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Additional Information

# High quality biowaxes from fatty acids and fatty esters: catalyst and reaction mechanism for accompanying reactions

Borja Oliver-Tomas, Michael Renz\*, Avelino Corma\*

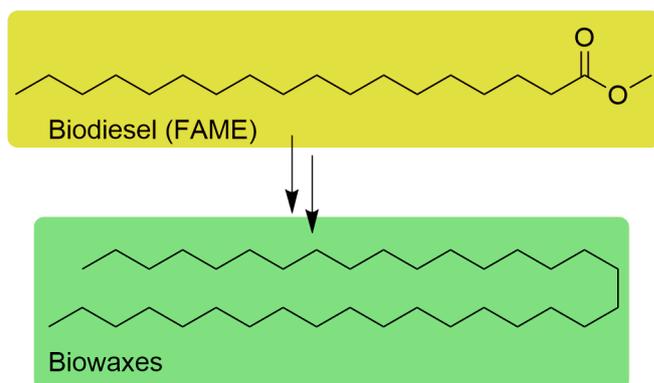
Instituto de Tecnología Química, Universitat Politècnica de Valencia-Consejo Superior de Investigaciones Científicas (UPV - CSIC), Av. de los Naranjos s/n, E-46022 Valencia, Spain

Tel.: +34 96 387 7800, Fax: +34 96 387 9444, mrenz@itq.upv.es; acorma@itq.upv.es

## Keywords

synthesis of biowaxes, ketonic decarboxylation, fatty acids and esters to waxes

## Graphical abstract



## **Abstract**

Biowaxes are interesting materials for pharmaceutical industry and consumer goods. Here the production of waxes from alternative renewable resources has been evaluated on the basis of the ketonic decarboxylation of fatty acids. The latter converts carboxylic acids (or its derivatives) into ketones with almost double chain length. Hence, sunflower oil was employed as starting material and passed over monoclinic zirconium. A wax fraction of 43% yield was obtained, though high content of molecules with more than 30 carbon atoms was not achieved due to prevalent carbon chain degradation. However, reaction of methyl stearate over zirconium oxide gave 60% of a wax fraction. Together with the waxes, an almost oxygen-free diesel fraction was obtained in more than 25% yield. Labeling experiments showed that the ketone intermediate is degraded by a radical chain mechanism. It is further concluded that methyl stearate radical formation is induced by carbon-carbon bond scission at high temperature whereas the glycerol part of the triglyceride may act as radical initiator. As a consequence, long linear alkane waxes should be produced in the absence of glycerol (moieties). The exploitation of the side-product as high quality diesel together with the waxes improves the economic feasibility of the process.

## Introduction

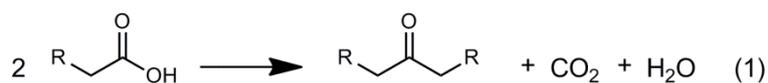
Increasing carbon dioxide concentration in the atmosphere originated by combustion of fossil carbon is supposed to contribute to the climate change. Therefore, in recent years the social actors have tried to mitigate global warming by substitution of fossil raw materials by renewable ones. For instance, production of biodiesel (FAMES) by transesterification of vegetable oils and animal fats has been promoted as well as the production of lignocellulosic ethanol as gasoline replacement.<sup>1-4</sup> The use of bioplastics has been stimulated and polylactic acid obtained from biochemical processes is an outstanding example for the industrial application of renewable materials.<sup>5-7</sup>

Apart from fuels and polymers, a further classical type of petroleum-derived products are waxes.<sup>8</sup> Paraffin waxes are separated from crude petroleum with the aim to improve its flow properties for direct use as a base oil.<sup>9</sup> Synthetic waxes are obtained from Ziegler Natta polymerization of petroleum-derived ethylene<sup>10</sup> or from the Fischer-Tropsch process with syngas from fossil methane.<sup>11,12</sup> However, waxes from renewable sources are also marketed. Over thousands of years beeswax has been obtained from honeycombs,<sup>13</sup> and, more recently, other higher value added natural waxes from plants such as carnauba wax from palm trees<sup>14,15</sup> or candelilla wax from the candelilla plant have been used.<sup>16</sup> Nevertheless, the available raw materials for the production of the renewable waxes are already exploited to a maximum, and, either the growth of the precursors has to be reinforced or natural formation processes have to be mimicked from alternative renewable materials.

Candelilla wax (CW) is a biowax material obtained from the candelilla plant that might be produced from alternative natural sources. CW is used as a glazing agent, as a binder for chewing gums, as a component of lip balm or of varnishes.<sup>17,18</sup> CW consists of *n*-alkanes (approx. 50%) with 29 to 33 carbon atoms, high molecular weight esters (up to 30%) and other compounds.<sup>17</sup> The market volume of vegetable waxes is orders of magnitude smaller than the volume of vegetable oils and it would be interesting to find a process that could transform fatty acids and esters present in vegetable oils into renewable waxes.<sup>19,20</sup> To achieve that, vegetable oils have to be modified to adapt functional properties, texture and stability. Hence, in the present work a straightforward way to transform vegetable oils into renewable biowaxes will be presented.

