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Enzymatic Valorization of Fatty Acids in Oleochemical Synthesis

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Keywords: biocatalysis | epoxidation | fatty acids | hydroxylation | oxyfunctionalization | reduction

ABSTRACT

Fatty acids derived from renewable resources, such as vegetable oils, serve as essential feedstocks in various industries, including surfactants, cosmetics, lubricants, and polymers. Although current industrial applications of fatty acids are mainly centered around carboxylate group transformations, recent advancements in biocatalysis have opened new possibilities for converting fatty acids into valuable chemical building blocks. This contribution critically assesses novel biocatalytic transformations of fatty acids, including hydroxylation of the alkyl chain, epoxidation of C=C double bonds, reduction of the carboxylate group, and decarboxylation. These reactions hold great potential for producing important intermediates for chemical synthesis.

Practical Application: The enzymatic valorization of fatty acids offers transformative potential for sustainable oleochemical synthesis, presenting practical applications across various industries. Hydroxylated and epoxidized fatty acids are promising precursors for the production of polyesters, bio-based lubricants, and surfactants. Sophorolipids, derived from hydroxylated fatty acids, are gaining attraction as renewable biosurfactants with applications in detergents and cosmetics. Epoxidized fatty acids serve as intermediates for eco-friendly adhesives, coatings, and polymers. Furthermore, decarboxylation reactions yield alkanes, viable as biofuels, whereas reductions of carboxyl groups enable selective synthesis of aldehydes and alcohols for fragrances and pharmaceutical intermediates. The scalability of these biocatalytic transformations, combined with their mild operational conditions and high specificity, can substantially reduce environmental impact and production costs. These applications highlight biocatalysis as a pivotal technology for advancing the chemical industry toward sustainable practices.

1 | Introduction

Fatty acids, oils, and fats are essential raw materials for a wide range of chemical industries [1–4]. More than 200 M ton of vegetable oil-derived fatty acids are produced annually worldwide [3]. Beyond food applications, these fatty acids serve as valuable feedstocks for the production of surfactants, cosmetics, paints, coatings, lubricants, polymers, adhesives, and more [3]. Today, classical chemical technologies prevail in the conversion of fatty acids into chemicals [5, 6]. Biocatalysis, however, offers unique advantages over chemocatalysis. Enzymes operate under mild conditions, reducing energy input and preventing undesired side reactions. Their high selectivity reduces by-products [7], simplifying downstream processing. Furthermore, they enable

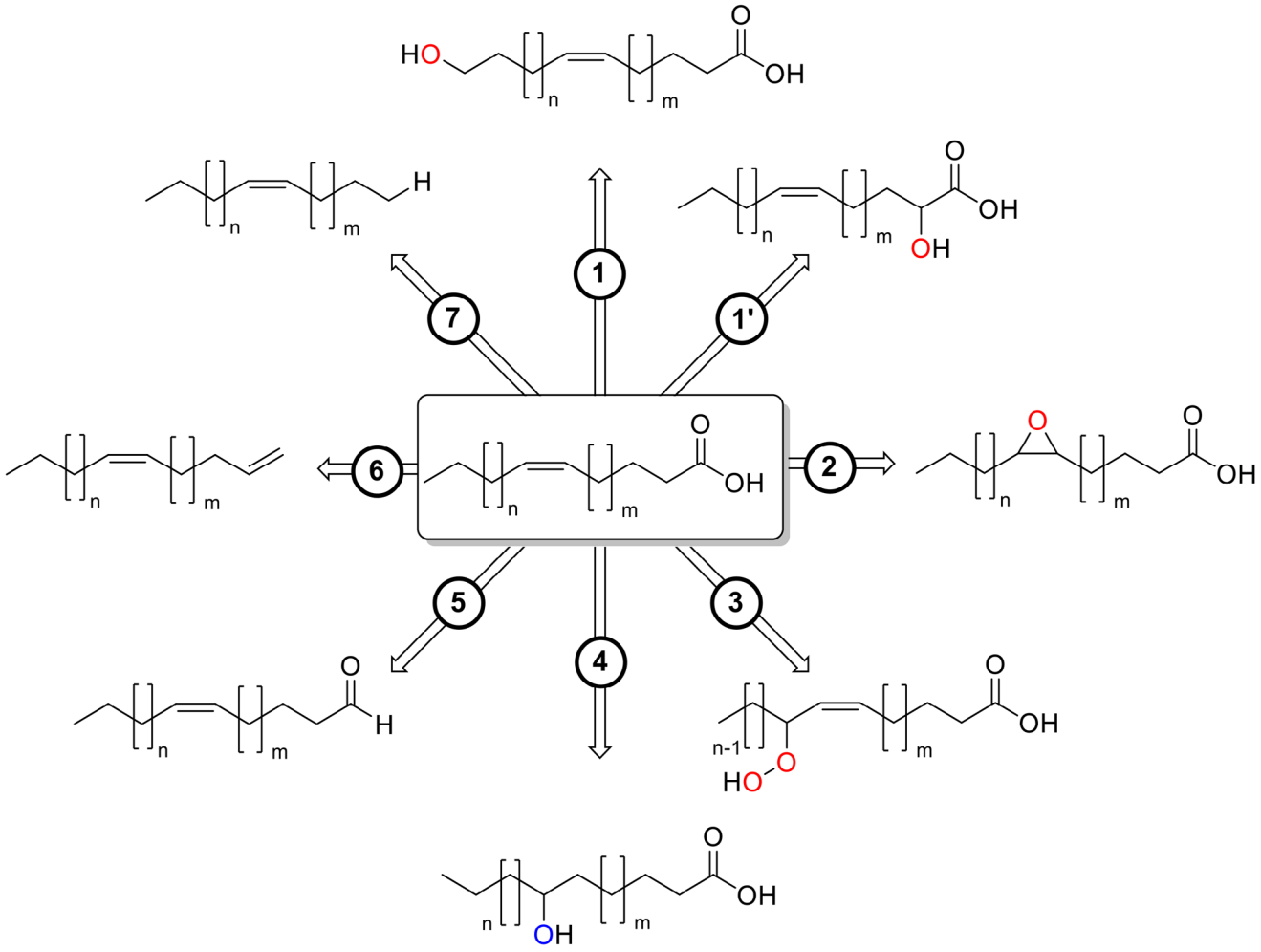

FIGURE 1 | Selection of fatty acid transformations discussed in this contribution: 1: hydroxylation reactions, 2: epoxidations, 3: allylic hydroperoxidation, 4: C═C double bond hydratation, 5: carboxylate reduction, 6: oxidative decarboxylation, 7: decarboxylation.

regio- and stereoselective transformations that are challenging for traditional chemical methods, offering innovative routes to value-added fatty acid derivatives for diverse applications.

