

Perspective

# Oxidative Cleavage of Fatty Acid Derivatives for Monomer Synthesis

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**Abstract:** Oxidative cleavage of fatty acids and fatty acid derivatives is a practical way to obtain bifunctional molecules that can be used in polycondensation reactions. Diacids, hydroxyacids, and amino acids can then be used to produce polyesters or polyamides and also a large range of other products, such as lubricants and plasticizers. Ozonolysis has long been the sole industrial process for oxidative cleavage, but recently, routes using hydrogen peroxide as a clean oxidant have regained interest. Hydrogen peroxide is easier to use, but the kinetics of the catalyzed reactions are still slow. Although several catalytic systems have been described in the literature, tungsten-based catalysts are still the preferred choices. Different catalysts can trigger different mechanisms, such as a radical mechanism instead of a catalytic reaction. In addition, some side products and co-products often disregarded in the literature, such as shorted cleavage products, indicate the presence of side reactions that affect the quality of the final products. The oxidative cleavages in continuous and batch processes have significant differences, which are discussed with an illustration of our understanding of the process used by *Matrica S.p.A.*

**Keywords:** oxidative cleavage; fatty acid; diacid; hydrogen peroxide; catalyst; tungsten

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## 1. Introduction

### *Industrial Oils*

The advantages of industrial vegetable oils are linked to their physicochemical characteristics, which make them and their fatty acids' contents useful for industrial and other non-food applications. These characteristics are, for example, the chain length, the degree or nature of unsaturation, or the presence of special functional groups on the fatty acid chain. Known to be a valuable source of carbons with world-wide availability and relatively low prices (especially for edible oils), natural oils and fats are consumed by the oleochemical industry. The most common oils and fats are triacylglycerols (i.e., esters of glycerol with three fatty acids, which are specific for each source).

Free-fatty acids can be easily obtained by hydrolysis of triacylglycerols. As highly functionalized molecules, fatty acids are valuable renewable building blocks for the synthesis of monomers for specific polymer's properties. The double bonds of the triacylglycerols can be epoxidized or converted into hydroxyl groups. Epoxidized oils are used as secondary plasticizers, and the hydroxyl-rich oils are used, for example, for polyurethane. The two configurations of the double bond, *cis* or *trans*, lead to different properties (such as melting points), which might be important for the different applications. The *cis* fatty acids are the most common natural products but are also

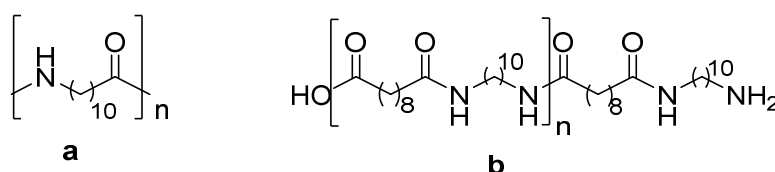
thermodynamically less stable than the *trans* fatty acids. Fatty acids are also classified as monounsaturated fatty acids (MUFAs) and polyunsaturated fatty acids (PUFAs). MUFAs are more appealing for the production of high-value monomers, because fewer co-products and by-products are produced (Table 1).

**Table 1.** Fatty acid composition of common edible and non-edible oils, extracted from and expressed as percentage mass-fraction of total fatty acids [1].

Oil	SFA				MUFA				PUFA		Others
	16:0	18:0	20:0	22:0	16:1	18:1	20:1	22:1	18:2	18:3	18:1-OH
$\Delta$					9	9	11	13	9, 12	9, 12, 15	9
Rapeseed	4	2				62			22	10	
Crambe	1.8–2.2	0.7				16.5–17.2	3.4–4.7	56.2–62.5	8.7–9.5	4.8–5.2	
Soybean	10	4	0.4	0.4		23	0.3		54	7.5	
Camelina	5.2–7.0	2.2–3.2				14.5–18.5	14.4–17.6	2.4–4.0	14.7–20.4	29.9–35.1	
Castor	1.0–2.0					4.0–9.0					85–90
Linseed	5.5	3.5				17			15	60	
Palm	40.1–47.5		<1.0	<0.6	<0.6	36–44			6.5–12	<0.5	
Stearin	48.4–73.8	3.9–5.6	0.3–0.6	>0.2	>0.2	15.6–36			3.2–9.8	0.1–0.6	
Safflower	4.8	1.3				75.3			14.2		

( $\Delta$ ) = position of the double bonds from the acid group.

The growing interest in the use of the fatty acids as monomer precursors is driven not only by their renewability, but also because of the polymer technical properties, which are strongly dependent on the carbon chain length [2]. Arkema (Colombes, France) is a world leader of bio-based polymer production, with several brands of polymers for different applications [3,4]. The polyamide Rilsan (PA 11) and Rilsan T (PA10.10) (Figure 1) are extraordinary examples of 100% bio-based polymers made from castor seed oil, respectively through thermal and alkaline cleavage chemistries.



**Figure 1.** Chemical structure of (a) polyamide 11 (Rilsan) [3] and (b) polyamide 10.10 (Rilsan T) [5].

The oxidative cleavage of the double bond of monounsaturated fatty acids can be considered to be a greener alternative to the process used industrially to produce these “specialty monomers”.

Valuable difunctional molecules that can be produced by oxidative cleavage of fatty acids and derivatives include Azelaic acid (DC9) and Brassylic acid (DC13). However, currently, these molecules have a limited market application. They have to compete with Sebacic acid (DC10) and Dodecanedioic acid (DC12), which are well established. DC10 is already bio-based and made from castor oil [6]. DC12 is commonly produced from fossil resources (from a butadiene derivative), but also by fermentation of parafins (by companies in China and formerly in Japan). Recently, the company Verdezyne was building a plant in Malaysia to produce DC12 by fermentation of Lauric acid (C12:0) ester, but due to a lack of financial resources, the production plan has been halted. DC10 and DC12 [7] already have market applications and would be relevant to produce. Unfortunately, there are no significant sources of fatty acids with a single double bond at the 10th or 12th carbon that would allow a direct oxidative cleavage to these relevant diacids. The other relevant monomers to produce would be the Aminoundecanoic acid (A11) and the Aminododecanoic acid (A12), because they would directly allow the production of polyamides 11 and 12, which are currently on the market. PA11 is produced by Arkema [4], while there are several producers, including Arkema, for PA12 [3]. In addition to these two polyamides, which have current applications, it is worth mentioning PA9, which was produced in the past under the name of Pelargon [8]. A11 is already bio-based and made from castor oil through a thermal cleavage process. For A12, there have been some attempts to make a monomer by fermentation by Evonik [9] and others. Although there are several options to produce

