ACS Sustainable Chemistry & Engineering

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Research Article

Toward Sustainable Chemical Synthesis: Metathesis of Sunflower-Derived Ethyl Esters and Evaluation of the Surfactant Potential of the Product Mixtures

Published as part of ACS Sustainable Chemistry & Engineering special issue "Sustainable Research Spotlight: Sub-Saharan Africa".

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Cite This: ACS Sustainable Chem. Eng. 2024, 12, 15472−15483

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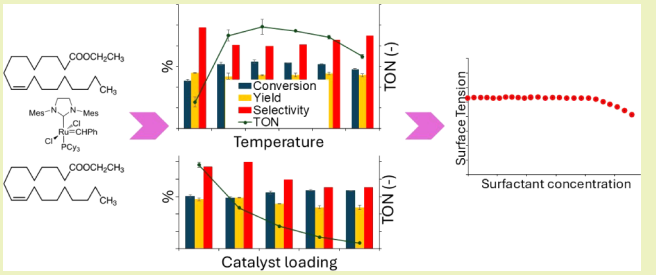
ABSTRACT: Metathesis of functionalized alkenes from sustainable biological feedstocks like plant oils is an important chemical reaction pathway, that could contribute toward improving the environmental sustainability of the chemical synthesis industry. In this study, the metathesis of unsaturated fatty acid ethyl esters derived from higher purity ethyl oleate (HPEO) and sunflower oil-based ethyl esters (SB) using the Grubbs second-generation catalyst was investigated, and the potential of the metathesis-enriched product mixture to act as a surfactant was evaluated. The product distribution of the metathesis reaction and the surfactant potential of the product mixtures were determined. Metathesis of the HPEO performed best at 50 °C and 0.2 mol % catalyst loading, resulting in 67.4% conversion of unsaturated fatty acid esters and a yield of 47.7% (based on the formation of 9-octadecene and diethyl 9-octadecene). For the SB feedstock, 87.8% feedstock conversion was achieved under optimum conditions (0.4 mol % catalyst loading at 50 °C) but at lower yields of ∼11.6%, due to the complexity of the feedstock and the multiple coproducts that can form. Surfactant studies showed that the surfactant potential of the reaction mixtures obtained from the feedstocks was upgraded through metathesis (C_{20} of 8305 mg/L for HPEO compared to C_{20} of 4995 mg/L for metathesized HPEO, and C_{20} of 8.90 mg/L for SB compared to C_{20} of 0.08 mg/L for metathesized SB). The C_{20} of some of the reaction product mixtures was in the same order as that of the industrial surfactant Flotanol (C_{20} of 7742 mg/L), although product mixtures lacked the foaming capacity of the industrial surfactant, making them suitable for specific applications where nonfoaming surfactants are desired, like paper making or textile dyeing industries. The study confirmed that the metathesis of unsaturated ethyl esters from sunflower oil generates a range of useful chemical products, which can make an important contribution toward the chemical synthesis industry moving away from fossil-based inputs.

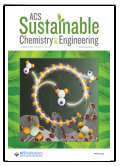


KEYWORDS: *renewable resources, plant oils, metathesis, value-added chemical intermediates, sustainable chemistry*

1. INTRODUCTION

Alkene metathesis is a powerful catalytic method that is used industrially for the generation of petrochemicals, polymers, oleochemicals, and specialty chemicals.[1] However, conventional fossil-derived feedstocks remain the major raw material, with alkenes forming a major proportion thereof.[2] The need to reduce fossil-based carbon emissions in the chemical industry, which contributes approximately 18% to industrial carbon dioxide emissions and 5% to global greenhouse gas emissions, necessitates the development of environmentally friendly catalytic pathways.[3−5] Metathesis of plant-based organic molecules provides such a catalytic pathway as it adheres to a number of the principles of green chemistry: it utilizes a renewable feedstock, and it has high atom economy as all atoms present in the starting materials are incorporated into the final product, reducing waste generation.[1] Metathesis of nonfunctionalized alkenes has been well studied, as the catalysis with metal carbene catalysts shows low tolerance for some functional groups. However, well-defined ruthenium complexes have been developed that show an improved tolerance toward functional groups, thereby allowing for

Received: June 10, 2024
Revised: September 25, 2024
Accepted: September 26, 2024
Published: October 4, 2024



successful metathesis of functionalized alkenes.[6] Schrock, Grubbs, and the Hoveyda−Grubbs catalysts have been applied in metathesis of functionalized and nonfunctionalized alkenes, with the Grubbs catalyst being viewed as the standard against which new catalysts are compared.[7]

Natural fats and oils and their derivatives provide a potential feedstock for alkene metathesis since some of the fatty acids that make up the natural oils, contain the unsaturated carbon−carbon double bonds required for a metathesis reaction. Plant oils are a particularly suitable renewable feedstock for metathesis, and cross-metathesis of seed oil is already employed in a biorefinery plant, providing access to oleochemicals, specialty chemicals, and alkenes.[6] Self-metathesis of plant oil leads to the formation of a mixture of internal alkenes, diesters, and ethyl esters,[8] each with its own potential use. Diesters are used in the synthesis of biosourced materials such as polymers (polyamides and polyesters), adhesives, coatings, and cosmetics.[9] Fatty acid esters can serve as biofuels and are used to synthesize fuel additives, lubricants and metal working fluids, coatings, cosmetics, personal care products, detergents, and surfactants.[10,11] An important application of internal alkenes is the production of chiral aldehydes, which is an important starting point for pharmaceutical products.[12−14] However, in plant oils, unsaturated fatty acids (UFAs) are chemically bonded to glycerol, which could become a chemical nuisance since it could result in the formation of undesirable cyclic products. The UFAs can be chemically removed from glycerol using various methods, with base-catalyzed transesterification being the one considered in this study. Methanol is the most often used alcohol reagent, but in this study, ethanol is used, which is more renewable than methanol in the sense that it can be produced on a large scale from renewable bioresources,[15,16] and ethanol is less toxic than methanol.[17] Using these natural feedstocks could decrease the carbon intensity of the chemical industry, reducing environmental impacts and contributing to a sustainable chemical industry.[10,18,19]

One of the drawbacks of employing a mixed starting substrate like UFAs from a natural feedstock is the formation of a mixture of products, which may require further separation, driving up production costs. One application that may not require such separation is for surfactant applications, where mixtures of compounds are often employed in industrial surfactant formulations. Co-surfactancy is frequently employed to address various applications within a formulation. For instance, stabilizers and spreader surfactants are used together in a foliar fertilizer formulation to enhance the stability, sprayability, and coating efficiency. Depending on the exact product distribution, products from self-metathesis of fatty acid esters obtained from transesterification from plant oils could potentially have surfactant properties. Sunflower oil contains a higher concentration of linoleic acid compared to canola oil and might therefore result in a wider range of metathesized products. However, to determine a specific market for such mixtures, the surfactant potential of such a reaction mixture needs to be ascertained.[20]

There is a lack of literature focusing on the metathesis of mixtures of functionalized alkenes, particularly from renewable resources. There is extensive literature on the metathesis of pure UFAs obtained from plant oils, but purification of UFAs from plant oils before metathesis increases overall production costs; limited studies explore the metathesis of mixed UFAs without initial purification. This work aimed to investigate the metathesis of unsaturated fatty acid ethyl esters (FAEEs) using the Grubbs second-generation catalyst (Grubbs 2) and evaluate the potential of the metathesis-enriched product mixture to act as a surfactant. The effect of the reaction conditions (reaction temperature and catalyst loading) was determined for a higher purity ethyl oleate (HPEO) and a sunflower-based (SB) feedstock and compared. Possible catalyst deactivation was evaluated for the SB feedstock. Finally, the surfactant properties for both feedstocks were evaluated for the unmodified reaction product stream, and permeate and retentate streams when the reaction product mixture was subjected to one or two stages of membrane nanofiltration.

