

Continuous Flow Metathesis for Direct Valorization of Food Waste: An Example of Cocoa Butter Triglyceride

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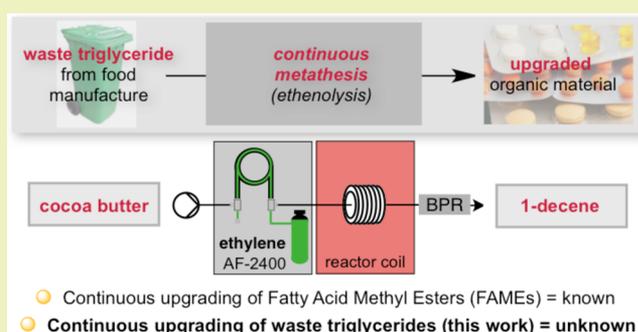
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Supporting Information

ABSTRACT: The direct chemical conversion of cocoa butter triglycerides, a material available as a postmanufacture waste stream from the food industry, to 1-decene by way of ethenolysis is reported. The conversion of the raw waste material was made possible by use of 1 mol % of the [RuCl₂(iBu-phoban)₂(3-phenylindenyl)] catalyst. The process has been investigated in both batch and flow conditions, where the latter approach employs a Teflon AF-2400 tube-in-tube gas–liquid membrane contactor to deliver ethylene to the reaction system. These preliminary studies culminate in a continuous processing system, which maintained a constant output over a 150 min period tested.

KEYWORDS: Food waste, Valorization, Metathesis, Triglycerides, Green chemistry, Flow chemistry



INTRODUCTION

Biofeedstocks in general and biowaste in particular represent an attractive source of useful chemical functionality, which to date is still largely untapped in terms of its application in the fine chemicals industry. This is particularly the case for the construction of elaborate molecular architectures such as those found in many functional materials, in pharmaceuticals and agrochemicals. However, in recent years, the conversion of biowaste materials into chemical feedstock compounds and added-value chemical commodities has become an intense area of research.^{1–4} The valorization of biologically derived waste into upgraded chemical materials is of paramount importance in order to reduce indirectly the global dependence on fossil feedstocks by entering the chemicals supply chain with biologically premade structures. This approach is, however, up against a wealth of knowledge and understanding of how to extract, manipulate and process fossil feedstocks on vast scales, a process that has been finely tuned over many decades in order to maximize both energy and monetary output from the entire petrochemical process. Thus, the challenge for the emerging field of biobased chemistry is not only in identifying new viable feedstocks but also in simultaneously developing new catalytic systems and process technologies that would ultimately compete with a petrochemical supply chain.

Within the range of compounds produced from biofeedstocks, triglycerides form one of the largest classes, with

primary applications in the food, healthcare, cosmetics and industrial lubricant sectors.² To maintain this demand, there exists a significant industry for production of triglycerides. Triglycerides from primary biomass are increasingly used as first-generation biofuels, which directly compete with food and other applications for land.⁵ There exist secondary sources of triglycerides, following their primary use. Thus, used cooking oils have been intensively investigated as a feedstock for biodiesel production.⁶ We have identified another source of waste triglycerides from food manufacturing: food ingredients that are discarded after primary food manufacturing. One such material, albeit having a relatively modest annual volume of ca. 4000 metric tonnes waste from a single plant, is cocoa butter.

For this study, cocoa butter was obtained as a waste product from the food industry, at present destined for landfill as it cannot be returned back to primary manufacturing. Thus, it is not the primary biomass that enters food production. Cocoa butter is primarily composed of triglycerides, of which there are a variety of combinations of glycerol with palmitic (P), stearic (S) and oleic (O) acids. Other acid residues are present in lower quantities (palmitoleic acid, myristic acid, arachidic acid and linoleic acid). The ratios of triglycerides vary as a response

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to numerous effects, major factors being the geographical source of the bean and the time of year at harvest, typically variations are within 1–4%. Of the six major triglycerides present (16 have been identified), all contain oleic or linoleic unsaturated acid residues.⁷ The transformation of interest in this work is the production of 1-decene, a useful intermediate in surfactants manufacturing, via a cross-metathesis with ethylene known as ethenolysis, which also leaves the remaining triglyceride as a functionalized terminal alkene.