A9 from natural resources, the polymer is no longer on the market, and it would take a lot of time to reintroduce it. For PA11 and P12, there are routes through metathesis or hydroformylation, which have been investigated, and also through oxidative cleavage [10,11]. For example, the oxidative cleavage of the gondoic nitrile (C20:1, delta-11) leads to a nitrile acid intermediate that can be further hydrogenated. Similarly, the oxidative cleavage of the nitrile obtained from the 12-hydroxystearic acid (itself made by hydrogenation of ricinoleic acid C18:1, OH derived from castor oil) leads to nitrile acid intermediates with 11 and 12 carbons, which can be further hydrogenated into amino acids [12]. Because high purity monomers need to be obtained, the selectivity of the process is of the utmost importance. A good understanding of the reaction mechanism and process condition is necessary.

## 2. Oxidative Cleavage of Unsaturated Fatty Acids

High-value monomers can also be obtained by oxidative cleavage of the double bond of unsaturated fatty acids. Oxidative scission leads to bifunctional (e.g., diacids) and monofunctional (e.g., monoacid or aldehyde) compounds, which serve as intermediates. For example, the reductive ozonolysis of oleic acid/ester leads on one side to nonanal, which can be used in the perfume and fragrance industry, and on the other side, to a bifunctional aldehyde-acid/ester, which could be used in the polymer industry through reductive amination [12] or hydrogenation [13]. These can also be oxidized to the corresponding acids or hydrogenated to alcohols, leading to valuable starting materials for the synthesis of polymer plasticizers. The oxidation of 9-oxononanoic acid leads to azelaic acid (1,9-nonadioic acid), a precursor of plasticizers, lubricants, and polymers such as Polyamide-6,9 [14,15]. Respectively, nonanal can be oxidized to pelargonic acid (nonanoic acid), which is used as herbicide [16] or lubricant [14,15].

### 2.1. Ozonolysis

Oxidative cleavage of unsaturated fatty acids is mostly accomplished by ozonolysis. Oxidation of the olefins by ozone ( $O_3$ ) has been proposed as a clean and efficient reaction for use in the production of bio-based aldehydes (reductive ozonolysis) and acid monomers (oxidative ozonolysis). This oxidative cleavage process, the only operational process applied in the chemical industry (*P2 Science* [17], *Emery Oleochemicals* [18], and *Croda Sipo* [19]), presents some disadvantages, such as high-energy (high electricity) consumption and the need for a special technology for the production of ozone (ozone generator). The dilution of the ozone in the feed (1.5–2 wt.% ozone when air is the oxidant) also implies slow reaction kinetics [20]. However,  $O_2$  instead of air can be used, and ozone generators are common in the paper industry. As an alternative, oxidative cleavage using hydrogen peroxide has been studied since 1945 as a potentially cheaper substitute to ozone.

### 2.2. Hydrogen Peroxide

Hydrogen peroxide is a strong reducing and oxidizing agent usually used in bleaching. Discovered in 1818 by the French chemist Louis-Jacques Thenard, it is used for many applications such as chemical synthesis [21], textile treatment, and paper bleaching. The demand in the paper and pulp industry will lead to an estimated market in 2024 of US \$2.5 billion. Arkema is among the top three world producers of  $H_2O_2$ , with three different brands in the market, ALBONE®, PEROXAL® and VALSTERANE®, and with production plants in Asia, Europe, and North America [22]. This oxidant is also a natural metabolite of many organisms and is a clean oxidant, because its decomposition produces only  $O_2$  and  $H_2O$  [23]. The content of active oxygen depends on the concentration of  $H_2O_2$  (Table 2).

However, hydrogen peroxide decomposition is quite exothermic ( $\Delta H^\circ = -100.4$  kJ/mole), making it a hazardous reagent. The physical properties of  $H_2O_2$  change with the concentration, as do the associated risks; for example, the use of a highly concentrated aqueous solution (>70 wt.%) can generate serious hazards [24–26,27].

**Table 2.** Physical properties of different concentrations of hydrogen peroxide [22].

Property	70 wt.%	50 wt.%	35 wt.%
H <sub>2</sub> O <sub>2</sub> , g/L	902	597	395
Liters of O <sub>2</sub> at 0 °C/760 mm Hg released by liter of H <sub>2</sub> O <sub>2</sub> at 20 °C	298	197	130
Active O <sub>2</sub> content, %	32.8	23.5	16.4
Freezing point, °C	−55	−51	−32
Boiling point at 760 mm Hg, °C	119	114	108
Viscosity, centipoises at 25 °C	1.20	1.17	1.10

The fact that the water freezes and evaporates quicker than H<sub>2</sub>O<sub>2</sub> promotes the increase of the concentration of H<sub>2</sub>O<sub>2</sub> in a water solution. In this case, the lower the concentration of hydrogen peroxide transported, the lower the transportation hazards [28,29]. However, higher reactivities are achieved with higher concentrations of H<sub>2</sub>O<sub>2</sub>.

Hydrogen peroxide reacts well with organic compounds. This activation can occur by nucleophilic, electrophilic, radical activation or transition metal activation forming a metal-oxo complex or metal-peroxo complexes.

The application of this oxidant, to our knowledge, in the epoxidation of  $\alpha,\beta$  unsaturated acids, was initiated by Payne in 1958 [30].

