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(54) Title: PRODUCTION OF OXYGENATES AND OXYGENATED DIMERS

(57) **Abstract:** The invention provides an oxygenated compound composition obtained by oxygenating the dimerisation reaction products of a Fischer-Tropsch dimerisation process, which oxygenated compound composition has on average between 0.9 and 3 branches per molecule. The dimerisation process is carried out in the presence of a metallocene/aluminoxane catalyst. Typically the oxygenated compound composition includes at least some branched alcohol and/or aldehyde selected from the group including monomethyl branched alcohol, dimethyl branched alcohol, trimethyl branched alcohol, monomethyl branched aldehyde, dimethyl branched aldehyde, and trimethyl branched aldehyde.

PRODUCTION OF OXYGENATES AND OXYGENATED DIMERS

Field of the Invention

This invention relates to oxygenated products of a process for the production of dimers from an olefinic feedstock. More particularly, the invention relates to oxygenated products of a process suitable for the production of a product having the general formula $R'R''=CH_2$, in which R' and R" are alkyl groups, from an olefinic feedstock, the oxygenated products having the general formula $R'CH_3R''CHO$ and/or $R'CH_3R''CH_2OH$.

Summary of the Invention

According to the invention there are provided oxygenated products of a dimerisation process for the production of dimers from an olefinic feedstock containing α-olefins, the dimerisation process comprising contacting the feedstock with a metallocene/aluminoxane catalyst, thereby selectively to dimerise α-olefins in the feedstock by means of a metallocene-catalysed dimerisation reaction, the feedstock being in the form of a Fischer-Tropsch-derived olefinic feedstock comprising a mixture of Fischer-Tropsch-derived hydrocarbons made up of at most 90% by mass of linear and branched α-olefins e.g. between 10% and 60% branched, at least 5% by mass of olefins, other than α-olefins, selected from internal olefins, cyclic olefins, dienes, trienes and mixture thereof, and at least 5% by mass of constituents, other than olefins, selected from paraffins, oxygenated hydrocarbons, aromatic hydrocarbons and mixtures thereof, the metallocene-catalysed dimerisation reaction taking place while the olefins which are dimerised form part of the mixture constituted by the feedstock.

By a Fischer-Tropsch-derived olefinic feedstock is meant an olefinic feedstock which is a product obtained by subjecting a synthesis gas comprising carbon monoxide and hydrogen to Fischer-Tropsch reaction conditions in the presence of a suitable Fischer-Tropsch catalyst, which catalyst may be iron-based, cobalt-based or iron/cobalt-based. In particular the Fischer-Tropsch derived olefinic feedstock may be one which, after production thereof from the synthesis gas, has been subjected to no substantial further treatment, purification or processing thereof to remove unwanted constituents such as non-α-olefins therefrom, other than cutting so that a suitable cut of the Fischer-Tropsch-derived product will typically be selected for use as the feedstock to the dimerisation process.

The feedstock may comprise 50 - 90% by mass of said linear and branched α-olefins, for example 60 - 80% by mass thereof; it may comprise 5 - 20% by mass of said olefins other than α-olefins, for example 9 - 16% by mass thereof; and it may comprise 6 - 30% by mass of said constituents other than olefins, for example 13 - 22% by mass thereof.

By way of example, the feedstock may comprise 50% by mass of linear and branched α-olefins, 20% by mass olefins other than α-olefins, and 30% by mass of constituents other than olefins. The metallocene/aluminoxane catalyst may have an aluminoxane component which is methylaluminoxane, and a metallocene component which is a compound of the general formula $(Cp)_2MY_2$ in which Cp represents a cyclopentadienyl group, M is a metal selected from zirconium, hafnium and titanium, and Y is selected from hydrogen radicals, halogen radicals (preferably chlorine radicals), alkyl groups (preferably methyl groups) and mixtures thereof. The metallocene component preferably comprises a single compound of said formula $(Cp)_2MY_2$, but it may instead comprise a mixture of several said compounds of formula $(Cp)_2MY_2$.