The aim of this contribution is to critically assess some of these transformations (Figure 1).

Well-established biocatalytic (trans)esterification and (trans)amidation reactions have been reviewed extensively [2–4, 8–14] and will not be discussed here.

2 | Hydroxylation Reactions

Hydroxylation of fatty acids produces bifunctional hydroxy acids, promising building blocks for polyester synthesis. Notably, cytochrome P450 monooxygenases have been identified for their role in fatty acid hydroxylation [15–18]. Typically, regioselectivity can be categorized on the basis of the hydroxylation at positions near the carboxyl terminal, the alkyl terminus, or along the fatty acid chain (Figure 2).

Selective α-hydroxylation has been demonstrated, for example, using the P450 monooxygenase from *Sphingomonas paucimobilis*

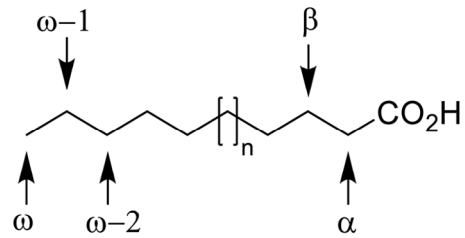

FIGURE 2 | Position nomenclature in fatty acids.

($P450_{SP\alpha}$) [19, 20]. This enzyme functions as a peroxygenase, utilizing preformed H_2O_2 as a cosubstrate [21]. Kroutil and colleagues demonstrated gram-scale transformations of substrates such as octanoic acid [22]. A self-sufficient cascade for direct conversion of fatty acids into α-keto acids was achieved by coupling H_2O_2-consuming P450SPα with H_2O_2-generating oxidases [23, 24]. The α-keto acid can be captured by reductive amination resulting in nonnatural fatty amino acids (Figure 3) [25].

β-Hydroxylation of fatty acids has also been reported but is somewhat underrepresented. The synthetic potential of enantiomerically pure β-hydroxy acids, such as those produced via $P450_{Bs\beta}$-catalyzed β-hydroxylation, as starting materials for

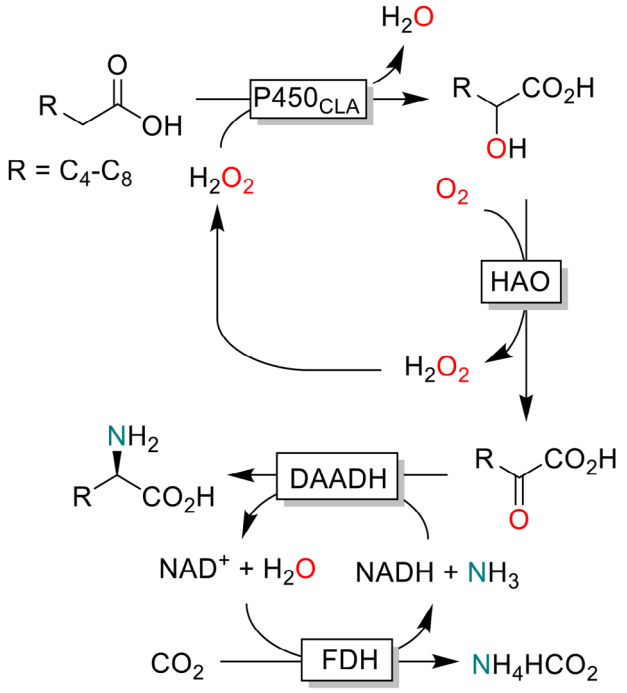

FIGURE 3 | Enzyme cascade transforming carboxylic acids into α-amino acids using a combination of $P450_{CLA}$ (in the peroxide shunt mode), an α-hydroxy acid oxidase (HAO, also supplying the H_2O_2 needed for the P450 step) followed by reductive amination using a D-amino acid dehydrogenase (DAADH) together with an in situ NADH regeneration system.

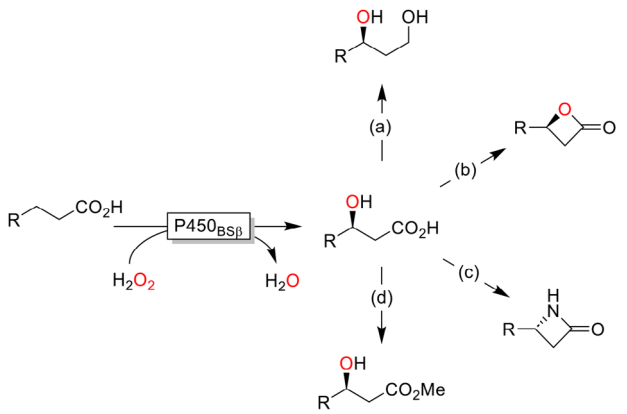

FIGURE 4 | Chiral β-hydroxy acids obtained from P450BSβ-catalyzed hydroxylation as building blocks: (a) Reduction to the β-diol; (b) lactonization; (c) Mitsunobu reaction and lactamization; and (d) esterification [26].

further chemical synthesis was impressively showcased by Wang and colleagues (Figure 4) [26].

