

**Biomass Valorization**

# Catalytic Biorefining of Natural Oils to Basic Olefinic Building Blocks of Proven Chemical Valorization Schemes

 Stefanie de Roo<sup>+</sup>, Felix Einsiedler<sup>+</sup>, and Stefan Mecking\*

**Abstract:** Catalytic transformation of renewable plant oils including microalgae and waste oil into industrially relevant  $\alpha$ -olefins in the  $C_3$  to  $C_{10}$  regime is demonstrated. The biorefinery concept is comprised of a catalytic sequence of ethenolysis, double bond isomerization, and a subsequent ethenolysis, thereby cutting and rearranging the fatty acid chains into valuable chemical building blocks. A benign extraction and reaction solvent, supercritical carbon dioxide ( $scCO_2$ ), is utilized.

## Introduction

As an alternative to today's crude oil based petrochemical refineries, a biorefining of renewable feedstocks has been much discussed.<sup>[1–6]</sup> Yet, a biorefinery concept that provides provenly established building blocks in a direct fashion is lacking. Rather, renewable feedstocks are converted to hydrocarbon oils to replace fossil-based naphtha feedstock as an input to a petrochemical refinery, or carbohydrate-based platform chemicals like 5-hydroxymethylfurfural with a limited scope of follow-up chemistry are pursued.<sup>[7–9]</sup> We now demonstrate how the essential  $\alpha$ -olefin building blocks for practiced valorization pathways can be generated from common plant oils by directed sequential breaking and rearrangement of their hydrocarbon chains through one-pot ethenolysis metathesis and isomerization.

In the established petrochemical industry, a combination of olefin metathesis and isomerization is employed most prominently in the Shell Higher Olefin Process,<sup>[10]</sup> which generates  $C_{11}$  to  $C_{18}$  olefin products from ethylene. Here, cycles of isomerization and metathesis serve to convert also the lower  $C_{\leq 10}$  and higher  $C_{\geq 20}$  end of the Schulz–Flory distribution of chain lengths obtained from

ethylene oligomerization into the desired product range. Metathesis and isomerization of the non-functionalized purely hydrocarbon feedstock are performed in separate gas phase reactors, with traditional heterogeneous catalysts not compatible with functional group-containing renewable feedstocks.

Our biorefining concept targets terminal unsaturated products in the  $C_3$  to  $C_{10}$  regime by breaking down the fatty acid chains of plant oil feedstock, as most products and intermediates today are based on these building blocks' further conversion by established follow-up chemistry. To this end, an initial ethenolysis<sup>[11–13]</sup> step halves the chain length, with subsequent further sequential isomerization and ethenolysis to the final desired products (Figure 1a and b). As an environmentally benign reaction medium supercritical carbon dioxide ( $scCO_2$ ) is employed. This can also simplify the overall biomass to product process as  $scCO_2$  is particularly well suited to selectively extract lipids from biomass, and the extraction solution may be fed to the catalytic conversions without the need for changing solvents and other work-up.<sup>[14–16]</sup>

