

ALKENE PRODUCTION

FIELD OF THE INVENTION

The present invention relates to a method of producing alkenes. In particular, the method involves the production of at least one alkene from at least one ketone in the presence of at least one ketonisation catalyst.

BACKGROUND OF THE INVENTION

Various methods have been studied to transform biomass into valuable chemical compounds that can be used as sustainable alternatives to petroleum. Petroleum, the main source for chemical building blocks and transportation fuel, is being continuously depleted, and the prices perpetually fluctuating. Accordingly, there is a need to find an alternative energy source. One such energy source is alkenes.

For example, short and medium chain α -olefins serve as not only biofuels but also as polymer building blocks. In particular, alkenes may be used broadly for making lubricants, polymers and detergents.

Fatty acids are the preferred starting materials for production of alkenes as they contain carbon at low oxidation state. Also, fatty acids can usually be obtained in large quantities at low prices from natural resources, such as fats. However, there is always a need to find other new starting materials from which alkenes can be formed to have alternative means of producing alkenes in the event fatty acids become too expensive or are depleted.

Further, the current methods used in the production of alkenes from fatty acids are chemical in nature where α -olefins are formed from saturated unbranched fatty acids ($\geq C_{11}$). These methods usually require expensive and/or toxic metal-based catalysts and high temperatures ($>130^\circ\text{C}$).

There is thus a need in the art for an improved efficient method of producing alkenes from an alternative starting material.

DESCRIPTION OF THE INVENTION

The method according to any aspect of the present invention solves the problems above by using at least one ketone as a starting material for the production of at least one corresponding alkene. In particular, the ketone is in a gaseous state and method is carried out in the presence of at least one ketonisation catalyst and a hydrogen releasing agent or hydrogen agent at a temperature of at least 350°C . It was found that, surprisingly, at this temperature, an alkene was formed from a ketone in the gaseous state. Further, increasing the temperature above 350°C resulted in higher production of the alkene and reduction of the ketone in the reaction mixture comprising the ketone and the ketonisation catalyst.

According to one aspect of the present invention, there is provided a method of producing at least one alkene from at least one ketone, the method comprising the step of:

- contacting at least one gaseous ketone with at least one ketonization catalyst in the presence of at least one hydrogen releasing agent or hydrogen at a temperature of at least 350°C to produce a corresponding alkene

The term 'gaseous ketone' as used herein refers to ketones which are in a gaseous state. At room temperature, ketones are usually in a solid or liquid state depending on the size of the molecule of the ketone. For example, low molecular weight ketones such as acetone are liquids at room temperature, whereas higher molecular weight ketones may be solids. However, the method according to any aspect
5 of the present invention is carried out at a temperature of at least 350°C. This high temperature is higher than most boiling points of ketones and therefore, the ketone used in the method according to any aspect of the present invention, is present in a gaseous state.

