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Nickel-catalyzed reductive decarboxylation of fatty acids for drop-in biofuel production†

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An operationally simple and highly selective method for the decarboxylation of fatty acids under remarkably mild conditions is described herein. The activation of the aliphatic carboxylic acids by esterification with *N*-hydroxyphthalimide (NHPI) enabled efficient deoxygenation to synthesize *n*-alkanes in up to 67% yield, employing inexpensive PMHS as a hydrogen source, $NiCl_2\cdot 6H_2O$, bipyridine, and zinc in THF. In contrast to the conventional thermo-catalytic approaches, this protocol does not require high temperature and high pressure of hydrogen gas to deoxygenate biomass-derived carboxylic acids, thus representing an attractive alternative for producing drop-in biofuels.

Introduction

Extensive consumption of fossil fuels to meet the global energy demand has intensified environmental concerns regarding the increase in emissions of CO_2 and other greenhouse gases. In 2018, petroleum-based fuels were responsible for 94% of the energy use of the global transportation sector.[1,2] In particular, the aviation industry, for example, accounts for approximately 2% of global CO_2 emissions each year, which highlights the necessity of broadening the use of alternative low-carbon biofuels for preventing air pollution.[3]

Vegetable oils are one of the most prominent types of renewable feedstock to produce biofuels such as biodiesel.[4] However, as well as the crude oils, the fatty esters are still associated with poor fuel properties such as low heating value, high viscosity, and low oxidative stability.[5,6] Additionally, the high oxygen content of this biofuel also results in poor cold flow properties, strongly limiting their use as blends with fossil fuels for diverse applications.[7] Therefore, technical approaches for deoxygenating vegetable oils and their derived biofuels are important targets for increasing their compatibility with petroleum-based fuel infrastructure.

Several protocols have demonstrated the utility of vegetable oils for the production of biofuels through deoxygenation pathways.[8–11] These reactions enable the conversion of biobased triglycerides, fatty acids, or esters into mixtures of renewable hydrocarbons that are able to either partially or completely replace fossil fuels as they are functionally equivalent to them.[12] Remarkably, among the various types of suitable substrates for deoxygenation, fatty acids obtained upon hydrolysis of vegetable oils have met biofuel application more promisingly due to their low cost, availability, and carbon number lying within the range of fossil hydrocarbons.[13,14]

Depending on the biomass employed as feedstock, many technological routes such as hydroprocessing, catalytic hydrothermolysis, alcohol-to-jet, and gasification combined with the Fischer–Tropsch process are available for accomplishing the synthesis of renewable hydrocarbons.[15,16] Particularly for the conversion of fatty acids and their derivatives, hydroprocessing has been a widely exploited approach[17–19] (Scheme 1A). Although hydroprocessing has become increasingly relevant in petrochemical industry settings,[20] it demands high temperatures (>250 °C) and high pressure (>10 bar) of hydrogen gas, which is usually obtained from non-renewable sources.[21,22] Thermo-catalytic pyrolysis is a useful alternative that allows conversion without hydrogen. However, this process lacks selectivity, resulting in mixtures of products that require further upgrading to provide suitable biofuels.[23–25] Hence, efficient deoxygenation methods that are operational in low temperature and ambient pressure under a hydrogen-free atmosphere are highly desirable.

In the past few years, radical decarboxylation of redox-active esters (RAE) using metal catalysts under mild conditions has become a promising approach for forging C–C, C–X, and C–H bonds, introducing complexity in a variety of molecules with remarkable selectivity.[26,27] Recently, Baran and coworkers reported the use of a Ni-based catalyst for the decarboxylation of RAEs in the presence of phenylsilane or Michael acceptors to

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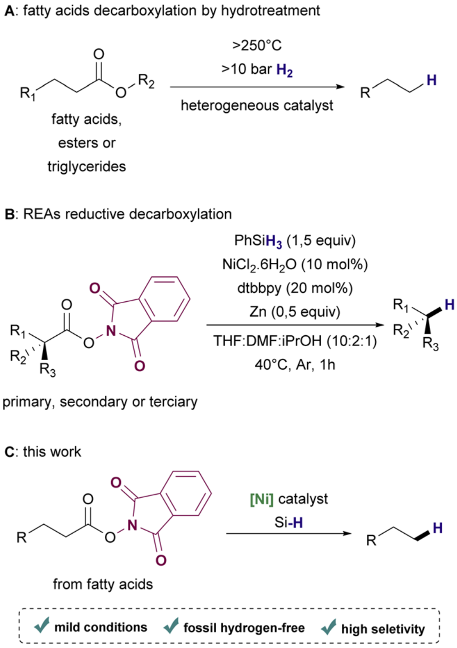


Scheme 1 Reaction approaches for the decarboxylation of carboxylic acids.

afford hydrocarbons or coupling products respectively[28] (Scheme 1B).

