 345 to 425°F).

Residue Stripper (omitted from drawings): Overhead $P = 5$ to 80 mmHg (*e.g.*, 15 to 65 mmHg or 15 to 50 mmHg), Bottoms $T = 400$ to 550°F (*e.g.*, 420 to 525°F or 450 to 515°F).

Small variations in the above may be made to accommodate desired stream compositions.

Separating the secondary mercaptans from the crude stream to provide the make-up stream may take place at a temperature from about 0 to 500°C and a pressure from about -15 to $+15$ psig. Typically, the crude stream contains substantially no tertiary mercaptans.

Figure 7 shows another exemplary embodiment of the process to produce linear primary mercaptans. In this embodiment, the reactor system and the linear primary mercaptan purification system can be the same as shown in Figure 6. However, the crude linear primary mercaptan separation system can have a different arrangement than shown in Figure 6. In Figure 7, the crude linear primary mercaptan separation system can include an olefin separation unit and a crude linear primary mercaptan separation unit. These two separation units can be distillation columns (also called towers). As shown in Figure 7, the crude linear primary mercaptan stream emerging from the flash vaporizer can be fed to the crude mercaptan separation unit. The crude linear primary mercaptan separation unit can be configured to produce the linear primary mercaptan product stream out the bottom and an olefin and a first by-product stream out the top as overhead. The overhead olefin and first by-product stream emerging from the crude linear primary mercaptan separation unit can be fed to the bottom of the olefin separation unit. The olefin separation unit can be configured to separate the olefin stream to produce a by-product stream as bottoms and the olefin recycle stream as overhead. The olefin recycle stream can be fed back to the reactor system. As shown in this embodiment, the crude linear primary mercaptan product stream emerging from the bottom of the crude linear primary mercaptan separation unit can be fed to the bottom of the product linear primary mercaptan purification unit (a distillation column, also called a “tower”), which is the same arrangement as in Figure 6. The product linear primary mercaptan purification unit can be configured to separate the pure product linear primary mercaptan as the overhead and a second by-product in the bottoms. In this embodiment, a sulfide cracking and stripping unit configured to further separate the bottoms out of the product purification unit is not used but could be utilized in another embodiment.

Optional Pre-Purification of the Make-Up Stream of the Linear Primary Mercaptan Process

The composition of the by-product of linear primary mercaptan process, such as the NDM process, can comprise secondary mercaptans, linear branched dodecyl mercaptans, decyl mercaptans, dodecane, dodecenes and tetradecenes, *inter alia*. In some embodiments, a pre-purification step may be included, in which the by-product of the linear primary mercaptan production unit can be first purified before being sent to the tertiary mercaptan production unit. The goal of this purification would be to remove undesired by-products and/or co-products, such as decyl mercaptans, dodecane, dodecenes, tetradecenes, and the like.

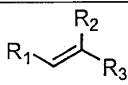
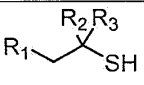
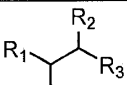
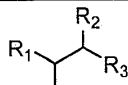
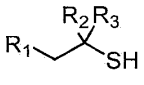
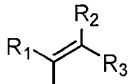
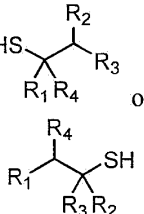
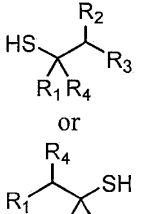
Additionally or alternatively, the make-up stream may optionally be further purified before being fed to the intermediate stream of the acid catalyzed process that produces the blend of tertiary and secondary mercaptans to produce the final product mixture comprising tertiary mercaptans and secondary mercaptans. This optional additional purification step may remove the optional linear and/or branched primary mercaptans, for example.

Summary of Reactions of Olefins with H₂S

Table 1 provides a summary of the olefins types and exemplary expected products for the two above reactions: production of intermediate stream including tertiary mercaptans and secondary mercaptans via acid catalysis and production of crude stream including primary linear mercaptans, primary branched mercaptans, and secondary mercaptans via photochemical catalysis/radical pathway.