## Results and Discussion

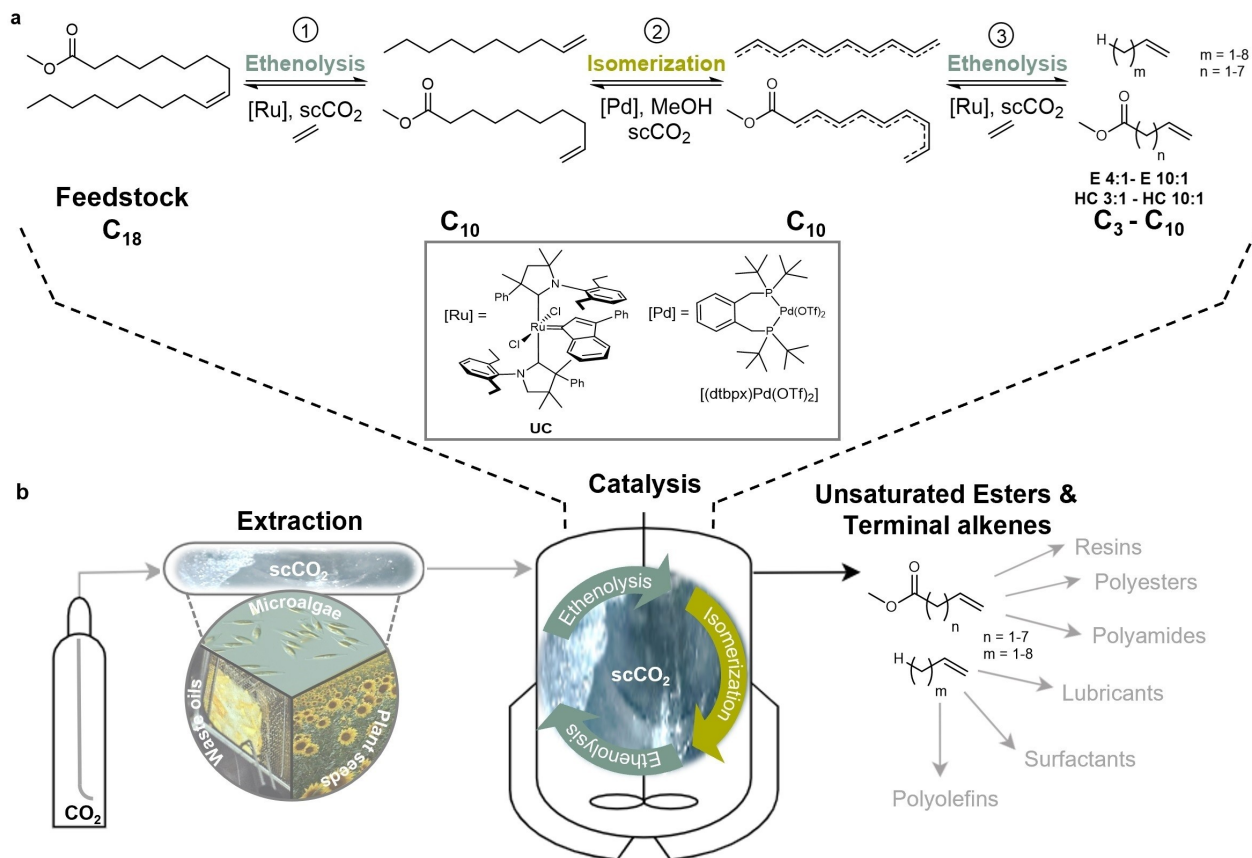
### Ethenolysis and isomerization efficiency

To realize this concept in a one-pot sequential ethenolysis-isomerization-ethenolysis catalysis (SEIEC), a custom-built semi-batch reactor system that allows for the controlled addition of substrates and catalysts into dense carbon dioxide was designed (see Supporting Information Figure S1a and S1b). As a starting point, ethenolysis and isomerization reactions were separately analyzed using transesterified high oleic sunflower oil (HOSO) as a model substrate to identify catalysts with a high performance in  $scCO_2$ . Since ruthenium-alkylidene metathesis catalysts are known to be compatible with fatty acids and  $scCO_2$ ,<sup>[17–19]</sup> state-of-the-art Hoveyda-Grubbs type catalysts as well as Ru-alkylidene catalysts with cyclic alkyl amino carbene ligands (CAAC)<sup>[20]</sup> were screened for ethenolysis in  $scCO_2$  (see Supporting Information Figure S3a, S3b, S3e and Figure S24). Conversions and selectivities achieved with the CAAC-substituted "Ultracat" catalyst (UC, Figure 1) stand out. Under optimized reaction conditions (10 ppm of commercial UC, 10 bar ethylene,  $p_{total} = 450$  bar, 55 °C, 6 h), the ethenolysis of the transesterified natural oil proceeded with a turn over number (TON) of up to 78000 and selectivities of over 97% (Figure S3b). This catalyst

[\*] S. de Roo,<sup>+</sup> F. Einsiedler,<sup>+</sup> Prof. Dr. S. Mecking  
 Department of Chemistry, University of Konstanz  
 Universitätsstrasse 10, 78464 Konstanz (Germany)  
 E-mail: stefan.mecking@uni-konstanz.de

[†] These authors contributed equally to this work

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**Figure 1.** Catalytic biorefinery approach. a), b) Biorefining concept comprising sequential ethenolysis, isomerization and ethenolysis catalysis (SEIEC) to provide target linear 1-olefins and esters in the  $C_3$  to  $C_{10}$  regime by selectively breaking down fatty acid chains of plant oil feedstocks. This is illustrated for the discrete examples of transesterified high oleic sunflower oil (FAME 18:1). This catalysis is performed in supercritical carbon dioxide ( $scCO_2$ ) as a selectivity-enhancing and environmentally benign reaction medium, which is also an established selective extraction medium for lipids<sup>[15,16]</sup> in the upstream extraction of biomass. E X:1 mono-unsaturated methyl ester with x carbon atoms. HC X:1 linear 1-olefin with x carbon atoms.

performance is on par with reported data in neat substrates,<sup>[21]</sup> illustrating the excellent suitability of UC for the ethenolysis of fatty acid esters in  $scCO_2$  as a medium.