### 2.3. Safety

#### **Attention! Concentrated H<sub>2</sub>O<sub>2</sub> is dangerous** [24–26]!

In addition to the environmentally-friendly nature of an agent, safety should always be taken into account. The decomposition of hydrogen peroxide, as mentioned above, releases heat. In concentrated solutions, the heat raises the temperature of the solution, accelerating the decomposition rate. Because of this, stabilizers are added during the manufacture of all the grades [22] to inhibit the catalytic decomposition effect of metals and other impurities that may accidentally contaminate the oxidant during shipment, storage, and handling. Still, no additive will prevent decomposition if excessive contamination occurs. In addition, at high H<sub>2</sub>O<sub>2</sub> concentrations, the mixture with organic compounds might cross the flammability limits. The safety procedures to consider are as follows:

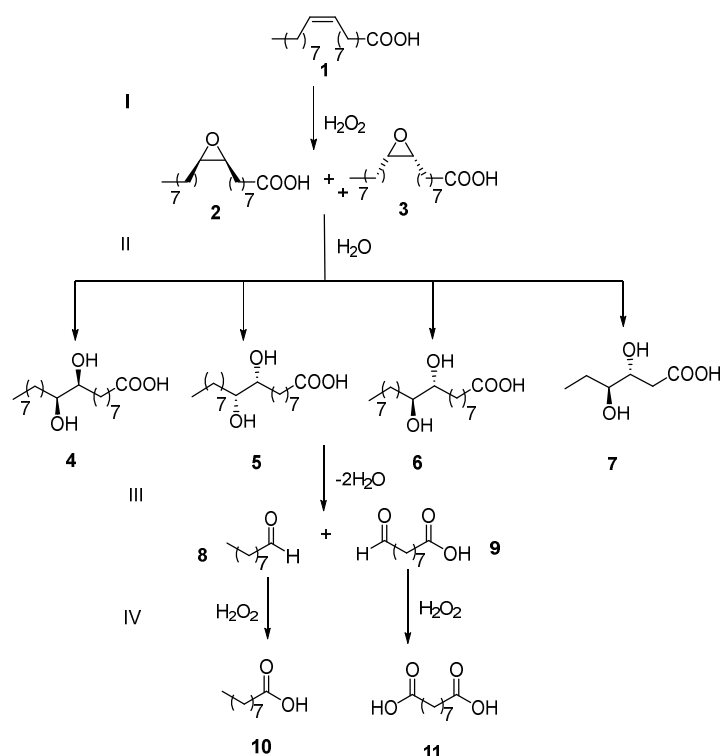
All containers with H<sub>2</sub>O<sub>2</sub> solution must be properly vented and properly stored away from sources of direct heat and combustible materials.

Adequate ventilation and a sufficient water supply should be provided for thorough flushing in case of an accidental leak on the property or spillage on the worker. In addition, H<sub>2</sub>O<sub>2</sub> is not considered an explosive. However, in contact with organic substances at significant concentrations and compounds containing catalysts such as silver, lead, copper, chromium, mercury, and iron oxide rust, rapid decomposition of the oxidant can occur, and an explosive pressure rupture of the containing vessel can occur if the vessel is not properly vented.

### 2.4. Reaction Mechanism

Historically, the use of H<sub>2</sub>O<sub>2</sub> in oxidative cleavage started with studies of hydroxylation of unsaturated fatty acids. The direct conversion of these to the corresponding  $\alpha,\beta$ -glycols was studied in 1949 by Mugdan and Young [31] from Distillers Company Ltd. (Great Burgh, Epsom, Surrey, UK), where they found that pertungstic acid catalyzes the addition of 2 OH in the *R,S* and *S,R* position. The reaction is facilitated by increasing the nucleophilic character of the double bond involving, in the case of oleic acid, the formation of an epoxide specie as the first intermediate. This reaction is considered by Swern [32] to be an ionic addition reaction, followed by epoxide ring fission because of the nucleophilic attack of the OH group on one electrophilic carbon atom, known as Walden inversion [33]. As a result, the isomers *R,S* and *S,R*-diols are formed. Contrary to Mugdan, some authors [34–36] have claimed that the first step of the reaction with this kind of catalyst is non-stereoselective, yielding in the first step (I) the epoxide (2 and 3) and giving place to the racemic mixtures of *syn* diols (4 and 5) or *anti*-diols (6 and 7) via non-enantioselective hydrolytic cleavage (II). To achieve oxidative cleavage, the reaction should proceed by the cleavage of the C–C bond releasing

water (III), with the formation of the corresponding aldehydes (8 and 9) and further oxidation to yield carboxylic acids (IV) (Figure 2).



**Figure 2.** Oxidative cleavage intermediate steps with hydrogen peroxide and tungstic acid.

## 2.5. Catalyst

Many catalysts have been applied to this type of reaction [37–40]. For example, a niobium oxide catalyst has been recently used in the oxidative cleavage of methyl linoleate to obtain aldehydes as a major product. The reaction occurred through a radical mechanism with the initial formation of hydroperoxyl radicals ( $\text{HOO}\cdot$ ), formed by the interaction between  $\text{Nb(V)}$  and  $\text{H}_2\text{O}_2$ . A conjugated hydroperoxide radical was formed, reacting consequently with the molecular oxygen formed by the  $\text{H}_2\text{O}_2$  decomposition in the presence of niobium. The reaction proceeded through a Hock-type rearrangement with water elimination and the formation of protonated hemiacetals, which fragment to form aldehydes compounds. This radical-type mechanism, followed by isomerization and hydroperoxide formation, was proposed due to the fact that, in tests pursued with methyl oleate and methyl linoleate, only the latter provided a significant quantity of aldehydes (40 mol%) [37].

Tungsten-based catalysts are the most common preference in studies of oxidative cleavage with  $\text{H}_2\text{O}_2$  [41–43].

### 2.5.1. Tungsten-Based Catalysts

Tungsten, as a mineral, was first mentioned in the scientific literature in 1574, under the name Wolfram. It is recovered from nature as trioxide  $\text{WO}_3$  (anhydrous) or  $\text{WO}_3 \cdot n\text{H}_2\text{O}$  (hydrate), and it exhibits very strong Bronsted acid sites [44,45]. The relatively low point of zero charge (PZC) complies with its high surface acidity. The oxidation states of tungsten from  $-2$  to  $+6$  lead to several W species that are applied to different reactions, such as tungsten carbide in the hydrogenation of olefins [46], tungsten sulfide (as NiWS) in hydrotreatment/hydrodenitrogenation [47], and tungsten oxide in acid catalyzed reactions, such as glycerol dehydration to acrolein [48].

Based on the experiments of Swern work [32], Luong T. and coworkers [49] reported a new method of preparation of the  $\alpha,\beta$ -glycols by means of a hydrogen peroxide-tungstic acid system at  $\text{pH} = 0\text{--}1$ . However, they reported that with the addition of  $\text{H}_2\text{O}_2$  at concentrations below 70 wt.% at

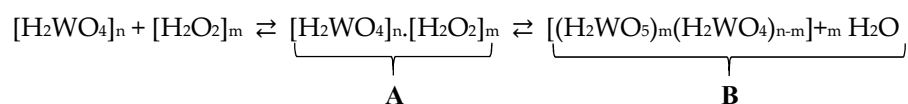
55 °C, the reaction kinetics were extremely low, followed by a high exothermic and uncontrollable reaction. The main reaction occurring was the decomposition of H<sub>2</sub>O<sub>2</sub>.