Notably, the use of fatty acid esters as a source of long-chain terminal alkenes via ethenolysis has fueled significant interest in this reaction. Several homogeneous catalysts have been reported for self- and cross-metathesis of fatty acid esters, where selectivity between the two reactions and its origin, and the attainment of high turnover numbers (TONs) were the primary focus.^{8,9} Dow has set a commercial target of >50 000 TON for the reaction to be deemed economically viable, based on the price of homogeneous catalysts.¹⁰ Ethenolysis of fatty acid esters has also been reported using supported Re_2O_7 catalysts, leading to good selectivity toward cross-metathesis products over self-metathesis.^{11–13}

Despite the many examples of the use of fatty esters in the metathesis reaction, the cost of isolation of a pure, single unsaturated fatty ester starting materials from the feedstock triglycerides can be a significant drawback for industrial application. In this regard, the direct metathesis of triglycerides is an attractive option for an ethenolysis reaction.¹⁴ However, despite the fact that the direct use of triglyceride substrates would be very useful, the presence of different combinations of polyunsaturated fatty acid moieties on the triglyceride skeleton, often leads to the formation of a mixture of metathesis products. Therefore, traditionally, the use of a single fatty ester, obtained from transesterification and subsequent purification of the triglyceride starting material is preferable. In fact, very few examples of the direct use of triglycerides in metathesis have been reported in the literature.^{14–19} Thus, in the case that a clean source of a waste triglyceride with a significant proportion of a single unsaturated fatty acid structure is available, the direct metathesis of the triglyceride material is potentially a better overall option. The remaining triglyceride then contains a terminal double bond, which in itself is a useful functional group, for example for polymer formation. Epoxidation and further polymerization of such triglycerides sources from cocoa butter is the subject of a separate study.

Most of the published studies concerning the metathesis of biorenewable resources were performed in batch reactors. However, translation of batch chemistry to a continuous flow approach frequently results in more efficient processes due to either improved selectivity, reduced inventory of reagents through solvent and catalyst recycling, use of more intensive reaction conditions (elevated temperature and pressure), improved mass and heat transfer and/or improved mixing.^{20–25}

There are scant reports on metathesis under continuous flow conditions.^{26–30} A comparison of batch, continuous stirred tank reactors and tubular continuous flow reactors for ring-closing metathesis has recently been presented.³¹ This work clearly shows the impact of different types of residence time distributions characterizing batch, continuous stirred tank and plug-flow reactors on transformations with reaction orders over unity, and the possibility to attain high space-time yields in continuous reactors. Plug-flow reactors with heterogeneous catalysts offer the simplicity of catalyst separation, as well as the frequently desired plug-flow regime. However, immobilization

of homogeneous catalysts is often complicated by a reduction in activity or selectivity, or gradual loss of metal through leaching.³² Several approaches for immobilization of metathesis catalysts to develop a heterogeneous-type continuous metathesis process have been reported, either using covalent grafting²⁸ or noncovalent interactions to heterogenize the active organometallic precatalyst or catalyst onto a solid support.^{26,33,34} A truly heterogeneous catalyst based on supported Re_2O_7 was reported in a continuous scCO_2 flow self-metathesis reaction.³⁰

In addition, a continuous gas phase metathesis has been reported using an ionic liquid supported catalyst, in which the catalyst is immobilized on a thin film of an ionic liquid.^{35,36} Moreover, in the case of higher olefins, the use of a second liquid phase, immiscible with an ionic liquid, has been suggested such as a monolith biphasic continuous reactor.²⁷