Double bond positional isomerization of non-functionalized alkenes with heterogeneous catalysts is an established industrial process, and double bond isomerization is a ubiquitous undesired side reaction with many soluble catalysts.<sup>[22–24]</sup> Notwithstanding, catalysts capable of efficient isomerization of double bonds along a fatty acid ester substrates' chain are scarce. We found  $[Pd(\mu\text{-Br})t\text{-Bu}_3P]_2$ , used by Gooßen et al. in their pioneering simultaneous isomerization/metathesis approach which opposite to SEIEC is based on concomitant tandem catalysis that yields mixtures of internal unsaturated compounds, suited for the generation of bio-based Diesel fuel replacements,<sup>[25]</sup> to be inactive towards transesterified HOSO in  $scCO_2$  even at a temperature of 70 °C.

By contrast,  $[(dtpbx)Pd(OTf)_2]$  (Figure 1)<sup>[26]</sup> displayed a high activity and fully equilibrated the double bond isomers after 3 h at 35 °C (see Supporting Information Figure S4a and S4b). As in a sequential process of ethenolysis-isomer-

ization-ethenolysis the isomerization would take place with the primary ethenolysis products of an oleate substrate, 1-decene and methyl 9-decenoate, further isomerization experiments with  $[(dtpbx)Pd(OTf)_2]$  were performed on these two compounds as model substrate. As a reference point, equilibrium distributions<sup>[27,28]</sup> were obtained by exhaustive isomerization in organic solvents (see Supporting Information Table S2, S4 and Figure S4c, S4d, S5, S9, S10). Whereas the isomerization of 1-decene and methyl 9-decenoate in the absence of ethylene led to an equilibrium mixture (0.4 mol % catalyst per double bond,  $p_{\text{total}} = 350$  bar, 55 °C), the isomerization in the presence of 10 bar ethylene under otherwise identical conditions resulted in an isomer distribution that was far from the expected equilibrium. This reflects the preferred unproductive coordination and addition of the active Pd H species<sup>[29]</sup> to ethylene, slowing down the double bond isomerization of the designated substrates. However, elevated temperatures of 85 °C and reduced ethylene pressures of 3 bar led to a satisfactory double bond isomerization and an isomer distribution close to equilibrium (see Supporting Informa-

tion Figure S4c, S4d and S5). This underlines the suitability of  $[(\text{dtpbx})\text{Pd}(\text{OTf})_2]$  for the isomerization of unsaturated esters and olefins in  $\text{scCO}_2$ , even in the presence of ethylene. Note the observed attainment of an equilibrium of the olefin isomers starting from 1-decene and methyl 9-decenoate at the catalyst loadings employed corresponds to  $>10^4$  catalytic events per active site of olefin insertion into a Pd-H bond and subsequent  $\beta$ -H elimination (assuming a statistical nature of the direction of the individual insertion or elimination event within the substrate chain). A further requirement for the targeted sequential one-pot process is the compatibility with the catalyst from the previous step, that is of the olefin metathesis with the isomerization catalyst and vice versa. To this effect, the impact of  $[(\text{dtpbx})\text{Pd}(\text{OTf})_2]$  as well as of methanol (required for the activation of the Pd-complex)<sup>[30]</sup> on the ethenolysis activity was elucidated (see Supporting Information Figure S3c and S3d). Whereas the presence of methanol does impact ethenolysis performance (0.5 vol % MeOH led to a reduced ethenolysis conversion of 65 %), at minimum methanol concentrations found to be sufficient for activation of the isomerization catalyst (see Supporting Information Figure S4d), ethenolysis is not affected. Excess  $[(\text{dtpbx})\text{Pd}(\text{OTf})_2]$  vs. **UC** could also impact the latter's ethenolysis performance. Notwithstanding, at suitable conditions (0.1 vol % MeOH, 0.4 mol % per double bond of **UC** and  $[(\text{dtpbx})\text{Pd}(\text{OTf})_2]$ , respectively) high conversions and selectivities of 88 % and 96 %, respectively, were obtained in the ethenolysis. Vice versa, a potential impact of **UC** on the isomerization performance was illuminated by comparing the isomer distribution after isomerization of 1-decene and methyl 9-decenoate model substrate to the distribution obtained after ethenolysis of HOSO and a subsequent one-pot isomerization under identical conditions (see Supporting Information Figure S6). No significant difference in the isomer distribution was observed, suggesting a negligible impact of **UC** on the isomerization performance.