Table 1: olefin type, structure and products derived from acid catalyzed or photo catalyzed addition of sulfhydryl source (H₂S) to olefins.

Olefin Type	Structure	Acid Catalysis pathway		Photochemical Catalysis/radical pathway	
		Major	Minor	Major	Minor
I (Major Olefin type in linear alpha-olefin for NDM process)					
II			n/a		n/a
III					

IV (Major Olefin type in tetramer for TDM process)					
V			n/a		n/a

As shown in the Examples section, a fresh catalyst yielded product designated as “TDM” with ~20 mol% secondary mercaptan, and the secondary mercaptan concentration eventually reducing to ~8 mol%, in spite of the feed stream being a propylene tetramer with a stable olefin type content (which was attributed to the catalyst aging/deactivating over time).

Combining Secondary and Optionally Linear and/or Branched Primary Mercaptans from the Linear Primary Mercaptan Process with the Product (Intermediate) Stream of the Tertiary (and Secondary) Mercaptan Blend Process

The process can include a step of combining at least a portion of the make-up stream comprising secondary mercaptans and optionally linear and/or branched primary mercaptans from the production of the linear primary mercaptans with the intermediate stream from the acid catalyzed process that produces a blend of tertiary and secondary mercaptans to produce the product mixture comprising tertiary mercaptans, secondary mercaptans, and optionally linear and/or branched primary mercaptans.

The secondary tower of the linear primary mercaptan process can be designed to separate a linear primary mercaptan product from a by-product stream containing secondary mercaptans and optionally linear and/or branched primary mercaptans. As disclosed herein, the secondary tower overhead (STO) stream from the free-radical process to produce linear primary mercaptans may be fed to a storage tank so that at least a portion of it as a make-up stream may be fed to the intermediate stream of the acid catalyzed process that produces the blend of tertiary and secondary mercaptans to produce the final product mixture comprising tertiary mercaptans, secondary mercaptans, and optionally linear and/or branched primary mercaptans. Additionally

or alternatively, at least a portion of the make-up stream may be fed directly to the intermediate stream of the acid catalyzed process that produces the blend of tertiary and secondary mercaptans to produce the final product mixture including tertiary mercaptans, secondary mercaptans, and optionally linear and/or branched primary mercaptans, rather than from a storage tank.

- 5 A goal of this combining step can be to maintain constant composition of tertiary and secondary mercaptans (and optionally primary mercaptans, if desired) in the product mixture stream from the integrated process.

 Depending upon various factors, an amount/proportion of (the portion of) the make-up stream combined with the intermediate stream can be selected such that a mole percent of
10 secondary mercaptans relative to tertiary mercaptans in the product stream does not vary by more than 10 mol% (*e.g.*, by more than 9 mol%, by more than 8 mol%, by more than 7 mol%, by more than 6 mol%, by more than 5 mol%, by more than 4 mol%, by more than 3 mol%, by more than 2 mol%, or by more than 1 mol%) over about 500 hours. Additionally or alternatively, the product mixture can comprise 5 mol% or less of linear primary mercaptans, branched primary
15 mercaptans, secondary mercaptans, or a combination thereof (in particular, 5 mol% or less of secondary mercaptans). In some embodiments, the amount/proportion of the make-up stream can be from 0.1 to 50 wt% (*e.g.*, from 1 to 30 wt%, from 1 to 20wt%, or from 1 to 10 wt%), based on the weight of the intermediate stream.

 Figure 8 shows a simplified tertiary mercaptan production unit including various feed
20 point options where at least a portion of the make-up stream comprising secondary mercaptans and optionally linear and/or branched primary mercaptans (*e.g.*, the inclusion of primary mercaptans generally or linear primary mercaptans specifically potentially resulting from an imperfect separation process) from the production of the linear primary mercaptans points can be combined with the intermediate stream from the acid catalyzed process to produce the product
25 mixture blend of tertiary and secondary mercaptans. In Figure 8, the high pressure and low pressure separators have been removed for simplicity. Figure 8 also shows the options (I-IV) of the various feeding locations of the secondary mercaptan make-up stream portion into the tertiary mercaptan process.