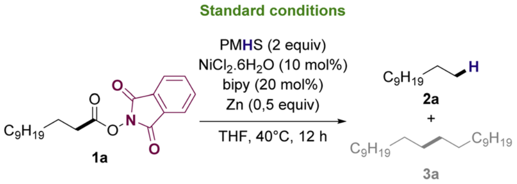
Although this protocol proved to be efficient to synthesize a variety of useful products from several examples of structurally diverse carboxylic acids, fatty acids were not included in the scope of the reductive method for hydrocarbon synthesis. Based on this important work, we envisioned the production of renewable hydrocarbons from bioderived fatty acids by reductive decarboxylation of RAEs under mild conditions using a Ni catalyst and a silane as the hydrogen source (Scheme 1C).

Results and discussion

Based on previously reported protocols for the decarboxylation of RAE's,[28] we started the optimization by employing $NiCl_2 \cdot 6H_2O$ as the catalyst, bipyridine as ligand, Zn as the reductive agent and inexpensive poly(methylhydrosiloxane) (PMHS) as the hydrogen source. PMHS has been previously reported as an efficient hydrogen source for other reductive decarboxylation processes[29–32] and has a lower cost compared to other silanes already reported for similar transformations.[33] It is a non-toxic, air and moisture stable reagent that can be easily obtained as by-product of silicon chemical industries.[34,35] RAE **1a** was selected as the model substrate to study the reductive deoxygenation since its corresponding fatty acid (lauric acid) is one of the major compounds in the composition of useful biofuel feedstocks such as coconut, licuri and babaçu oils.[36–38]

Initial optimization studies revealed, after extensive solvent screening (see ESI for full details†), that THF was the ideal solvent for the transformation, resulting in the conversion of RAE into the desired hydrocarbon in 45% yield along with trace amounts of radical homocoupling byproduct (see Table ES1 in ESI†). Remarkably, the use of a mixture of THF : DMF : iPrOH (10 : 2 : 1) (Table 1, entry 2), which was advantageous for the decarboxylation of a range of RAEs reported by Baran and coworkers,[28] decreased the yield of **2a** to 22%. Other Ni-based catalysts such as $NiBr_2$ and $Ni(OAc)_2 \cdot 4H_2O$ (Table 1, entries 3 and 4) as well as other ligands such as dtbbpy and DPPB (Table 1, entries 5 and 6) also proved to be less effective to afford the decarboxylation product. Increasing the stoichiometry of both Ni and ligand diminished the yield of **2a** (Table 1, entry 9).

Table 1 Optimization of RAE reductive decarboxylation for production **2a**[a]

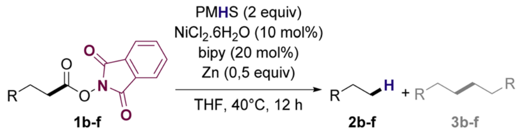


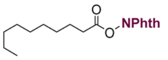
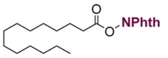
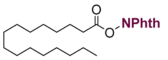
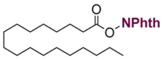
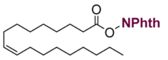
		Yield[b] (%)	
Entry	Modification from standard conditions	2a	3a
1	None	45	2
2	THF : DMF : iPrOH (10 : 2 : 1)	22	0
3	$NiBr_2$ as catalyst	19	0
4	$Ni(OAc)_2 \cdot 4H_2O$ as catalyst	10	2
5	Dtbbpy as ligand	28	0
6	DPPB as ligand	6	0
7	$PhSiH_3$ as hydrogen source	28	26
8	TMDSO as hydrogen source	0	0
9	20 mol% $NiCl_2 \cdot 6H_2O$ + 40 mol% bipy	6	0
10	Mn as reducing agent	0	0
11	Addition 3 equiv. K_2CO_3	46	7
12	Reaction concentration of 0.2 M (0.5 mL)	36	0
13	Reaction at 70 °C	35	8
14	No nickel or ligand	0	0
15	No PMHS	0	0
16	Methyl laureate or lauric acid instead of NHPI ester	0	0