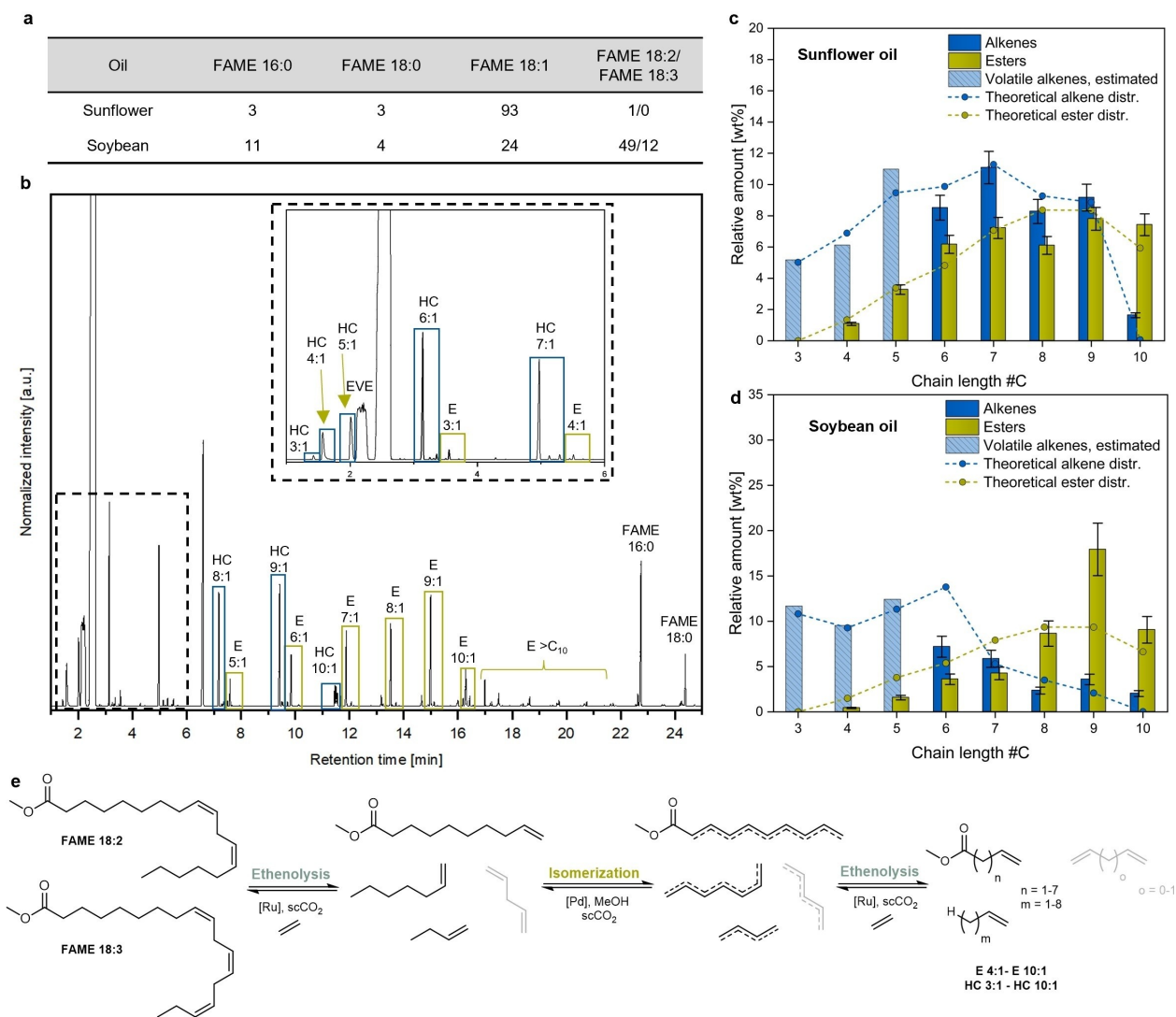
### One-pot sequential catalytic conversion with seed oil feedstocks

In order to establish an alternative to the production of proven platform chemicals from crude oil, an applicability of our approach to a variety of renewable oils as a broad feedstock basis is desired. Established seed oil crops as one possible source of renewable fatty acids offer the advantage of an already existing supply chain. Especially, soybean and sunflower oil are of interest, since sunflowers exhibit particularly high oil contents whereas soybean crops are produced worldwide in outstanding large volumes.<sup>[31]</sup> In addition, they contain high amounts of unsaturated fatty acids of up to 80 %, advantageous for the targeted biorefinery approach (Figure 2a). High oleic sunflower oil mainly consists of a single unsaturated fatty acid, which facilitates an analysis and interpretation of the formed product distribution. Therefore, transesterified HOSO was used to establish the SEIEC approach. The first ethenolysis step of SEIEC was conducted at a low ethylene pressure of 3 bar in view of the unfavorable effect of high ethylene