The basis for this transformation is the ketonic decarboxylation of a carboxylic acid or carboxylic esters. In fact, it is possible to join two molecules of carboxylic acid (with *n*

carbon atoms) by carbon-carbon bond formation to obtain a linear molecule with  $2n-1$  carbon atoms and carbon dioxide and water as innocuous by-products (Eq. 1).<sup>21,22</sup> In general the process can be carried out in a continuous flow reactor at temperatures in the range of 350 to 400 °C without the need of a solvent, and *monoclinic* zirconium oxide has been identified as very suitable catalyst for this reaction. The mechanism has been studied by theoretical and experimental means and it has been shown that a beta-keto acid is favored as intermediate.<sup>23,24</sup> When this reaction is applied to a mixture of palmitic and stearic acids, ketones with 31 to 35 carbon atoms are obtained which is very close to the carbon atom number of the paraffins of CW. The ketones can then be hydrogenated to the corresponding linear alkanes (Eq. 2).<sup>25,26</sup> In the same hydrogenation double bonds can be saturated which expands the scope of raw materials from saturated to unsaturated fatty acids, i.e. from stearic acid to e.g. oleic acid. As a consequence, fatty acids from vegetable oil, or the vegetable oils themselves, can be included in the group of suitable raw materials.



In recent years the ketonic decarboxylation of carboxylic acids has been studied with the aim to produce fuels from the free acids.<sup>25-28</sup> The reaction can also be applied directly to esters,<sup>29-31</sup> but these compounds have aroused less interest for the production of fuels since the selectivities to the ketone observed were lower than for the free carboxylic acids. Furthermore, hydrocarbons and shorter ketones were obtained as by-products when using the esters.

Herein, we have studied the conversion of fatty acid esters and vegetable oils into waxes, and more specially Sunflower oil and stearic acid methyl ester. The products obtained were evaluated for their wax content while the hydrocarbons with a smaller number of carbon atoms were considered as an oxygen-free feedstock for renewable, high quality diesel fuel. The catalyst employed was zirconium oxide which has been identified as a material with excellent intrinsic catalytic activity and selectivity for the ketonic decarboxylation with carboxylic acids as substrates.<sup>23,25</sup>

## Experimental Part

### *General*

Methyl stearate (96%) and oleic acid (tech. grade, 90%) were received from Sigma–Aldrich. Isotopically-labelled methanol (99%  $^{13}\text{C}$ ) and stearoyl chloride (97%) were acquired from ABCR (Germany). Sunflower oil was purchased from a local supermarket. All reagents were used without any further purification. *Monoclinic* zirconium oxide ( $m\text{-ZrO}_2$ ) and alumina ( $\text{Al}_2\text{O}_3$ ) were purchased from ChemPur (Germany) as pellets. The pellets were crushed and sieved, and the 0.4 – 0.8 mm fraction was employed as catalyst.  $\text{H}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$  (99%, Aldrich) was employed as noble metal precursors for the impregnation of the alumina.

### *Catalytic Reactions (except for Hydrogenation Reaction)*

All reactions were carried out in a tubular fixed-bed continuous-flow reactor. The whole set-up has been described before.<sup>25</sup> The reagents were placed in a syringe and in the case of methyl stearate the syringe was heated to 50 °C. Sunflower oil and oleic acid were fed at room temperature. The reactor was filled with 2.50 g of  $m\text{-ZrO}_2$  diluted with silicon carbide. The reactions were carried out at temperatures between 400 and 550 °C at atmospheric pressure. Hydrogen gas (100 mL/min) was employed as carrier gas and the substrate was fed with 0.15 mL/min (WHSV of 3.02 h<sup>-1</sup> for methyl stearate, 3.31 h<sup>-1</sup> for sunflower oil and 3.20 h<sup>-1</sup> for oleic acid) during 33 min in each experiment. The products were condensed at the exit of the reactor using an ice bath. Liquid products (yields stated in Table S1) were analyzed off-line by gas chromatography on different GC apparatus, three of them equipped with a FID detector. The instruments were an Agilent 7890A with split injection equipped with a HP-5 column (30 m x 0.320 mm x 0.25 μm), a Varian CP-3800 apparatus with on-column injection equipped with a Varian's Select Biodiesel for Glycerides (10 m x 0.320 mm x 0.10 μm) and a simulated distillation gas chromatograph Bruker 450-GC equipped with an Agilent J&W GC Column CP-SimDist (10 m x 0.53 mm x 2.65 μm). The substances were identified with a GC-MS apparatus Agilent 6890 N equipped with a HP-5 column (30 m x 0.320 mm x 0.25 μm) and a mass selective detector Agilent Technologies 5973 Network. Non condensable gases were analyzed off-line on a GC apparatus equipped with three channels (columns + detectors). Hydrogen was analyzed with a 2 m molecular sieve 5 Å column and TCD detector, while permanent gases such as CO and CO<sub>2</sub> were separated on a 2.5 m molecular sieve 13X column and

quantified with a TCD detector. Low molecular weight hydrocarbons were separated with a 50 m Plot/Al<sub>2</sub>O<sub>3</sub> column and analyzed with a FID detector.

#### *Hydrogenation Reaction*

The reaction was performed in a fixed-bed tubular continuous-flow reactor with a back-pressure regulator for pressure control as described in detail elsewhere.<sup>25</sup> The reagent was placed in a syringe and was fed at room temperature. Pt(2 %wt)/Al<sub>2</sub>O<sub>3</sub> (1.50 g) was employed as catalyst mixed with silicon carbide as diluent and placed in the reactor. The hydrogenation reactions were carried out at 400 °C and 40 bar. Hydrogen gas (150 mL/min) was passed as carrier gas and 7.41 g/h (WHSV of 4.94 h<sup>-1</sup>) of substrate was fed during 70 min. Substrate and liquid products were analyzed off-line by two dimensional gas chromatography with an Agilent 7890 GC apparatus equipped with a HP Innowax column (30 m x 0.250 mm x 0.25 μm) as first column and a DB-5 as second column (5 m x 0.250 mm x 0.25 μm), with a modulator between both columns. The system is connected to two detectors, a fast detection FID and a mass selective detector (Agilent Technologies 5977 A).