They assumed that tungstic acid requires a period of pre-conditioning with aqueous hydrogen peroxide before it can act as a catalyst. The solution of H<sub>2</sub>O<sub>2</sub> and tungstic acid was stirred at room temperature for 20 min. This can be explained by the fact that in presence of H<sub>2</sub>O<sub>2</sub>, tungstic acid is oxidized to pertungstic acid, the active intermediate specie to the oxidation process. The work done by Sapunov and Lebedev showed the kinetics and the catalytic mechanism of olefin epoxidation with H<sub>2</sub>O<sub>2</sub> in the presence of tungsten salts [50]. They demonstrated that the peroxotungstate defines the epoxidation rate. The catalytic specie would be the anion HWO<sub>5</sub><sup>-</sup>. The rapid decomposition of H<sub>2</sub>O<sub>2</sub> neutralized the active tungsten anion, and its activity was substantially reduced.

Luong T. and coworkers' hypothesis was that a reaction product was formed, altering the characteristics of the emulsion, facilitating the interaction between oleic acid, hydrogen peroxide, and catalyst. If tungstic acid is omitted from the reaction media, no oxidation occurs because the decomposition of H<sub>2</sub>O<sub>2</sub> is faster than the reaction itself. They favored the option of pre-conditioning with hydrogen peroxide–tungstic acid for 5 h before a 19 h reaction at 55 °C, probably leading to the formation of pertungstic acid.

The first intermediate detected from oleic acid was the 9,10-epoxystearic acid (EpSA), with consecutive conversion to *threo*-9,10-dihydroxystearic acid (DHSA). In those studies, it was observed that the rate of oxidation did not accelerate until some accumulation of the DHSA had occurred. The researchers found that this specie probably acted as a phase transfer agent in the oleic acid oxidation. This statement was proven by dissolving 2 wt.% *threo*-DHSA in oleic acid and conducting the oxidation at 55 °C. Nevertheless, as the oxidation proceeded, the system became pasty and hardened. With the addition of 2.5 mL of water to the solution, they achieved, for the first time, small quantities of cleavage product [49]. On our side, we confirmed these observations: when the conditions are appropriate to avoid the accumulation of the DHSA as a pasty/solid material, cleavage products are produced [51].

With respect to pre-conditioning with hydrogen peroxide and tungstic acid, a complex (A) is formed between the hydrogen peroxide and tungstic acid, proceeding with an oxygen transfer to form a polyperoxytungstic acid (B), as follows:



Two different mechanisms were proposed: (1) When pre-conditioning is not employed, DHSA acid is observed, a complex is formed, and the hydroxyl species facilitates the transfer of oxygen from H<sub>2</sub>O<sub>2</sub> to the tungsten catalyst and to the double bond through B complex; (2) When pre-conditioning is used and hydroxyl intermediate is absent, B is formed as the primary oxidant. After starting the oxidation reaction, some diol intermediate species are formed, and the oxidation proceeds via complex A giving B, while the reaction kinetics were favored with pre-conditioning and DHSA present at the beginning of the reaction. Tungstic acid is not well dissolved in H<sub>2</sub>O<sub>2</sub>, and this is consistent with our own observations.

### 2.5.2. Peroxo-Tungstate Complexes in Oxidative Cleavage of Unsaturated Fatty Acids

Metal catalyzed oxidations with hydrogen peroxide can be conveniently divided into two categories, involving peroxometal and oxometal species as the active oxidant [52].

MacKenzie et al. [53] applied, for the first time, a system comprising cobalt salt instead of tungsten and a portion of DHSA (between 1 mol% and 3 mol%), using propanol as a solvent. The use of cobalt salts, such as cobalt acetate or naphthenate, was guided by the high catalytic activity that remained for long periods of time using oxygen as an oxidant, but also certainly by the lower oxidant cost.

This method is also described by De Vries and Schors [54]. They were able to oxidize  $\alpha,\beta$ -vicinal diols to the corresponding acids, with a combination of H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub>, using cobalt as a catalyst.

### 2.5.3. W/Co System

In 1974, *Procter & Gamble* released two patents [55,56], in which the oxidative cleavage of vicinal diols was achieved using a combination of tungstic acid and cobalt in the presence of a polar aprotic (dimethylacetamide) solvent and oxygen. They prepared a solution of 70 wt.%  $\text{H}_2\text{O}_2$  and tungstic acid, which was stirred for 3 h at 35–50 °C and left overnight (the solution passed from yellow to a cloudy-white or gray color). To this, was added, at the beginning of the reaction, a small amount of DHSA, dimethylacetamide, and cobalt. Oxygen was used as a co-oxidant, and the slurry of tungstic acid and hydrogen peroxide was added drop-wise over 4 h. The reaction temperature rose to a maximum of 100 °C.

Following this principle, E. Santacesaria et al. [57,58] proposed a reaction in two consecutive steps. The first step is comprised by the reaction between the oleic acid with 60 wt.%  $\text{H}_2\text{O}_2$ , in the presence of tungstic acid to form the  $\alpha,\beta$ -diol species. The second step corresponds to the oxidative cleavage with molecular oxygen, under pressure, of the  $\alpha,\beta$ -diol species, in the presence of the in situ-formed catalyst, obtained by the reaction between the remaining tungsten catalyst of the first step and the metastable form of cobalt acetate added before the beginning of the second step. The reaction was performed with addition of oxygen, under moderate pressure in autoclave, giving place, therefore, to a triphasic system, gas–liquid–liquid.

In the second step of the reaction, in the presence of  $\text{O}_2$  (absence of  $\text{H}_2\text{O}_2$ ), the tungstic acid was not active without the addition of cobalt acetate, and cobalt acetate was not active alone (note that in this case, there is not enough  $\text{H}_2\text{O}_2$  to continue the oxidation and that the sole source of the oxidant is  $\text{O}_2$ , which then must interact with the Co moiety). According to the authors, by mixing both, a new catalytic species was then formed, but which is still not clearly defined.

Cobalt ions can also act as a templating agent for the formation of polyoxometalate (POM) with a well-defined structure, such as Keggin, Dawson, or Anderson structures. Anderson structures are easily formed by reacting molybdate, cobalt, and hydrogen peroxide. However, these results are much less known with respect to tungsten [59].