concentrations in the subsequent isomerization. Under these conditions, 0.06 mol % of **UC** were necessary to reach similar high conversions and selectivities in the ethenolysis. To allow for a following efficient isomerization, the reaction temperature was increased to 85 °C when  $[(\text{dtpbx})\text{Pd}(\text{OTf})_2]$  was added into the reaction mixture along with low amounts of methanol for activation. For the subsequent second ethenolysis step, the reactor was fed with additional 15 bar of ethylene along with the introduction of fresh **UC** to reach high conversions and selectivities. Under these overall reaction conditions, both ethenolysis reactions proceeded with high conversions of up to 97 % with a selectivity for ethenolysis products of 97 % (see Supporting Information Table S7). In addition, the analysis of the product mixture by gas chromatography (Figure 2b) revealed the formation of all desired 1-olefins (HC 3:1 to HC 10:1) and terminal unsaturated esters (E 3:1 to E 10:1) with a selectivity of 96 % for products with chain lengths  $<C_{10}$ . Note that in the decompression of the  $\text{scCO}_2$  with evaporation of  $\text{CO}_2$  and collection of the products for analysis, losses of low boiling olefins propylene to pentene (HC 3:1 to HC 5:1) are inevitable which hampers their quantitative detection (see Supporting Information Figure S14). Therefore, their portions in the overall distribution were determined via mass balance, a procedure that is supported by the self-consistency of the data (see Supporting Information).

To evaluate the obtained product distributions, theoretical distributions from 100 % complete and fully selective ethenolysis steps, and ideal double bond isomerization to equilibrium were calculated (cf. Supporting Information for details of calculation procedure). A comparison with the experimentally achieved product distributions show these are close to these theoretically expected values (Figure 2c, dashed line) for all products, methyl esters E 4:1 to E 10:1 and olefins HC 3:1 to HC 10:1. This underlines a successful isomerization to an isomer distribution close to equilibrium as well as high conversions in the ethenolysis steps in the one-pot approach. Moreover, the close correlation indicates that no further undesired isomerization occurred during the second ethenolysis step. This is further reflected by a high selectivity for terminal alkenes and unsaturated esters of over 90 % (see Supporting Information Table S7). Performing the one-pot SEIEC in dichloromethane and MeOH as a reaction medium under otherwise identical reaction conditions afforded a product mixture with a lower selectivity of 55 % for terminal products. This can be accounted for by a more pronounced deceleration of the double bond isomerization by the presence of ethylene in  $\text{scCO}_2$  due to unproductive occupancy of the catalyst by ethylene (vide supra), suppressing any undesired simultaneous isomerization and ethenolysis. Thus, the utilization of  $\text{scCO}_2$  as solvent not only facilitates an integration of biomass extraction and catalytic upgrading but also a more selective reaction towards terminal products.

The utilization of soybean oil as a feedstock poses an additional challenge due to the large portion of multiple unsaturated fatty acids (Figure 2a). These are converted



**Figure 2.** Sequential catalysis (SEIEC) of plant oils. a) Fatty acid methyl ester (FAME) composition of high oleic sunflower and soybean oil. b) Gas chromatogram of the obtained product mixture (HC3:1 to HC 10:1 corresponds to alkenes and E3:1 to E10:1 to esters) starting from transesterified high oleic sunflower oil, EVE corresponds to the ethyl vinyl ether used as a quenching agent during workup. c) Product distribution for alkenes (blue) and unsaturated esters (yellow) starting from high oleic sunflower oil and d) Soybean oil. Dots represent the theoretical product distributions from complete ethenolysis and isomerization in methanol (the connecting line is only a guide for the eye). Biorefining concept comprising sequential ethenolysis, isomerization and ethenolysis catalysis (SEIEC) for the polyunsaturated FAME18:2 and FAME 18:3 (e). Reaction conditions: (1) ethenolysis 0.06 mol % UC, 55 °C, 3 bar ethylene,  $p_{\text{total}}$  250 bar, catalyst added as solution in 6 mL DCM (dichloromethane), 24 h; (2) isomerization 0.4 mol % [(dtpbx)Pd(OTf)<sub>2</sub>] per double bond, 85 °C,  $p_{\text{total}}$  500 bar, catalyst added as solution in 5.9 mL DCM and 0.1 mL methanol, 48 h; (3) ethenolysis 0.4 mol % UC per double bond, 55 °C, 15 bar ethylene,  $p_{\text{total}}$  450 bar, catalyst added as a solution in 6 mL DCM, 24 h. e) Transformation of polyunsaturated fatty acids in the SEIEC process.

amongst others to 1,4-pentadiene in the ethenolysis (Figure 2e), which can form stable allylic Pd-complexes<sup>[29]</sup> with the isomerization catalyst and thereby impede the double bond isomerization. The SEIEC with transesterified soybean oil led to all desired products with an uncompromised high selectivity of 97 % for chain lengths < C<sub>10</sub> and 95 % of terminal unsaturated products. This is enabled by a high ethenolysis performance in the primary as well as final ethenolysis step, with conversions and selectivities over 96 % and up to 86 %, respectively. By doubling the reaction times of the isomerization step, a high degree of isomer-

ization leading to all double bond isomers could be achieved, though a full isomer equilibrium was not reached. This reflects in lower amounts of the unsaturated esters at the lower end of the spectrum of chain lengths (up to ca. C<sub>6</sub>) in the found product distribution than expected for a complete isomerization (Figure 2d).