#### *Catalyst characterization*

Powdered catalyst samples were characterized by X-ray diffraction at room temperature with a PANalytical CubiX diffractometer using a monochromatic K $\alpha$  radiation. The X-ray pattern confirms the monoclinic phase of the catalyst (Figure S1). Nitrogen adsorption isotherms were measured at 77 K using a Micrometrics ASAP 2020 apparatus. The Brunauer–Emmett–Teller (BET) method was used for the determination of the catalyst surface area. A surface area of 104 m<sup>2</sup>/g was determined for the fresh catalyst.

#### *Hydrogenation catalyst preparation*

The Pt(2 %wt)/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by the incipient wetness impregnation method. The surface area of the Al<sub>2</sub>O<sub>3</sub> support was determined by nitrogen adsorption to be 222 m<sup>2</sup>/g. An aqueous solution of H<sub>2</sub>PtCl<sub>6</sub> · 6 H<sub>2</sub>O was prepared with the corresponding concentration to achieve the desired metal content in the solid. The Al<sub>2</sub>O<sub>3</sub> used as support was impregnated as pellets (0.4 – 0.8 mm), dried at room temperature in vacuum during 2 h and afterwards in an oven overnight at 100 °C. Chemisorption experiments revealed that the dispersion of the Pt was 97% and the average particle size was 1.2 nm. At 250 °C all platinum was reduced as evidenced by temperature programmed reduction (TPR). The metal-containing catalyst was activated (reduced) in-situ in the reactor. The catalyst was heated to 400 °C employing a heating ramp of 9

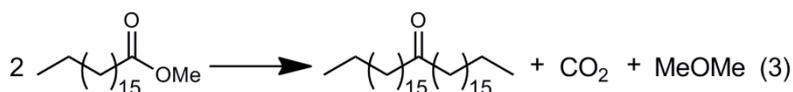
K/min at a hydrogen pressure of 40 bar and a hydrogen flow of 150 mL/min. The final temperature was maintained for two hours.

#### *Isotopically-labelled methyl stearate synthesis*

Following a literature procedure,<sup>32</sup> 90 mL of anhydrous dichloromethane and 1.00 g of isotopically labeled MeOH (99% <sup>13</sup>C) were placed into a round bottom flask and stirred magnetically. 6.7 mL of triethylamine and 9.45 g of stearoyl chloride were added dropwise to the mixture cooled in an ice water bath. The mixture was kept reacting for 2 h, then the solvent was removed in vacuum and the crude product was obtained. The latter was purified by column chromatography using dichloromethane as eluent. Isotopically-labeled methyl stearate was obtained in 88% yield and with 99% labelled <sup>13</sup>C carbon in the alcohol position of the ester.

#### *Mass balance and yields calculations and liquid fuel classification*

In the case of the transformation of methyl stearate the initial reaction should be the ketonic decarboxylation of the ester as described in Eq. 3:



Methyl stearate

MW: 298.50 g/mol

MW: 506.94 g/mol

Thereby, carbon dioxide and dimethyl ether are produced which were not condensed in the liquid phase with our experimental set-up. Therefore, a maximum weight balance for the liquid phase (liquid yield) of 85% can be expected. The theoretical maximum yield of carbon dioxide from ketonic decarboxylation (following Eq. 3) is 7.4%, and 7.7% for dimethyl ether.

The following formulas were employed to calculate the liquid yield [%] and the product yield [%]:

$$\text{Liquid yield [\%]} = (\text{Mass of liquid product collected} / \text{Mass of substrate fed}) \cdot 100$$

$$\text{Product yield [\%]} = \text{Liquid yield [\%]} \cdot (\text{Concentration of the product in the liquid collected, in weight}) / 100$$

$$\text{Total gas yield [\%]} = (\text{Mass of the gaseous products collected} / \text{Mass of substrate fed}) \cdot 100$$

$$\text{Normalized concentration of gas products} = (\text{Mass yield of gas compound at given temperature} / \text{Total mass yield of gases at reference temperature}) \cdot 100$$

A combination of gas yields, determined by a GC with a refinery gas analyzer (RGA) configuration, with the <sup>12</sup>C and <sup>13</sup>C compounds distribution, determined by mass

spectroscopy, was employed for the calculations of the yields of isotopically-labelled gases.

The fuel properties of the components of the organic liquid have been classified with respect to their boiling point as detailed in Table 1

Table 1. Liquid fuel classification used in this work based on the boiling point.

	Temperature range / °C
Gasoline	36 – 171
Diesel	171 – 359
Waxes	> 359

## Results and discussion

### *Catalytic transformation of sunflower oil into vegetable waxes*

Sunflower oil was chosen as substrate with a fatty acid chain length distribution of 93 : 7 of 18 and 16 carbon atoms, and it was reacted using *monoclinic* zirconium oxide as catalyst in the 400 to 500 °C temperature range. The main product expected was the ketone with 35 carbon atoms ( $2n-1$ ), i.e. 18-pentatriacontanone ( $C_{35}H_{70}O$ ), together with smaller amounts of 16-tritriacontanone ( $C_{33}H_{66}O$ ) and 16-hentricontanone ( $C_{31}H_{62}O$ ). The corresponding alkanes have melting points in the range of 68 to 75 °C and boiling points from 458 to 490 °C.