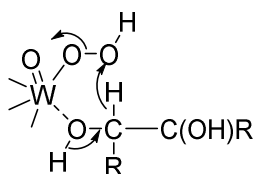
Santacesaria argued that the activity of this complex catalyst was not due to the original well-structured polyoxometalates (POMs) formed but due to lacunary POMs successively formed, in which the cobalt atoms are directly accessible to the reagent, and so, the tungsten atoms have the capacity to activate the cobalt catalyst. Two different mechanisms were proposed: (1) direct C–C bond cleavage with the formation of an aldehyde group as the intermediate with consequent oxidation to acids; and (2) formation of W-hydroxy ketone by the initial oxidation of the OH group and successive oxidation to acid. The second proposal was supported by the detection of hydroxyketone specie by GC-MS. This process has been developed by the bioplastic firm *Novamont S.p.A.* [57,58,60,61] and is now produced by their joint venture *Matrica*.

### 2.5.4. W/P System

Heteropoly-acids and anions are those that contain one or two atoms of another element in addition to tungsten, oxygen, and hydrogen. They consist of combinations of octahedral  $\text{WO}_6$  groups, so that the conversion of  $\text{WO}_4^{2-}$  into polyanions requires an increase in coordination number. The polymerization of its oxo-ions metal constitution can be related to the metal and oxygen orbitals' abilities to overlap, giving a strong  $\pi$  bonding ( $\text{M}=\text{O}$ ). Cotton and Wilkinson [62] state that tungstic acid is polymeric  $(\text{H}_2\text{WO}_4)_n$ . The lower the pH employed, the higher the aggregation expected. This statement was proved by X-ray patterns.

Venturello et al. reported the importance of aqueous hydrogen peroxide in conjunction with catalytic amounts of tungstate and phosphate ions under acidic conditions.

The reaction proceeds via an initial C–H bond fission of the  $\alpha,\beta$ -diol unit to form  $\alpha$ -hydroxy ketone followed by oxidative cleavage of the latter yielding aldehydes with further oxidation to obtain carboxylic acids. They supposed that this intermediate probably arises from the decomposition of an adduct formed by the interaction of the diol with the anionic tungsten-peroxo species present in the acid solution [63] (Figure 3).



**Figure 3.** Complex formed between the anionic tungsten peroxo specie and the diol intermediate.

### 2.5.5. Induction Time/Mass Transfer Concerns

In 2011, *Novamont* described in its patent that the oxidative cleavage reaction mechanism of the vicinal diols with oxygen is of a radical type due to the observed reaction acceleration. From their point of view, the reaction showed an induction time in which the hydroxyl radicals started propagating exponentially and in an uncontrolled manner, leading to a lack of selectivity, with the formation of by-products of different chain length [64].

The activity of organometallic complexes of W has been found to be limited to homogeneous catalysts in a medium containing  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$ , catalyst, olefin, and the organic solvent. The olefins are in general insoluble in an aqueous phase. The best cleavage results were obtained at concentration of 70 wt.%  $\text{H}_2\text{O}_2$ . Low concentration oxidant solution led to a slow reaction, low productivity of the oxidized products, low conversions, and selectivity due to the limited solubility of  $\text{H}_2\text{O}_2$  in the homogeneous solvent/olefin/catalyst system.

Aqueous hydrogen peroxide is rapidly decomposed by catalytic metal compounds, reducing the ability of the peroxide to proceed with the oxidation reaction. To avoid faster decomposition, *tert*-butanol can be added, but it can also form *tert*-butyl hydroperoxide. The need for a long induction time, described by Venturello, suggests the requirement of the use of a new active catalyst, phase transfer catalyst (PTC), to not only solve the dissolution problem but also to stabilize  $\text{H}_2\text{O}_2$  against decomposition [65,66].

### 2.5.6. Phase Transfer Agent System

MacKenzie [53] did optimize the oxidation of internal olefins. However, in his studies, he noticed that by adding small amounts (1–3 mol%) of the intermediate product of the reaction (DHSA), the kinetics of the reaction were improved. Following this studies, Edmund Pultinas et al. [56] also found that the fastest rates were obtained with pre-conditioning ( $\text{H}_2\text{O}_2$  and catalyst) and with hydroxyl intermediate present at the beginning of the reaction, confirming that the hydroxyl intermediate could be acting as a phase transfer agent.

The function of hydroxyl species in accelerating the reactions could also be that of a surfactant or a complexing agent for the polyperoxy acid acting as a phase transfer catalyst (PTC) allowing higher surface contact between the aqueous phase ( $\text{H}_2\text{O}_2$  + catalyst) and the organic phase (internal olefin).

### Onium Salts

According to Bortolini [67], in the presence of hydrogen peroxide, tungstic acids are transformed in the corresponding peroxo-derivatives. In a protic medium, these derivatives are partially dissociated according to the acid–base equilibrium. Neutral and anionic species have different oxidizing characteristics. The former is suitable for oxidizing systems rich in electrons, such as olefins, transforming them into epoxides and into the hydrolysis product thereof: vicinal diols.

The company *Continental Oil* [66,68] claimed, for the first time, the application of quaternary salts in a heterogeneous system.

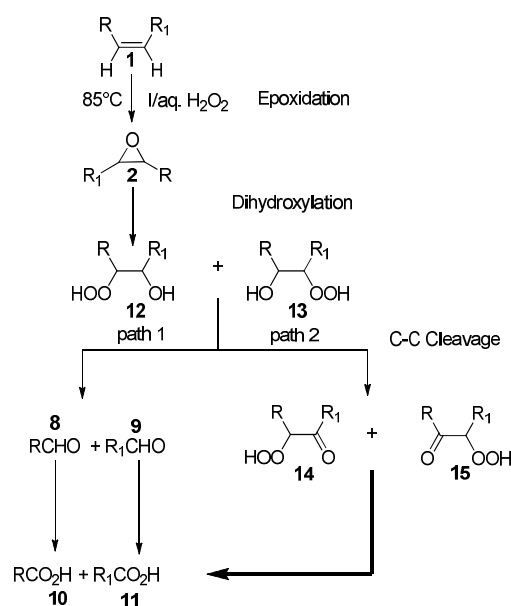
The Italian company *Montedison S.p.A* [69,70], through extensive studies made by Venturello et al. [63,65,71], claims a new method based on a system where the catalytic specie was an onium salt of hetero-pertungstic acid, prepared *ex situ* and confirmed by X-Ray crystallography (catalyst I:  $\text{Q}_3\{\text{XO}_4[\text{W}(\text{O})(\text{O}_2)_2]_4\}$ , where X represents P or As atoms). Q represents the cation of a quaternary



onium salt with the formula  $n(\text{C}_6\text{H}_{17})_3\text{NCH}_3^+$ . This structure shows 2 peroxy species per tungsten atom, present at the solid state [71].