### Microalgae as a feedstock

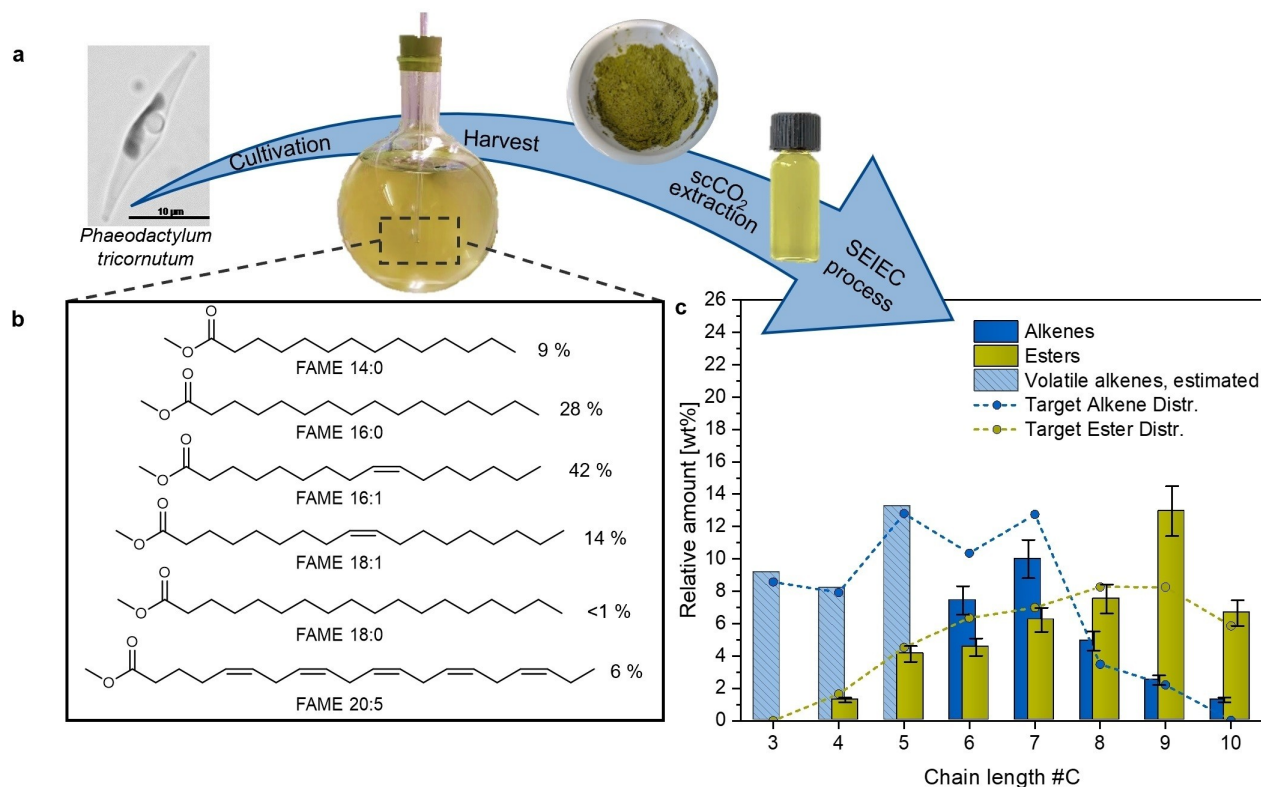
Microalgae feature high growth rates and short harvesting cycles and can deliver one or two orders increased yields per area compared to traditional oilseed crops.<sup>[32–34]</sup> They do not require arable land but can be grown in a range of aquatic habitats including rivers, lakes and even wastewater and generally are tolerant towards growth conditions.<sup>[34]</sup> The potential of microalgae as a feedstock has been realized so far in pilot projects for e.g. the production of aviation fuels, and in the industrial production of surfactants.<sup>[35]</sup>

The extraction of dry microalgae powder in a continuous flow of scCO<sub>2</sub> at 90 °C and 600 bar (corresponding to a density  $\rho(\text{CO}_2) \approx 0.89 \text{ g mL}^{-1}$ ) yielded an oil with an unsaturated fatty acid content of ca. 60%, which served as a substrate for the SEIEC (Figure 3a). Whereas the conversion in both ethenolysis steps reached values over 96 and 84%, respectively, the isomer equilibrium was not completely reached as concluded from the lower amounts

of shorter chain length ( $C_{\leq 6}$ ) esters and intermediate ( $C_5$ ,  $C_6$ ) chain length olefins (Figure 3c). As outlined for soybean oil, multiple unsaturated compounds slow down isomerization. Microalgae oil prominently contains five-fold unsaturated eicosapentaenoate (FAME 20:5, Figure 3b) present in limited but relevant amounts. Notwithstanding, a high selectivity of 97% for products with chain length  $< C_{10}$  as well as a high share for terminal products of 90% was reached, underlining the suitability of microalgae feedstock for our biorefining approach.

