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Upgrading Biodiesel from Vegetable Oils by Hydrogen Transfer to its Fatty Esters

Zhiyao Lu, Valeriy Cherepakhin, Talya Kapenstein, and Travis J. Williams*

Donald P. and Katherine B. Loker Hydrocarbon Institute and Department of Chemistry, University of Southern California, 837 Bloom Walk, Los Angeles, California, 90089-1661, United States

Abstract

Conversion of vegetable-derived triglycerides to fatty acid methyl esters (FAMEs) is a popular approach to the generation of biodiesel fuels and the basis of a growing industry. Drawbacks of the strategy are that (a) the glycerol backbone of the triglyceride is discarded as waste, and (2) most available natural triglycerides in the U.S. are multi-unsaturated or fully saturated, giving inferior fuel performance and causing engine problems. Here we show that catalysis by iridium complex **1** can address both of these problems through selective reduction of triglycerides high in polyunsaturation. This is realized using hydrogen from methanol or those imbedded in the triglyceride backbone, concurrently generating lactate as a value-added C3 product. Additional methanol or glycerol as a hydrogen source enables reduction of corn and soybean oils to > 80% oleate. The cost of the iridium catalyst is mitigated by its recovery through aqueous extraction. The process can be further driven with a supporting iron-based catalyst for the complete saturation of all olefins. Preparative procedures are established for synthesis and separation of methyl esters of the hydrogenated fatty acids, enabling instant access to upgraded biofuels.

TOC image

The one-pot catalytic process converts biodiesel waste glycerol to lactate while hydrogenating polyunsaturation in the fatty acids.

*Corresponding author: Travis J. Williams, travisw@usc.edu.

Supporting Information

Details of reactivity screening studies, optimization studies, substrate scope studies. Data on NMR studies to probe mechanism. Graphical NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Notes

The authors declare no competing financial interests.

Keywords

Biodiesel; transfer hydrogenation; lactate; iridium

INTRODUCTION

U.S. biodiesel production is proliferating at a brisk pace, with an average annual growth of 29% since 2009.¹ In contrast to fossil fuels, which emit significant net carbon, sulfur and aromatic pollutants, biodiesel that is produced from vegetable oils enables an environmentally-benign fuel cycle that involves carbon fixation.^{2,3,4,5}

Key properties of the biodiesel depend almost entirely on its chemistry;^{6,7,8} it is popular to convert vegetable oils (triglycerides) to low molecular weight fatty acid methyl esters (FAMEs), although cleavage of the linking glycerol moiety from the triglyceride leaves this fragment, ca. 10% of the mass of the feedstock, as waste.^{9,10,11} Still, these FAMEs are not ideal drop-ins for diesel fuel due to their polyunsaturation properties. In the U.S., over 80% of FAMEs (or equivalents) are produced from the two dominant vegetable feedstocks, soybean and corn oils.¹ These oils are heavily unsaturated, with characteristic high content of linoleic acid (18:2) and linolenic acid (18:3).¹² This is problematic, because polyunsaturation lowers fuel stability, fuel energy density and lubricity, increases viscosity and gum formation, and causes slow ignition and high emission of hydrocarbons.^{13, 14} Corn and soybean will maintain a major role in US biodiesel, because they comprise more than half of the total acreage of farmed land in the US.¹⁵ While heterogeneous hydrogenation is possible (e.g. Pd),^{16, 17, 18, 19, 20, 21} this involves cost and safety issues associated with high pressure. Further, non-selective hydrogenations yield fully saturated FAMEs that have undesirable high melting points and high propensity to precipitate in diesel blends.^{22,23}

While polyunsaturation or full saturation in fatty acids can cause long-term use issues, FAMEs that have high content of oleate (18:1) are an advantageous biodiesel.²² High oleate FAMEs give useful stability and low-temperature performance. Therefore, the purpose of this work is to provide a selective catalytic method that enables conversion of soybean and corn oils to high oleate biodiesel without glycerol waste. We propose that we can do this by transferring hydrogen selectively from triglyceride backbone and an external reductant to unsaturation in the lipids to produce high oleate biodiesel. This is conceptualized in scheme 1.