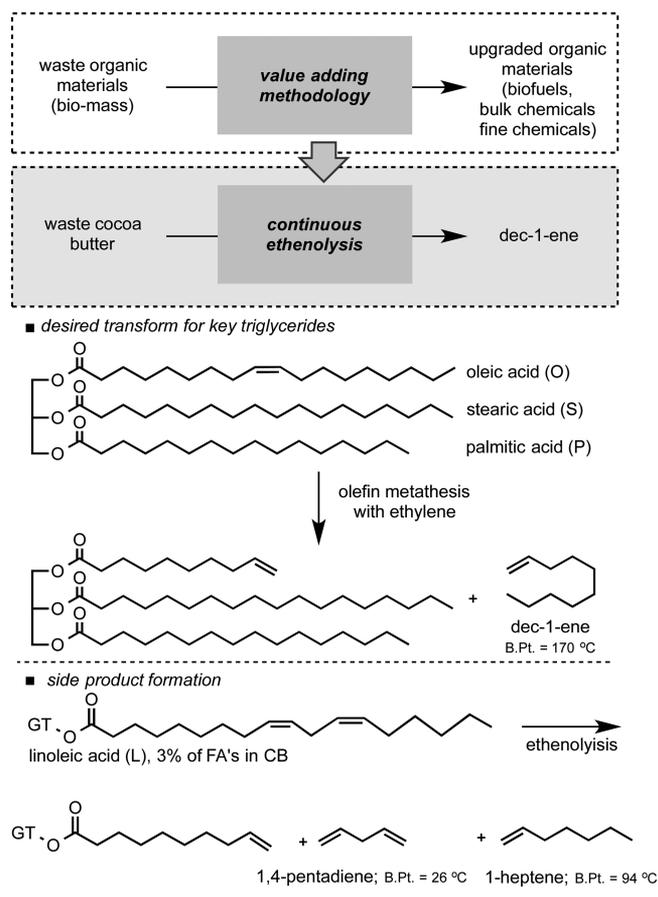
In the present instance, cross-metathesis with ethylene requires the controlled addition of a gaseous reactant to the liquid phase mixture of reactant and catalyst in order to render the desired product conversion and afford longevity of catalyst. For this, a hollow fiber membrane contactor offers an alternative technology to conventional trickle-bed reactors.^{37,38} However, such processes frequently suffer from poor chemical resistance of the fiber membrane or significant mass transfer limitations. With the recent introduction of thin and chemically resistant membrane contactors based on Teflon AF-2400 (poly(tetrafluoroethylene-co-2,2-bis(trisfluoromethyl)-4,5-difluoro-1,3-dioxole)) by DuPont, the scope of applications and efficiency of membrane contactors has improved significantly.³⁹ Such tube-in-tube membrane contactors have now been applied in several important synthetic reactions and are becoming a generally accepted tool of mesoscale flow chemistry.^{40–58} Very recently, ring-closing metathesis was shown to be effectively performed in such a reactor, whereby the ethylene produced could be removed by applying a vacuum across the porous polymeric Teflon AF-2400 membrane.⁵⁹ This technology offers an efficient alternative to the heterogenization of metathesis catalysts allowing truly continuous operation of an optimized catalytic system under its best conditions, we therefore designed our flow system to incorporate the porous membrane gas–liquid contactor design by employing the Teflon AF-2400 tube-in-tube reactor.

In this context, we report here the direct ethenolysis of raw cocoa butter triglyceride as a waste material from a food manufacturer to provide 1-decene as the major lower weight alkene product. In addition to the desired ethenolysis of the oleic acid containing triglycerides, we hypothesized that the bis-alkene containing linoleic acid residues would undergo complete cross-metathesis with ethylene leading to a mixture of 1-heptene and 1,4-pentadiene (as long as the system was not starved of ethylene, Scheme 1). The product mixture would thus be composed of lightweight alkenes with sufficiently differing boiling points that they could then be separated at scale by distillation. The reaction was performed both in batch mode to screen the catalysts and in the flow mode, using a tube-in-tube membrane contactor.

■ EXPERIMENTAL SECTION

Materials. The cocoa butter was sourced from Kraft Foods (UK). For the particular sample of cocoa butter used in this study, the fatty acid composition as determined by gas chromatography (GC) is shown in Table 1, together with the fraction of total double bonds represented by each component.