Still more particularly, the feedstock may comprise olefins other than linear and branched α-olefins which include internal olefins, cyclic olefins, dienes and trienes, and constituents of the feedstock other than olefins may include paraffins, aromatics and small amounts of oxygenates. There may be an Al:M atomic ratio between aluminium in the aluminoxane component of the catalyst and the metal M in the metallocene component of the catalyst of 1:1 - 100:1, preferably 40:1 - 80:1, e.g. 60:1 - 70:1. As the Al:M atomic ratio increases, the degree of conversion and reaction rate increase, while the selectivity with regard to dimer production decreases, while a reducing Al:M atomic ratio reduces the degree of conversion and the reaction rate, and increases the selectivity for dimer production. An optimum or acceptable Al:M atomic ratio may accordingly be selected by routine experimentation, bearing practical and economic considerations in mind.

It is preferred to have the feedstock in a liquid state during the contacting of the catalyst with the feedstock, and the contacting may take place at a reaction temperature, and at a reaction pressure, both of which can vary within broad limits, the reaction time being determined by the period required to obtain a desired degree of conversion. Thus, reaction temperatures of -60°C to 280°C, e.g. 20 - 120°C have been found to be suitable, and absolute reaction pressures of 1 atmosphere or less, up to 500 atmospheres or more, may be used. In a particular case, the feedstock may be in a liquid state during the contacting of the feedstock with the metallocene/aluminoxane catalyst, the contacting taking place at a reaction temperature of -60°C to 280°C and at an absolute reaction pressure of 1 - 500 atmospheres, usually at or slightly above 1 atmosphere; and in the case the reaction temperature is preferably 20 - 120°C, the process being carried out under an inert atmosphere. Once again, routine experimentation may be used to establish optimum or acceptable reaction conditions with regard to temperature, pressure and reaction time.

The aluminoxane component of the catalyst, dissolved in an organic solvent (conveniently the organic solvent used in the preparation of the aluminoxane component) may be admixed with a well-stirred suspension of the metallocene component of the catalyst in an organic liquid which may be inert with regard to the metallocene/aluminoxane catalyst, or conveniently may be in the form of the feedstock used for the dimerisation reaction. When the feedstock is used to suspend the metallocene component, the dimerisation reaction proceeds in earnest as soon as the admixture thereof with the aluminoxane solution becomes substantially homogeneous. The dimerisation is conveniently carried out under an inert atmosphere, e.g. an argon atmosphere, at atmospheric pressure.

The dimer reaction products of the described dimerisation process are further reacted, for example in a hydroformylation reaction zone, to produce oxygenated products such as aldehydes and alcohols. An isomerising cobalt catalyst may be used for the hydroformylation of these dimmer reaction products in order to obtain primary alcohols.

The hydroformylation products may be branched. Typically, the hydroformylation products include mono- and/or di- and/or tri-methyl branched oxygenated products.

Where the feedstock to the dimerisation process is primarily linear α-olefinic, then the oxygenated products are predominantly monomethyl branched, for example, monomethyl branched alcohols and aldehydes.

Where the feedstock to the dimerisation process includes predominantly linear α-olefins and a minor fraction e.g. 10% to 25%, typically 15% to 20%, of monomethyl branched α-olefins, then the oxygenated products are predominantly monomethyl branched with a minor fraction being dimethyl branched, for example, mono- and di-methyl branched alcohols and aldehydes . Typically, the monomethyl branched oxygenated products will predominate.

Where the feedstock to the dimerisation process includes predominantly linear α-olefins and a major proportion e.g. 25% to 50% of the remainder of the feedstock are monomethyl branched α-olefins, then the oxygenated products include monomethyl branched, dimethyl branched and trimethyl branched oxygenated compounds, for example, mono-, di, and tri-methyl branched alcohols and aldehydes. Typically, the monomethyl branched fraction of the oxygenated products will exceed the dimethyl branched fraction of the oxygenated products which in turn will exceed the trimethyl branched fraction of the oxygenated products.