In particular, the method according to any aspect of the present invention is carried on in a reactor and
10 the gases in the reactor are moving at gas hourly space velocity (GHSV) of 1 to 1000 m³/(m x h). More in particular, reactor may be a heated continuous flow-bed reactor. The GHSV refers to the speed of gases moving in the reactor per hour, particularly to the speed of gases moving over the catalyst. In particular, the gases in the reactor are at least ketone and/or the hydrogen releasing agent. More in particular, the gases in the reactor are at least ketone and hydrogen. The GHSV is 2 to 1000, 3 to 1000, 4 to 1000, 5 to
15 1000, 10 to 1000, 15 to 1000, 20 to 1000, 25 to 1000, 30 to 1000, 35 to 1000, 40 to 1000, 45 to 1000, 50 to 1000, 55 to 1000, 60 to 1000, 65 to 1000, 70 to 1000, 75 to 1000, 80 to 1000, 85 to 1000, 90 to 1000, 95 to 1000, 100 to 1000, 5 to 900, 10 to 900, 15 to 900, 20 to 900, 25 to 900, 30 to 900, 35 to 900, 40 to 900, 45 to 900, 50 to 900, 55 to 900, 60 to 900, 65 to 900, 70 to 900, 75 to 900, 80 to 900, 85 to 900, 90 to 900, 95 to 900, 100 to 900, 5 to 800, 10 to 800, 15 to 800, 20 to 800, 25 to 800, 30 to 800, 35 to 800,
20 40 to 800, 45 to 800, 50 to 800, 55 to 800, 60 to 800, 65 to 800, 70 to 800, 75 to 800, 80 to 800, 85 to 800, 90 to 800, 95 to 800, 100 to 800, 5 to 700, 10 to 700, 15 to 700, 20 to 700, 25 to 700, 30 to 700, 35 to 700, 40 to 700, 45 to 700, 50 to 700, 55 to 700, 60 to 700, 65 to 700, 70 to 700, 75 to 700, 80 to 700, 85 to 700, 90 to 700, 95 to 700, 100 to 700, 5 to 600, 10 to 600, 15 to 600, 20 to 600, 25 to 600, 30 to 600, 35 to 600, 40 to 600, 45 to 600, 50 to 600, 55 to 600, 60 to 600, 65 to 600, 70 to 600, 75 to 600, 80 to 600, 85 to 600, 90 to 600, 95 to 600, 100 to 600, 5 to 500, 10 to 500, 15 to 500, 20 to 500, 25 to 500,
25 30 to 500, 35 to 500, 40 to 500, 45 to 500, 50 to 500, 55 to 500, 60 to 500, 65 to 500, 70 to 500, 75 to 500, 80 to 500, 85 to 500, 90 to 500, 95 to 500, or 100 to 500 m³/(m x h). In particular, the GHSV is 5 to 500, 5 to 400, 10 to 400, 15 to 400, 20 to 400, 25 to 400, 30 to 400, 35 to 400, 40 to 400, 45 to 400, 50 to 400, 55 to 400, 60 to 400, 65 to 400, 70 to 400, 75 to 400, 80 to 400, 85 to 400, 90 to 400, 95 to 400, or
30 100 to 400, 5 to 300, 10 to 300, 15 to 300, 20 to 300, 25 to 300, 30 to 300, 35 to 300, 40 to 300, 45 to 300, 50 to 300, 55 to 300, 60 to 300, 65 to 300, 70 to 300, 75 to 300, 80 to 300, 85 to 300, 90 to 300, 95 to 300, or 100 to 300, 5 to 200, 10 to 200, 15 to 200, 20 to 200, 25 to 200, 30 to 200, 35 to 200, 40 to 200, 45 to 200, 50 to 200, 55 to 200, 60 to 200, 65 to 200, 70 to 200, 75 to 200, 80 to 200, 85 to 200, 90 to 200, 95 to 200, or 100 to 200, 5 to 150, 10 to 150, 15 to 150, 20 to 150, 25 to 150, 30 to 150, 35 to 150,
35 40 to 150, 45 to 150, 50 to 150, 55 to 150, 60 to 150, 65 to 150, 70 to 150, 75 to 150, 80 to 150, 85 to 150, 90 to 150, 95 to 150, or 100 to 150 m³/(m x h). In particular, the GHSV is 5 to 500 m³/(m³ x h). More in particular, the GHSV is 10 to 150 m³/(m³ x h). It is especially advantageous when the gases in the reactor are moving at this speed as then the ketone has sufficient time to be in contact with the catalyst and be converted into the alkene. The GHSV of the gaseous ketone may be measured using any
40 means known in the art. In particular, the GHSV may be measured using a flow indicator. Namely, an

indicator that can be used to measure the gas volume or the mass of the gases in the reactor where the method according to any aspect of the present invention is carried out.

Any ketone may be used as the starting material in the method according to any aspect of the present invention. In particular, the ketone has a structure $R-C(=O)-R'$, where R and R' can be a variety of carbon-containing substituents. Ketones contain a carbonyl group $-C(=O)-$ (which contains a carbon-oxygen double bond $C=O$). In particular, the ketone may comprise at least three carbon atoms. More in particular, the ketone in the method according to any aspect of the present invention may be a C_3 to C_{31} ketone. In one example, the ketone is at least one 6-undecanone which is a dialkyl ketone with formula $(CH_3(CH_2)_4)_2CO$.