2. EXPERIMENTAL SECTION

2.1. Materials. Commercial sunflower oil (Spar brand) was obtained from a local retail outlet (Stellenbosch, South Africa). For acid-catalyzed esterification: sulfuric acid (98.9%), ethanol (99.9%), oleic acid (≥88.5%), technical grade linoleic acid (58−74%), hexane (≥99%), and ethyl acetate (98%) were supplied by Sigma-Aldrich (South Africa). For base-catalyzed transesterification: sodium hydroxide (99.7%), ethanol (99.9%), and 3 Å molecular sieves (20 wt % absorption capacity) were supplied by Sigma-Aldrich (South Africa). For metathesis: Grubbs 2 catalyst (shown in Figure 1, 99% purity),

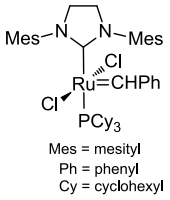


Figure 1. Chemical structure of the Grubbs 2 catalyst.

ethyl vinyl ether, and dichloromethane (99.9%) were supplied by Sigma-Aldrich (South Africa). PuraMem 280 organic solvent nanofiltration (OSN) flat sheet membranes were supplied by Evonik (Germany). Silica gel 60 F254 and RP-18W/UV254 thin-layer chromatography (TLC) plates were supplied by Merck (Germany) and Macherey-Nagel (Germany), respectively. Furthermore, gas chromatography (GC) reference standards dodecane (99.9%), ethyl palmitate (99%), ethyl stearate (≥99%), ethyl oleate (98%), ethyl linoleate (99%), ethyl linolenate (≥98%), and ethyl arachidate (≥99%) were all obtained from Sigma-Aldrich (South Africa). All of these chemicals were used without any further purification. GC reference standards for 9-octadecene and diethyl 9-octadecenedioate were synthesized (see Supporting Information). For the surfactant investigations, Flotanol was supplied by Clariant (South Africa).

2.2. Methods. *2.2.1. Preparation of the Metathesis Feedstock from Oleic Acid.* A higher purity ethyl oleate (HPEO) feedstock was prepared from technical grade oleic acid (≥88.5%) through an acid-catalyzed esterification reaction. Oleic acid (*ca.* 100 mL) was weighed accurately and transferred to a 250 mL flat-bottomed flask, fitted with a reflux condenser (using water as coolant). A heating mantle with a thermocouple and a magnetic stir bar was used to control the reaction temperature at 80 °C and stirring speed at 500 rpm, respectively. The fatty acid was preheated to 80 °C, after which ethanol (3:1 molar ratio of ethanol to oleic acid)

https://doi.org/10.1021/acssuschemeng.4c04758
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and finally 0.25 M sulfuric acid were added. Molecular sieves (3 Å) were added to the reaction mixture to remove the water that formed during the reaction. The esterification reaction was allowed to continue for 90 min, whereafter the reaction mixture was allowed to cool to room temperature, followed by the addition of hexane and distilled water in equal volumes. The entire reaction mixture was centrifuged at 14 000 rpm for 5 min, ensuring complete separation of the organic and aqueous phases. The top organic phase was transferred to a vacuum distillation setup, and the hexane was boiled off at a temperature of 71 °C (in industrial settings, should this esterification route be utilized, the possible toxicity of hexane could be avoided by using a different nonpolar solvent to extract the FAEE from the reaction mixture). The fatty acid ethyl ester (FAEE) mixture was then heated (under vacuum) to 120 °C for 10 min to remove any residual moisture present in the mixture. This FAEE mixture was analyzed using the method described in Section 2.2.5, and the esterification yield (Y_E) was calculated based on the mass of oleic acid converted to ethyl oleate (see eq 1). The mass of ethyl oleate was quantified by gas chromatography−mass spectrometry (GC−MS), whereas the mass of oleic acid was determined based on specifications obtained from the supplier.

$$Y_E\,(\%) = \frac{\text{mass of ethyl oleate}}{\text{mass of oleic acid in standard}} \times 100 \quad (1)$$

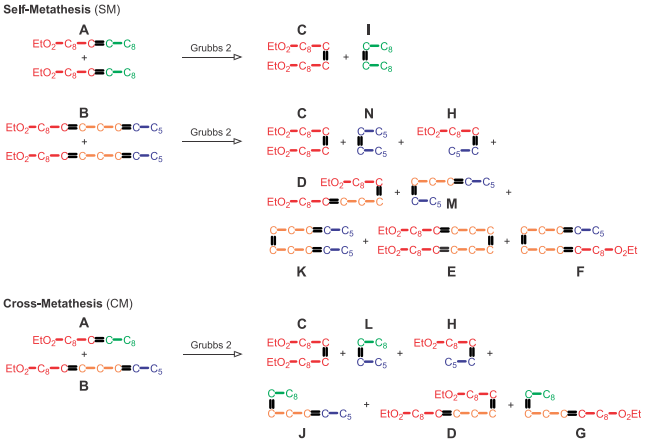
2.2.2. Preparation of the Metathesis Feedstock from Sunflower Oil. A sunflower-based (SB) feedstock was prepared from commercial sunflower oil through a base-catalyzed transesterification reaction. Sunflower oil (*ca.* 100 mL) was weighed accurately and transferred to a flat-bottomed flask, fitted with a reflux condenser (using water as coolant). A heating mantle with a thermocouple and a magnetic stir bar was used to control the reaction temperature at 60 °C and the stirring speed at 500 rpm, respectively. Ethanol (6:1 molar ratio of ethanol to oil) and NaOH (0.8 wt % of the oil) were mixed in a glass beaker until the NaOH dissolved completely, forming a sodium ethoxide solution. Thereafter, 3 Å molecular sieves (75% of the bed volume of ethanol used) were added to the sodium ethoxide solution to absorb any residual water. After 20 min, the solution was decanted into the flat-bottomed flask, which was preheated to a reaction temperature of 60 °C. After 90 min, the reaction mixture was decanted into a 250 mL gravity-separation funnel, allowing for the separation of the glycerol from the FAEEs. The FAEE phase was removed and washed with hot water (60 °C) until the pH of the wash water was approximately 7. The FAEE mixture was then decanted into a 300 mL glass beaker and heated to 120 °C for 15 min, allowing for the evaporation of any residual water present in the mixture. This FAEE mixture was analyzed using the method described in Section 2.2.5, and the transesterification yield (Y_{TE}) was calculated as the mass of UFAs in the oil converted to FAEEs (see eq 2). The mass of FAEEs was quantified by GC−MS, and the mass of UFAs was determined based on specifications obtained from the supplier.

$$Y_{TE}\,(\%) = \frac{\text{mass of FAEEs}}{\text{mass of UFAs in oil}} \times 100 \quad (2)$$

2.2.3. Metathesis Reactions. The metathesis reactions of the two feedstocks were carried out in sealed Falcon tubes in the temperature range of 20−100 °C and with a catalyst loading of 0.025−0.4 mol %. The lower limit of 20 °C was selected due to the low activity of the Grubbs 2 catalyst below this temperature, and the upper limit of 100 °C was selected based on the tendency of the Grubbs 2 catalyst to deactivate beyond this temperature.[21,22] The catalyst loading range was selected as the range mostly used for fatty acid or ester feedstocks.[23−26] Optimum metathesis reaction conditions were determined by (a) varying the reaction temperature while the catalyst loading was kept at 0.1 mol % and (b) varying the catalyst loading while the reaction temperature was kept at 50 °C. A reaction time of 60 min was used based on preliminary experiments (data not shown).