The reaction is conducted in a biphasic aqueous/organic system, in which the organic phase is constituted by the catalyst I and the olefin and the aqueous phase is comprised of  $\text{H}_2\text{O}_2$  and water.

Given the lipophilic character of the catalyst and its epoxidizing ability, the epoxidation of the alkene is regarded as the initial stage of the reaction (**epoxidation**, Figure 4). By this, the reaction is believed to involve the formation of a  $\beta$ -hydroxyperoxide alcohol intermediate (**12** and **13**) upon acid hydrolysis (Figure 4) of the epoxide formed from the olefin oxidation, opposite to the  $\alpha,\beta$ -diol formation shown in Figure 2.



**Figure 4.** Proposed mechanism adapted from the study by Venturello et al. [67].

This  $\beta$ -hydroxyperoxide alcohol is then oxidized into  $\alpha$ -hydroxyperoxide ketone (**14**, **15**), which undergoes C–C bond fission by hydrogen peroxide, leading to the mono- and di-acids. This pathway is denominated as “perhydrolytic” (**path 2**) instead of a hydrolytic pathway (**path 1**) due to the increase of the stability of the epoxide with an increase of the carbon number. However, **path 1** can also explain the appearance of shorter carboxylic acids obtained at the end of the reaction. This can be due to an over-oxidation of the first products of the oxidative cleavage, the aldehydes **8** and **9**. Once the heteropolymetalate catalyst is put in contact with water in the biphasic system, enough acidity is generated (by phosphotungstic moieties).

Nevertheless, this catalyst I is important to the epoxide opening by hydrogen peroxide/water, mainly as a Bronsted acid, through the acidic species coming from its partial hydrolytic degradation. Venturello et al. alleged that the major route for the two phases of oxidation passed through a perhydrolytic pathway, **path 2** (Figure 4).

Godard et al., based on these studies, later proposed a non-stereospecific oxidative cleavage process with the formation of an in situ catalytic species composed of a peroxy-tungsten complex  $\text{Q}_3\{\text{PO}_2[\text{WO}(\text{O}_2)_2]_4\}$  as a phase transfer catalyst (PTC) and a co-oxidant in solvent-free conditions. Due to its lipophilic nature, the pyridinium ion can efficiently transfer the peroxy anion from the aqueous phase to the organic phase [72].

The stoichiometry of the oxidative cleavage requires 4 molar equivalents of hydrogen peroxide, to achieve carboxylic acids, whereas oleic acid generates only 1 molar equivalent of azelaic acid. *DSM* [73] and *Arkema* [74] proposed that the production of azelaic acid can be higher if the starting material is 9-octadecenedioic acid (i.e., a symmetric unsaturated diacid (or derivative)), because this generates 2 molar equivalents of azelaic acid for the same amount of hydrogen peroxide and no side products, thereby contributing to the reduction of the production cost.

In 1993, *Novaol* patented a method of oxidative cleavage, using a solely ionic phase transfer agent dimethyldioctadecylammonium chloride (Arquad 2HT) [61] in organic solvent-free conditions. The reaction is performed between 100–104 °C for 6h, and the yields obtained for pelargonic and monomethyl azelate from methyl oleate are 80 mol% and 77 mol%, respectively. The co-products are not disclosed.

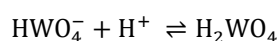
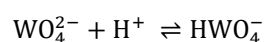
### 3. Reaction Conditions

#### *pH*

The ring opening of epoxy-alkanes fails when carried out in the presence of neutral aqueous hydrogen peroxide only [65,71].

The pH meter readings in an aqueous solution of hydrogen peroxide are lower than the real pH, and the difference increases with the increasing addition of H<sub>2</sub>O<sub>2</sub>. Such behavior has been linked, by thermodynamic calculations, to the difference in the free energy of solvation of the proton in water and pure H<sub>2</sub>O<sub>2</sub> (about 9 kcal/mole). It was proven that the proton is more firmly bounded to the water. Due to the interaction with the H<sub>2</sub>O<sub>2</sub> molecules, the apparent acidity of the water is increased. The extension of such phenomenon varies with the concentration of H<sub>2</sub>O<sub>2</sub> in the aqueous medium [75].

The efficiency of the oxidation depends on the pH of the reaction. The best results were obtained at pH = 3 [36,71,72]. In the Beg and Ahmad [50] kinetic studies with tungsten salt, it was shown that in acid medium an oxyanion is formed as follows:



It was proven that the [HWO<sub>4</sub><sup>-</sup>] is at its maximum at pH = 4.7 but decreases rapidly thereafter. The results of their work demonstrated an intramolecular, concerted mechanism. Despite the lower acidity of the medium, salts of tungstic acid (e.g., Na<sub>2</sub>WO<sub>4</sub>) intensify epoxidation due to their high stability in water. In this mechanism, the electrophilic attack on the olefin double bond happens by intramolecular hydrogen bond and the presence of a partial positive charge at peroxide oxygen atom (Figure 5).

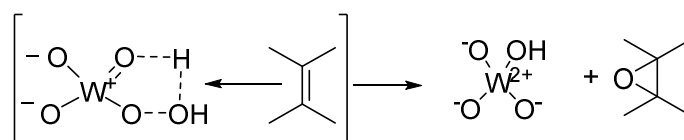


Figure 5. Epoxidation of the C=C bond mechanism.