In-chain hydroxylation of fatty acids has recently gained more attention due to its potential to produce lactonizable products, which are valuable as flavor and fragrance compounds. For instance, Flitsch and colleagues reported the regio- and stereoselective C5 hydroxylation of decanoic acid to (*S*)-5-hydroxydecanoic acid using the P450 monooxygenase (CYP116B46) from *Tepidiphilus thermophilus* [27]. Similarly,

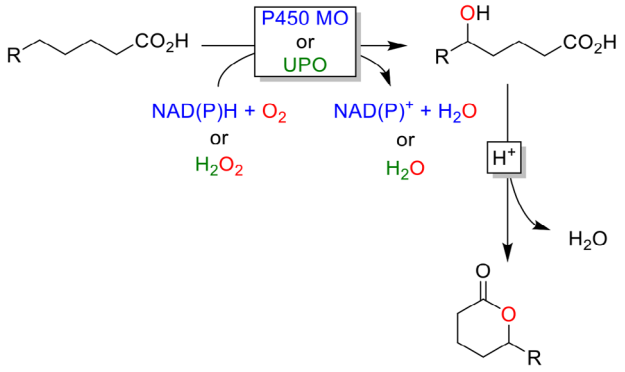

FIGURE 5 | Selective C5-hydroxylation of carboxylic acids followed by acid-catalyzed lactonization.

CYP505E3 from *Aspergillus terreus* catalyzes selective ω-7 hydroxylation, which, in the case of dodecanoic acid, results in C5-hydroxylation [28–30]. Additionally, an ω-1-selective variant of the UPO from *Agrocybe aegerita* (*Aae*UPO-Fett) has been used for the selective C5-hydroxylation of hexanoate [31]. Upon mild acid treatment, these C5-hydroxylated acids can spontaneously form lactones (Figure 5) [32, 33].

Achieving selective ω-hydroxylation of fatty acids is challenging, largely due to the greater stability of terminal C—H bonds compared to the methylene C—H bonds found within the chain [34]. However, this lower reactivity can be overcome when the enzyme positions the terminal CH_3-group near the catalytically active oxo-species. P450 monooxygenases have been extensively studied in this context [35, 36], as well as the non-heme iron alkane monooxygenase from *Pseudomonas putida* GPo1 (AlkGBT), which catalyzes highly regioselective ω-hydroxylation of carboxylic acids and their esters [37, 38].

Fungal P450 monooxygenases from *Candida* species, in particular, have shown notable ω-selective hydroxylation activity. *Candida tropicalis* has garnered significant industrial interest for converting fatty acids into ω-hydroxy acids or dicarboxylic acids, which are potential building blocks for polyesters [39–42]. Through engineered strains overexpressing multiple P450 monooxygenases and exhibiting reduced β-oxidation activity, Gross and colleagues successfully produced various dicarboxylic acids at concentrations of up to 100 g per liter [41]. The *Candida*-mediated ω-hydroxylation of fatty acids has been commercialized by Cathay Biotech at an annual scale of 40 000 t for the production of biobased long-chain dicarboxylic acids [13].

The intermediate aldehyde opens up further synthetic possibilities such as the reductive amination yielding ω-amino acids as building blocks for polyamides. Bühler and coworkers, for example, established a whole-cell system converting natural fatty acids into lactams (Figure 6) [38, 43–46]. Especially, the final lactamization step proved to be challenging due to unfavorable (de)protonation of the amino acid as well as the thermodynamically favored amide hydrolysis. Starting from activated methyl esters as well as operating under alkaline conditions enabled the authors to obtain the desired laurolactam in approx. 10%–15% yield.

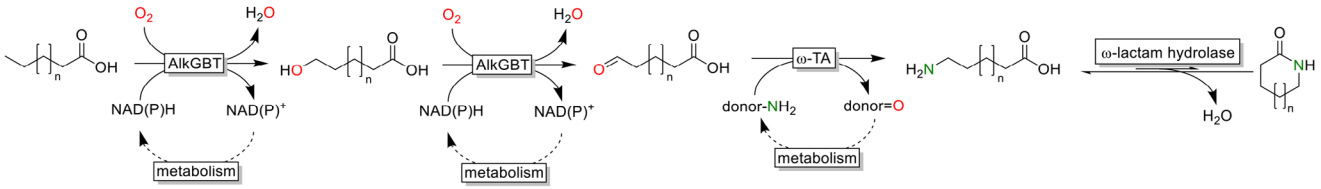

FIGURE 6 | Lactam synthesis from fatty acids involving AlkGBT-catalyzed ω-hydroxylation, "over oxidation" to the aldehyde (either catalyzed by AlkGBT or via endogenous dehydrogenases, not shown), reductive amination using an ω-transaminase (ω-TA using metabolic amino acids as amine donors) and a cyclization step mediated by an ω-lactam hydrolase.

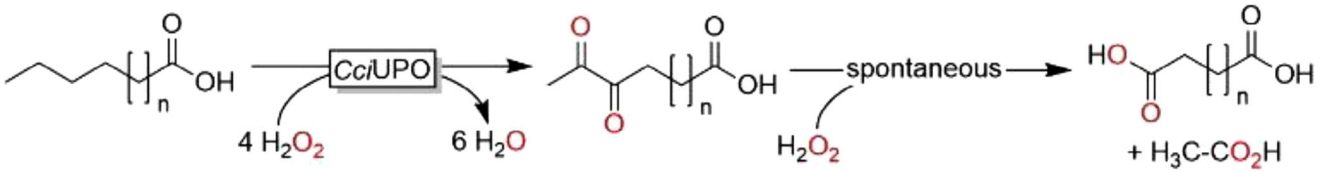

FIGURE 7 | Fourfold oxidation of fatty acids followed by H_2O_2-driven oxidative cleavage of the intermediate diketone.

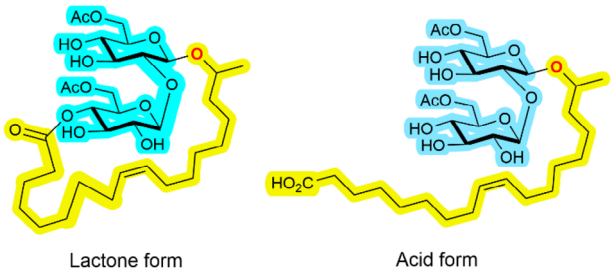

FIGURE 8 | Example for an oleic acid-derived sophorolipid. Partially acetylated sophorose (blue background) represents the hydrophilic part, whereas oleic acid (yellow background) represents the hydrophobic part. Both parts are linked as an acetal between the reducing carbohydrate end and the (ω- or ω-1-hydroxylated fatty acid). The hydroxylation-O-atom is highlighted in red. Sophorolipids exist in either an open (acid) form or as internal ester (lactone form).