The ketonization catalyst used according to any aspect of this present invention may be a heterogeneous catalyst. In particular, the ketonization catalyst may be any metal oxide catalyst or mixtures thereof. More in particular, the catalyst may be selected from the group consisting of heteropoly acid ($H_3PW_{12}O_{40}$) catalyst, niobium oxide (Nb_2O_5) catalyst, titanium oxide (TiO_2) catalyst, cerium oxide (CeO_2) catalyst, zinc-chromium (Zn-Cr) mixed oxide catalyst, manganese oxide (MnO_x) catalyst, lanthanum oxide (La_2O_3) catalyst, magnesium oxide (MgO) catalyst, iron oxide (FeO , FeO_2 , Fe_2O_3 , Fe_3O_4 , Fe_4O_5 , Fe_5O_6 , Fe_5O_7), silicon-aluminium (Si_yAl_zO) mixed oxide catalyst, aluminium oxide (Al_2O_3) catalyst and zirconia (ZrO_2) catalyst. The 'x' in MnO_x may be 1, 2 or 4. The 'y' and 'z' in Si_yAl_zO may refer to any number where the ratio z/y is any number between 0 to 1. The metal oxide ketonization catalyst as confirmed in the examples did not produce products where the double bond has been hydrogenated. Instead, surprisingly, with use of these metal oxide ketonization catalysts in the method according to any aspect of the present invention, alkene formation due to Norrish Type fragmentations is seen.

It would be within the knowledge of a skilled person to determine the suitable conditions for the use of the different ketonization catalysts in the method according to any aspect of the present invention. In particular, the ketonization catalyst may be a zirconia catalyst and may be used in the conversion of a ketone to the corresponding alkene. In particular, the temperature has to be at least $350^\circ C$ for the ketone to be converted to the corresponding alkene. More in particular, the temperature may be maintained at about 350, 355, 360, 365, 370, 375, 380, 385, 390, 395, or $400^\circ C$ during the method according to any aspect of the present invention. Even more in particular, the reaction temperature may be 350-420, 350-415, 350-410, 350-405, 350-400, 350-395, 350-390, 350-385, 350-380, 350-375, 350-370, 350-365, 350-360, 355-420, 355-415, 355-410, 355-405, 355-400, 355-395, 355-390, 355-385, 355-380, 355-375, 355-370, 355-365, 355-360, 360-420, 360-415, 360-410, 360-405, 360-400, 360-395, 360-390, 360-385, 360-380, 360-375, 360-370, 360-365, 365-420, 365-415, 365-410, 365-405, 365-400, 365-395, 365-390, 365-385, 365-380, 365-375, 365-370, 370-420, 370-415, 370-410, 370-405, 370-400, 370-395, 370-390, 370-385, 370-380, 370-375, 375-420, 375-415, 375-410, 375-405, 375-400, 375-395, 375-390, 375-385, 375-380, 380-420, 380-415, 380-410, 380-405, 380-400, 380-395, 380-390, 380-385, 385-420, 385-415, 385-410, 385-405, 385-400, 385-395, 385-390, 390-420, 390-415, 390-410, 390-405, 390-400, 390-395, 395-420, 395-415, 395-410, 395-405, 395-400, 400-420, 400-415, 400-410, or $400-405^\circ C$. More in particular,

the method according to any aspect of the present invention is carried out at a temperature between 350°C and 390°C. Even more in particular, alkenes are produced from ketones using a zirconia catalyst as the ketonization catalyst at reaction temperatures of 350°C – 390 °C. The zirconia catalyst is preferably prepared by peletisation, having 0.5 to 3mm diameter and 1 to 5 mm length. The surface is in the range of 10 to 300 m²/g.

The method according to any aspect of the present invention further comprising a hydrogen releasing agent or hydrogen. The hydrogen releasing agent may be any compound that donates a H atom to the ketone to produce the corresponding alcohol and from there the alkene. In particular, the hydrogen releasing agent may be hydrogen or at least one carboxy acid or organic acid. More in particular, the hydrogen releasing agent is at least one alkanolic acid comprising 1 to 22 carbon atoms. The hydrogen releasing agent may therefore be at least one alkanolic acid comprising 1 to 22 carbon atoms or hydrogen. In particular the alkanolic acid is selected from straight chain alkanolic acids comprising 4 to 18, preferably 5 to 12, carbon atoms. More in particular, the alkanolic acid is hexanoic acid.