[a] Reactions were run on a 0.1 mmol scale. [b] Yield determined by GC-MS using hexadecane as internal standard. PMHS: poly(methylhydrosiloxane); bipy: 2,2-bipyridine; dtbbpy: 4,4-di-*tert*-butyl-2,2-dipyridyl; DPPB: 1,4-bis(diphenylphosphino)butane; $PhSiH_3$: phenylsilane; TMDSO: 1,1,3,3-tetramethyldisiloxane. See ESI for additional details.

Replacing PMHS with different hydrogen sources commonly reported for this type of transformation[39,40] significantly decreased the formation of the desired product under this set of conditions (Table 1, entries 7 and 8). Notably, other reductive agents such as Mn (Table 1, entry 10) completely inhibited the decarboxylation. The presence of a base such as K_2CO_3 as an additive (Table 1, entry 11) did not improve the yield of **2a**, favoring radical homocoupling instead. Furthermore, increasing either reactants concentration or reaction temperature to 70 °C was also prejudicial to the formation of **2a** (Table 1, entries 12 and 13). Control studies confirmed the necessity of Ni catalyst, ligand, and hydrogen source for the reaction to occur (Table 1, entries 14 and 15). Additionally, no product of

Table 2 Reductive decarboxylation of fatty acids derived RAEs[a]



Entry	Feedstock	Principal product	Yield[b] (%)	
			2a	3a
1	 from capric acid **1b**	n-C$_9$ **2b**	45	2.5
2	 from myristic acid **1c**	n-C$_{13}$ **2c**	65	4.9
3	 from palmitic acid **1d**	n-C$_{15}$ **2d**	67	4.2
4	 from stearic acid **1e**	n-C$_{17}$ **2e**	54	1.7
5	 from oleic acid **1f**	n-C$_{17:1}$ **2f**	33	0

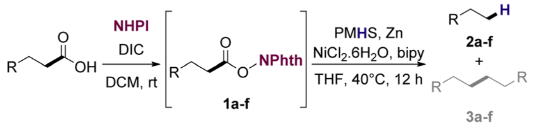
[a] General decarboxylation reaction conditions: 0.1 mmol of redox-active ester, 0.2 mmol of PMHS, 0.01 mmol of NiCl$_2\cdot$6H$_2$O, 0.02 mmol of bipyridine, 0.05 mmol of zinc in 1 mL of THF (0.1 M). [b] Yield determined by GC-FID using calibration curve. NPhth: N-phthalimide.

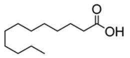
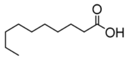
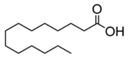
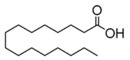
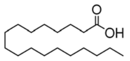
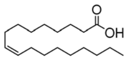
decarboxylation was observed when using either the methyl laureate or lauric acid as substrates, proving that NHPI esters are crucial reactants to enable efficient reactivity (Table 1, entry 16).

After optimization experiments, the efficiency of the reductive deoxygenation of **1a** using PMHS (2 equiv.), NiCl$_2\cdot$6H$_2$O, bipyridine, and Zn in THF at 40 °C was confirmed by GC-FID with a calibration curve, which allowed to determine that **2a** could be synthesized in 51% yield. It is noteworthy that, under the applied conditions, the reaction exclusively afforded hydrocarbons as products. Both undecane (n-C11) and docosane (n-C22) are valuable biofuel candidates since they have carbon number in the jet-fuel and diesel range, respectively. Furthermore, the N-phthalimide formed during the reaction work up, can be recovered and utilized to synthesize more N-hydroxyphthalimide[41] that can be converted into **1a** upon reaction with lauric acid.

With suitable conditions in hand, the generality of the decarboxylation method was evaluated. The scope of the fatty acids-derived RAE was examined by employing substrates with different carbon chain lengths. Reaction yield was determined by GC-FID using a calibration curve. The devised protocol proved to be effective for converting RAE **1b**, which was synthesized from capric acid, into n-nonane in 45% yield, and octadecane in 2.5% yield (Table 2, entry 1). A better result was observed for the synthesis of n-tridecane (65% yield) after decarboxylation of **1c**, which also resulted in the formation of the homocoupling product in a 4.9% yield (Table 2, entry 2). The reaction of the RAEs derived from palmitic and stearic acids delivered n-pentadecane in a 67% yield, and n-heptadecane in a 54% yield while the formation of the respective byproducts was diminished to less than 5% (Table 2, entries 3 and 4).