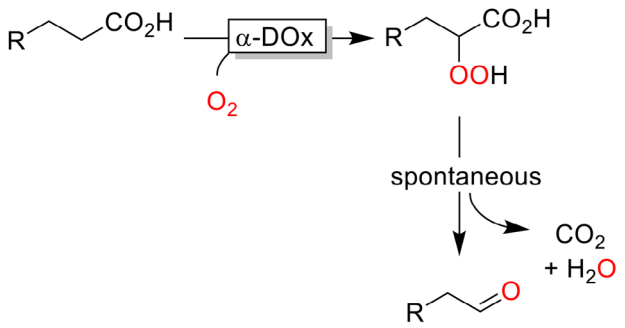

FIGURE 9 | α-Dioxygenase-catalyzed oxidative decarboxylation of fatty acids.

Next to monooxygenase-catalyzed ω-hydroxylation, peroxygenases offer an alternative access to α,ω-dicarboxylic acids starting from fatty acids [47]. An interesting hydroxylation of fatty acids catalyzed by the peroxygenase from *Coprinopsis cinerea* gives access to C2-shortened dicarboxylic acids [48]. The proposed mechanism includes fourfold oxidation of the fatty acid (ω-1- and ω-2-hydroxylation and overoxidation) followed by non-catalyzed H_2O_2-oxidation of the 2,3-diketone (Figure 7).

Another interesting class of hydroxylated fatty acid derivates are the sophorolipids [49–52] that currently are receiving a lot of interest as biosurfactants. In sophorolipids, hydroxy fatty acids (typically ω-1) are glycosylated with the carbohydrate sophorose (Figure 8). However, different hydroxylation sites are known from *Candida kuoi* (ω) or *Candida borogeniensis* (in-chain). In addition, engineering of *Starmerella bombicola* was done to produce hydroxy acids [53, 54].

Sophorolipids and rhamnolipids (containing rhamnose as carbohydrate element) are gaining attention for their renewability, biodegradability, and low toxicity compared to synthetic surfactants. Fermentatively produced sophorolipids are commercialized by various companies, for example, Evonik.

3 | Hydroperoxidation Reactions

Next to hydroxylation reactions, hydroperoxidation of activated positions (particularly α-C-H bonds and allylic C-H bonds) in fatty acids is known.

In this context, α-dioxygenases (α-DOx) are worth mentioning (Figure 9) [55]. The primary reaction products (α-hydroperoxy acids) spontaneously decarboxylate into aldehydes. However, given that aldehydes are highly versatile starting materials for a wide range of chemical transformations, it is likely that this enzyme class will attract increasing interest in the future.

To date, only a limited number of studies have explored the synthetic applications of α-DOx [56, 57].

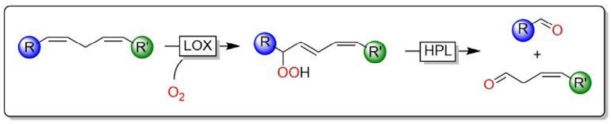

FIGURE 10 | General reaction scheme of the lipoxygenase (LOX) hydroperoxide lyase (HPL) system.

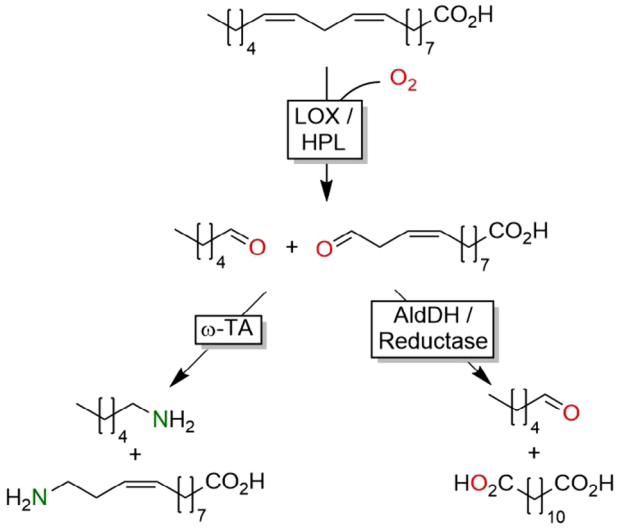

FIGURE 11 | Selected examples for the LOX/HPL system to provide polymer building block precursors.

More widespread than α-DOx are lipoxygenases catalyzing the hydroperoxidation of the *cis*, *cis*-1,4-pentadiene moiety, generally the successive cleavage of the intermediate by a hydroperoxide lyase (Figure 10). The combination of lipoxygenase and hydroperoxide lyase is an established enzyme system in the flavor and fragrance industry to produce C6 odor compounds, the so-called green-leaf volatiles [58].

In recent years, also applications for the transformation of unsaturated fatty acids into bifunctional polymer building blocks have received more attention (Figure 11) [59, 60].

Finally, so-called diol synthases should be mentioned in this context. Similar to lipoxygenases, they catalyze an allylic hydroperoxidation reaction. The resulting hydroperoxides, however, are directly used as oxygen-donor for an intramolecular hydroxylation reaction (Figure 12).

Diol synthases, for example, with 1,2- [61], 1,3- [62], or 1,4- [63] selectivity, relative to the hydroperoxidation position, are known.

Unfortunately, these exciting enzymes have so far not found widespread interest in the biocatalysis community.

4 | Carboxylate Reduction Reactions

Carboxylic acid reductases (CARs) catalyze the reduction of acids. The poor reactivity of carboxylic acids (especially under ambient aqueous conditions) necessitates in situ activation of the carboxylate group. CARs achieve this by the ATP-dependent thioester formation. The resulting thioester can undergo NADPH-dependent reduction [64–66].