Our lab has been involved in catalytic dehydrogenation for some time,^{24,25,26,27,28,29,30} and we recently reported a catalytic, acceptorless dehydrogenation of glycerol.³¹ Here we show that we can realize the proposal in scheme 1, a tandem process which has an output of high oleate FAMEs and no glycerol waste stream. Because there is only one equivalent of H₂ in the triglyceride's backbone and six degrees of unsaturation in corn and soybean triglycerides, we will introduce an external reductant to realize full conversion of polyunsaturation. As exemplified in scheme 2, corn oil is converted to hydrogenated biodiesel and lactide in presence of an alcohol reductant, with perfect atom economy from the oil, good isolated yields of lactide and FAMEs, and high catalyst turnover number. We will also show that addition of a (Macho)Fe catalyst can enable full reduction of unsaturated

triglycerides without loss of selectivity for conversion of the backbone to lactate. Thus, this work adds value to biodiesel production in two ways: 1) high oleate FAMEs can be produced from the abundant feedstocks, corn and soybean oils; 2) a large volume of waste glycerol is converted to a valuable fine chemical, lactate.³²

RESULTS AND DISCUSSION

We began by characterizing representative samples of natural corn and soybean oils. Other oils such as red palm and coconut oils also seem to work under our conditions, but they have limited applicability due to their low unsaturation levels. We were able to measure natural oils' fatty acid composition using ¹H-NMR (Table 1).

To test our tandem reaction, neat corn oil and iridium complex **1** were combined in a sealed vessel with NaOH, and the solution was heated (Table 2). Hydrogen pressure evolved, and double bonds of the fatty acids were reduced. Only polyunsaturated fatty acids were reduced under our conditions. The selectivity is striking. In both corn and soybean oils, polyunsaturated acids can be completely hydrogenated to monounsaturated acids (e.g. oleic acid (18:1)). Simultaneously, oleic acid stays intact. The degree of hydrogenation reported in table 2 therefore describes the portion of polyunsaturated acids that are reduced. In our case, the product is FAMEs with 84-92% monounsaturation. The stability of monounsaturation through the reduction is significant, because it provides low-temperature fluidity and resistance to precipitation, which are problems with fully saturated fatty acids (e.g. 16:0 and 18:0).

In a first-pass experiment (Table 2, entry 1), both lactate (15%) and fatty acid hydrogenation were observed. The glyceride fragment of corn oil cannot provide enough reducing equivalents of hydrogen, and in about an hour the reaction mixture turns into a biphasic soapy mass and stops stirring. Only 5% of olefins were reduced. We addressed both problems with the addition of either methanol (entry 2) or glycerol (entry 3) to serve as both an external reductant and a solvent. Each works well, enabling complete hydrogenation and improved lactate yields. High conversion and selectivity are observed in the presence of methanol, which also enabled us to esterify crude fatty acid to yield FAMEs directly in an overall isolated yield of 65%. In reactions with glycerol as the reducing agent, a longer reaction time enables a higher yield of lactate: compare entries 3 and 4. These observations are not limited to corn oil; we observe comparable results for soybean oil (entry 5). Complex **1** also has good longevity under our catalytic conditions. Using only 30 ppm of **1** provides satisfying results, delivering over 230,000 turnovers in a single catalytic run (entry 6).

While we found C—N-ligated complex **1** to be the best catalyst precursor for glycerol to lactate conversion³¹ and it performed well in this tandem process, we examined several related iridium(I) precursors for comparative and control purposes. These are sketched in table 2. Complex **2** is a bulkier, CO-ligated version of **1** prepared in an analogous way. Complex **3** is a P—N homolog of **1** that works well in our hands in dehydrogenation of formic acid and alcohols.^{24b} **4** is Crabtree's catalyst, presented here as an acyclic homolog of **3**, and **5** is the iridium precursor from which our chelates are prepared.