The invention thus provides an oxygenated compound composition obtained by oxygenating the dimerisation reaction products of the abovementioned dimerisation process, which oxygenated compound composition has on average between 0.9 and 3 branches per molecule. Typically the oxygenated compound composition includes at least some branched alcohol and/or aldehyde selected from the group including monomethyl branched alcohol, dimethyl branched alcohol, trimethyl branched alcohol, monomethyl branched aldehyde, dimethyl branched aldehyde, and trimethyl branched aldehyde.

Typically the composition includes primary alcohols and/or primary aldehydes.

The alcohols and/or aldehydes of the invention may be between C_4 and C_{40}, typically between C_{10} and C_{20}.

The oxygenate, for example alcohol or aldehyde, broadly in accordance with the invention, has one more methyl branch than the dimerisation reaction product, e.g. vinylidene , which is the intermediate feedstock for the oxygenate, which intermediate in turn has one more methyl branch than the α-olefin feedstock to the dimerisation process from which the intermediate feedstock is derived.

Typically, one unbranched and one monomethyl branched α-olefin is dimerised to produce a monomethyl branched vinylidene from which a dim ethylated oxygenate may derived.

Typically, two monomethyl branched α-olefins are dimerised to produce a dimethyl branched vinylidene from which a trimethylated oxygenate may derived.

The oxygenated products may be represented by R'R"C-CHO and/or R'R"C-CHOH in which R' and R" are alkyl groups and may be the same of different.

The oxygenated products derived from the dimer being formed from the ∝-olefins R' - CH_2 and R" each typically have C_2 -C_{30} carbon atoms, preferably C_5 - C_{10} carbon atoms.

The oxygenated products of dimer reaction products of the dimerisation process, of the present invention, are useful as starting materials for the production of detergents, surfactants, plasticizers or the like.

While the invention is suitable for use with any dimer derived from Fischer-Tropsch-derived olefinic feedstock, it is particularly suitable for such feedstock when derived from a high temperature Fischer-Tropsch process carried out at a temperature above 280°C, preferably above 300°C, for example at 330°C, as contrasted with feedstocks derived from low temperature Fischer-Tropsch processes, typically carried out at about 220°C.

Description of Examples of the Invention

The invention will now be described, by way of non limiting illustration, with reference to the following Examples:

Example 1

A metallocene/aluminoxane catalyst was prepared by admixing 3.07g of a 30% by mass methylaluminoxane solution in toluene with 0.24g of $(CP)_2ZrCl_2$ (zirconocene dichloride) with stirring at room temperature for about 15 minutes under argon, that catalyst having an Al:Zr atomic ratio of 66:1.

31.89g of Fischer-Tropsch-derived C_7 out (containing about 74% by mass of 1 heptene) and 11,82g of a Fischer-Tropsch-derived C_9 cut (containing about 65% by mass of 1-nonene) were admixed with the catalyst under argon in a reaction vessel in the form of a 300ml flamed-out Schlenk flask, followed by stirring at room temperature and atmospheric pressure under argon for about 4 hours, before being quenched with a 10% by mass solution was stirred for a further 30 minutes and was then washed with water and concentrated with regard to dimer reaction product. Gas-chromatographic analysis of the concentrated washed product showed a degree of conversion of > 85% and a mole ratio of dimerisation and cross-dimerisation products of C_{14}:C_{16}:C_{18} of 1:2:1 where C_{14} represents the dimerisation product of two of the heptene molecules, C_{18} represents the cross-dimerisation product of one of the heptene molecules with one of the nonene molecules.

Example 2

Example 1 was repeated using 3.552g of the methylaluminoxane and 0.22g of the $(Cp)_2ZrCl_2$ with 79.19 of a Fischer-Tropsch-derived C_8 out (containing about 40% by mass of 1-octene). The gas-chromatographic analysis showed that the degree or conversion to a C_{16} product was > 77%.