When sunflower oil was reacted under these reaction conditions, conversion of the triglyceride was complete but the reaction was not selective and a complex product mixture was obtained. In a first approximation, the products obtained were grouped into three fractions by simulated distillation (Figure 1): gasoline, diesel and waxes. In Figure 1 it can be seen that the yield of waxes obtained was 43%, which is a fair yield but it was lower than expected. There is no clear temperature plateau in the target boiling point region from 450 to 500 °C which would indicate considerable amounts of the aimed ketones. With increasing temperature the wax fraction is reduced significantly from 43 to 26 and 11% yield for 400, 450 and 500 °C, respectively.

Figure 1. a) Simulated distillation curves of the liquid product obtained in the transformation of sunflower oil over zirconium oxide as catalyst at different reaction temperatures and b) Product yields for fractions of gasoline (light grey), diesel (medium grey) and waxes (dark grey). Conversion of sunflower oil was complete in all cases as confirmed by GC with on-column injection.

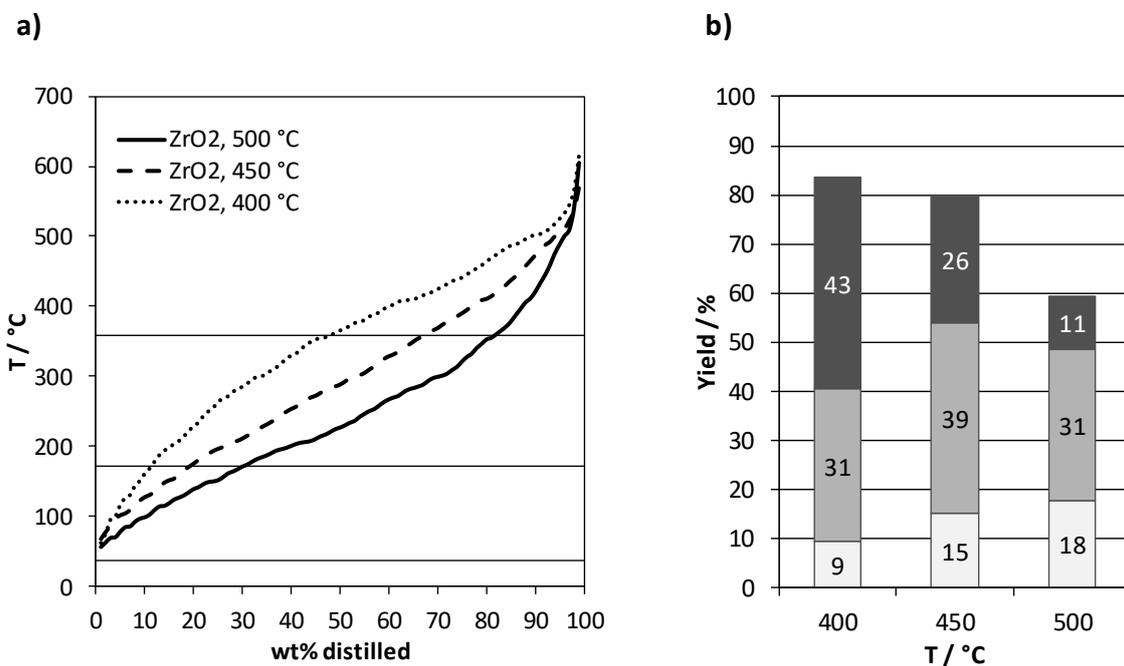
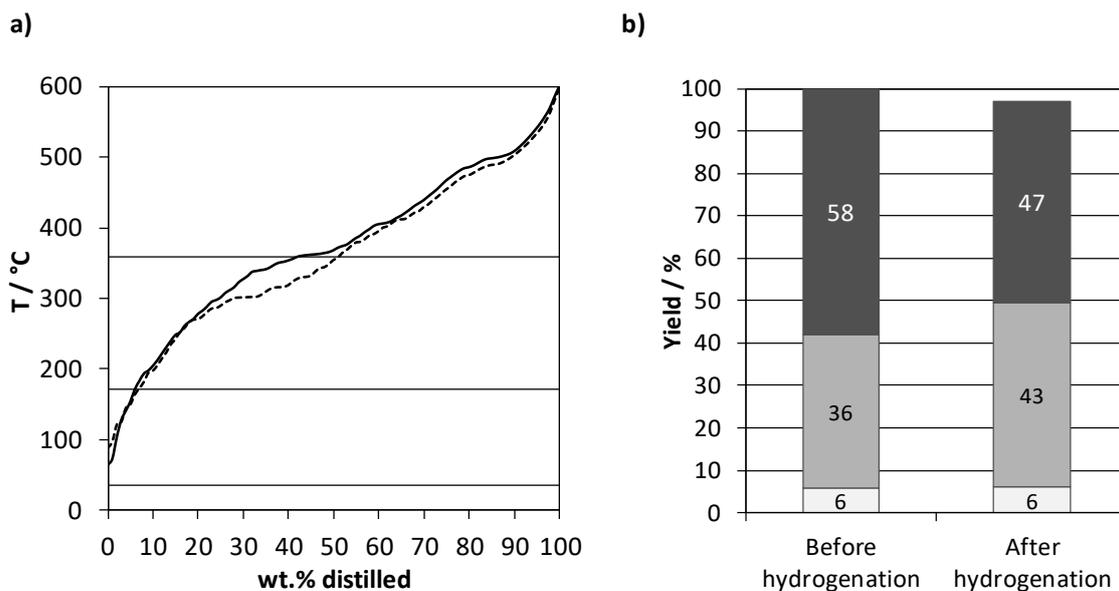


Figure 2. a) Simulated distillation curves of the joined product mixtures obtained when sunflower oil was passed over zirconium oxide (continuous line) and after hydrogenation of this mixture employing Pt/Al<sub>2</sub>O<sub>3</sub> as catalyst at 400 °C and 40 bar (dashed line; mass balance 97%); and b) Composition of the liquid when divided into gasoline (light grey), diesel (medium grey) and waxes (dark grey).