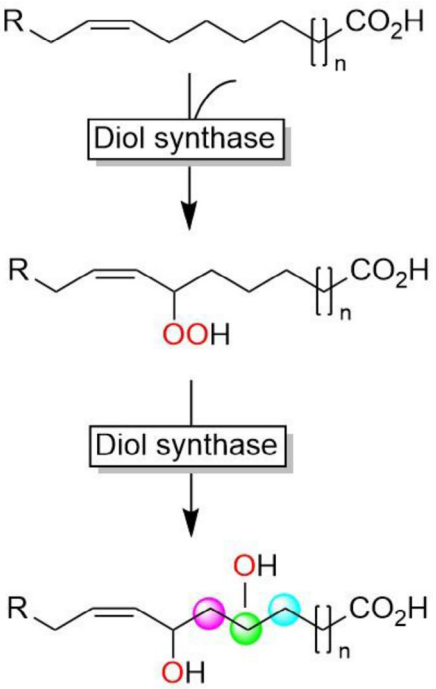

FIGURE 12 | Diolsynthases catalyze first allylic hydroperoxidation of unsaturated fatty acids followed by an intramolecular peroxygenase-like hydroxylation. Different regioselectivities for the second step are known (indicated by the colored C-atoms).

The multiple cofactor dependency of CARs, however, makes cell-free applications challenging, and whole-cell reactions are preferred. Under these conditions, however, acid reduction generally proceeds to the alcohol level (due to the presence of endogenous alcohol dehydrogenases). If aldehydes are the desired products, in situ extraction into a hydrophobic organic layer is a viable approach to prevent the subsequent reduction (Figure 13) [65].

So-called aldehyde oxidoreductases (AORs) represent an alternative enzyme system for the reduction of carboxylic acids [67, 68]. AORs are tungsten-containing enzymes. The unique chemistry of tungsten offers a simpler, ATP-independent, access to acid reduction. Indeed, H_2- and even CO-driven reduction of carboxylic acids has been reported [69, 70]. However, today, recombinant expression systems for the production of tungsten-dependent enzymes, for example, in *Escherichia coli* are rare and limits AOR-catalysis, so far, to wild-type organisms.

5 | Reactions With the C=C Double Bond

Unsaturated fatty acids offer further possibilities for chemical modification.

Hydratation of the C=C double bond to the corresponding alcohols is enabled by so-called fatty acid hydratases [71]. Especially the hydratation of oleic acid to (*R*)-10-hydroxystearic acid has been investigated intensively because of its

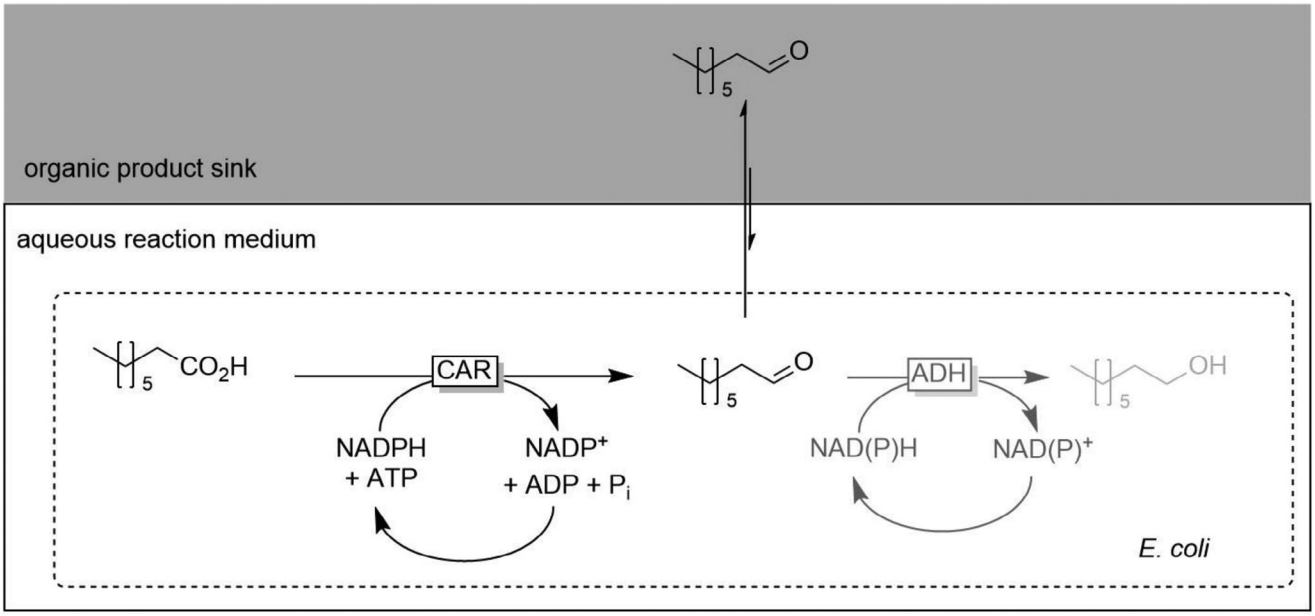

FIGURE 13 | Selective reduction of octanoic acid to octanal using recombinant *Escherichia coli* and heptane as in situ extractant for the aldehyde product.

applications as lubricant, in cosmetic formulations, and as potential building block for polyesters. Since the discovery of microbial oleate hydratase (Ohy) activity in the 1960s, its application for the production of hydroxy fatty acids has been explored [72] reaching impressive productivities and product titers.

Several enzymatic cascade reactions following Ohy-catalyzed hydration have been developed to enhance the substrate scope (Figure 15). Park and colleagues pioneered cascades where the alcohol group is oxidized to a ketone by secondary alcohol dehydrogenases. These ketones can be further processed into valuable products like esters using Baeyer–Villiger monooxygenases (BVMOs), yielding bio-based monomers for polyesters or fatty amines through transaminase-catalyzed reductive amination. Co-expression of Ohy, ADH, and BVMO in *E. coli* has led to efficient biocatalytic cascades for producing bio-based building blocks [73–78].