The hydrogen releasing agent may be supplied together with the ketone.

The ketone may be any ketone with 3-31 carbon atoms. In one example, the ketone is undecanone and the alkene is undecene.

The method according to any aspect of the present invention may comprise a further step of extracting the alkene produced. Any method known in the art may be used to extract the alkene. In particular, distillation may be used to extract the alkene.

According to a further aspect of the present invention, there is provided a method of improving yield of production of at least one alkene from at least one ketone using the method according to any aspect of the present invention compared to carrying out the method at a different temperature with a different gas hourly space velocity (GHSV) in the reactor.

The term “contacting”, as used herein, means bringing about direct contact between the gaseous ketone with at least one ketonization catalyst according to any aspect of the present invention in the medium in step (a). For example, the ketone, and the ketonisation catalyst may be in different compartments and brought together in step (a).

According to yet another aspect of the present invention, there is provided an alkene produced from the method according to any aspect of the present invention.

According to a further aspect of the present invention there is provided a use of a ketonization catalyst for the production of at least one alkene from at least one ketone. In particular, the ketone is undecanone and the alkene is undecene. The ketone is a gaseous ketone and has a gas hourly space velocity

(GHSV) of 1 to 1000 $\text{m}^3/(\text{m}^3 \times \text{h})$ in the reaction. In particular, the ketonization catalyst is a zirconia catalyst.

Unless stated otherwise, all percentages (%) given are percentages by mass.

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The term 'about' as used herein refers to a variation within 20 percent. In particular, the term "about" as used herein refers to $\pm 20\%$, more in particular, $\pm 10\%$, even more in particular, $\pm 5\%$ of a given measurement or value.

- 10 The examples adduced hereinafter describe the present invention by way of example, without any intention that the invention, the scope of application of which is apparent from the entirety of the description and the claims, be restricted to the embodiments specified in the examples.

EXAMPLES

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Example 1

Example for GHSV: $121 \text{ m}^3/(\text{m}^3 \times \text{h})$, $T > 350^\circ\text{C}$

- The reaction was conducted in a heated continuous flow-bed reactor. Gaseous hexanoic acid ($1.2 \text{ m}^3/\text{h}$) was continuously fed to a reactor charged with zirconium oxide on silica (95 wt.%, 10.2 kg or 0.01 m^3) at 20 365°C. The catalyst has a diameter of 1 mm and a length of 3 mm. The gaseous out stream was collected and analyzed by nuclear magnetic resonance spectroscopy (NMR) for its composition. In total, 3 kg of hexanoic acid was fed to the reactor, leading to a 2.3 kg mixture consisting of 15% undecene and 75% 6-undecanone and 10% of byproducts, alongside 0,5 kg of carbon dioxide and 0,2 kg water. The residual amount of hexanoic acid was lower than the detection limit. Figure 1 and Table 1 show the reaction 25 outcome prior to any derivatization and confirms that there is no formation of undecane observed. All structures have been suggested by the NIST database and isomers have not been specified further in terms of the position of any functional group. Figure 2 and Table 2 show the reaction outcome after subsequent hydrogenation.

Peak	Start	RT	End	Height	Area	Area%	Area% _{norm.}	Chemical Structure
1	4.936	4.963	5.016	199606.69	290237.95	13.24	4,04	Heptanone
2	5.016	5.035	5.054	34382.21	49049.57	2.24	0,68	Nonene
3	5.054	5.068	5.139	42268.33	77927.24	3.55	1,08	Nonene
4	6.925	6.954	7.016	42268.33	486291.91	22.18	6,77	Nonanone
5	7.068	7.102	7.164	507275.28	2024132.14	92.34	28,20	Undecene
6	7.178	7.192	7.240	1632920.82	41395.99	1.89	0,58	Undecene
7	7.240	7.264	7.287	41600,09	25622.3	1.17	0,36	Methyldecene
8	7.549	7.564	7.592	24697,2	96294.73	4.39	1,34	Tetradecyne
9	7.592	7.616	7.639	104644.53	27679.11	1.26	0,38	Methylundecene
10	7.649	7.664	7.721	273535.23	177741.07	8.11	2,48	Methylundecene
11	7.897	7.916	7.981	191575.2	35719.52	1.63	0,50	Methylundecene
12	8.225	8.245	8.302	26326.58	2192047.24	100	30,54	Undecanone
13	8.483	8.497	8.567	259449.55	35583.44	1.62	0,49	Tetradecene
14	8.850	8.873	8.902	30084.11	1368241.58	62.42	19,06	Tetradecene
15	9.287	9.302	9.350	1673103.24	249440.92	11.38	3,48	Hexadecene