Example 3

The catalyst system consists of cobalt neodecanoate (0.833g of 13wt% cobalt) and 2.009g eicosyl phoban. The dimerisation product of example 1 was separated from the unreacted material. 100g of the fractionated dimerised product in example 1, the described catalyst system and 0.059 g potassium hydroxide were mixed in a 450ml Parr pressure reactor. A syngas composition of 2:1 (H_2:CO) was used and the reactor was pressurised to 75 barg. The reaction temperature was 170°C and the total reaction time was 66 hours. Mainly monomethyl branched alcohols with a small percentage dimethyl and trimethyl alcohols were obtained. The monomethyl branched alcohols made up between 80% and 85% of the mixture, the dimethyl branched alcohols made up 13% to 18% of the mixture and the trimethyl branched alcohols made up about 2% of the mixture.

Example 4

The attached compound structures of Figures 1 and 2, further illustrate the feedstock useable to produce the oxygenated products of the invention.

An advantage of the invention is that the Applicant has discovered that, surprisingly, a high degree of ∝-olefinic feedstock purity is not required for an-effective dimerisation and thus for producing monomethyl branched, dimethyl branched, and trimethyl branched oxygenated products of the dimerisation reaction products. Instead, a Fischer-Tropsch-derived olefinic feedstock containing substantial proportions of non-∝-olefinic constituents may be employed without any substantial treatment, purification or processing thereof, other than the selection of a suitable cut or cuts thereof containing ∝-olefins predominantly of the desired number or numbers of carbon atoms, to produce oxygenated products of the desired number or numbers of carbon atoms.

Claims

1. An oxygenated compound composition obtained by oxygenating dimerisation reaction products of a dimerisation process for the production of dimers from a Fischer-Tropsch-derived olefinic feedstock comprising a mixture of Fischer-Tropsch-derived hydrocarbons made up of at most 90% by mass of linear and branched α-olefins, at least 5% by mass of olefins other than α-olefins, and at least 5% by mass of constituents other than olefins, the dimerisation process comprising contacting the feedstock with a metallocene/aluminoxane catalyst thereby selectively to dimerise α-olefins in the feedstock by means of a metallocene-catalysed dimerisation reaction, the metallocene-catalysed dimerisation reaction taking place while the olefins which are dimerised form part of the mixture constituted by the feedstock, which oxygenated compound composition has on average between 0.9 and 3 branches per molecule.

2. An oxygenated compound composition as claimed in claim 1, wherein the oxygenated compounds of the composition are predominantly monomethyl branched when the feedstock to the dimerisation process is primarily linear α-olefinic.

3. An oxygenated compound composition as claimed in claim 1 or claim2, wherein the oxygenated compounds of the composition are predominantly monomethyl branched with a minor fraction being dimethyl branched when the feedstock to the dimerisation process includes predominantly linear α-olefins and a minor fraction of monomethyl branched α-olefins.

4. An oxygenated compound composition as claimed in claim 3, wherein the oxygenated products of the composition include mono- and di-methyl branched alcohols and./or aldehydes.

5. An oxygenated compound composition as claimed in claim 1 or claim 2, wherein the oxygenated compounds of the composition include monomethyl branched, dimethyl branched and trimethyl branched oxygenated compounds when the feedstock to the dimerisation process includes predominantly linear α-olefins and a major proportion of the remainder of the feedstock are monomethyl branched α-olefins.

6. An oxygenated compound composition as claimed in claim 5, wherein the oxygenated products of the composition include mono-, di-, and tri-methyl branched alcohols and/or aldehydes.

7. An oxygenated compound composition as claimed in claim 5 or claim 6, wherein a monomethyl branched fraction of the oxygenated compounds exceeds the dimethyl branched fraction of the oxygenated compounds which in turn exceeds the trimethyl branched fraction of the oxygenated compounds.

8. An oxygenated compound composition as claimed in claim 1, wherein the composition includes primary alcohols and/or primary aldehydes.

9. An oxygenated compound composition as claimed in any one of claims 4, and 6 to 8, wherein the alcohols and/or aldehydes include from C_4 to C_{40}.

10. An oxygenated compound composition as claimed in claim 9, wherein the alcohols and/or aldehydes include from C_{10} to C_{20}.