A very interesting whole-cell transformation of oleic acid was reported by Borodina and coworkers (Figure 14) [79]. By metabolic engineering, the strain's β-oxidation preferentially formed C12-fatty acid-CoA, which (presumably spontaneously) underwent intramolecular lactonization.

The cascades discussed above for the valorization of oleic acid bear the intrinsic disadvantage of producing stoichiometric amounts of either nonanoic acid (pelargonic acid) or 1-octanol as byproducts, which if bifunctional polymer building blocks are desired represent undesired byproducts lowering the overall atom economy of the reactions. A similar situation arises starting from ricinoleic acid [17, 80]. To solve this problem, Xu and coworkers designed a modular approach to ω-hydroxylate nonanoic acid (Figure 16) [81, 82]. This way, oleic acid can be converted entirely into ω-hydroxy nonanoic acid and other bifunctional polymer building blocks [83].

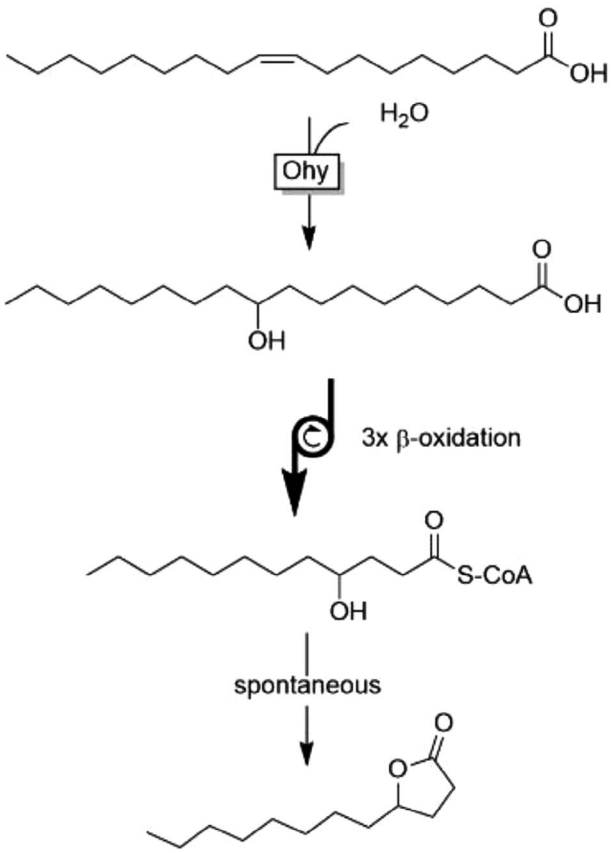

FIGURE 14 | Conversion of oleic acid into γ-dodecalactone using engineered Yarrowia lipolytica.

Epoxidation. The reactive oxirane group in epoxidized fatty acids makes them valuable compounds used in various ways as plasticizers, coatings and adhesives, lubricants, surfactants, and emulsifiers [84]. Some heme-containing enzymes such as P450

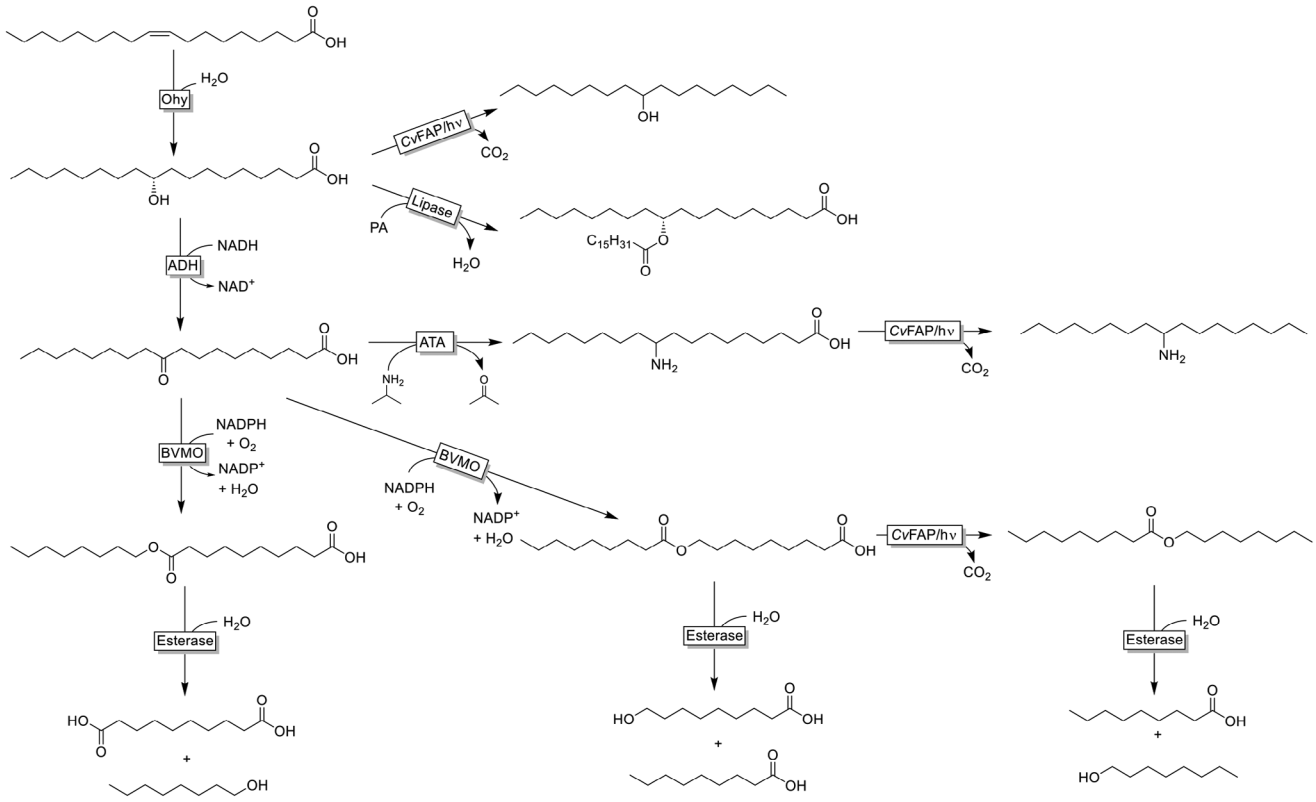

FIGURE 15 | Overview of some cascade transformations initiated by the oleate hydratase (Ohy)-catalyzed hydratation of oleic acid.