Generally, iridium complexes **2-5** are less effective than **1** in the tandem reaction. Under the same reaction conditions, less fatty acid was hydrogenated and less lactate was produced in each case (Table 2, entry 7-10). Owing to its bulky mesityl group, **2** reacts more slowly than **1** (entry 7). The (P—N)Ir complex **3** showed the closest reactivity to **1** (entry 8), although its acyclic congener (**4**) is less efficient (entry 9). This shows that the supporting C—N or P—N ligand on the iridium plays an important role in the reactivity. Along these lines, iridium precursor **5** proved to be poor in both hydrogenation and dehydrogenation (Table 2, entry 10).

Although monounsaturated FAMES have higher value as biofuels, we still wanted to identify conditions for complete reduction of vegetable oils. Starting from our original conditions, increasing the loading of **1** to 6 mol% and raising the reaction temperature to 150 °C, we observe over 95% hydrogenation of unsaturated fatty acids (Table 3, entry 1). We perceive that our active iridium species is prone to decomposition and deactivation under these conditions. To obviate this problem (and mitigate the cost of iridium), we show that the addition of a second catalyst can enable total reduction without requiring high [Ir] loading. We find iron complex **6** to be quite useful in this role (entries 3-5). By adding **6** along with **1**, up to 90% of total hydrogenation could be achieved.

In order to gain insight of the catalysis, we have measured several key parameters of the reaction. First, we determined whether there is double bond migration coinciding with catalytic turnovers. Using structural NMR tools such as TOCSY and NOESY, we are confident that there is no migration, and the majority of the 1-degree unsaturated product is oleate (see Supporting Information for graphic spectra).

In varying the methanol loading, we observed near quantitative hydrogenation of fatty acid and near perfect glyceride to lactate conversion when 15 to 25 equivalents methanol are used (Figure 1A). In each case, formate appears as the side product. Further increasing methanol concentration beyond 25 equivalents resulted in lower conversion. This appears to result from catalyst deactivation in presence of high concentrations of methanol (high volume of methanol/total volume). We have observed the same in a previous study: although **1** provides an active methanol dehydrogenation catalyst and a robust catalyst for glycerol dehydrogenation, in concentrated aqueous methanol solution the catalyst is deactivated after only a few hundred turnovers. However, we see that if methanol loading is limited, the catalyst can dehydrogenate methanol through thousands of turnovers. To our knowledge, such prolific transfer hydrogenation is uncommon when glycerol or methanol is the hydrogen source,^{33,34,35,36,37} notwithstanding the potential to work under base-free conditions, as in our tandem runs (Figure 1C&D).

Unlike methanol, glycerol is benign to the catalytic species. When varying the concentration of glycerol in our tandem system, a linear correlation is observed between yield and glycerol loading. The lactate yield scales well without optimizing reaction conditions (Figure 1B).

A base loading study showed no formation of lactate up to 2.5 equivalents of NaOH, even though > 90% hydrogenation of the fatty acids was observed (Figure 1C). This means that stoichiometric base is not required for olefin hydrogenation. This observation implies that a

fast, base-independent transfer hydrogenation route from methanol to fatty acid is available. Such a transfer hydrogenation path can also explain the reactivity observed for iridium complexes **2**, **3**, **4**, and **5** in which a relatively high degree of hydrogenation is observed with a relatively low level of lactate yield. However, under base-free conditions, more glycerol (20%) is derivatized than methanol (<5%). This evidence suggests that glycerol in the backbone may be derivatized faster than methanol in runs where lactate formation is not observed (e.g. left side of Figure 1C). In the same sense, when glycerol is used as sole reductant and base is absent, we observe olefin hydrogenation faster than lactate formation (Figure 1D). We rationalize this observation by considering that the formation of lactate is a multi-step process that requires base, whereas the transfer hydrogenation is likely facile and base-independent (see detailed steps in Scheme 3).