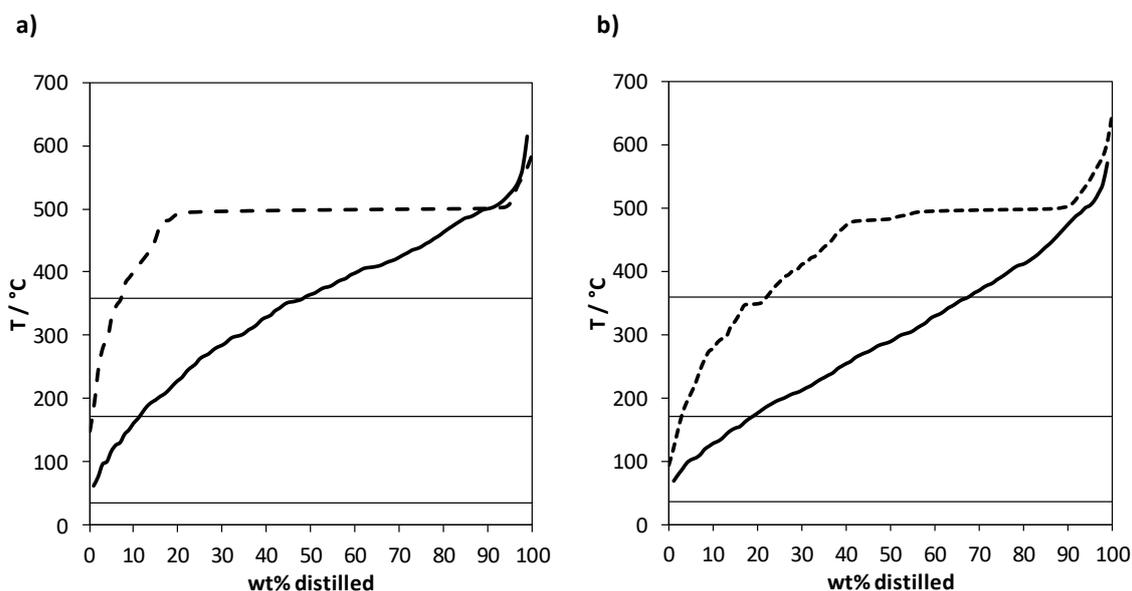
Fatty acid esters such as mono- or diglycerides are undesired products and their presence in the wax fraction should be excluded. These intermediates have to be considered as incompletely converted starting material rather than products since they still involve a short carbon chain of maximum 18 carbon atoms and are less stable than linear alkanes. Hence, we investigated the amount of oxygenated molecules remaining in the wax fraction by two-dimensional gas chromatography. The total content of the oxygenated molecules was estimated to be approximately 65 wt% of the liquid phase, but their nature could not be established unequivocally. Therefore, several crude product mixtures were joined and the resulting mixture was hydrodeoxygenated over Pt/Al<sub>2</sub>O<sub>3</sub> catalyst and the composition was compared before and after hydro-treatment. From Figure 2 it can be seen that the wax content decreased from 58 to 47% in the oxygen-free liquid product. This high wax content in the absence of ester functionalities is a clear indication of carbon-carbon bond formation during the treatment with ZrO<sub>2</sub> since hydro-treatment of triglycerides or fatty acid esters provide linear alkanes up to 17 carbon atoms which correspond to the diesel fraction (max. boiling point of 302 °C).<sup>33-36</sup> The liquid product was analyzed again by GCxGC (Table S2) which confirmed the absence of oxygenated compounds. The hydrogenated product mixture was composed mainly of alkanes (72.4 wt%), aromatic compounds with a single benzene ring (monoaromatics, 15.5 wt%), cycloalkanes (5%), bicyclic fused aromatics (3%) and other minority compounds (4.1%). Aromatic compounds could be produced by Diels-Alder reactions from unsaturated alkyl fragments, followed by dehydrogenation and aromatization.<sup>37</sup>

The hydrodeoxygenation experiment confirmed that ketonic decarboxylation occurred and the desired product was obtained as a major product fraction, but still, the relatively high diesel yield indicate that fragmentation reactions or other side reactions were also favored with the substrate. These reactions may be induced by the double bonds of the alkyl chain, or the glycerol part of the triglyceride since stearic acid can be converted into the corresponding ketone in the presence of magnesium oxide<sup>38</sup> or zirconium oxide<sup>23</sup> in approximately 90% yield. With the aim to identify the origin of the lower selectivity when using triglycerides instead of fatty acids as reactant, first, oleic acid, incorporating a double bond in the alkyl chain, was passed over the present system, i.e. a catalytic fixed bed charged with *monoclinic* zirconium oxide, at 400 and 450 °C. When this was done (Figure 3), it can be seen in the distillation curve that the expected temperature plateau for the corresponding C<sub>35</sub>-ketone was observed for the reaction at 400 °C. At 450 °C reaction temperature, the temperature plateau in the distillation curve was shortened

considerably but still almost 80% of the liquid product fell into the wax fraction. This result confirmed that the presence of double bonds in the alkyl chain was not the unique cause for the loss of selectivity to waxes when sunflower oil was processed, at least at 400 °C.