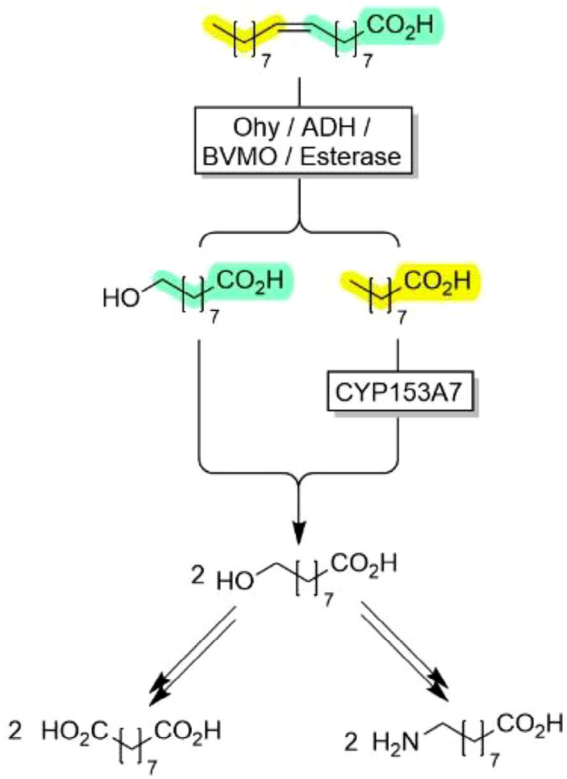

FIGURE 16 | Convergent cascade merging nonanoic acid and ω-nonanoic acid to attain full atom economy.

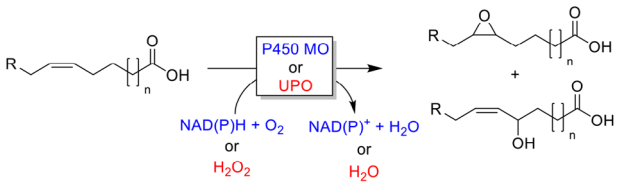

FIGURE 17 | Heme-oxygenase-catalyzed epoxidation of unsaturated fatty acids, including the generally observed, undesired allylic hydroxylation.

monooxygenases and peroxygenases [85–88] have been reported to mediate epoxidation of unsaturated fatty acids. The high reactivity of these enzymes, however, also causes sometimes undesired allylic hydroxylation (Figure 17).

More commonly, chemoenzymatic epoxidation via the perhydrolase activity is used. In this approach, a hydrolase catalyzes the in situ formation of a reactive peracid which then undergoes spontaneous Prilezhaev epoxidation of the C═C double bond (Figure 18) [89, 90].

An interesting chemoenzymatic cascade transforming high oleic acid content sunflower oil into azelaic and pelargonic acid was reported by Casali et al. (Figure 19) [91].

6 | Decarboxylation Reactions

Oxidative decarboxylation of fatty acids yielding terminal alkenes has been reported with a range of heme-containing monooxyge-

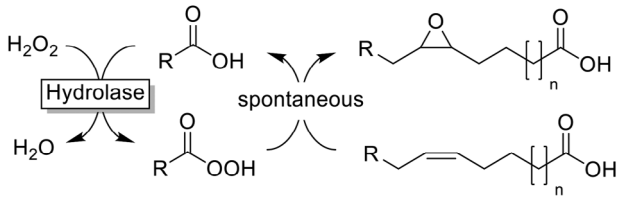

FIGURE 18 | Chemoenzymatic epoxidation of unsaturated fatty acids.

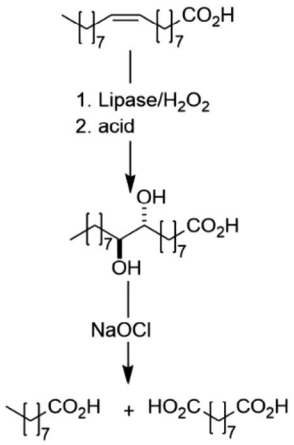

FIGURE 19 | Chemoenzymatic cascade to transform oleic acid into azelaic and pelargonic acid.

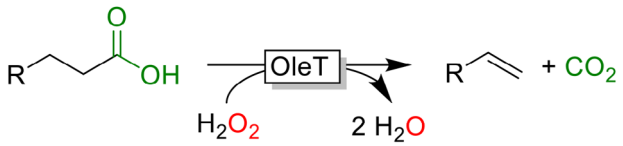

FIGURE 20 | Oxidative decarboxylation using OleT.

nases. This activity was first reported with a P450 monooxygenase from *Jeotgalicoccus* sp., OleT$_{Je}$) (Figure 20) [92] but has also been observed as side reaction, for example, with P450$_{BS\beta}$ [26] and other P450 monooxygenases [93–95]. Moreover, non-heme-Fe-containing decarboxylases such as UndB from *Pseudomonas* sp. are known [96–99].

An interesting approach synthesizing terminal alkenes from triglycerides was suggested combining OleT with an alditol oxidase (Figure 21) [100, 101] suggesting a holistic approach to valorize natural triglycerides.

Fatty acid photodecarboxylases (FAPs) represent a novel class of enzymes first having been reported by Beisson and coworkers in 2017 [102, 103]. Ever since, the FAP from *Chlorella variabilis* (*Cv*FAP) has been attracting a lot of attention especially envisioning the production of alkane biofuels but also because of the unusual mechanism involving photoactivation of the flavin prosthetic group. Compared to classical fatty acid methyl ester (FAME)-based biodiesel, alkanes exhibit several advantages such as the ease and irreversibility of the reaction and the higher caloric value of the product (Figure 22).