Scheme 1. Reaction Scheme of Cocoa Butter Metathesis with Ethylene as Upgrading of a Food Industry Waste Stream^a



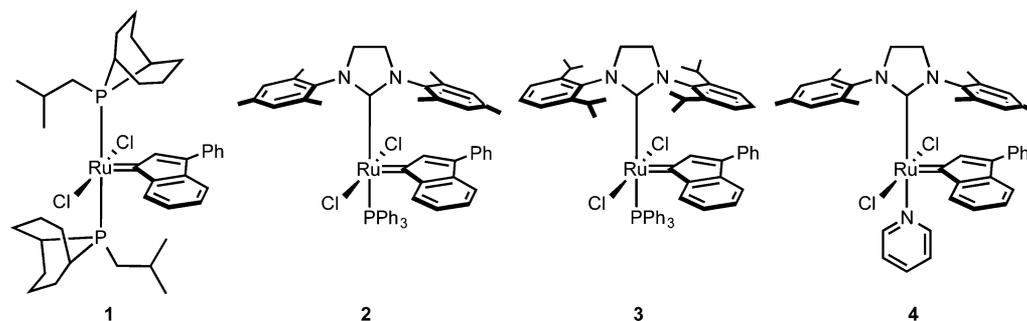
^aPotential byproducts are shown.

Table 1. Composition of Cocoa Butter

fatty acids	fatty acids in CB (%)	double bonds in CB (%)
palmitic (C16:00)	25.8	0
palmitoleic (C16:1n7)	0.3	0.8
stearic (C18:00)	37.9	0
oleic (C18:1n9c)	32.2	84.1
linoleic (C18:2n6c)	2.9	15.1
arachidic (C20:00)	0.9	0

Ethylene was purchased from BOC Ltd. (UK). Solvents and reagents were obtained from Sigma-Aldrich and used without further purification.

Scheme 2. Catalysts Screened for Ethenolysis of Cocoa Butter



Methods. A selection of ruthenium indenylidene catalysts, shown in Scheme 2, were screened in batch conditions.

The catalyst (1 mol %; 0.0025 mmol) and a stirrer bar were added to a 5 mL vial in an argon-filled glovebox. The vial was closed using a plastic septa cap. Next, this vial was removed from the glovebox. Then, 216.7 mg of cocoa butter (0.25 mmol, average M_w of cocoa butter) was added into a second 5 mL vial and the vial was closed using the septa cap (outside of the glovebox). The cocoa butter vial was purged with argon from a Schlenk line before addition of 1 mL of dry and oxygen-free solvent was introduced via syringe into the cocoa butter vial. The cocoa butter was dissolved and then added via syringe into the catalyst vial. The vial was then stirred with an ethylene purge from a balloon. After the allotted time, the reaction was quenched with ethyl vinyl ether, before drying under reduced pressure to constant mass and analyzing by ¹H NMR.

For >1 Bar Pressure of Ethylene. The charged reaction vial was then loaded into the autoclave. The autoclave was connected to an ethylene cylinder. After the allotted time, the reaction was quenched with ethyl vinyl ether, before drying under reduced pressure and analyzing by ¹H NMR.

It should be noted that by conducting the same reaction using nondried glassware, without a glovebox and with THF from a standard column type solvent purification system, conversions within 5–10% of those reported were routinely achieved.

Flow Procedure. Flow experiments were conducted using a Uniqsis Flowsyn. The mixture of cocoa butter, catalyst and THF was injected into the sample loop and the valve position switched to place the sample inline. The sample was then carried into the lumen side of the Teflon AF-2400 membrane. The tube-in-tube reactor was constructed from an inner Teflon AF-2400 tube (o.d. 1.0 mm and i.d. 0.8 mm) and an outer PTFE tube (OD 3.18 mm and ID 1.59 mm). The sample then flowed into a 20 or 10 mL residence coil and then through a back-pressure-regulator (BPR) rated to 6.9 barg (100 psi). The collected sample was flushed with argon to remove dissolved ethylene and to stop the reaction before drying under reduced pressure to constant mass and analyzing by ¹H NMR.