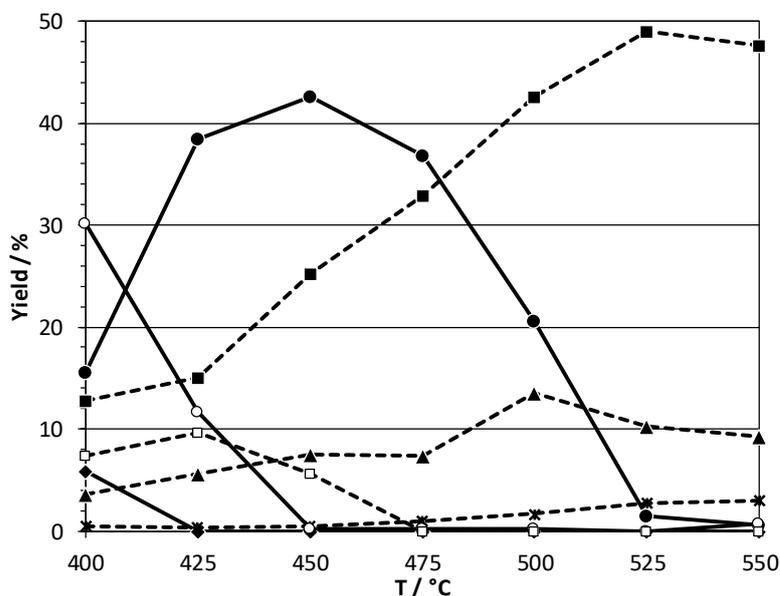
As a consequence, it can be stated that the fragmentation reaction should be induced by the alcohol part of the ester. With the aim to determine the reactions occurring under the present conditions, a simpler model compound was employed, namely methyl stearate, and the temperature range extended from 400 to 550 °C.

Figure 3. a) Simulated distillation curves of the product mixture obtained when sunflower oil (continuous line) and oleic acid (dashed line) were passed over zirconium oxide at a) 400 °C and b) 450 °C.



In Figure 4 the yield to different products, determined by GC, are depicted *versus* the reaction temperature. At the lowest temperature, i.e. at 400 °C, the conversion of the methyl ester was 94%, being that completely converted at higher temperatures. At 400 °C, the main product observed was the C<sub>35</sub> ketone (approx. 30% yield) which is obtained from the ketonic decarboxylation reaction. Increasing temperature, the yield of the C<sub>35</sub> ketone gradually decreased until it became zero at 450 °C. In this temperature range, C<sub>35</sub> hydrocarbons (mainly alkenes) were observed as the main product, with the maximum yield (> 40%) occurring at 450 °C. Raising above 500 °C the reaction temperature, the yield of the C<sub>35</sub> hydrocarbon fraction sharply decreased to almost zero (Figure 4).

Figure 4. Product yields for cracking/transformation of methyl stearate over zirconium oxide catalyst at different temperatures.  $\blacklozenge$  methyl stearate,  $\circ$   $C_{35}$ -ketone,  $\bullet$   $C_{35}$ -hydrocarbons,  $\blacktriangle$   $C_{21}$  –  $C_{34}$ -hydrocarbons,  $\blacksquare$   $C_{11}$  –  $C_{20}$ -hydrocarbons (diesel),  $*$   $\leq C_{10}$ -hydrocarbons (gasoline),  $\square$  oxygenated compounds. Reactions (5 mL of feed, 33 min reaction time) were carried out subsequently at each temperature without intermediate activation procedure, starting at the lowest temperature.



Plateaus were observed in the distillation temperature for the organic liquids produced at 450 and 500 °C (Figure S2). The boiling point of these plateaus (approx. 500 °C) is in accordance with  $C_{35}$  compounds which are the expected and desired products. For the product obtained at a reaction temperature of 550 °C, this plateau disappeared indicating further fragmentation of the  $C_{35}$  carbon chain. Interestingly, an important amount of olefins with 35 carbon atoms were formed that account for more than 40% yield at 450 °C (Figure 4).

The olefin should be produced from the corresponding ketone in a similar way as the formation of monoalkenes from methylketones which has been reported in the presence of activated alumina<sup>39–41</sup> and in presence of titania.<sup>42</sup> Probably, in these cases the ketone is reduced to the alcohol which then can be easily dehydrated. The double bond reducing agent has not been identified unambiguously but it has been proposed that different components of the product mixture contribute to the reduction.<sup>42</sup> In the present case the methanol might also act as reducing agent. Although hydrogen was used here as carrier gas, we have seen that hydrogen was not the principal reductant and the product composition did not alter significantly when changing the carrier gas from hydrogen to nitrogen.

Over the whole temperature range from 400 to 525 °C, formation of hydrocarbons with eleven to twenty carbon atoms, i.e. the diesel fraction, augmented when increasing reaction temperature. Although diesel has a lower economical value than waxes, commercialization of these compounds as biodiesel is straightforward since oxygen content was almost zero so that it can be used directly (or after a short standard hydro-treatment of the oil refinery) as drop-in fuel. It should be considered that the diesel obtained is mainly formed by linear (and slightly branched) alkanes with the corresponding high cetane number (Table S2).

#### *Carbon-carbon bond scission reactions*

The boiling point range of the products derived from methyl stearate was higher than from vegetable oil, when processed at the same temperature. For instance, at 450 °C 60% of waxes (Figure S2) was obtained starting with methyl stearate whereas the value decreased to 36% when starting with the vegetable oil (Figure 1). This indicated that the fragmentation reactions have to be studied at higher temperature in the case of the mono-ester since with this substrate the fragmentation reactions were induced most notably at higher temperature.