### Perspective catalyst developments

These findings show that a broad feedstock basis can be converted by our biorefining approach, and further to achieve maximum flexibility enhanced isomerization performance is desirable. To probe the viability of improvements to this end, beyond commercially available diphosphines, the novel complex  $[(\text{dabpx})\text{Pd}(\text{OPFBS})_2]$ <sup>[36]</sup> was



**Figure 3.** Extraction and catalytic transformation of microalgae oil. a) Schematic representation of microalgae processing starting from cultivation of a *Phaeodactylum tricornutum* species via harvesting and scCO<sub>2</sub> extraction to the catalytic refining process of microalgae oil. b) Fatty acid composition of extracted microalgae oil and c) obtained product distribution for alkenes (blue, (solely derived from monounsaturated compounds formed in the primary ethenolysis step)) and unsaturated esters (yellow) of extracted microalgae oil after sequential catalysis. For the calculation of the theoretical amounts of HC3:1 to HC5:1 (light blue bars), an isomer distribution of the primary ethenolysis products was used which was obtained in a reference isomerization under the same reaction conditions. Dots represent the theoretical product distributions from complete ethenolysis and isomerization in methanol (the connecting line is only a guide for the eye). Reaction conditions: (1) ethenolysis 0.06 mol% UC, 55 °C, 3 bar ethylene,  $p_{\text{total}}$  250 bar, catalyst added as solution in 6 mL DCM, 24 h; (2) isomerization 0.4 mol%  $[(\text{dtpbx})\text{Pd}(\text{OTf})_2]$  per double bond, 85 °C,  $p_{\text{total}}$  500 bar, catalyst added as a solution in 5.9 mL DCM and 0.1 mL methanol, 48 h; (3) ethenolysis 0.4 mol% UC per double bond, 55 °C, 15 bar ethylene,  $p_{\text{total}}$  450 bar, catalyst added as a solution in 6 mL DCM, 24 h.

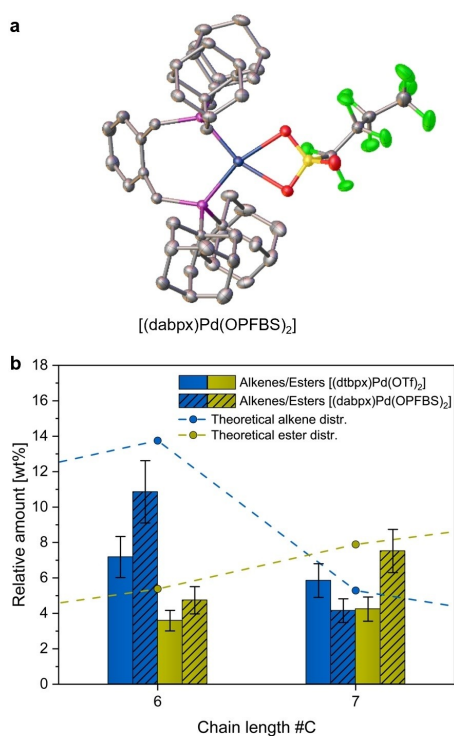
explored. This combines an adamantyl-phosphine motif, known to be generally more stable than its *tert*-butyl analogue<sup>[37]</sup> with perfluorinated sulfonate anions that can enhance solubility and dissociation due to their lyophilicity concerning *scCO*<sub>2</sub> (Figure 4a and Figure S2).<sup>[38–40]</sup> Indeed, the isomerization of decene and methyl decenoate model substrates into the double bond equilibrium occurred significantly faster with [(dabpx)Pd(OPFBS)<sub>2</sub>] compared to the [(dtbpx)Pd(OTf)<sub>2</sub>] catalyst (see Supporting Information Table S3 and Figure S7, S8a, S8b). In the SEIEC on soybean oil as an example of a challenging substrate, the incomplete double bond isomerization could be overcome by utilizing [(dabpx)Pd(OPFBS)<sub>2</sub>], as evidenced by the observed product distribution matching theoretical values calculated for the case of full equilibration in the isomerization step (Figure 4b, for complete distribution see Fig-

ure S17). At the same time high conversions in both ethenolysis steps (98 and 88 %, respectively) and a high selectivity for products with a chain length < C<sub>10</sub> (94 %) as well as for terminal products (97 %) were not compromised. The latter, in particular, underlines that despite a faster isomerization, no undesired simultaneous isomerizing ethenolysis occurred in the final stage.