Analytical Methods. ¹H NMR spectra were recorded on either a Bruker Avance DPX-400 or DRX-600 (in the case of raw cocoa butter) spectrometer with the residual solvent peak as the internal reference; resonances are reported to the nearest 0.1 ppm. Details of calculations of conversion on the basis of NMR are given in the Supporting Information.

RESULTS AND DISCUSSION

Catalyst Screening. To screen for catalyst activity and performance and develop analytical methods for the ethenolysis of raw cocoa butter waste, a series of reactions were conducted in batch mode with catalysts shown in Scheme 2. These catalysts generally demonstrate increased activity and stability compared with their benzylidene counterparts. There is a straightforward procedure to synthesize these catalysts, making them relatively inexpensive compared with other congeners.^{60,61}

We were pleased to find that the metathesis catalysts employed showed activity with the raw waste material during preliminary experiments. Catalysts **1** and **2** demonstrated effective catalytic turnover (Table 2 entries 1 and 2), whereas

Table 2. Screening of Catalysts for Ethenolysis of Cocoa Butter

entry	catalyst ^a	solvent	pressure (bar)	time (h)	T (°C)	conversion (%)
1	1 (1)	toluene	1	2	r.t.	30%
2	2 (1)	toluene	1	2	r.t.	21%
3	3 (1)	toluene	1	2	r.t.	~1%
4	4 (1)	toluene	1	2	r.t.	~1%
5	1 (1)	toluene	1	16	r.t.	36%
6	1 (1)	DCM	1	16	r.t.	46%
7	1 (1)	THF	1	16	r.t.	45%
8	1 (1)	THF	1	16	50	35%
9	1 (1)	THF	2	16	r.t.	49%
10	1 (1)	THF	2	1	r.t.	34%
11	1 (0.25)	THF	2	1	r.t.	24%
12	1 (0.5)	THF	2	1	r.t.	25%

^aCatalyst loading (mol %) shown in parentheses.

catalysts **3** and **4** appeared to deactivate after the first cycle (Table 2, entries 3 and 4). Indeed, the use of bisphosphine catalyst (**1**) gave the best results for this transformation. This is likely due to the increased stability of the methylidene intermediate formed during the ethenolysis reaction, reducing the possibility for decomposition pathways. In fact, generally, the bisphosphine methylidene complexes bearing electron-donating phosphines are more stable than their heteroleptic analogues.⁶²

On the basis of these results, [RuCl₂(*i*Bu-phoban)₂(3-phenylindenyl)] (**1**), was selected for further optimization of the parameters. An increase in reaction time from 2 to 16 h resulted in a modest increase in yield (Table 2, entries 1 and 5). A solvent screening highlighted dichloromethane as optimum in terms of yield; however, the option of THF was preferred (Table 2, entries 5, 6 and 7). Notably, an increase in reaction temperature from ambient to 50 °C resulted in a decrease in yield, presumably due to catalyst decomposition (Table 2, entries 7 and 8). Increasing the pressure of ethylene, a practice that requires a significant effort and poses a safety hazard in batch mode, appeared to increase the reaction rate, furthermore, an excess of ethylene is essential to prevent homodimerization, thus the ability to work at increased pressures is an important consideration.

Flow Experiments. In the preliminary setup, HPLC piston pumps of a Uniqsis FlowSyn were used in conjunction with the

in built 6-port 2-position switching valve bearing a 10 mL loading loop. In a typical experiment, the loop was loaded with a 0.5 M segment of cocoa butter in THF with 1 mol % of catalyst. This was then switched inline (by changing the position of the valve) and the segment was carried initially through a Teflon AF-2400 tube-in-tube module (liquid in the inner tube), where the outer surface of the gas permeable tube was exposed to ethylene gas from the cylinder.^{40,52} The gas-rich homogeneous segment then passed into a 20 mL residence coil, where it resided for 60 min (flow rate of 0.33 mL min⁻¹) before passing through a back pressure regulator where the media outgassed to form slugs of liquid and gas, signifying that excess gas remained after the reaction, see Figure 1.