- Option I represents feeding the at least a portion of the makeup stream from the free radical process to the acid-catalyst reactor feed line and blending with fresh and recycle olefin streams.

- Option II represents feeding the at least a portion of the makeup stream from the free radical process at the outlet of the acid-catalyst reactor to mix in with the crude reactor feed into the residue tower.

- Option III represents feeding (the portion of) the makeup stream from the free radical process in the product tower feed stream of the acid-catalyzed process.

- Option IV represents feeding (the portion of) the makeup stream from the free radical process in the final (intermediate) product of the acid-catalyzed process.

Figure 9 shows a simplified tertiary mercaptan production unit where the by-product (make up stream) from the linear primary mercaptan production unit can be first purified by distillation to remove unwanted co-products/reactants, such as olefin, hydrocarbons and/or lower boiling mercaptans. Also shown are the various feed points options from the storage tank to the tertiary mercaptan production unit. High pressure and low-pressure separators such as shown in Figure 1 have been removed for simplicity.

Additionally or alternatively, the make-up stream from the linear primary mercaptan process may be sent directly to the tertiary mercaptan process. Alternatively to what Figure 8 is illustrating, the by-product (make-up) stream from the linear primary mercaptan production unit could be sent directly to the tertiary mercaptan production unit (Figure 10) and introduced at any feed point illustrated in Figure 11.

Figure 10 shows a simplified flow diagram of the linear primary mercaptan production unit where the by-product (make-up stream) from the secondary tower of the linear primary mercaptan production unit can be sent directly to the tertiary mercaptan production unit.

Figure 11 shows a simplified tertiary mercaptan production unit where the by-product (make-up stream) from the linear primary mercaptan production unit can be directly fed to the tertiary mercaptan production unit. Also shown are the various feed points options from the linear primary mercaptan production unit to the tertiary mercaptan production unit. High-

pressure and low-pressure separators such as shown in Figure 5 have been removed for simplicity.

Apparatus

An apparatus is also provided. The apparatus can include:

5 a first reactor configured and arranged to react a first olefin stream comprising an asymmetric branched olefin or oligomer thereof with a first sulfhydryl source stream in the presence of a catalyst to provide an intermediate stream including tertiary mercaptans and secondary mercaptans;

10 a second reactor configured and arranged to react a second olefin stream including a linear alpha-olefin with a second sulfhydryl source stream (which may be the same or different in nature as the first sulfhydryl source stream) to provide a crude stream including linear primary mercaptans, branched primary mercaptans, and secondary mercaptans;

a separation apparatus configured and arranged to:

15 separate the secondary mercaptans and optionally some or all of the linear and/or branched primary mercaptans from the crude stream to provide a make-up stream including secondary mercaptans and optionally linear and/or branched primary mercaptans; and

20 combine at least a portion of the make-up stream with the intermediate stream to produce a product mixture including tertiary mercaptans, secondary mercaptans, and optionally linear and/or branched primary mercaptans.

25 Within this specification, embodiments have been described in a way which enables a clear and concise specification to be written, but it is intended and will be appreciated that embodiments may be variously combined or separated without departing from the disclosure. For example, it will be appreciated that all preferred features described herein are applicable to all aspects of the disclosure herein.

In some embodiments, the disclosure herein can be construed as excluding any element of process step that does not materially affect the basic and novel characteristics of the compositions, materials, products, and articles prepared therefore and methods for making and

using such articles. Additionally, in some embodiments, the disclosure can be construed as excluding any element or process step not specified herein.

Although the disclosure is illustrated and described herein with reference to specific embodiments, the invention is not intended to be limited to the details shown. Rather, various
5 modifications may be made in the details and the scope and range of equivalents of the claims and without departing from the invention.