To perform the metathesis reactions, feedstock (3 mL) was added to a Falcon tube and heated to the required reaction temperature in a water bath. Based on the molar amount of UFAEs in the feedstock, Grubbs 2 catalyst was added to the feedstock to initiate the reaction. Samples (200 μL) were collected by syringe at 0, 2.5, 5, 10, 15, 30, 45, and 60 min and transferred to sample vials. Ethyl vinyl ether (500 mol equiv) was added to each vial to terminate the metathesis reaction. The samples were prepared for GC−MS analysis according to the method described in Section 2.2.5. The metathesis efficiency was expressed in terms of the conversion (X_M), effective turnover number (TON), the average molar conversion rate (X_{ave}), and the yield (Y_M) using eqs 3−7. For the calculation of yield and selectivity, the molar amounts of 9-octadecene and diethyl 9-octadecenedioate (**I** and **C**, respectively, in Scheme 1) were used, as these were the only two metathesis compounds for which GC reference standards were available.

Scheme 1. Expected Primary Metathesis Products of Ethyl Oleate and Ethyl Linoleate



$$X_M\,(\%) = \frac{\text{moles UFAEs}_{\text{Reacted}}}{\text{moles UFAEs}_{\text{Initial}}} \times 100 \quad (3)$$

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ACS Sustainable Chem. Eng. 2024, 12, 15472−15483

$$X_{ave}\,(\text{mmol/h}) = \frac{\text{millimoles UFAEs}_{\text{Reacted}}}{\text{Time to reach equilibruim (h)}} \quad (4)$$

$$\text{TON} = \frac{\text{moles of UFAEs}_{\text{Reacted}}}{\text{moles of catalyst}} \quad (5)$$

$$Y_M\,(\%) = \frac{\text{moles of } \mathbf{C} \text{ and } \mathbf{I}_{\text{Final}}}{\text{moles UFAEs}_{\text{Initial}}} \quad (6)$$

$$\text{Selectivity}\,(\%) = \frac{\text{Yield}}{\text{Conversion}} = \frac{\text{moles of } \mathbf{C} \text{ and } \mathbf{I}_{\text{Final}}}{\text{moles UFAEs}_{\text{Initial}}} \quad (7)$$

2.2.4. Surfactant Investigations. The preparation of the metathesis reaction mixtures for the surfactant investigations is described in this section. Upon completion of the metathesis reactions, the catalyst was removed from the reaction mixtures using organic solvent nanofiltration (OSN).[27] The product streams were also partially fractionated using OSN (data on the composition of the fractionated streams are available in the Supporting Information).[27] The surfactant potential of the metathesis reaction mixtures was investigated (i) visually through frothing tests and (ii) quantitatively through tensiometry measurements. Flotanol, an industrial surfactant used in the mining industry as a flotation frother, served as a benchmark for comparison.

Frothing tests were conducted in a flotation cell with a mixing blade rotating at 3500 rpm and air sparged into the solution at 5 L/min. The solution was prepared by adding the required amount (to achieve a specific concentration) of the product to 3 L of water.[28] Surface tension measurements were conducted at 25 °C using the du Noüy ring (platinum−iridium ring) method. A KRÜSS force tensiometer K100 (KRÜSS-scientific, Germany) was used for these measurements.

In preparation for tensiometry testing, 10 mL of the sample (with a known mass) was added to 35 mL of deionized water, followed by thorough mixing in a 50 mL Schott bottle. Given the hydrophobic nature of the compounds under investigation, which may exhibit limited solubility in water, the mixture was transferred to a 100 mL separating funnel. This setup was left undisturbed for 24 h to facilitate phase separation. The process was designed to isolate insoluble oils from the aqueous phase under the premise that surface-active agents (surfactants)—known for their ability to lower the surface tension of water—would predominantly partition into the aqueous phase, leaving behind the hydrophobic, water-insoluble compounds on top of the water surface. Post separation, the aqueous phase was transferred to a 50 mL glass reservoir, which was then positioned in the tensiometer. The procedure for surfactant dilution was automated through the employment of two microdispensers: one dedicated to the addition of water and the other to the removal of diluted surfactant solution. Before use, the glass reservoir and platinum ring were cleaned with acetone, rinsed with deionized water, and dried over a flame. The final surface tension values were recorded after five consecutive measurements were obtained for a single surfactant concentration, achieving a standard deviation below 0.1 mN/m.

2.2.5. Sample Analysis. Chemical analysis of samples was done using a GC−MS. An Agilent 7890A gas chromatograph (GC) equipped with an Agilent 7693 auto-injector and an Agilent 5975C MSD triple-axis detector was used. The GC was fitted with a Zebron ZB-1701 (60 m, 0.25 mm ID, 0.25 μm film thickness) column. A split/splitless front inlet was used with an injection volume of 1.0 μL and a split ratio of 70:1. The injector settings were as follows: inlet temperature at 300 °C and a helium carrier gas flow rate of 15 mL/min at a pressure of 23.787 psi. The oven was programmed as follows: initial temperature of 54 °C (hold time 1 min) followed by an increase in temperature by 5 °C/min until 270 °C (hold time 14 min). The internal calibration method was used to quantify samples with GC response factors being determined experimentally. Samples for quantification were prepared as follows: 30 μL of dodecane (internal standard) and 80 μL of the sample were diluted with 1.5 mL of dichloromethane in a clean GC vial. Thereafter, 100 μL of the diluted sample was transferred into a new GC vial and diluted again with an additional aliquot of 1.5 mL of dichloromethane.

3. RESULTS AND DISCUSSION

3.1. Preparation of the Metathesis Feedstocks. The esterification of oleic acid achieved a high yield of 98.7%, and the transesterification of sunflower oil resulted in a yield of 82.1%. The HPEO feed contained 83.9 wt % ethyl oleate, 4.36 wt % ethyl linoleate, and 2.78 wt % saturated fatty acid ethyl esters (SFAEs). The SB feed contained 22.2 wt % ethyl oleate, 51.3 wt % ethyl linoleate, and 8.6 wt % SFAEs, in line with the more diverse fatty acid profile in the sunflower oil compared to the oleic acid. During base-catalyzed transesterification, the introduction of ethanol instead of methanol for reagent preparation resulted in considerable difficulty in obtaining high yields. Utilizing ethanol resulted in increased process complexity due to lower reactivity compared to methanol, and soap formation took place which led to reduced reaction yields and difficulty in phase separation between FAEE and crude glycerol. The use of 3 Å molecular sieves during the preparation of the ethoxide reagent was shown to be an effective way of catering for this added complexity. This method effectively reduces the free moisture content, shifting the equilibrium toward sodium ethoxide formation, thereby decreasing residual hydroxides. Removal of moisture and unreacted hydroxides from the reagent reduces the possibility that these reagents can hydrolyze the triglycerides in the oil, which will result in saponification of fatty acids and the formation of soaps. The transesterification yield of this study (82.1%) as well as other studies (81.4−93.1%),[16,29] are in range with yields obtained for base-catalyzed transesterification using methanol (80−97.4%).[30−32] Considering the environmental benefit of using ethanol over methanol, additional effort is warranted.