Table 1 Providing details of the products of the chromatogram in Figure 1

Peak	Start	RT	End	Height	Area	Area%	Area% _{norm.}	Chemical Structure
1	4.949	4.973	5.054	129362.75	218792.93	6.4	3.35	Heptanone
2	5.068	5.097	5.144	37687.64	50677.2	1.48	0.77	Nonane
3	6.940	6.959	7.021	250713.65	272005.05	7.96	4.16	Nonanone
4	7.132	7.159	7.216	1230725.78	1004807.57	29.39	15.38	Undecane
5	7.521	7.535	7.563	108251.27	97475.37	2.85	1.49	Methylundecane
6	8.225	8.249	8.311	4129422.43	3418517.18	100	52.32	Undecanone
7	8.849	8.873	8.935	1655218.18	1273784.41	37.26	19.49	Tetradecane
8	9.278	9.297	9.359	222357.16	198442.73	5.8	3.03	Methylnonadecane

5 Table 2 Providing details of the products of the chromatogram in Figure 2

Example 2

Example for GHSV: $117 \text{ m}^3/(\text{m}^3 \times \text{h})$, $T < 350^\circ\text{C}$

- 10 The reaction was conducted in a heated continuous flow-bed reactor. Gaseous hexanoic acid ($1.2 \text{ m}^3/\text{h}$) was continuously fed to a reactor charged with zirconium oxide on silica (95 wt.%, 10.15 kg) at 343°C . The gaseous out stream was collected and analyzed by gas chromatography (GC) for its composition. In total, 3 kg of hexanoic acid was fed to the reactor, leading to a 2.2 kg mixture consisting of 99% 6-undecanone and <1% hexanoic acid, alongside 0,6 kg of carbon dioxide and 0,2 kg water.

15 **Example 3**

Example for GHSV: $4,6 \text{ m}^3/(\text{m}^3 \times \text{h})$, $T < 350^\circ\text{C}$

- 20 The reaction was conducted in a heated continuous flow-bed reactor. Gaseous hexanoic acid ($3.6 \times 10^{-5} \text{ m}^3/\text{h}$) was continuously fed to a reactor charged with zirconium oxide on silica (95 wt.%, $7.9 \times 10^{-6} \text{ m}^3$) at 348°C . The gaseous out stream was collected and analysed by nuclear magnetic resonance spectroscopy (NMR) for its composition. In total, 89 mg of hexanoic acid was fed to the reactor, leading

to a 66 mg mixture consisting of 9% undecene, 13% 6-undecanone and 78% hexanoic acid, alongside 17 mg of carbon dioxide and 7 mg water.

Example 4

5 *Example for GHSV: $4,6 \text{ m}^3/(\text{m}^3 \times \text{h})$, $T > 350^\circ\text{C}$*

The reaction was conducted in a heated continuous flow-bed reactor. Gaseous hexanoic acid ($3.6 \times 10^{-5} \text{ m}^3/\text{h}$) was continuously fed to a reactor charged with zirconium oxide on silica (95 wt.%, $7.9 \times 10^{-6} \text{ m}^3$) at 355°C . The gaseous out stream was collected and analysed by nuclear magnetic resonance

10 spectroscopy (NMR) for its composition. In total, 89 mg of hexanoic acid was fed to the reactor, leading to a 66 mg mixture consisting of 20% undecene, 1% 6-undecanone and 79% hexanoic acid, alongside 17 mg of carbon dioxide and 7 mg water.