EXAMPLES

Lab scale synthesis of tert-dodecyl mercaptan from propylene tetramer and sulfhydryl source (H₂S) using acid catalysis

10 TDM product was synthesized using an adapted method based on U.S. Patent No. 4,102,931, the contents of which are hereby incorporated by reference, particularly for the disclosure relevant to the synthesis method. A tubular reactor was charged with ~28 cm³ of LZY-64, a type Y zeolite catalyst (~16.6 g), representing a bed height of about 16 cm. The reactor was loaded onto a lab set up and pressure rated using nitrogen. The reactor was heated to ~90°C
15 while flowing H₂S at ~42 NL/h (Normal Liters/hour) at a pressure of about 15 bara. The liquid feed, comprised of ~95 wt% propylene tetramer and ~5 wt% TDM was fed through the reactor using a top to bottom flow of ~20 g/h during ~1,000 hours. Approximately a +2°C exotherm was observed in the reactor after introduction of the liquid feed. The feed was essentially constant throughout the ~1000-hour test, and no recirculation was done through the reactor. Samples were
20 taken at various intervals, and the conversion was measured by gas chromatography and mercaptan sulfur titration (argentometric potentiometry).

Mercaptan types in lab scale produced tert-dodecyl mercaptans

Table 2 reports the composition of TDM product produced at lab scale using an approximately constant feed of raw materials. There was substantially no change in raw material
25 composition for the duration of the experiment. The temperature, pressure, and flow rates were kept roughly constant, and therefore the decrease in secondary mercaptans from ~20.2 mol% to ~17.5 mol% in ~500 hours of operations was presumptively attributed to the aging (and thus partial deactivation/inefficiency) of the LZY-64 zeolite catalyst. Mercaptan type can be determined by known methods, such as NMR (*e.g.*, UOP935-94, available from ASTM).

Table 2: Mercaptan distribution in lab scale TDM synthesis using a constant feed composition.

Sample Time Point	Primary Mercaptan (mol%)	Secondary Mercaptan (mol%)	Tertiary Mercaptan (mol%)
~30 hours	n.d.	~20.2	~79.8
~500 hours	n.d.	~17.5	~82.5

Mercaptan types in commercial tert-dodecyl mercaptan and tert-nonyl mercaptan products

Table 3 reports the concentration of secondary mercaptans and tertiary mercaptans in commercial tert-dodecyl mercaptan (TDM) products as well from alternative TDM production samples from various processes.

Table 3

Cat. life (days)	Process	Finished TDM Product	
		2° -SH (mol%)	3° -SH (mol%)
12	Process A	~20.2	~79.8
31	Process A	~19.8	~80.2
37	Process A	~18.8	~81.2
109	Process A	~14.7	~85.3
115*	Process A	~16.8	~83.2
189	Process A	~11.9	~88.1
217	Process A	~11.7	~88.3
219**	Process A	~15.7	~84.3
429	Process A	~11.0	~89.0
667	Process A	~6.9	~93.1
	Process B	~2.4	~97.6
	Process B	~2.8	~97.2
	Process C***	~11.8	~88.0
	US 2010/0249366 Process	~10.5	~89.5
	Process D	~1.2	~98.8

*catalyst cookout performed before this day, explaining increase in secondary mercaptan

** added fresh catalyst capacity in the reactor, explaining increase in secondary mercaptan

*** ~0.2 mol% primary mercaptans not included in Table

As shown in Table 3, samples of commercial TDM produced throughout the lifetime of the catalyst were sampled directly from production units. In some instances, an increase of secondary mercaptans over the course of the catalyst life was observed. In Table 3, this was presumptively attributed to such occurrences as catalyst cookouts being performed on the catalyst (*e.g.*, between day 109 and 115) and addition of another catalyst bed in the process (*e.g.*,
5 between day 217 and 219).

The secondary mercaptan content in the (TDM) product can be impacted by the number of catalyst beds online in the reactor. The Process A reactor utilized five catalyst beds from which the liquid could be fed. At a beginning of a campaign, the reactor can be operated using the last bed (or set of beds). When the conversion of that bed (those beds) lowers, the feed may
10 then be changed to the penultimate bed (or set of beds). The same procedure can be applied until the feed is fed to the first bed (or set of beds) in the reactor. If the previous bed (or set of beds) can be isolated during the use of other beds, in some embodiments, that bed (those beds) can have their catalyst rejuvenated or replaced with fresher catalyst, *e.g.*, to enable continuous/semi-continuous operation of the reactor.
15

In Table 3, Process A samples for days 12 to 217 were taken when the reactor operated using the final two beds. Process A samples for days 219 and 429 were taken when the reactor operated using the final three beds of catalyst. Finally, the sample at day 667 was taken when the reactor operated on all five beds of catalyst.