3.2. Expected Primary Metathesis Products. The expected primary metathesis products due to the self-metathesis (SM) and cross-metathesis (CM) reactions of ethyl oleate and ethyl linoleate (key components in the HPEO and SB feedstocks) are illustrated in Scheme 1. The SM of two molecules of ethyl oleate will yield compounds **C** (diethyl 9-octadecenedioate) and **I** (9-octadecene) as products. Similarly, the SM of two molecules of ethyl linoleate will yield **C**, **D**, **E**, **F**, **H**, **K**, **M**, and **N** as products. The CM of ethyl oleate and ethyl linoleate will yield **C**, **D**, **G**, **H**, **J**, and **L** as products. The product mixtures resulting from the metathesis of HPEO and SB feedstocks are therefore likely to be complex, as metathesis can result in the formation of internal alkenes, unsaturated diethyl diesters, and unsaturated FAEEs. The primary metathesis products can undergo further secondary metathesis reactions (not illustrated) *via* self-metathesis, cross-metathesis,

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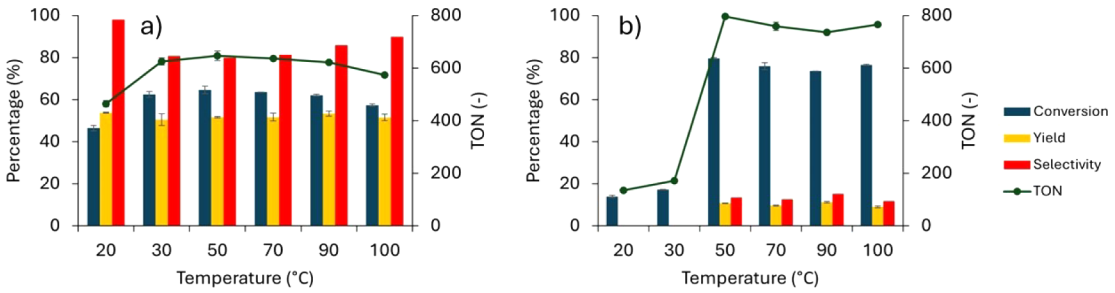

Figure 2. Effect of the reaction temperature on the conversion, yield, selectivity, and TON for the metathesis of the HPEO (a) and SB (b) feedstocks, using the Grubbs 2 catalyst at a 0.1 mol % catalyst loading.

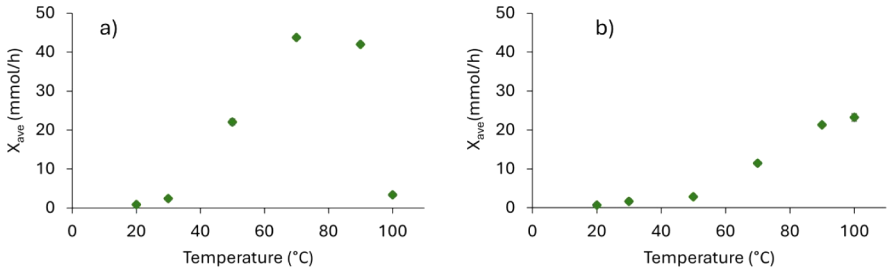

Figure 3. Effect of the reaction temperature on the average molar conversion rate of UFAEs for the HPEO (a) and SB (b) feedstocks, using the Grubbs 2 catalyst at a 0.1 mol % catalyst loading.

and ring-closing metathesis routes, leading to enhanced complexity in the product mixture.[8] The HPEO and SB feedstocks also contain small amounts of metathesis-unreactive SFAEs (no carbon−carbon double bonds are present). Downstream separation of the product mixture may therefore be challenging if individual compounds need to be recovered. Nonetheless, within the expected metathesis products, valuable diesters, and mono- and polyunsaturated internal alkenes are formed.[9,10,12]

In the work presented here, the goal is not to produce individual target compounds but rather to evaluate how the entire metathesis reaction product mixture (or membrane-processed product mixtures) can act as a surfactant. This approach complicates the calculation of green chemistry metrics. However, under the assumption that the diester products may be the desired reaction targets and all other metathesis products are viewed as byproducts, the molecular weight-based *E*-factors are as follows: for the SM of ethyl oleate, it is 1.46; for the SM of ethyl linoleate, it is 0.55; and for the CM of ethyl oleate and ethyl linoleate, it is 0.62.

3.3. Optimization of the Metathesis Reaction Conditions. *3.3.1. Effect of Reaction Temperature.* The effect of the reaction temperature on the reaction parameters for the metathesis of the HPEO (a) and SB (b) feedstocks is shown in Figure 2.

In Figure 2a, there is a similar trend for the reaction conversion and TON concerning the reaction temperature for the HPEO feedstock. As the temperature increases from 20 °C, the conversion increases from 46.4% at 20 °C to a maximum conversion of 64.6% at 50 °C. However, as the temperature continues to increase beyond this point, the conversion begins to decline, eventually reaching a conversion of 57.4% at 100 °C. This trend correlates well with literature findings where a different type of feedstock was subjected to the same catalyst.[2,21] The maximum conversion of this work (64.6%) surpasses previous results, which ranged between 45 and 50% with catalyst loadings varying from 0.0001 to 0.2 mol %, despite using high-purity methyl fatty acid esters as the feedstock.[21,23,26,33] Similar to conversion, the TON increased with temperature to a maximum of 646 at 50 °C. However, as the temperature continued to increase to 100 °C, the TON gradually decreased to 574. The maximum TON achieved in this work, 646, is modest when compared to the 440 000 TON reported in the use of a low catalyst loading of 0.0001 mol % for metathesis of methyl oleate.[21] However, the conversion of 64.6% achieved here outperforms the 45% reported by Dinger and coworkers, indicating a more efficient conversion despite the lower TON. Similarly, for investigations on CM of methyl oleate and 2-butene, high conversions and TONs were only achieved when the raw material was further refined (TON of 470 000 at 0.0002 mol %).[34] The increase in the TON as reaction temperature increases up to 50 °C is consistent with 1-octene metathesis using the same Grubbs 2 catalyst.[2] The decrease in conversion for temperatures higher than 50 °C may *inter alia* be due to thermal deactivation, although reduced activity and increased isomerization were only seen previously at temperatures of 90−100 °C.[22,27,36]

In Figure 2b, the trends of the reaction conversion and TON for the metathesis of the SB feedstock are also similar. At lower temperatures of 20 and 30 °C, conversion rates were modest at 13.9 and 17.1%, respectively. However, a substantial enhancement in conversion was observed upon elevating the temperature from 30 to 50 °C, with conversion increasing to 79.6%. Further temperature increases to 100 °C led to a marginal reduction in conversion, from 79.6 to 76.5%. The significant increase in reaction conversion between 30 and 50 °C is likely related to the activation energy for the metathesis of this feedstock, suggesting that this temperature range is critical for optimizing the reaction efficiency. The maximum conversion (79.6%) is lower than previously observed, where SM of unsaturated fatty acid methyl esters from soybean oil reached 89% using 0.1 mol % Grubbs 2 catalyst and a reaction temperature of 53 °C.[24] The total unsaturated fatty acid ester content of the soy methyl esters reached 80.4% (21% methyl

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ACS Sustainable Chem. Eng. 2024, 12, 15472−15483