Example 5

Example for GHSV: $4,6 \times 10^4 \text{ m}^3/(\text{m}^3 \times \text{h})$, $T > 350^\circ\text{C}$

15 The reaction was conducted in a heated continuous flow-bed reactor. Gaseous hexanoic acid ($0.36 \text{ m}^3/\text{h}$) was continuously fed to a reactor charged with zirconium oxide on silica (95 wt.%, $7.9 \times 10^{-6} \text{ m}^3$) at 355°C . The gaseous out stream was collected and analyzed by nuclear magnetic resonance spectroscopy (NMR) for its composition. In total, 893 g of hexanoic acid was fed to the reactor, leading to a 655 g mixture consisting of 96% 6-undecanone and 4 % hexanoic acid, alongside 169 g of carbon

20 dioxide and 69 g water. The amount of undecene was lower than the detection limit.

Example 6

Example for GHSV: $0.3 \text{ m}^3/(\text{m}^3 \times \text{h})$, $T > 350^\circ\text{C}$

25 The reaction was conducted in a heated continuous flow-bed reactor. Gaseous hexanoic acid ($2.2 \times 10^{-6} \text{ m}^3/\text{h}$) was continuously fed to a reactor charged with zirconium oxide on silica (95 wt.%, $7.9 \times 10^{-6} \text{ m}^3$) at 355°C . The gaseous out stream was collected after 72 h and analyzed by gas chromatography for its composition. In total, 0.14 mg of hexanoic acid was fed to the reactor, leading to a product mixture consisting of 80% 6-undecanone and 9 % undecane, alongside carbon dioxide and water.

CLAIMS

1. A method of producing at least one alkene from at least one ketone, the method comprising the step of:
 - 5 (a) contacting at least one gaseous ketone with at least one ketonization catalyst in the presence of at least one hydrogen releasing agent or hydrogen at a temperature of at least 350°C to produce a corresponding alkene, wherein the gases have a gas hourly space velocity (GHSV) of 1 to 1000 m³/(m³ x h), and wherein the ketonization catalyst is a metal oxide catalyst or mixtures thereof.
- 10 2. The method according to claim 1, wherein the temperature is between 350°C and 390°C
3. The method according to either claim 1 or 2, wherein the metal oxide catalyst or mixtures thereof is selected from the group consisting of heteropoly acid (H₃PW₁₂O₄₀) catalyst, titanium
15 oxide (TiO₂) catalyst, cerium oxide (CeO₂) catalyst, zinc-chromium (Zn-Cr) mixed oxide catalyst, manganese oxide (MnO₂) catalyst, lanthanum oxide (La₂O₃) catalyst, magnesium oxide (MgO) catalyst, iron oxide (FeO, FeO₂, Fe₂O₃, Fe₃O₄, Fe₄O₅, Fe₅O₆, Fe₅O₇), silicon-aluminium (Si-Al) mixed oxide catalyst and zirconia (ZrO₂) catalyst.
- 20 4. The method according to any one of the preceding claims, wherein the ketonization catalyst is a zirconia catalyst.
5. The method according to any one of the preceding claims, wherein the hydrogen releasing agent is an acid, preferably a carboxy acid or inorganic acid.
- 25 6. The method according to claim 5, wherein the acid is at least one alkanoic acid comprising 1 to 22 carbon atoms.
7. The method according to any one of the claims 1 to 6, wherein in step (a) the gaseous ketone
30 is brought into contact with the ketonization catalyst in the presence of hydrogen.
8. The method according to claim 7, wherein in step (a) at least one alkanoic acid comprising 1 to 22 carbon atoms is introduced.
- 35 9. The method according to any one of the preceding claims, wherein the alkanoic acid is hexanoic acid.
- 40 10. The method according to any one of the preceding claims, wherein the ketone is undecanone and the alkene is undecene.

11. An alkene produced from the method according to any one of the claims 1 to 10.
- 5 12. Use of a ketonization catalyst for the production of at least one alkene from at least one ketone.
13. Use according to claim 12, wherein the ketone is undecanone and the alkene is undecene.
- 10 14. Use according to either claim 12 or 13, wherein the ketone is a gaseous ketone and has a gas hourly space velocity (GHSV) of 1 to 1000 m³/(m x h) in the reaction.
15. Use according to any one of the claims 12 to 14, wherein the ketonization catalyst is a zirconia catalyst.