As described in Table 3, by holding the reactor coil at room temperature and varying the pressure of ethylene (*P*₁), by altering the regulator pressure on the cylinder, it was found that 6 bar provided optimal results. Interestingly, at both higher and lower pressures, the conversion was notably lower. The same pressure trend was observed as the reactor coil temperature was increased to 40 °C, (Table 3 entries 6–10) where now at 6 bar pressure, a 38% conversion could be obtained. Interestingly, and in accord with the batch results obtained at 50 °C (Table 2, entry 8), the conversion decreased at reactor coil temperatures of 60 °C (Table 3, compare entries 8 and 11), this is likely as a consequence of thermal decomposition of the catalyst.

A plot of the trend of pressure and temperature against conversion is shown in Figure 2. At 40 °C and 6 bar pressure, halving the catalyst loading also reduced the conversion by approximately half (Table 3, entries 8 and 12). Halving the concentration of cocoa butter also did not result in improved conversion. However, increasing the residence time in the reaction coil to 2 h by halving the flow rate afforded increased conversion to 49%. It is possible that this increase is attributable to an increase in retention time in the tube-in-tube reactor, resulting in a greater uptake of gas in to the liquid stream. This hypothesis was therefore, tested by maintaining the flow rate but changing the volume of the reaction coil to half that of the original (i.e., to 10 mL from 20 mL). If no effect was to be observed from gas uptake or mass transfer limitations, then essentially no difference compared to the original should be seen. In fact, this configuration also delivered an increased conversion relative to the original conditions, suggesting that the ethylene uptake was also an important factor (Table 3, compare entries 8, 14 and 15).

Using these conditions, a longer continuous reaction was performed to verify the stability of the system under a continuous rather than segmented run. This was done by simply bypassing the 6-port, 2-position valve and loading loop, and instead pumping from a reservoir bottle containing the

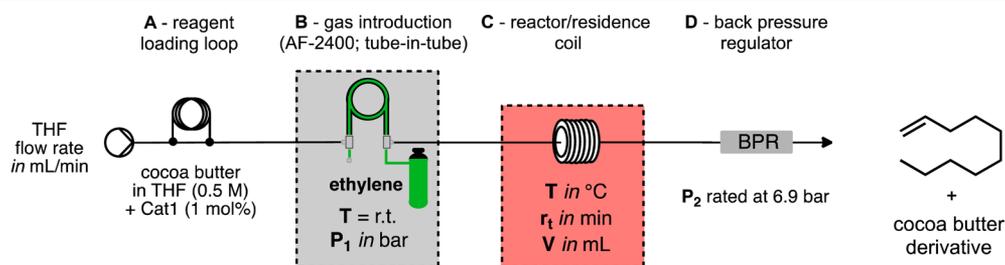


Figure 1. Scheme of flow reactor system for ethenolysis of cocoa butter (*r*_t is residence time in the reactor coil; *V* is the volume of the reaction residence coil).

Table 3. Ethenolysis of Cocoa Butter in Tube-and-Tube Reactor and a Scheme of Flow Reactor System for Ethenolysis of Cocoa Butter^a

entry	flow rate (mL min ⁻¹)	P ₁ (bar)	T (°C)	t _r (min)	V (mL)	conversion ^a
1	0.33	2	r.t.	60	20	10% (9%)
2	0.33	4	r.t.	60	20	15% (13%)
3	0.33	6	r.t.	60	20	25% (21%)
4	0.33	10	r.t.	60	20	22% (18%)
5	0.33	14	r.t.	60	20	17% (15%)
6	0.33	2	40	60	20	22% (18%)
7	0.33	4	40	60	20	26% (23%)
8	0.33	6	40	60	20	38% (32%)
9	0.33	10	40	60	20	31% (26%)
10	0.33	14	40	60	20	28% (24%)
11	0.33	6	60	60	20	32% (28%)
12 ^b	0.33	6	40	60	20	26% (22%)
13 ^c	0.33	6	40	60	20	20% (17%)
14	0.17	6	40	118	20	49% (41%)
15	0.17	6	40	59	10	46% (39%)

^a¹H NMR conversion to terminal alkene products, number in parentheses represents 85% of this value as a measure of the quantity of 1-decene present. ^bCatalyst loading = 0.5 mol %. ^cCocoa butter concentration = 0.25 M.