11. An oxygenated compound composition as claimed in any one of claims 1 to 10, wherein the oxygenated compounds of the composition have one more methyl branch than the dimerisation reaction product, which in turn has one more methyl branch than the α-olefin feedstock to the dimerisation process from which the dimerisation reaction product is derived.

12. An oxygenated compound composition as claimed in any one of claims 1 to 11, including a dimethylated oxygenate derived from a monomethyl branched vinylidene which is in turn derived from dimerisation of one unbranched and one monomethyl branched α-olefin.

13. An oxygenated compound composition as claimed in any one of claims 1 to 11, including a trimethylated oxygenate derived from a dimethyl branched vinylidene which is in turn derived from dimerisation of two monomethyl branched α-olefins.

14. An oxygenated compound composition as claimed in any one of claims 4 and 6 to 13, wherein the monomethyl branched alcohols make up from 60% to 90% of the alcohols of the composition, the dimethyl branched alcohols make up from 9% to 35% of the alcohols of the composition and the trimethyl branched alcohols make up up to about 5% of the alcohols of the composition.

15. An oxygenated compound composition as claimed in any one of claims 4, and 6 to 13, wherein the monomethyl branched alcohols make up from 80% to 85% of the alcohols of the composition, the dimethyl branched alcohols make up from 13% to 18% of the alcohols of the composition and the trimethyl branched alcohols make up up to about 2% of the alcoghols of the composition.

16. An oxygenated compound composition as claimed in any one of claims 4, and 6 to 13, wherein the monomethyl branched aldehydes make up from 60% to 90% of the aldehydes of the composition, the dimethyl branched aldehydes make up from 9% to 35% of the aldehydes of the composition and the trimethyl branched aldehydes make up up to about 5% of the aldehydes of the composition.

17. An oxygenated compound composition as claimed in any one of claims 4, and 6 to 13, wherein the monomethyl branched aldehydes make up from 80% to 85% of the aldehydes of the composition, the dimethyl branched aldehydes make up from 13% to 18% of the aldehydes of the composition and the trimethyl branched aldehydes make up up to about 2% of the alcohols of the composition.

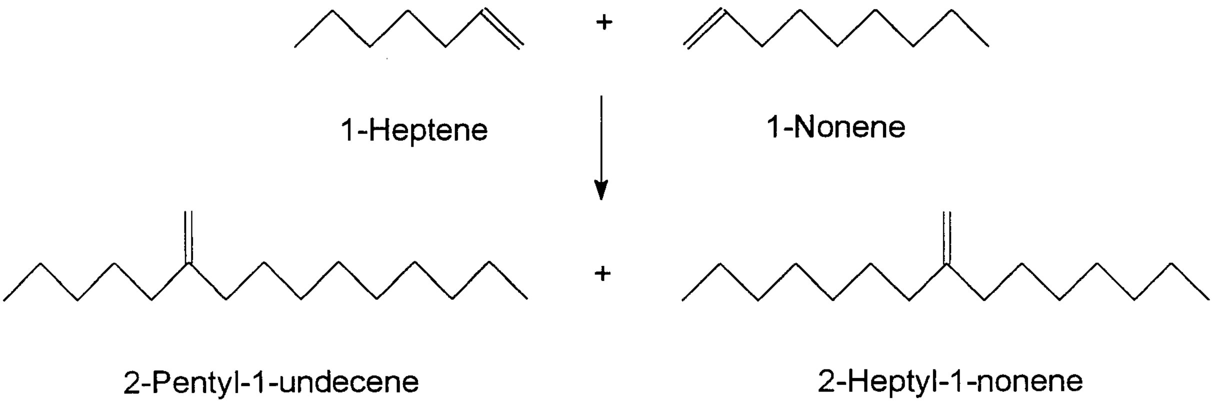
18. Detergents when derived from an oxygenated compound composition as claimed in any one of claims 1 to 17.