Table 3 One-pot scope of the *in situ* REA to reductive decarboxylation[a]



Entry	Feedstock	Principal product	Yield[b] (%)	
			2a	3a
1	 lauric acid	n-C$_{11}$ **2a**	48	4.8
2	 capric acid	n-C$_9$ **2b**	28	1.2
3	 myristic acid	n-C$_{13}$ **2c**	27	<1
4	 palmitic acid	n-C$_{15}$ **2d**	51	2.3
5	 from stearic acid	n-C$_{17}$ **2e**	24	1.7
6	 from oleic acid	n-C$_{17:1}$ **2f**	10	0

[a] Activation *in situ* conditions: fatty acid (0.1 mmol), N-hydroxyphthalimide (0.11 mmol), DIC (0.11 mmol) in DCM at rt, then 0.2 mmol of PMHS, 0.01 mmol of NiCl$_2\cdot$6H$_2$O, 0.02 mmol of bipyridine, 0.05 mmol of Zn in 1 mL of THF (0.1 M). [b] Yield determined by GC-FID with calibration curve. NPhth: N-phthalimide.

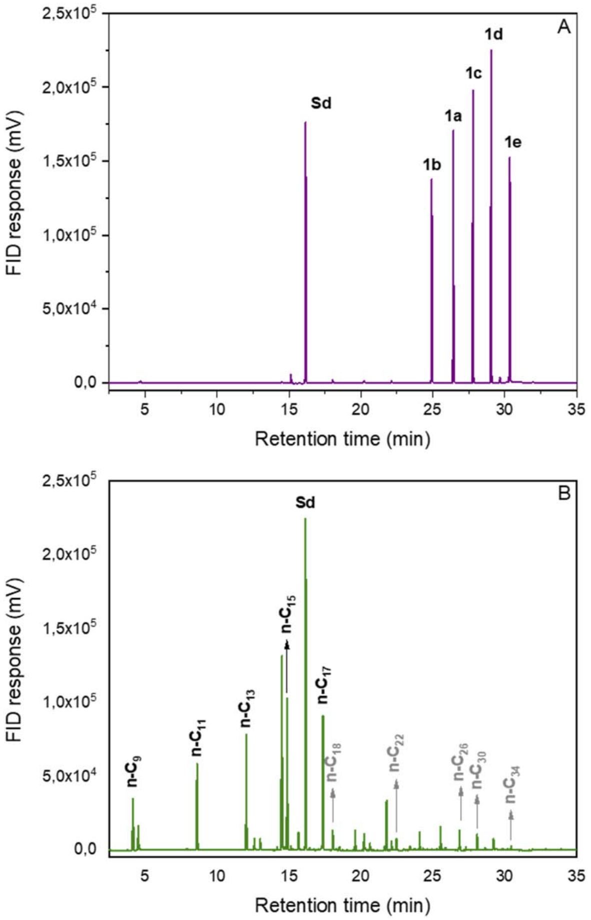
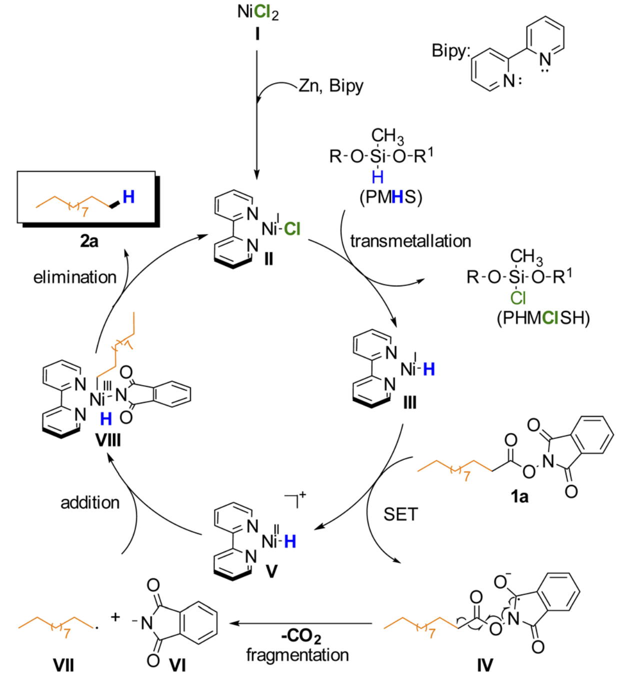


Fig. 1 Chromatograms of the decarboxylation reaction of REAs mixture derived from fatty acids. (A) Initial reaction sample; (B) final reaction sample; Sd: internal standard.