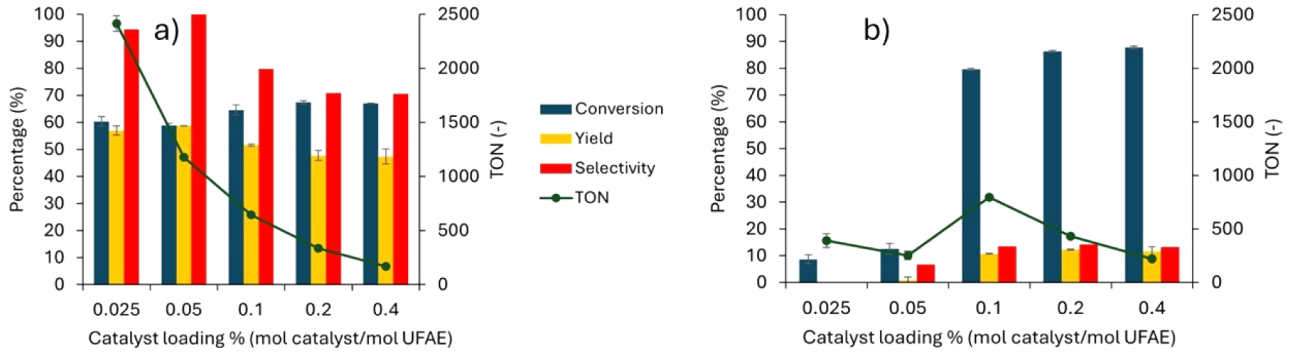

Figure 4. Effect of the catalyst loading on the conversion, yield, selectivity, and TON for the metathesis of the HPEO (a) and SB (b) feedstocks, using the Grubbs 2 catalyst at 50 °C.

oleate, 52% methyl linoleate, and 7.4% methyl linolenate) and was significantly higher than the 73.3% unsaturated fatty acid ester content (22.2% ethyl oleate and 51.3% ethyl linoleate) of our SB feedstock, which is likely the reason why higher conversions were achieved for the soybean feedstock. The TON showed the same trend as the conversion when the reaction temperature was increased (135 at 20 °C, 796 at 50 °C, and 765 at 100 °C). TONs for metathesis with similar feedstocks were not reported in literature but comparing it to the work of Ngo and Foglia (TON of 890 at a 0.1 mol % loading, based on 89% conversion),[23,24] the maximum TON (796) is lower for the same reason as discussed for the conversion.

The yield and selectivity results are less insightful. The yield remained more or less constant (~52%) for the HPEO feedstock (Figure 3a), even though it was slightly higher than that observed for the metathesis of methyl and ethyl oleates.[23,26,33] The slightly higher yield in this work is simply a result of higher conversions compared to the above-mentioned work. For the SB feedstock (Figure 3b), no metathesis products were detected at the lower temperatures (20 and 30 °C), and yields and selectivities remained similar at temperatures of 50−100 °C. The yields and selectivities achieved (9−11.2 and 12.7−15.2%, respectively) are also rather low compared to 60% yield when using soybean methyl esters as raw material.[25] The low yield and selectivity are likely a result of SM and CM occurring simultaneously with the SB feedstock.

The effect of the reaction temperature on the average UFAE molar conversion rate (X_{ave}) is presented in Figure 3 for the HPEO (a) and SB (b) feedstocks.

The average UFAE molar conversion rate for the HPEO feedstock (Figure 3a) increased almost linearly from 0.9 at 20 °C to 43.7 at 70 °C, and then it decreased to 3.3 at 100 °C. A linear increase in the average molar conversion rate is expected with an increase in temperature (40−75 °C).[33] However, equilibrium was only reached much later at 100 °C compared to the other runs (presumably due to potential thermal catalyst deactivation), thereby significantly decreasing the molar conversion rate. The average UFAE molar conversion rate for the SB feedstock (Figure 3b) increased almost linearly from 0.67 mmol/h at 20 °C to 2.81 mmol/h at 50 °C, and then it increased again in an almost linear fashion from 2.81 mmol/h at 50 °C to 23.2 mmol/h at 100 °C, but at a steeper gradient. Increased temperature is expected to result in an increased average molar conversion rate, seeing that metathesis is an endothermic reaction.[37]

Comparing these results with those of the HPEO feedstock, the average molar conversion rate for the SB feedstock is less than half of that for the HPEO feedstock. This finding is in agreement with previous work that found the conversion rate to be higher when dealing solely with the SM of a compound, as compared to a mixture where both SM and CM takes place.[38−40] There are several possible explanations for why SM reactions are faster than CM reactions. During SM, interactions between carbon atoms occur among identical reactants at concentrations higher than those observed during CM. Secondly, steric hindrance could play a relatively larger role during certain CM reactions, where the hindrance could make it more challenging for two CM reactants to approach each other. Thirdly, during CM, the catalyst must activate two different substrates, potentially lowering reaction rates. Finally, during CM, the different reactants may have substantially different electronic and steric properties, which could make it more challenging to reach an energetically favorable transition state leading to slower reaction kinetics.[41]

3.3.2. Effect of Catalyst Loading. The effects of the catalyst loading on the reaction parameters for the metathesis of the HPEO (a) and SB (b) feedstocks are illustrated in Figure 4.

For the HPEO feedstock (Figure 4b), the conversion increased from 60.4% at a 0.025 mol % catalyst loading to 67.4% at a 0.2 mol % catalyst loading, with a similar conversion of 67.0% achieved at a 0.4 mol % catalyst loading. The trends for conversion and TON correlate well with literature when using a heterogeneous catalyst at different catalyst loadings, where conversion was 15% at 0.43% HG/SiO_2, 44% at 0.87% HG/SiO_2, and 50% at 1.21% HG/SiO_2.[33,35] The maximum conversion of 67.4% at a 0.2 mol % catalyst loading observed in this work is higher than the 50% obtained for metathesis of 99% ethyl oleate at a 0.2 mol % loading.[26] The simultaneous SM and CM reactions of ethyl oleate and ethyl linoleate are again the potential reason for this increased conversion. The TON decreased from 2414 at a 0.025 mol % loading to 168 at a 0.4 mol % loading, confirming the higher catalytic efficiency at lower catalyst loadings.[2,27]

For the SB feedstock (Figure 4b), the conversion increased from 8.7% at a 0.025 mol % catalyst loading to 87.8% at a 0.4 mol % catalyst loading. The maximum conversion correlates well with previous work where 89% conversion was achieved at a 0.1 mol % catalyst loading, but at low catalyst loadings, the conversions are much lower than the 50% conversion seen at 0.01 mol %.[24] It was suspected that the low conversions at low catalyst loadings were due to chemical catalyst deactivation, and this possibility was investigated and reported in Section

https://doi.org/10.1021/acssuschemeng.4c04758
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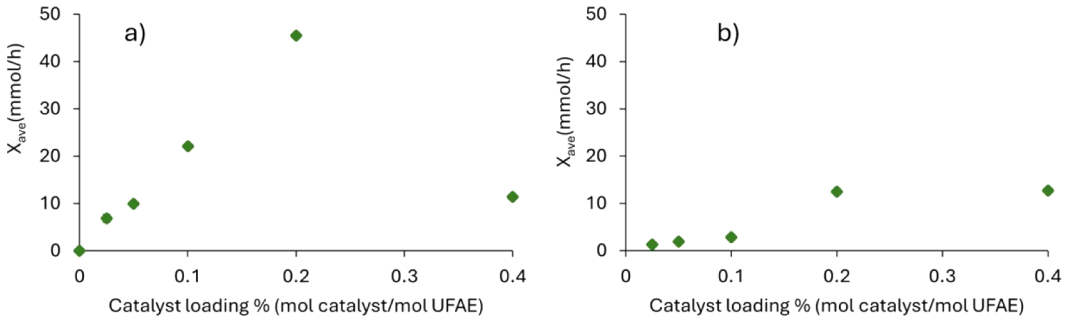

Figure 5. Effect of the catalyst loading on the average molar conversion rate of the UFAEs for the HPEO (a) and SB (b) feedstocks, using the Grubbs 2 catalyst at 50 °C.