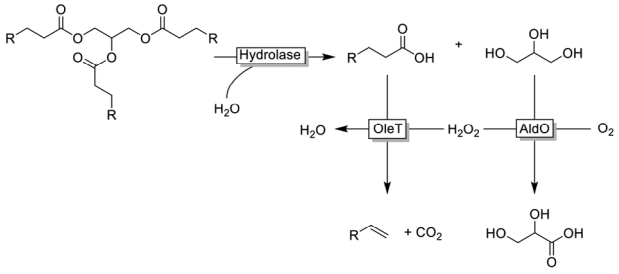

FIGURE 21 | 'Double utilization' of triglycerides for the synthesis of terminal alkenes. In a first step, the triglyceride is hydrolyzed into glycerol and fatty acids. The latter are further converted by OleT into terminal alkenes by partially utilizing H_2O_2 provided by the oxidation of glycerol to glyceric acid (catalyzed by alditol oxidase, AldO).

Despite the enormous potential of FAP-derived "next generation biodiesel," their implementation is severely challenged by the poor photostability of FAPs [104]. As a consequence, the operational stability of the enzymes does not enable economic feasible synthesis especially of low-value products such as fuels. In-depth understanding of the inactivation mechanisms and enzyme engineering will be necessary to attain economic feasibility.

Several innovative strategies have been developed to incorporate FAPs into synthesis pathways for higher-value products (Figure 23). Various research groups engineered *Cv*FAP to enhance its selectivity for different compounds, particularly in light-driven kinetic resolution reactions. For instance, Wu and colleagues engineered *Cv*FAP for the kinetic resolution of α-substituted carboxylic acids [13] and for differentiating between *cis*- and *trans*-unsaturated fatty acids [105].

7 | Conclusions

Biocatalysis holds significant potential for the valorization of fatty acids. These applications range from high-value-added products, such as flavors and fragrances or pharmaceutical building blocks, to bulk products like polymer precursors. For many of the transformations presented in this contribution, no competitive alternative exists. This is particularly true for products derived from oxyfunctionalization chemistry. However, even for reactions such as reductions and seemingly simple esterifications, the mild reaction conditions of biocatalysis offer substantial advantages on an industrial scale. This has been exemplified, for instance, by Thum and colleagues, who compared the chemocatalytic and biocatalytic synthesis of myristyl myristate on an industrial scale [106].

Nevertheless, a considerable gap remains between the potential of biocatalysis and its industrial applicability for the majority of transformations. For example, product titers reported in academic studies are often in the lower millimolar range, making them unsuitable for industrial implementation. Similarly, catalyst usage, a critical factor in industrial processes, is frequently overlooked in academic research.

Closer collaboration between academic researchers and industrial developers is urgently required to facilitate the transition

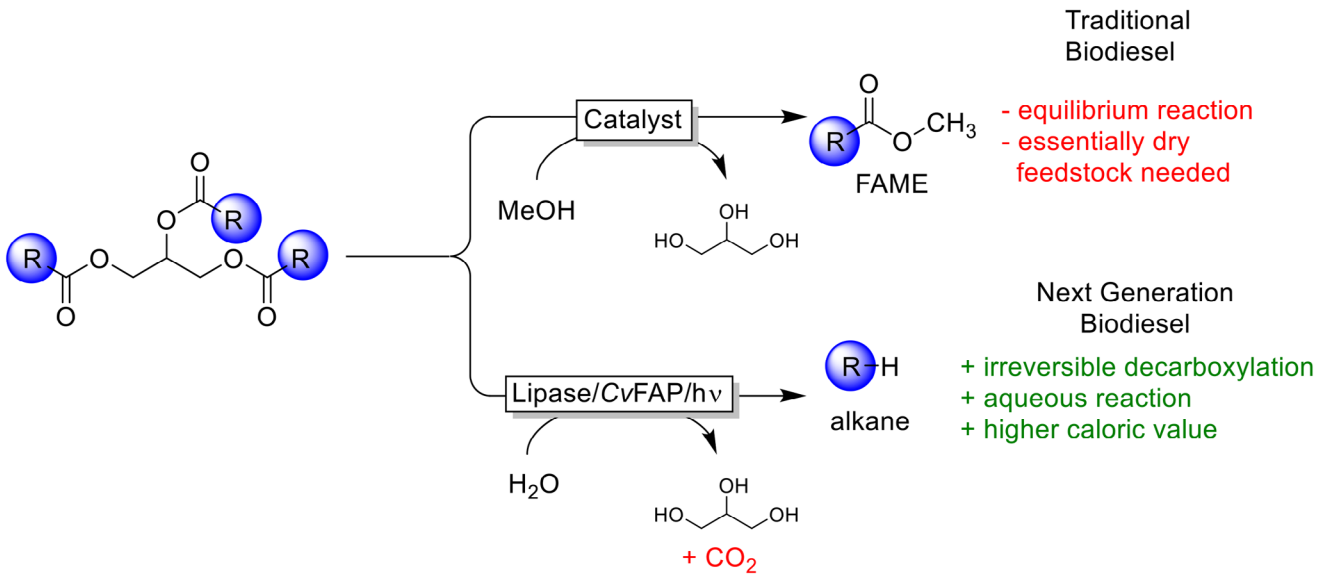

FIGURE 22 | Qualitative comparison of traditional biodiesel and bioalkanes as obtained via decarboxylation.

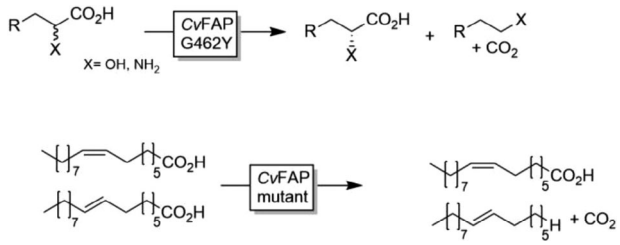

FIGURE 23 | Applications of engineered FAPs for the kinetic resolution of fatty acid stereoisomers such as chiral a-substituted acid or E/Z-isomers.

of the many exciting chemistries discussed here into practical applications.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

Data sharing not applicable to this article as no datasets were generated or analyzed during the current study.

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