TDM products from processes A, B, C, and D were produced from propylene tetramer and sulfhydryl source comprising H₂S. An alternative tertiary dodecyl mercaptan grade was produced from tri-n-butene and sulfhydryl source comprising H₂S, the description of which process can be found in U.S. Patent Application Publication No. 2010/0249366 (and perhaps also in U.S. Patent Application Publication No. 2007/019774), which is (are) incorporated by
20 reference herein, particularly for their relevant description.
25

A similar analysis was done on the production of tertiary nonyl mercaptan (TNM). TNM product was produced from propylene trimer (nonene) and sulfhydryl source comprising H₂S, which can use the same or similar catalyst and reactor as the process to make TDM product. Similar trends can be seen where there is a decrease in secondary mercaptan between day 17 and
30 day 31. The samples collected on Day 8 were taken when the TNM reactor operated using a

single bed whereas the samples collected at day 17 and 31 of operation were collected when the reactor was operated using two beds of catalyst.

Table 4: secondary and tertiary mercaptans in TNM commercial product

Cat. life (days)	Finished TNM Product	
	2° -SH (mol%)	3° -SH (mol%)
8	~8.7	~91.3
17	~15.2	~84.8
31	~13.9	~86.1

Styrene polymerization using tert-dodecyl mercaptans and secondary dodecyl mercaptan blends.

5 *Materials.* Styrene, toluene and di-tert-butyl peroxide (DtBP) were purchased from Sigma-Aldrich. DtBP was used as received without any purifications. Styrene was purified by passing through a basic alumina column. The purified styrene and toluene were deoxygenated by nitrogen bubbling before polymerization. TDM and secondary dodecyl mercaptans (NDM by-product) were used as received from commercial sources.

10 *Mercaptan samples blends:* Commercial TDM samples and NDM secondary mercaptan with optional linear and/or branched primary mercaptan (make-up stream) from the overhead of the secondary tower were mixed together to achieve target secondary mercaptan content in the blends.

15 *Method:* Deoxygenated styrene (~11 mL) was placed in a ~50 mL round bottom flask equipped with a magnetic stir bar. About 1 mL of deoxygenated toluene/mercaptan stock solution was added as internal reference (~3,000 ppm by weight to styrene). Inert atmosphere was applied and the initiator solution (DtBP, ~0.4 mL) was added to the reactor in order to initiate polymerization. Reactions were conducted at ~130 °C for ~1 h, after which the reaction was cooled and exposed to air for termination.

20 *Purification.* After polymerization, ~20-30 mL of chloroform was added to the flask to dilute the polystyrene. The diluted PS was then precipitated against excess amount of MeOH (~300-400 mL) while stirring. Stirring was applied overnight before filtering the product on

filtration paper. Further drying of polystyrene was performed in a vacuum chamber for about two days.

Sampling for analysis. Before and after polymerizations, aliquot amounts of samples were taken and diluted with chloroform for GC analysis. Monomer conversion was determined by GC, by comparing peak areas corresponding to styrene before and after the reaction occurred (toluene as the internal standard). Dried products were analyzed by TGA and GPC.

GPC analysis of polystyrene samples:

Polystyrene samples were analyzed by gel permeation chromatography. The analyses were performed using a Waters 2695e instrument coupled to a Wyatt T-rEX Differential Refractometer equipped with Two PL Gel mixed C columns and a guard column (~7.8 mm I.D. × ~30 cm, ~5 μm). THF (HPLC grade, ~1.0 mL/min, ~35°C) was used as elution solvent. ~100 μL samples (~1.0 mg/mL) were injected without filtration. Twelve polystyrene standards were used ranging in peak molecular weight (Mp) from ~160 to ~47,000 g/mol. Analyses were done using ASTRA 7 software. Calibration data was fitted to a cubic polynomial with R² of at least 0.999.