Extending the scope to RAE **1f** resulted in the complete suppression of **3f** generation along with lower yields of **2f** in relation to the other synthesized hydrocarbons. It is possible that the formation of **2f** was limited by the reaction between the radicals formed upon decarboxylation and the unsaturation within the substrate, leading to a polymerization product that could not be detected by the employed technique.[14]

Although moderate yields were determined for the *n*-alkanes, all reactions proceeded with more than 98% conversion, except for ester **1f**, which afforded the respective product with an 85% conversion. These data indicate that the redox-active esters are likely to decompose under the reaction conditions, which is corroborated by the presence of fatty acids and phthalimide in crude reaction mixtures according to GC-FID analysis.

The optimized conditions were also employed to convert the fatty acids using a one-pot reaction approach. The decarboxylation protocol was applied to RAEs generated *in situ* to produce *n*-alkanes. Notably, the RAEs from lauric and palmitic acids (Table 3, entries 1 and 4) delivered the corresponding hydrocarbons in similar yields in relation to the protocol that starts from the isolated esters. For the other substrates, however, significantly lower yields were observed, especially in the decarboxylation of the RAE from oleic acid. Similar outcomes were already described for this type of transformation.[28,42,43]



Scheme 2 Proposed mechanism.

Finally, the developed method was applied to a mixture of RAEs synthesized from saturated fatty acids. Fortunately, the materials could be converted into a mixture of hydrocarbons (C_9–C_{17}) within the diesel and jet-fuel ranges in 67% yield (Fig. 1). This result demonstrates the potential of the decarboxylation methodology to produce *n*-alkanes compatible with drop-in biofuels from more complex matrixes such as mixtures of fatty acids originating from vegetable oils or animal fat.

Based on these results, the proposed mechanism is analogous to previously reported Ni-catalyzed reductive decarboxylation of RAE (Scheme 2).[27,44–46] On the basis of this mechanism the BiPy ligand is necessary to help stabilize the *in situ* formed Ni(I) catalyst **II** that undergoes transmetallation with PMHS to afford intermediate **III**. This complex would then donate an electron *via* SET to the RAE forming **V** and the radical anion **IV** which undergoes radical fragmentation (decarboxylation) yielding the primary alkyl radical **VII** and anionic phthalimide **VI**. Addition of radicals **VII** and **VI** to intermediate **V** gives intermediate **VIII** which after reductive elimination affords the desired alkane product and regenerates the catalyst.

Conclusions

A method for the smooth conversion of redox-active esters derived from fatty acids to selectively produce renewable hydrocarbons was demonstrated. Prior activation of substrates enabled the process to be performed with a simple bench setup at 40 °C in ambient pressure. This chemistry was also efficient for the decarboxylation of fatty acids in a one-pot sequential protocol, avoiding the necessity of prior purification of the RAE formed *in situ*. Remarkably, a non-toxic, inexpensive silane proved to be effective, allowing the synthesis of *n*-alkanes under hydrogen-free conditions. To the best of our knowledge, no studies on applying Ni-catalysts combined with PMHS for decarboxylation of fatty acids to produce C_{n-1} hydrocarbons with high selectivity under mild conditions have been reported. According to the results, hydrocarbons within the diesel and the jet-fuel ranges were synthesized at similar yields compared to conventional thermo-catalytic routes that apply harsh conditions for the deoxygenation of biomass.

Author contributions

Silva MSB: methodology, formal analysis, investigation, writing – review & editing, Araujo JGL; Bento JCCV; Azevedo AM: methodology, formal analysis, Anjos ASD; Araújo AMM: methodology, formal analysis, Souto CRO; Menezes FG: writing – review & editing, data curation, validation, Silva DR; Gondim AD: conceptualization, supervision, Cavalcanti LN: conceptualization, data curation, validation, review & editing, supervision.

Conflicts of interest

There are no conflicts to declare.

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