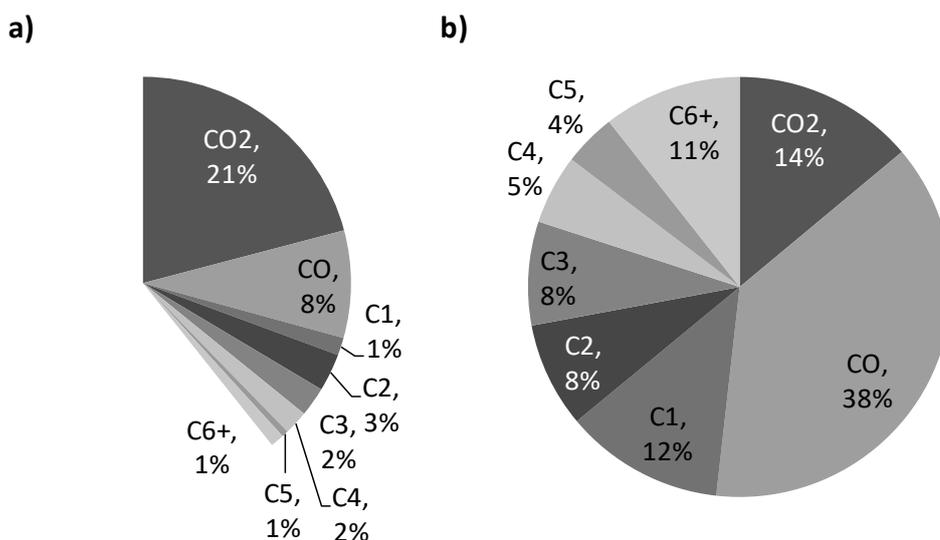
Interestingly, from the temperature curve of the simulated distillation of the liquid obtained at a reaction temperature of 550 °C it can be seen that the curve tags the different chain lengths of hydrocarbons throughout the whole range (Figure S2). From this it can be concluded that linear alkanes are the main products but without any predominant chain length, suggesting undifferentiated fragmentation of the carbon chain. As already explained above, the result for the reaction with the vegetable oil is similar to the one obtained with the methyl ester in the sense that no plateau was observed in the distillation curve (cf. Figure 1).

Apart from the liquid fraction, a gaseous effluent from the reactor was obtained. The yield was 17% for the transformation of the vegetable oil at 400 °C and 38% for methyl stearate at 550 °C. It can be seen that gas production was more than doubled for the reaction of the stearate at 550 °C (Figure 5). In both cases carbon dioxide was observed as a main product which is in accordance with the ketonic decarboxylation. A second gaseous product obtained in a significant amount is carbon monoxide. For the stearate case it almost triples the carbon dioxide yield (CO mass yield of 14.5%, 1.54 equiv.).

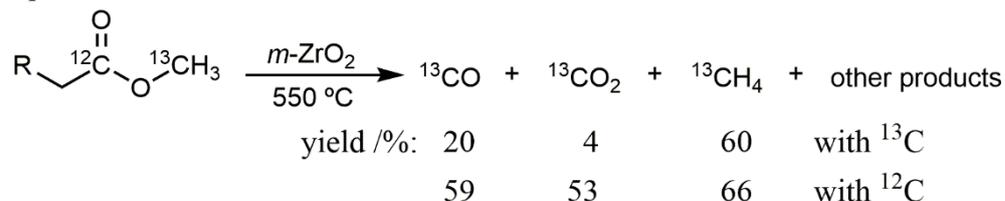
With the aim to clarify the mechanism by which degradation reactions occur, and to distinguish the products formed from the methoxy group and from the carbonyl group, an

isotopic labeling experiment was designed. Hence, isotopically labeled stearic acid methyl ester was prepared from stearoyl chloride and  $^{13}\text{C}$ -labelled methanol and reacted at  $550\text{ }^\circ\text{C}$ . With the isotopic labelled substrate, oxygenated products derived from the carbonyl group ( $^{12}\text{C}$ ) and from the methoxy group ( $^{13}\text{C}$ ) can be distinguished. From the product distribution (Scheme 1) it can be seen that the labelled carbon atom was involved at an important level within the permanent gases with one carbon atom, namely carbon monoxide (20%) and methane (60%), and a small amount of carbon dioxide (4%). In addition, the same products were observed in non-labelled form in 59%, 66% and 53%, respectively.

Figure 5. Output gas composition (wt%) for a) the transformation of sunflower oil over zirconium oxide catalyst at  $400\text{ }^\circ\text{C}$  (16.5% total yield; normalized to 38.3), and b) transformation of methyl stearate over zirconium oxide catalyst at  $550\text{ }^\circ\text{C}$  (38.3% total yield, normalized to 38.3%). Hydrogen, used as carrier gas, was excluded. Gas compositions at higher temperature are depicted in Figure S3 for sunflower oil.



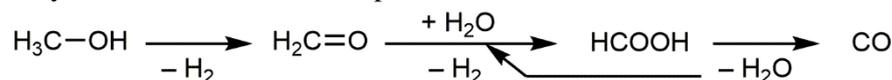
Scheme 1. Isotopically-labelled gaseous products obtained when transforming fatty acid methyl ester synthesized with  $^{13}\text{C}$  isotopically marked methanol. Yields stated with respect to one equivalent of the ester.



The formation of approximately 0.5 equiv. of un-labelled carbon dioxide was observed and this is in accordance with a quantitative formation of the ketone product which is observed as primary product at lower temperature. As a consequence, 0.5 equivalents of dimethyl ether has to be expected as third product (cf. Eq. 3). This ether, if actually desorbed as such, has to be formed on the surface by reaction of two methoxy species leaving behind a surface oxygen atom. Then, it can be concluded that labelled methanol adsorbed to the surface or desorbed labelled dimethyl ether are available for the formation of labelled methane and labelled carbon monoxide. Both transformations are straightforward and related literature examples can be found and are discussed below.