As described in Equation 3 and Table 5, the NDM secondary tower overhead (STO) stream (make-up stream) also contains primary branched mercaptans. The results show that blends of TDM and NDM STO may contain a certain percent of primary branched mercaptans. The major secondary mercaptan produced can be 2-dodecanethiol. The major primary branched mercaptans can include or be 2-ethyl-1-decanethiol and 2-butyl-1-octanethiol.

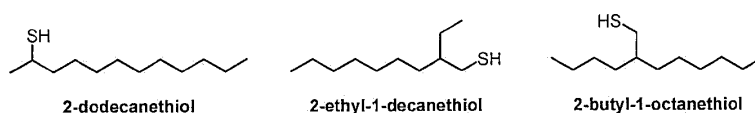


Table 5: Composition and GPC analysis of polystyrene made using commercial mercaptans/blends as chain transfer agents. See also Figure 12.

Sample	Blend	Primary Mercaptan (mol%)	Secondary Mercaptan (mol%)	Tertiary Mercaptan (mol%)	M _n (g/mol)
1	Commercial grade TDM	~0.0	~20.2	~79.8	~23,400
2	Commercial grade TDM	~0.0	~16.8	~83.2	~22,400
3	Commercial grade TDM	~0.0	~11.7	~88.3	~22,300
4	Commercial grade TDM	~0.0	~2.80	~97.2	~19,800

5	90 wt% Commercial grade TDM + 10 wt% NDM make-up	~3.6	~15.1	~81.3	~24,200
6	85 wt% Commercial TDM + 15 wt% NDM make-up	~6.1	~18.1	~75.8	~24,600

One practical use of commercial grade TDM is in polystyrene production from styrene monomer using TDM as the chain transfer agent. Figure 12 shows number-average molecular weight (Mn) of the polystyrene as a function of secondary mercaptans in the tertiary mercaptan-based chain transfer agent. Triangle data represent polystyrene made using commercial grade TDM produced by Arkema as chain transfer agent, and circle data represent polystyrene made using blends of commercial grade TDM and dodecyl mercaptans from the make-up stream as chain transfer agent.

TGA analysis of polystyrene samples made with mercaptan chain transfer agents:

Thermogravimetric analysis (TGA) measures the mass loss or gain of a material when subjected to a temperature program. Polystyrene powders were heated by TGA using a ramp rate of ~20°C/min in either air or nitrogen with masses ranging from ~7 mg to ~11 mg. The balance had a purge flow of ~10 mL/min with a sample purge of ~25 mL/min. The unit was first tarred with only the empty platinum pan having an Inconel bail and then the 100% mass setting was measured after the sample was loaded before heating. A TA Instruments 5000IR TGA was employed with Advantage/Universal Analysis (UA) Software. The unit was calibrated with Curie standards under a magnetic field resulting in an apparent mass change when passing through the magnetic transition. The Curie standards certified by TA Instruments used were Alumel, nickel and a Ni83Co17 alloy. The TGA balance was calibrated with a weight standard.

As described in Equation 3 and Table 6, the NDM STO stream also contains primary branched mercaptans. The result is that blends of TDM and NDM STO will contain a certain % of primary mercaptans. The major secondary mercaptan produced is 2-dodecanethiol. The major primary branched mercaptans are 2-ethyl-1-decanethiol and 2-butyl-1-octanethiol.

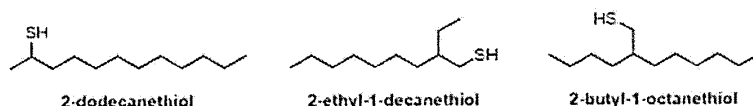


Table 6. Composition and TGA analysis of polystyrene made using commercial mercaptans/blends as chain transfer agents. See also Figure 13.