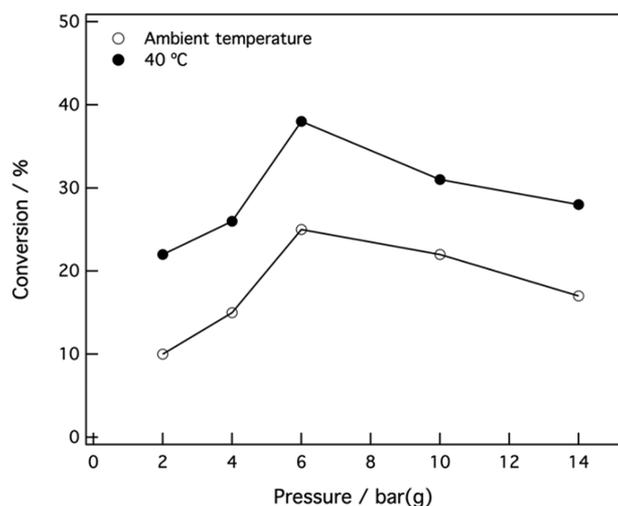


Figure 2. Conversion to alkenes as a function of ethylene pressure and reactor coil temperature. Lines are for convenience only.

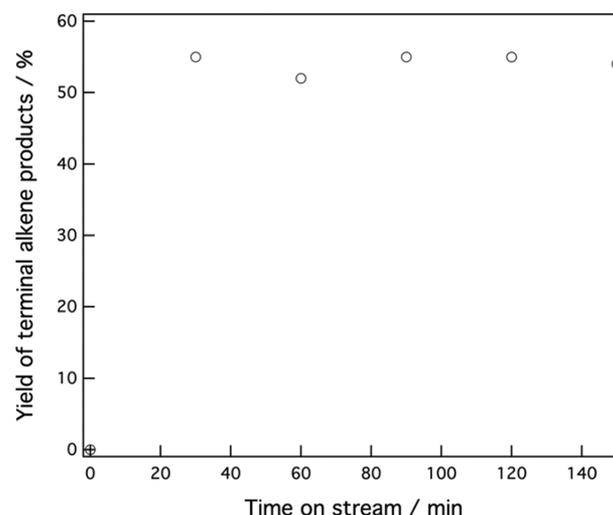


Figure 3. Longer run of cocoa butter continuous ethenolysis, with conversion "spot-checks" every 30 min.

cocoa butter and catalyst. Pleasingly, over a period of 2.5 h, the reactor output remained stable and constant, as detected by conversion spot-checks at 30 min intervals, Figure 3.

In conclusion, we have demonstrated a direct valorization of a waste triglyceride by way of ethenolysis of the unsaturated fatty acid components. A suitable catalyst that can operate with the specific raw waste material has been identified and the preliminary parameters of the reaction have been investigated in batch mode operation. The concentration and pressure of ethylene plays a clear and significant role that led us quickly to explore the use of flow methods employing a semipermeable Teflon AF-2400 tube-in-tube reactor whereby parameters could also be controlled to optimize the process, ultimately culminating in a proof-of-concept continuous run that displayed stability of output over a 2.5 h period. Future work will investigate larger scale processes with focus on achieving higher catalyst TONs, exploring more customized engineering solutions to provide responsive control of ethylene pressure, and inline purification of the 1-decene fractions. Exploration of the use of recyclable metathesis catalyst systems could also

contribute to further improving the present proof-of-concept study toward more readily scaled methods.

■ ASSOCIATED CONTENT

📄 Supporting Information

Details of general experimental procedure, batch and flow experiments and a detailed method of calculation of conversion based on ¹H NMR data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00397.

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The paper was written through contributions of all authors. All authors have given approval to the final version of the paper.

Notes

The authors declare no competing financial interest.

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