3.5. In our work, the conversions at 0.2 and 0.4 mol % catalyst loadings were similar (86.4 and 87.8%), and in line with previous work (89% at a 0.1 mol % loading).[24] The TON decreased from 392 at a 0.025 mol % loading to 252 at a 0.05 mol % loading, whereafter an increase (252−796) was experienced upon increasing the catalyst loading to 0.1 mol %; the TON then decreased to 219 upon a further increase in the catalyst loading to 0.4 mol %. The trend in the TON from a 0.1 mol % loading to a 0.4 mol % loading is expected;[2,27] however, the decrease in TON from a 0.025 mol % loading to a 0.05 mol % loading is not. This decrease in the TON reflects the overall low conversions achieved at these low catalyst loadings.

The trends for yield and selectivity of the HPEO feedstock (Figure 4a) contradict earlier observations.[2,26] Instead of an increase in yield and selectivity with an increase in catalyst loading, a decrease is experienced for catalyst loadings higher than 0.05 mol %. For the SB feedstock (Figure 4b), the yields and selectivities at catalyst loadings between 0.1 and 0.4 mol % lie within a narrow range with yields between 10.7 and 12.3% and selectivities between 13.2 and 14.3%. These values for yield are significantly lower compared to what was found previously (50% at a 0.01 mol % loading and 60% at a 0.1 mol % loading).[24]

When considering the relative contribution of the two main primary metathesis products 9-octadecene and diethyl 9-octadecenedioate, they contribute only 13.5−14.5% to the total chromatogram (Table 2), with 9-octadecene not being detected at any catalyst loading, possibly being consumed in secondary metathesis reactions. Conversely, other metathesis products contributed a further 39.3−45.7% to the total chromatogram area, with ethyl 9-pentadecenoate being particularly prominent. These results confirm that the two metathesis products that were quantified only constituted a relatively small proportion of the total amount of product formed, explaining the low yields and selectivities.

The effect of the catalyst loading on the average UFAE molar conversion rate (X_{ave}) is presented in Figure 5 for the HPEO (a) and SB (b) feedstocks.

The average molar conversion rate of the UFAEs for the HPEO feedstock (Figure 5a) increased from 6.83 mmol/h at a 0.025 mol % catalyst loading to 45.5 mmol/h at a 0.2 mol % catalyst loading, after which it decreased to 11.4 mmol/h at a 0.4 mol % catalyst loading. Although the actual values are not comparable to literature, the general trend for the average molar conversion rates of UFAEs corresponds to literature findings (3.9 mmol/h g_{cat} at a 0.43% HG/SiO_2 loading, 11.6 mmol/h g_{cat} at 0.87% HG/SiO_2 loading, 16 mmol/h g_{cat} at 1.21% HG/SiO_2 loading, and 22.2 mmol/h g_{cat} at 1.67% HG/SiO_2 loading).[33] At a 0.4 mol % catalyst loading, the average molar conversion rate of the UFAEs deviates from the trend and, contrary to expectation, decreases from the value obtained at 0.2 mol % loading. The reason for this decrease in the reaction rate for an increased catalyst loading for this feedstock is unclear.

The average molar conversion rate of UFAEs for the SB feedstock (Figure 5b) increased with an increase in the catalyst loading. There was an almost linear increase in the average conversion rate from 1.29 mmol/h at a 0.025 mol % loading, to 2.81 mmol/h at a 0.1 mol % loading. From 0.1 to 0.2 mol %, the rate increased from 2.81 to 12.4 mmol/h, and only increased slightly to 12.7 mmol/h when catalyst loading was further increased to 0.4 mol %. The general trend of increased molar conversion rates with an increase in catalyst loading corresponds to previous work.[36] Compared to the HPEO feedstock, the average molar conversion rates were much lower for the SB feedstock (1.29−12.7 mmol/h for SB *vs* 6.83−45.5 mmol/h for HPEO). When starting with a mixed feedstock, molar conversion rates are expected to be slower than for a purer compound, for the same reasons as discussed in Section 3.4.[38−40]

3.4. SB Feedstock Metathesis Product Distribution.

Reaction temperatures (Table 1) below 50 °C have no significant effect on the product composition, and it resembles the compositions before the metathesis reactions. The

Table 1. Product Distribution (%) of the Metathesis of the SB Feedstock at Different Reaction Temperatures Using Grubbs 2 at a 0.1 mol % Catalyst Loading

Compound	Reaction temperature (°C)					
	20	30	50	70	90	100
Ethyl palmitate	6.4	6.5	7.7	10.3	10.4	10.4
Ethyl stearate	6.1	6.3	8.8	9.8	10.2	10.1
Ethyl oleate (**A**)	29.3	30.2	31.3	27.1	28.1	26.9
Ethyl linoleate (**B**)	57.9	56.4	1.3	11.6	12.1	13.6
Diethyl 9-octadecenedioate (**C**)	-	-	13.5	10.3	9.8	9.5
9-Octadecene (**I**)	-	-	-	-	-	-
6-Dodecene(**N**)	-	-	3.9	3.5	2.9	3.2
Ethyl 9-pentadecenoate (**H**)	-	-	23.2	19.5	18.7	18.7
6,9-Pentadecadiene (**M**)	-	-	2.2	0.8	1.1	-
6-Pentadecene (**L**)	-	-	6.2	5.3	4.9	4.6
C_{20} Ethyl esters	-	-	3.8	0.9	0.3	0.8
Total area %	*99.8*	*99.5*	*101.8*	*99.0*	*98.6*	**97.7**

https://doi.org/10.1021/acssuschemeng.4c04758
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saturated FAEEs, ethyl palmitate and ethyl stearate, do show a slight increase as the temperature increases, most probably due to the loss of more volatile metathesis products. The relative amounts of ethyl oleate (**A**) remain almost constant at all temperatures; it does not seem to participate to any significant extent in the metathesis reactions. Further, from the absence of **I**, the SM of **A** does not seem to occur at all, indicating that the majority of the formation of diethyl 9-octadecenedioate (**C**) was driven by reactions involving ethyl linoleate (**B**). Among the detected products at 50 °C and above listed in Table 1, the SM of **B** results mainly in the formation of ethyl 9-pentadecenoate (**H**) and **C**, with small amounts of only two of the remaining SM products (*i.e.*, 6,9-pentadecadiene (**M**) and 6-dodecene (**N**)) forming. Apart from **C** and **H**, which may also result from the CM reaction, 6-pentadecene (**L**) was the only other CM product detected.

Similar trends for the saturated FAEEs are observed if the catalyst loading is varied at 50 °C (Table 2). No metathesis products were detected at a catalyst loading below 0.1 mol %. At a catalyst loading of 0.1 mol % and above, the major primary metathesis products are **H** and **C**, with **L**, **M**, and **N** as minor products. The only indication of secondary metathesis reactions is the formation of 1,4-cyclohexadiene at 0.2 mol % and above due to the ring-closing metathesis of the trienes **E**, **F**, and/or **K**.