Sample	Blend	Primary Mercaptan (mol%)	Secondary Mercaptan (mol%)	Tertiary Mercaptan (mol%)	10% Mass Loss temperature (°C)
7	Commercial TDM	~0.0	~20.2	~79.8	~397
8	Commercial TDM	~0.0	~16.8	~83.2	~395
9	Commercial TDM	~0.0	~11.7	~88.3	~397
10	Commercial TDM	~0.0	~2.80	~97.2	~398
11	99 wt% Commercial TDM + 1 wt% NDM make-up	~0.4	~11.0	~88.6	~340
12	97 wt% Commercial TDM + 3 wt% NDM make-up	~1.1	~12.1	~86.8	~340
13	90 wt% Commercial TDM + 10 wt% NDM make-up	~3.6	~15.1	~81.3	~338

Again regarding use of commercial grade TDM as chain transfer agent in mixtures with styrene monomer to form polystyrene, Figure 13 shows TGA in air of polystyrene plotted at ~10% mass loss temperatures as a function of secondary mercaptan concentration in TDM used as chain transfer agent. Triangle data represent polystyrene made using commercial grade TDM produced by Arkema as chain transfer agent, and circle data represent polystyrene made using blends of commercial grade TDM and dodecyl mercaptans from the make-up stream as chain transfer agent.

Figure 12 and Figure 13 demonstrated the impact of secondary mercaptan content in TDM on the activity of TDM/secondary mercaptan blend as a chain transfer agent. As the concentration of secondary mercaptan in TDM appears to increase, typically so does the Mn of the polystyrene produced using TDM as chain transfer agent. Moreover, as the concentration of secondary mercaptan appears to increase, the TGA ~10% mass loss temperatures of polystyrene tends to decrease.

These results are in line with what is expected based on the Dietrich *et al.* article: "Chain Transfer Constants of Mercaptans in the Emulsion Polymerization of Styrene," Journal of Applied Polymer Science, Vol. 36, 1129-1141 (1988).

Given the higher reactivity of secondary mercaptans, the polymerization appears to produce lower molecular weight polystyrenes as the secondary mercaptan content increases. The lower molecular weight polymers can decompose at lower temperatures compared to higher molecular weight polystyrenes.

- 5 This observation shows the impact of varied secondary mercaptan content on the product performance as a CTA and also highlights the need/benefit for making TDM product with consistent secondary mercaptan content, *e.g.*, to allow for consistent polymer properties.

CLAIMS

What is claimed is:

1. A continuous or semi-continuous process for producing a product mixture comprising tertiary and secondary mercaptans, the process comprising:
 - 5 reacting a first olefin stream comprising an asymmetric branched olefin or oligomer thereof with a first sulfhydryl source stream in the presence of a catalyst to provide an intermediate stream comprising tertiary mercaptans and secondary mercaptans;
reacting a second olefin stream comprising a linear alpha-olefin with a second sulfhydryl source stream to provide a crude stream comprising linear and/or branched primary mercaptans
10 and secondary mercaptans;
separating the secondary mercaptans and optionally some or all of the linear and/or branched primary mercaptans from the crude stream to provide a make-up stream comprising secondary mercaptans and optionally linear and/or branched primary mercaptans; and
combining at least a portion of the make-up stream with the intermediate stream to
15 produce the product mixture comprising tertiary mercaptans, secondary mercaptans, and optionally linear and/or branched primary mercaptans.
2. The process of claim 1, wherein: the portion of the make-up stream is selected such that a mole percent of secondary mercaptans relative to tertiary mercaptans in the product stream does not vary by more than 5 mole percent over 500 hours; a ratio of the makeup stream to the
20 intermediate stream is from 0.1 to 50 wt% by weight of the intermediate stream; or both.
3. The process of claim 1 or claim 2, wherein a sulfhydryl source in the first and second sulfhydryl source streams is each independently selected from the group consisting of hydrogen sulfide, thioacetic acid, t-butyl mercaptan, sodium mercaptan, and combinations thereof.
4. The process of any of claims 1-3, wherein the product mixture comprises 5 mol% or less
25 of linear primary mercaptans, branched primary mercaptans, secondary mercaptans; or a combination thereof.
5. The process of any of claims 1-4 wherein the catalyst comprises at least one of a zeolite, an acid compound, a metal oxide, a sulfonic acid resin, or a combination thereof.