Olah et al. reported the formation of methane from dimethyl ether in 40% yield in the presence of tungsten oxide supported on alumina between 300 and 350 °C.<sup>43</sup> So, it is reasonable to suggest that the same occurs on zirconium oxide at elevated temperatures of 550 °C and which has been confirmed by our experimental results. In addition, methane formation has also been identified theoretically as one of the major decomposition pathways of methanol occurring over silica.<sup>44</sup> The competing mechanism in that theoretical study was the dehydrogenation of methanol to formaldehyde (Scheme 2). The dehydrogenation of methanol to formaldehyde is an endothermic reaction<sup>45</sup> and is known to occur in the presence of supported metal catalysts at lower temperature (< 400 °C).<sup>46</sup> Moreover, the dehydrogenation of a primary alcohol to an aldehyde has also been observed on zirconium oxide at 450 °C.<sup>47,48</sup> In a subsequent step, formaldehyde can be oxidized to formic acid consuming a water molecule (Scheme 2), in an analogous way as described for the oxidation of heptanal to heptanoic acid over the zirconium oxide catalyst at 450 °C.<sup>47</sup> The water molecule is recovered immediately by dehydration of formic acid to carbon monoxide. The latter is the anhydride of formic acid and was observed as a product, during the reaction of the ester and also when methanol was passed over the fresh catalyst at 550 °C (33 vol% CO, together with 2 equivalents of hydrogen, 63 vol%).

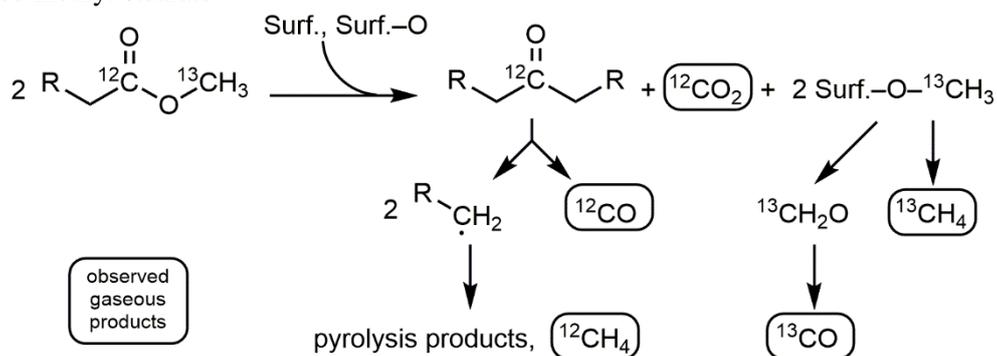
Scheme 2. Proposed conversion of methanol into carbon monoxide via dehydrogenation of methanol to formaldehyde, oxidation of the latter in the presence of water and subsequent dehydration of the formic acid product.



In this way, labelled methane and carbon monoxide can be formed from the labelled methanol part of the ester (Scheme 3). Apart from a small amount of labelled carbon

atoms in carbon dioxide (4%), the rest of labelled carbon could not be detected in the product mixture. It is assumed that due to the manifold olefin alkylation possibilities for the surface methoxy species, the non-quantified carbon is incorporated in various different products so that a clear detection with a statistical significance was not possible.

Scheme 3. Proposed formation pathways for labelled and un-labelled gaseous products from labelled methyl stearate.



Besides the labelled derivatives of carbon monoxide and methane, also the un-labelled forms of these products were detected (Scheme 1). Carbon monoxide formation can be explained by homogeneous bond splitting of the carbon-carbon bond in the ketone, between the carbonyl group and the adjacent methylene group (cf. Scheme 3). A similar behavior has been reported for cyclic ketones which achieve ring contraction by carbon monoxide removal.<sup>49,50</sup> Unlike the cyclic derivatives, the alkyl chains do not recombine but they undergo further free radical chain reactions. Under these conditions, also the formation of un-labelled methane can be assumed.

In summary, the experiment with the labelled substrate clearly demonstrates that the predominant fragmentation pathway was governed by a free radical mechanism. This was evidenced by formation of un-labelled carbon monoxide. Also in the transformation of vegetable oil carbon monoxide was observed as a product. This result also suggests a radical fragmentation of the ketone formed from the triglyceride, despite of the lower reaction temperature of 400 °C. This observation agrees with the results in the literature in where glycerol can be split into methanol and a C<sub>2</sub>-molecule over metal oxides at temperatures around 340 °C, involving a radical mechanism.<sup>51</sup>

## Conclusions

Sunflower oil has been considered as starting material for preparing vegetable waxes of the Candelilla type. Transformation of the oil over zirconium oxide at 400 °C yields a wax fraction in 43% yield.

When employing methyl stearate as starting material almost a 50% yield of linear C<sub>35</sub>-waxes was achieved. As by-product high quality diesel was obtained in more than 25% yield which has a high content of linear alkanes and is almost oxygen free.

A loss of selectivity, specially occurring at higher reaction temperature, is due to a radical mediated degradation mechanism. Thus, when starting from the triglyceride, the glycerol moiety might act as a radical initiator that can be responsible for lowering the yield of waxes. As a consequence, for industrial production of long-chain linear waxes the conversion of fatty acid mono-alcohol esters is preferred over the triglycerides (vegetable oil).

## Associated content

Supporting Information

The Supporting Information is available free of charge on the ACS Publication website at DOI:

XRD pattern of ZrO<sub>2</sub>, Simulated distillation curves and product yields, Gas compositions, Mass balances of liquids, and Product compositions obtained by GCxGC

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