Table 2. Product Distribution (%) of the Metathesis of the SB Feedstock at Different Catalyst Loadings Using the Grubbs 2 Catalyst at 50 °C

	Catalyst loading (mol %)				
Compound	0.025	0.05	0.1	0.2	0.4
Ethyl palmitate	6.5	6.9	7.7	10.6	10.3
Ethyl stearate	6.1	6.7	8.8	9.2	7.9
Ethyl oleate (**A**)	29.3	29.9	31.3	23.4	22.3
Ethyl linoleate (**B**)	58.3	55.3	1.3	-	-
Diethyl 9-octadecenedioate (**C**)	-	-	13.5	13.9	14.5
9-Octadecene (**I**)	-	-	-	-	-
6-Dodecene (**N**)	-	-	3.9	4.8	5.2
Ethyl 9-pentadecenoate (**H**)	-	-	23.2	25.8	27.6
6,9-Pentadecadiene (**M**)	-	-	2.2	-	-
6-Pentadecene (**L**)	-	-	6.2	7.2	7.6
C_{20} Ethyl esters	-	-	3.8	2.3	-
1,4-Cyclohexadiene	-	-	-	2.8	5.3
Total area %	*100.2*	*98.7*	*101.8*	*100.0*	*100.6*

The formation of compounds **N** and **M**, combined with the presence of **L**, therefore indicates that it is likely that both the SM of **B** and the CM of **A** and **B** take place simultaneously. The absence of some of the SM and CM primary metathesis products may also be attributed to secondary metathesis reactions of the primary products. This needs to be investigated further.

3.5. Chemical Catalyst Deactivation Investigation. Based on our prior results, nonthermal catalyst deactivation was suspected and subsequently investigated. An additional investigation was done at 50 °C using an initial catalyst loading of 0.1 mol %. After the reaction mixture was allowed to reach equilibrium, an additional aliquot of catalyst was added. Chemical deactivation caused by impurities in the feedstock could result in lower metathesis efficiencies.[41−46]

The initial metathesis reaction reached equilibrium within approximately 15 min, and the further addition of metathesis catalyst after 45 min of reaction time resulted in further reaction and a new equilibrium being established. The conversion increased from 75% at 45 min to 91% at 60 min, which is an indication that the catalyst activity was lost during the first 45 min reaction phase, pointing toward catalyst deactivation. The Grubbs 2 catalyst normally shows good temperature stability up to 100 °C, and our work indicated good conversion for temperatures higher than 50 °C for both feedstocks (see Section 3.3.1), thereby ruling out thermal catalyst deactivation. However, chemical catalyst deactivation could explain the loss of catalyst activity, and hence the low conversions (8.7% and 12.6%) achieved at the lower catalyst loadings (0.025 and 0.05 mol %) in Section 3.3.2. At low catalyst loadings, the impurities are likely to deactivate the majority of the available catalyst active sites, resulting in very low conversions, whereas at higher catalyst loadings there seems to remain sufficient catalyst activity to reach significant feedstock conversions, comparable to what was reported previously.

Potential chemically deactivating compounds are likely a result of fatty acid oxidation. Chemical impurities in the feedstock that have been implicated in catalyst deactivation include peroxides, phosphates, sulfates, carboxylate salts (soap), glycerides, and fatty acids.[47,48] Organic hydroperoxides form from autoxidation of unsaturated fatty acids in plant oils and poison the metathesis catalyst.[41−46] The SB feedstock

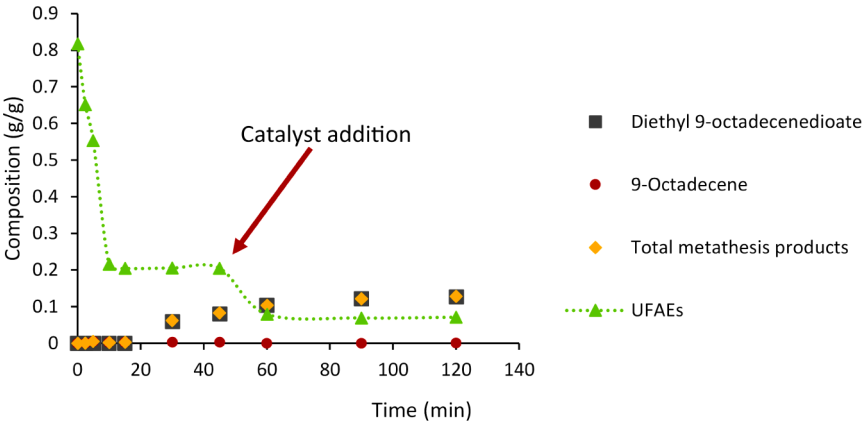

Figure 6. Catalyst deactivation test for the metathesis of the SB feedstock using the Grubbs 2 catalyst at 50 °C and a 0.1 mol % catalyst loading.

https://doi.org/10.1021/acssuschemeng.4c04758
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contained predominantly ethyl linoleate (51.3%), which includes two carbon−carbon double bonds, making the feedstock susceptible to autoxidation and hydroperoxide formation.

To investigate whether peroxides might be responsible for the lower TONs, conversions, and yields found for low catalyst loadings when using the SB feedstock, the peroxide content and metathesis performance of fresh SB feedstock were compared to the initial SB feedstock (which by this time showed some aging). A qualitative and quantitative test for peroxides was performed, where potassium iodide was added to acetic acid, and the mixture was added to each feedstock sample. In the presence of peroxides, the mixture reacts to form potassium hydroxide and darkly colored iodine. The aged sunflower oil (129 mequiv/kg oil) and the aged SB feedstock (309 mequiv/kg feedstock) contained considerably higher peroxide concentrations than the freshly prepared ones (19.0 mequiv/kg oil for fresh sunflower oil and 99.1 mequiv/kg feedstock for freshly prepared SB feedstock). The peroxide values can help explain the results shown in Figure 6, which could be due to chemical catalyst deactivation resulting from the presence of oxidation products. Here, we have tested only for peroxides, and there may also be other impurities in the feedstock that could cause chemical catalyst deactivation. Chemical catalyst deactivation could explain the low TON and yields, specifically for lower catalyst loadings. Comparison of metathesis using freshly prepared SB feedstock and aged feedstock resulted in the values presented in Table 3.

Table 3. Comparison of the Metathesis Performance Parameters for an Aged and Fresh Feed of the SB Feedstock Using the Grubbs 2 Catalyst at 50°C and a 0.1 mol % Catalyst Loading

Parameter	Aged feed	Fresh feed
Conversion (%)	79.6	89.1
Yield (%)	10.7	19.5
Selectivity (%)	13.5	21.9
TON	796	891

Compared to the aged feedstock, the conversion of fresh SB feedstock increased from 79.6 to 89.1%; the yield increased from 10.7 to 19.5%; the selectivity increased from 13.5 to 21.9%; and the TON increased from 796 to 891. The conversion and TON achieved with fresh feedstock are also comparable (89% and 890 at a 0.1 mol % loading) when performing metathesis of soy methyl esters.[24] There are prior indications that alkene metathesis could be significantly impacted by unknown factors, as high TON could only be achieved for specific batches of raw material.[34] Although the authors did not specifically pinpoint the possible reasons for batch-to-batch variation in TON and conversion, we pose the possibility that oxidation products may have played a role in this.