### 4. Purification Methodology

In *Emery's* process, to isolate the desired mono- and di-carboxylic acid, after the ozonolysis reaction, the solution is distilled to provide a first distillate comprising C<sub>2</sub> to C<sub>22</sub> carboxylic acids. The residue is distilled again to isolate the dicarboxylic acids. To separate the azelaic acid from the impure acids, liquid-liquid extraction is applied: hot water (between 79–110 °C) and a water-immiscible organic aliphatic solvent (such as pentane, octane, cyclohexane, etc.) are used. The impure acids (by-products) that are not soluble in water remain in the organic phase and are decanted. Azelaic acid, as well as shorter carbon chains (C<sub>4</sub> and C<sub>8</sub>) diacids, move to the aqueous phase, while the organic phase retains the monocarboxylic by-products from C<sub>9</sub> to C<sub>22</sub>. To separate lower chain diacids (C<sub>4</sub> to C<sub>8</sub>) from the longer chain diacids (C<sub>9</sub> or more) crystallization is applied, lowering the temperature of the water with different cooling stages from 60 °C to 41 °C, followed by 38 °C, and finally 18 °C. The shorter chain di-acids are retained in the mother liquid and removed by filtration. The crystallized azelaic acid-rich stream is then melted and transferred into a distillation unit to separate azelaic acid from higher length diacids. The purified azelaic acid is converted into flakes by cooling below its melting point and then is stored [76].

The *Novamont* process differs from the one patented by *Emery Oleochemicals*. After the reaction, the organic phase contains saturated mono acids and the derivatives of saturated carboxylic acids with more than one acid function (diacids), as well as the derivatives of the fatty acids present in the starting mixture, such as methyl linoleate, methyl stearate and methyl palmitate, and the  $\alpha,\beta$ -diol. The oily phase is dried, degassed, and transferred into a distillation column allowing the separation of monocarboxylic acid containing the lighter monocarboxylic acids (pelargonic and octanoic acid as main components) from the monomethyl azelate, methyl palmitate, methyl stearate, and esters of methyl dihydroxy stearate that were withdrawn from the bottom of the distillation column. This organic phase is then continuously fed into an emulsifier. The emulsion is hydrolyzed by feeding it into three consecutive columns filled with acidic ion exchange resin and heated at 100 °C for 6 h. Then, 4.3 kg of azelaic acid are recovered from the 8.5 kg of carboxylic acids obtained in the bottom of the column [64].

## 5. By-/Co-Products Formation

Most of the academic or patent publications do not disclose the side-products of the oxidative cleavage. However, it is quite common to obtain products with a lower number of carbons than expected, such as octanoic acid in addition to pelargonic acid and 8 carbons diacid in addition to azelaic acid, as well as some heavier products. In many cases, the carbon balance is not 100%, and it is not uncommon that less than 80% of the products are identified.

The difunctionalized compounds used in the polymerization process should have high purity, because even a small number of impurities will negatively influence the polymer properties, such as the molecular weight (with monofunctional molecules), color (if contamination with catalysts/metals), and crystallinity (with monomers of other chain lengths).

These impurities or co-products/by-products are the results of side-reactions governed by the process. The impurities reflect the difficulty of achieving high  $C_9$ -monomers yield in the oxidative cleavage of oleic acid.

Several hypotheses are proposed to explain the formation of these shorter acids/diacids.

### 5.1. Starting Material Purity

Most of the oleic acid used industrially has a maximum purity of 80%. It also contains some other MUFAs and PUFAs and saturated fatty acids.

At the end of the oxidative cleavage reaction, the saturated acids should remain in the reaction medium and may pose some separation issues due to similar boiling points of long-chain saturated acids and short-chain diacids, for example. On the other hand, all unsaturated fatty acids should have been oxidized/reacted during the process.

The low purity of oleic acid (presence of other unsaturated acids) can explain the different yields in oxidative cleavage products. Similarly, the production of hexanoic acid can be explained by the presence of linoleic acid along with the oleic acid (Figure 6) [23,74,77].

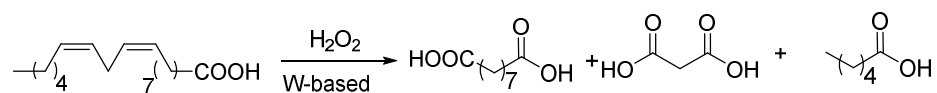


Figure 6. Oxidative cleavage of linoleic acid.

### 5.2. Intermediate Influence

#### 9,10-dihydroxystearic acid (DHSA)

As described above, the addition of the diol intermediate in small quantities, at the beginning of the reaction, can be a way to accelerate the oxidative cleavage of unsaturated fatty acids. Nevertheless, this method can lead to more by-product formation, such as esters and acetals [51]. Some studies describe that from the start of the reaction, a certain amount of cleavage products has already been produced. In the acid medium, the diol intermediate dubbed by Catia Bastioli et al. [78]

as the “reaction foot”, can react with the acids (or aldehydes as observed in our case), already formed, producing esters (or acetals) species.

In his extensive studies [63,65,69], Venturello et al. found a small amount of products with one carbon less than expected (2–5 wt.%). They stated that this arises from the cleavage of  $\alpha$ -hydroxy aldehyde formed by the C–H bond fission of the less reactive primary alcohol function of the starting diol. There has been speculation that these shorter acids could have been produced by the isomerization (shift) of the C=C bond in oleic acid and then the cleavage. However, that should lead to longer chains in the co-products. Because only shorter chains have been observed, the isomerization hypothesis can be ruled out. The ozonolysis of the starting materials, done in *Arkema*, also confirmed that the isomerization hypothesis was not relevant. Instead, the chain reduction of the cleavage products and intermediates is more probable.

### 5.3. Shorter Chain Products—Decarboxylation

In processes where no phase transfer catalyst was added, the same products with one fewer carbon [22,69] were quantified at the end of the process. Similarly in a two-step system, W/H<sub>2</sub>O<sub>2</sub> followed by Co/O<sub>2</sub>, shorter products were quantified [60,64,77]. The mechanism must then involve a decarboxylation of either the shorter acid/diacid or of the intermediate aldehyde compounds.

### 5.4. Isomerization

Another hypothesis of the by-product’s origin is the shift of the C=C double bond from the 9–10 position to the position 10–11, for example. However, it should be disregarded as in case of oleic acid; although octanoic acid was obtained, sebacic acid (DC10) was never described in the literature nor observed in our experiments.