19. Surfactants when derived from an oxygenated compound composition as claimed in any one of claims 1 to 17.

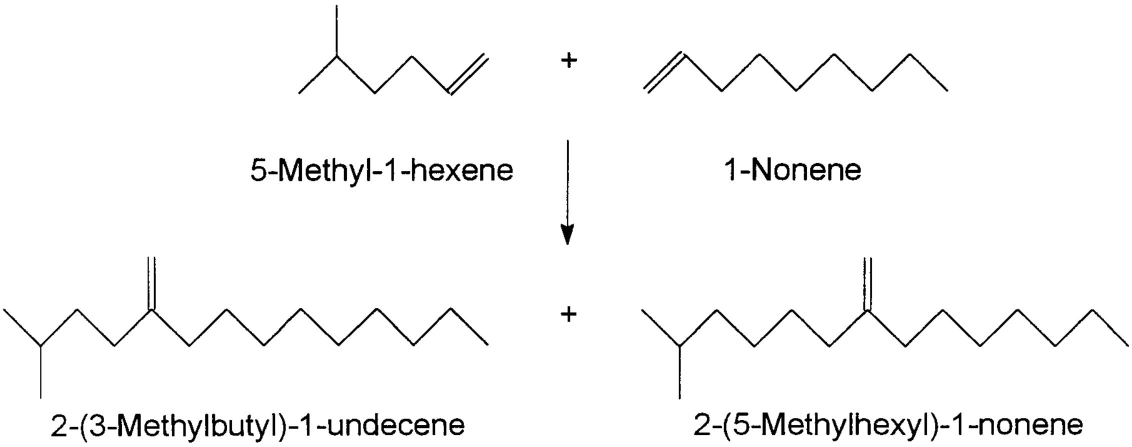
20 Plasticizers when derived from an oxygenated compound composition as claimed in any one of claims 1 to 17.