3.6. Surfactant Studies. The visual results from the frothing tests indicated that the metathesis reaction products had a higher foaming capacity compared to the feedstocks, but neither were comparable to the industrial standard employed (Flotanol). Results of the tensiometric quantification of the feedstock, and unfractionated and fractionated reaction products, are presented in Table 4.

In Table 4, a CMC was not observed for any of the mixtures **a**, **b**, **c**, **d**, **e**, **f**, and **g**. The industrial surfactant (**a**), which is a nonionic polyglycol-based compound, even at a very high concentration of 204 g/L, did not achieve a CMC. Since this is a formulated product of which the full composition is unknown, it might be that the commercial product is sold in an already diluted form, and therefore the CMC of the surfactant will be at a very high concentration. This result also shows that a surfactant does not necessarily have to be at its CMC for foaming purposes since Flotanol already formed a significant amount of foam at a 25 ppm dosage.

Table 4. Results of C_{20} and CMC for the UFAE Feedstocks and Unfractionated and Fractionated Metathesis Reaction Mixtures

Mixture	Surfactant	C_{20} (mg/L)	CMC (mg/L)
a	Flotanol	7742	-
b	HPEO feedstock	8305	-
c	SB feedstock	8.90	-
d	HPEO metathesis product mixture after 1st step filtration	4995	-
e	SB metathesis product mixture after 1st step filtration	0.08	-
f	HPEO metathesis product mixture after 2nd step filtration	4216	-
g	SB metathesis product mixture after 2nd step filtration	2.65	-

Mixtures **b**, **c**, **d**, **e**, **f**, and **g** contain a mixture of ethyl esters, diesters, and other compounds in the aqueous phase. Due to the long hydrocarbon chains and the hydrophobic nature of these mixtures, they have low water solubility. Low water solubility can explain why a CMC was not achieved for these mixtures, as there is a high probability that the solubility limit in water was reached before the CMC was achieved. The precise concentration of the compounds that partitioned into the water phase was not known since the mixture consisted of a mixture of surface-active and nonsurface-active compounds. These results showed that the compounds and mixtures evaluated exhibited surfactant properties since the surface tension of water was reduced upon the addition of each product evaluated. The C_{20} value denotes the lowest surfactant concentration required for reducing the surface tension of a solution by 20 mN/m. A lower C_{20} value represents a surfactant that is more efficient in reducing the surface tension of water since lower bulk concentrations of the surfactant are required to achieve a 20 mN/m reduction in the surface tension of water. Comparing the C_{20} values of mixtures **b** (8305 mg/L), **d** (4995 mg/L), and **f** (4216 mg/L), there is an increase in the surfactant efficiency as one goes from HPEO feedstock (**b**) to the first filtration of the reaction product (**d**), to the second filtration (**f**).

From the results presented in Table 4, mixtures **d** and **f** contain a diester and an alkene which are not present in **b**. Furthermore, mixture **f** had a higher mass fraction of diester, and it was also a more efficient surfactant than mixture **d**. This increase in surfactant efficiency as the mass fraction of the diester increases points toward the diester (formed during metathesis) being at least partially responsible for the increased surfactant efficiency of the mixture. The diester is more polar than the ethyl esters and alkenes, therefore increasing the probability of it partitioning into water and decreasing its surface tension. Another contributing factor for the increased surfactant efficiency in the presence of the diester is that the diester occupies a larger area at the air−water interface as the

https://doi.org/10.1021/acssuschemeng.4c04758
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surfactant must adjust (bend) its structure to incorporate both ester groups at the interface. This adjustment can lead to a rise in the system's overall bulk pressure, which in turn might lead to surfactants dispersing into the aqueous phase at reduced concentrations, leading to lower C_{20} values.

For mixtures **c**, **e**, and **g**, the surfactant potential of the feedstock was upgraded through metathesis. The surfactant efficiency of mixture **g** is lower than that of mixture **e**; however, due to the complexity of these mixtures, it is difficult to speculate about the exact reason for the differences in surfactant efficiency between the mixtures. Nonetheless, mixture **e** has a higher content of diester compared to mixture **g**, and the higher diester content corresponds with a higher surfactant efficiency. Comparing mixtures **c** and **b**, and **g** and **f**, the mixtures originating from the SB feedstock (**c** and **g**) are more efficient than the HPEO feedstock.

Overall, the product mixtures produced through metathesis showed clear surfactant properties, yet poor foaming capacity. This could be an advantage where specific applications require non- or low-foaming surfactants, such as in paper-making or textile dyeing industries.[49]

4. CONCLUSION

The work demonstrated the metathesis of functionalized alkenes in the form of fatty acid ethyl esters originating from plant-based oils, using the Grubbs 2 catalyst. The work characterized catalyst performance at different temperatures and catalyst loadings when employing a higher purity ethyl oleate feedstock and when using a sunflower oil-based feedstock and determined product distributions. Additionally, the potential of reaction mixtures to act as surfactants was evaluated. The results showed that optimal conversion of HPEO feedstock was achieved at a reaction temperature of 50 °C, although the highest selectivity was achieved at 20 °C, albeit at lower substrate conversions. Using the more complex SB feedstock, the highest feedstock conversion was again found at 50 °C with none of the desired diethyl 9-octadecenedioate forming at temperatures of 20 or 30 °C. The main pathways for the production of diethyl 9-octadecenedioate in the SB feedstock were the self-metathesis of ethyl linoleate and the cross-metathesis of ethyl oleate and ethyl linoleate; the self-metathesis of ethyl oleate seems to be slower than these two reactions and only plays a significant role in the formation of 9-octadecenedioate once ethyl linoleate is exhausted from the feedstock mixture. The feedstocks and reaction mixtures all displayed surfactant properties, and the metathesis of the HPEO and SB feedstocks resulted in increased surfactant efficiency. Metathesis generates a variety of alkenes and esters, increasing the complexity and functionality of the resultant molecules. Among these products, **C** and **H** are the most commonly formed. The SM of **A** or **B** to produce **C** results in a higher proportion of esters relative to those of hydrocarbons, thereby enhancing the hydrophilic−lipophilic balance of fatty molecules. This additional ester group improves the wetting ability of the resultant diester surfactants. Moreover, the SM of **B** or the CM of **A** and **B** to form **H** introduces a shorter carbon chain ethyl ester, which is crucial for enhancing the rapid spreading of surfactants through a medium. The synergistic effects of cosurfactancy between the metathesized and esterified products further improve their surfactant properties. This diversity in surfactants can enhance the stability of, for example, emulsions. The results confirmed the suitability of metathesis of feedstocks derived from renewable resources for the production of industrially relevant chemicals and demonstrated the utility of reaction product mixtures as surfactants. The research therefore makes a contribution toward developing catalysis pathways that move away from the use of fossil-based reactants and potentially toward more sustainable chemical industries.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.4c04758.

Synthesis and characterization of analytical standards, composition of mixtures used for surfactant investigations, and surfactant measurement setup (PDF)

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Author Contributions

C.L. performed experimental investigations, analyzed and processed the data, interpreted the results, and drafted the manuscript. H.C.M.V. and E.H.W. supervised the surfactant work and contributed to manuscript writing and revision. N.J.G. and M.T. supervised the research project and contributed to the writing of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge Ms. H. Botha, Mr. J. Van Rooyen, and Ms. L. Simmers for assistance with GC−MS analysis. We acknowledge funding from the NRF-DST Centre of Excellence in Catalysis (c*change) and Sasol.

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https://doi.org/10.1021/acssuschemeng.4c04758
ACS Sustainable Chem. Eng. 2024, 12, 15472−15483