### 5.5. Our Observations

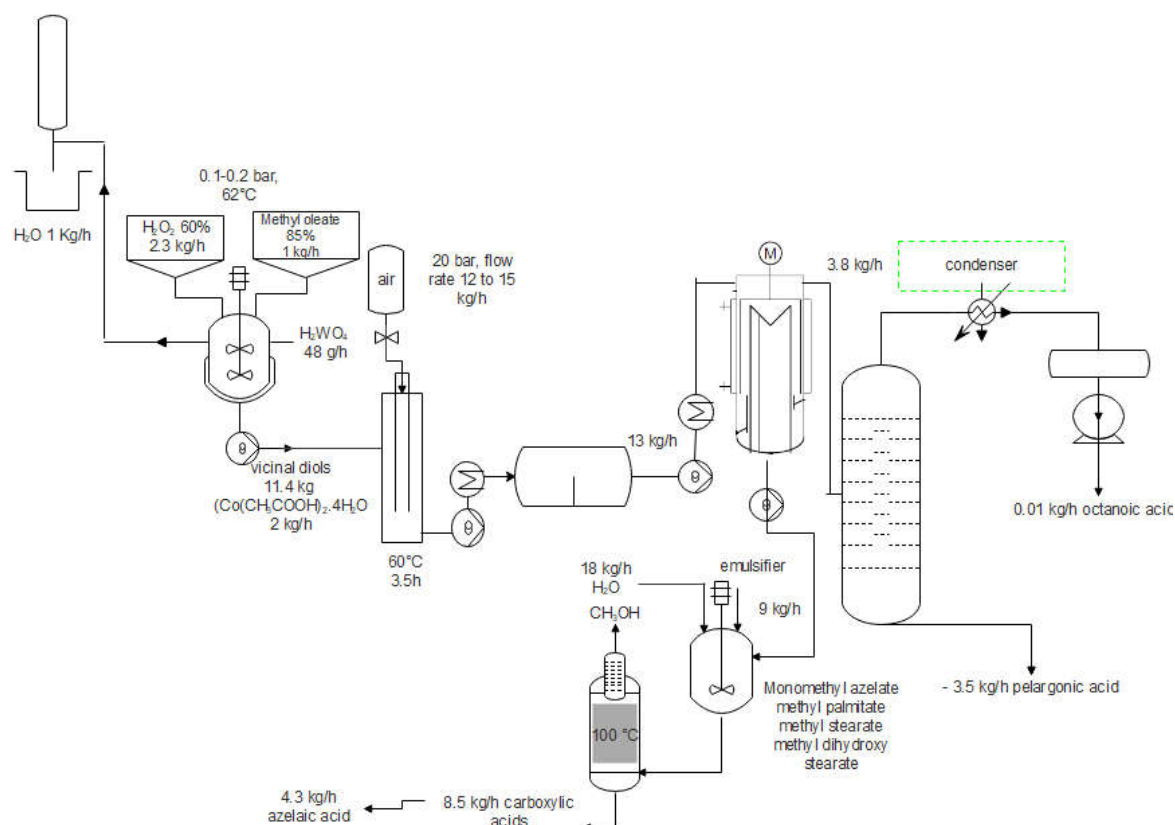
Our research group reproduced some experiments involving the oxidative cleavage of oleic acid at different conditions. We tested two different concentrations of H<sub>2</sub>O<sub>2</sub>, 69 wt.% and 35 wt.%, and two different working temperatures, 85 °C and 50 °C, over 5 h and 24 h of reaction time. We were able to identify at the end of the reaction, the existence of  $\alpha,\beta$ -diols, acetals [47] (formed by the reaction of the aldehydes with  $\alpha,\beta$ -diol) and mono-esters (products  $\alpha,\beta$ -diol esterification with pelargonic acid and azelaic acid). We were also able to identify acids with one fewer carbon (octanoic acid) but none with longer chains [51].

## 6. Industrial Application

To our knowledge, the Italian joint venture between *Versalis* and *Novamont, Matrica*, is the only company to operate the oxidative cleavage of vegetable oils with H<sub>2</sub>O<sub>2</sub> producing bio monomers and other products with a plant of 35,000 tons oil/year capacity.

### 6.1. Process Flow Sheet

The continuous process and most of the batch academic literature require very different process conditions. In the continuous process, using a stirred tank reactor for the first-step reaction, the composition of the reaction medium is equivalent to the composition that comes out of the reactor. This means that the synthesis is done in a stream rich in diol, while most of the batch reactions studied so far correspond to conditions where the stream is rich in oleic acid/ester at the beginning of the cycle. The same applies to the second-stage reaction, where in a continuous mode, with a loop reactor, the composition of the reaction medium is mostly cleavage products (pelargonic acid and azelaic acid/ester), in which a minute amount of diol is continuously fed. However, in batch experiments, the reaction starts in a diol-rich stream, which has to dissolve oxygen (or hydrogen peroxide) in order to initiate the cleavage reactions. The difference in the reaction medium affects not only the solubility of the oxidants, but also the viscosity, boiling points and many other physic-chemical properties and can favor the formation of side products such as the heavy esters of the diol.



**Figure 7.** Representation of our interpretation of the continuous oxidative cleavage process described in *Novamont's* patents [60,64,78].

## 6.2. Catalyst Recovery

The industrial oxidative cleavage is a continuous process in two consecutive phases. The first stage is the hydroxylation of the monoenoic double bond of oleic acid ester to yield the  $\alpha,\beta$ -diol intermediate, and the subsequent stage is the oxidative cleavage of the vicinal diols, obtaining at the end of the reaction a mixture of carboxylic acids. In the first stage, a tungsten catalyst is applied, while in the oxidation stage, a cobalt acetate is used.

The tungsten catalyst is only recovered at the end of the oxidative cleavage stage.

At the end of the reactions, the aqueous phase is separated from the organic phase and passed through a cation-exchange resin, fed by gravity, to retain the cobalt ions and to recover the tungstic acid in a concentration of 8000 ppm (kg/mL), which is then recycled to the first reaction step. The cobalt ions ( $\text{Co}^{2+}$ ) are desorbed from the ion-exchange column and recovered in a concentration of 9830 ppm (kg/mL) and recycled to the second stage of the reaction.

Such a process was developed by the bio-diesel company *Novaol* [78] and optimized by the bioplastic company *Novamont* [79].

## 7. Conclusions and Perspectives

Most relevant protocols for the oxidative cleavage of fatty acids and fatty acid derivatives have been herein reported and discussed. The existence of by-/co-products suggest the coexistence of different by-side reactions, such as decarboxylation (shorter carbon chain), but also acetalization and esterification (high molecular weight products), related to the starting material impurities and to the presence of  $\alpha,\beta$ -diol intermediate in the reaction media. The high industrial interest and the relevant economic impact have stimulated research in this field in search of new technologies. Among them, acoustic and hydrodynamic cavitation could promote such reactions by radical generation or improved mass transfer [80,81].

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**Conflicts of Interest:** The authors declare no conflicts of interest.

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