21. An oxygenated composition, substantially as herein described.

Monomethyl branched



Dimethyl branched



Trimethyl branched

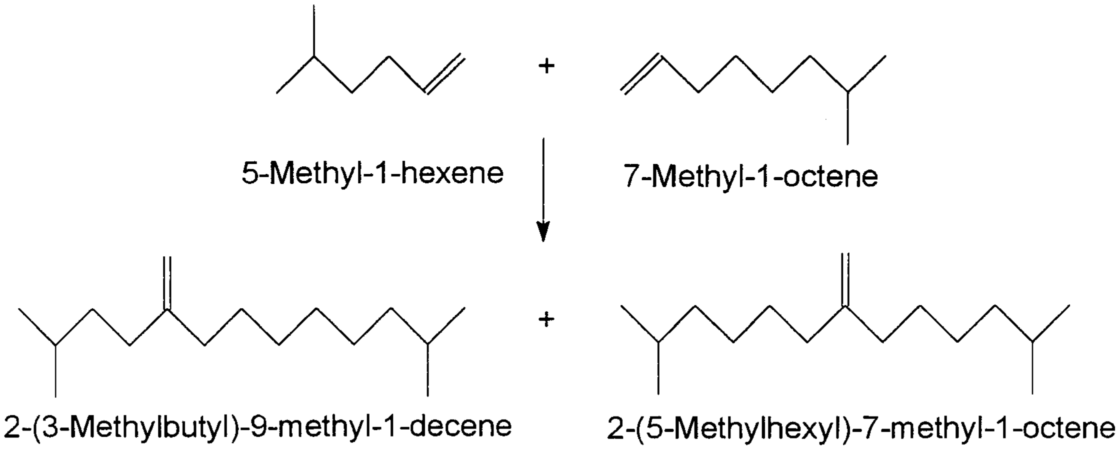


Figure 1

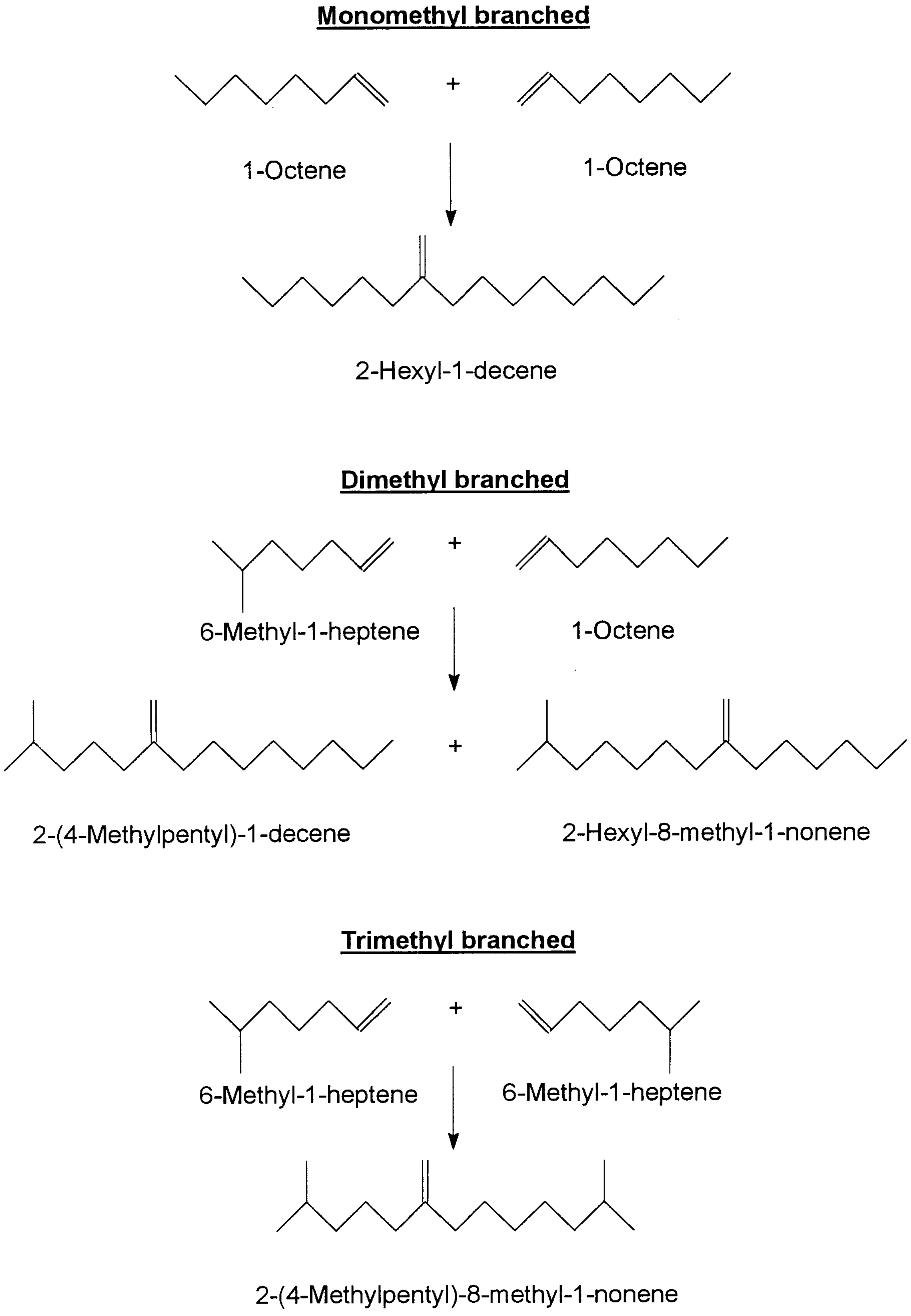

Monomethyl branched
+
1-Octene
1-Octene
2-Hexyl-1-decene
Dimethyl branched
+
6-Methyl-1-heptene
1-Octene
+
2-(4-Methylpentyl)-1-decene
2-Hexyl-8-methyl-1-nonene
Trimethyl branched
+
6-Methyl-1-heptene
6-Methyl-1-heptene
2-(4-Methylpentyl)-8-methyl-1-nonene

Figure 2

INTERNATIONAL SEARCH REPORT

Ir. ational Application No
PCT/ZA 00/00198

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C2/34 C07C11/02 C07C29/16 C07C31/125

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C

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

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

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search 28 February 2001	Date of mailing of the international search report 08/03/2001
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Authorized officer English, R

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/ZA 00/00198

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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1

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