6. The process of any of claims 1-5, wherein the catalyst comprises a synthetic zeolite comprising an alkali metal content (expressed as Na_2O) of less than 10% by weight.
7. The process of claim any of claims 1-6, wherein the catalyst comprises at least one of synthetic zeolite type X, synthetic zeolite type Y, sulfonic acid resin, or combination thereof.
- 5 8. The process of any of claims 1-7 wherein the first olefin stream and the first sulfhydryl source stream are continuously passed over the catalyst at a rate of from 5 to about 250 gram-moles of the first olefin stream per 24 hours per kilogram of catalyst.
9. The process of any of claims 1-8, wherein the first sulfhydryl source stream is present in a molar excess with respect to the first olefin stream and the reaction between the first olefin
10 stream and the first sulfhydryl source stream are carried out at above atmospheric pressure at a temperature of 20°C to 200°C.
10. The process of any of claims 1-9, wherein the first olefin stream comprises a branched, asymmetric olefin or oligomer thereof, the olefin having the formula $\text{R}_1\text{R}_2\text{C}=\text{CR}_3\text{R}_4$ where R_1 and R_2 are the same or different alkyl radicals, and R_3 and R_4 are independently either H or the
15 same or different alkyl radicals.
11. The process of claim 10, wherein the branched, asymmetric olefin or oligomer thereof comprises at least one of a C7 to C20 olefin, preferably propylene trimer, tri-n-butene, or propylene tetramer, most preferably propylene tetramer.
12. The process of any of claims 1-10, wherein the second olefin stream is reacted with the
20 second sulfhydryl source stream in the presence of a free radical initiator.
13. The process of claim 12, wherein the free radical initiator comprises at least one of peroxides, benzophenones, azo-initiators, or electromagnetic radiation having a wavelength from 10 nm to 600 nm, such as electromagnetic radiation having a wavelength from 100 nm to 300 nm or from 140 nm to 350 nm.
- 25 14. The process of any of claims 1-13, wherein the second olefin stream comprises a C4-C18 linear alpha-olefin, for example a C8-C18 linear alpha-olefin, a C12 linear alpha-olefin, or 1-dodecene.

15. The process of any of claims 1-14, wherein the secondary mercaptans comprise C4-C18 secondary mercaptans, for example C8-C18 secondary mercaptans or a C12 secondary mercaptan.

16. The process of any of claims 1-15, wherein the make-up stream further comprises
5 branched primary mercaptans.

17. The process of any of claims 1-16, wherein the second sulfhydryl source stream is present in a molar excess with respect to the second olefin stream.

18. The process of any of claims 1-17, wherein the second olefin stream is reacted with the second sulfhydryl source stream at a temperature from about -10 to 120°C and a pressure from
10 about 10 to 1,000 psig.

19. The process of any of claims 1-18, wherein separating the secondary mercaptans from the crude stream to provide the make-up stream comprising secondary mercaptans takes place at a temperature from about 0 to 500°C and a pressure from about -15 to +15 psig.

20. An apparatus comprising:
15 a first reactor configured to react a first olefin stream comprising an asymmetric branched olefin or oligomer thereof with a first sulfhydryl source stream in the presence of a catalyst to provide an intermediate stream comprising tertiary mercaptans and secondary mercaptans;
a second reactor configured to react a second olefin stream comprising a linear alpha-olefin with a second sulfhydryl source stream to provide a crude stream comprising primary
20 linear mercaptans, branched primary mercaptans, and secondary mercaptans; and
a separation apparatus configured to:
separate the secondary mercaptans and optionally some or all of the linear and/or
branched primary mercaptans from the crude stream to provide a make-up stream
comprising secondary mercaptans and optionally linear and/or branched primary
25 mercaptans; and
combine at least a portion of the make-up stream with the intermediate stream to produce a product mixture comprising tertiary mercaptans, secondary mercaptans, and optionally linear and/or branched primary mercaptans.