## Conclusion

1-olefins, together with ethylene and the aromatics benzene and *para*-xylene, are the basic building blocks of today's chemical industry.<sup>[41]</sup> Their central role in this proven valorization Scheme stems from their versatile reactivity which enables their conversion to major polymers, lubricants, surfactants and many other products. The biorefinery approach demonstrated here can provide these building blocks directly from a variety of feedstocks, comprising existing large scale oil crops as well as microalgae as a perspective resource. Preliminary studies of a waste frying oil as a substrate further underline the robustness of the catalytic procedure for different feedstocks (see Supporting Information Figure S18a and S18b). The final products originate for the largest part (ca. 80 wt. %) from the natural oil feedstock and only ca. 20 wt. % are derived from the ethylene co-reagent. The latter can also be generated on a renewable basis from bioethanol effectively. Concerning the portion of different chain length products, it is notable that our approach offers the additional possibility of fully adjusting these to a given demand by partial feeding of the products after downstream separation back into the process. The formation of these 1-olefins differs from simultaneous isomerization-metathesis with complete breakdown of methyl oleate starting material to yield propylene, the latter originating for the largest part from the ethylene coreagent.<sup>[42]</sup> The terminal unsaturated ester products formed in addition to the 1-olefin major products are valuable precursors for dicarboxylates like adipic, azelaic or sebacic acid, used amongst others as monomers for polyesters and polyamides.<sup>[43,44]</sup> Proven carbonylation chemistry can generate the dicarboxylates,<sup>[45,46]</sup> while 1-olefins and methyl decenoate<sup>[45]</sup> can be used as direct drop-in replacements of petrochemical sourced products.

Concerning the practicability of our approach, it is encouraging to note that both alkenolysis reactions<sup>[45]</sup> and olefin isomerizations<sup>[46,47]</sup> are both viable on an industrial scale (though as separated processes and with substrates different than the feedstocks used here), as are processes in supercritical media at elevated pressures.<sup>[48,49]</sup> Further improvements of catalyst performance are desirable to improve competitiveness with highly optimized traditional petrochemical procedures. Our findings underline the need for efficient olefin isomerization catalysts that are compatible with functional groups to enable the utilization of fatty acid feedstocks. Supercritical carbon dioxide, used as an environmentally benign solvent was found to also promote the high selectivity of the process. The additional benefit of simplifying the overall biomass-to-product process by



**Figure 4.** Use of [(dabpx)Pd(OPFBS)<sub>2</sub>] in sequential catalysis with transesterified soybean oil. a) Solid state structure of [(dabpx)Pd(OPFBS)<sub>2</sub>]<sup>[36]</sup> obtained by single crystal x-ray diffraction. Hydrogen atoms and the non-coordinating sulfonate anion are omitted for clarity. b) Distribution of selected alkene (blue) and unsaturated ester (yellow) products obtained by SEIEC with soybean oil feedstock using [(dabpx)Pd(OPFBS)<sub>2</sub>] vs. [(dtbpx)Pd(OTf)<sub>2</sub>] as a reference (for complete product distribution using [(dabpx)Pd(OPFBS)<sub>2</sub>] see Supporting Information Figure S17). Dots represent the theoretical product distributions from complete ethenolysis and isomerization in methanol (the connecting line is only a guide for the eye). Reaction conditions: (1) ethenolysis 0.06 mol% UC, 55 °C, 3 bar ethylene, *p*<sub>total</sub> 250 bar, catalyst added as solution in 6 mL DCM, 24 h; (2) isomerization 0.4 mol% [(dabpx)Pd(OPFBS)<sub>2</sub>] per double bond, 85 °C, *p*<sub>total</sub> 500 bar, catalyst added as a solution in 5.9 mL DCM and 0.1 mL methanol, 48 h; (3) ethenolysis 0.4 mol% UC per double bond, 55 °C, 15 bar ethylene, *p*<sub>total</sub> 450 bar, catalyst added as a solution in 6 mL DCM, 24 h.

harmonizing the solvent used for biomass extraction and for catalysis contributes to an efficient procedure. Beyond the application to microalgae biomass, this utilization of scCO<sub>2</sub> for extraction and sequential catalysis (SEIEC) was also demonstrated for sunflower seeds (see Supporting Information Figure S19a, S19b and S19c). We anticipate these findings will enable the transition to a chemical industry less dependent on fossil feedstocks. Further, it is notable that ethenolysis/isomerization has also been used most recently to upgrade plastic waste, a development that will further prompt advances of this powerful technology.<sup>[50,51]</sup>

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

**Keywords:** Biorefinery · Catalysis · Homogeneous Catalysis · Renewable Resources · Sustainable Chemistry

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