More effort was paid to understand the phenomenon. We attempted direct hydrogenation under basic and base-free conditions. In a typical run, a reaction was set up in which a solution of corn oil, NaOH or no base, and **1** (0.3 mol%) was charged with 1.0 atmosphere of H₂. After the reaction was stirred at 120 °C for 1 day, a strong contrast, 62% or 18% of hydrogenation for basic or base-free conditions, was observed. This shows that H₂ activation is effective with our catalyst and base, and can possibly account for the bulk of the reduction of fatty acids. Another possibility for the observed tandem dehydrogenation-hydrogenation is that it is a transfer-hydrogenation. To test this, we ran the reaction in a flask from which H₂ gas was vented. Here we observe 25% hydrogenation of olefins. Thus, base-free transfer hydrogenation is also possible for our olefin reduction, although it is slower than the direct hydrogenation.

In an extended utility study, the system shows useful water tolerance (Figure 1E). An even more critical extended utility issue, however, is the expense of iridium. Our homogeneous iridium catalyst is substantially soluble and thus can be recollected from aqueous-organic extraction and reused directly. We show our ability to extract the iridium catalyst from the reaction mixture and reuse it 4 times with only moderate loss of reactivity (Figure 1F). While there is reactivity loss that we are continuing to optimize, illustration of iridium recovery and reuse is an essential aspect of the merit of our system.

Based on the evidence above and knowledge from previous studies, we propose the catalyst initiation steps shown in scheme 3. In this mechanism, **1** is initiated by reduction and loss of its cyclooctadiene ligand to give **8**, which is observable by NMR, then **8** is deprotonated by base to an active species such as **8***. Although we can confirm the formation of **8*** in aprotic solvents by its signature dark color, we are unable to observe **8*** cleanly. We expect **8*** to dehydrogenate alcohol (or activate dihydrogen), more rapidly in presence of base, to hydrogenate alkenes to give **8**. When glycerol is dehydrogenated, 1,3-dihydroxyacetone is formed, then hydroxide is required for the transformations to finally yield lactate.

CONCLUSION

In conclusion, we present a high-utility process for the conversion of corn and soybean oils to value-added hydrogenated FAMES and lactate. The key step is a tandem fatty acid hydrogenation and glyceride dehydrogenation that is enabled by a (carbene)iridium

complex. The system has useful longevity and yield and is highly selective for the hydrogenation of polyunsaturated fatty acids. We further show that an iridium-iron catalysis cascade can almost completely hydrogenate the fatty acids. Ongoing work in our laboratory involves developing a detailed understanding of the initiation of hydrogenation pathways from **1**, **2**, and **3**; these data are soon to follow.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

Impact of methanol, glycerol, and NaOH concentration on the yield of reducing polyunsaturations. Conditions: 0.5 mL corn oil, 0.3 mol% Ir catalyst, 120 °C, 1 day. A. Variable methanol concentration, 5 eq. NaOH. B. Variable glycerol concentration, no MeOH, 1 eq. NaOH to glycerol (no less than 5 eq. to triglyceride). C. Variable NaOH loading, 15 eq. MeOH. D. Variable NaOH loading, 25 eq. glycerol. E. Variable H₂O loading, 15 eq. MeOH, 5 eq. NaOH. F. 5 eq. NaOH, 15 eq. MeOH, 1 day.

Scheme 1.
General Scheme for Triglyceride Utilization

Scheme 2.
Iridium Catalysis Enables Vegetable Oil Conversion to FAMES and Lactate

Scheme 3.

Proposed mechanism for iridium catalyzed tandem dehydrogenation of glycerol and hydrogenation of fatty acids.

Table 1Fatty Acid Composition of Natural Oils^a

	Palmitic (16:0)	Stearic (18:0)	Oleic (18:1)	Linoleic(18:2)	Linolenic (18:3)
Soybean	11.9%	4.2%	22.6%	53.5%	6.1%
Corn	6.5%	1.4%	39.9%	50.1%	0.6%

^aDetermined in triplicate by ¹H-NMR.

Table 2

Catalytic Hydrogenation of Polyunsaturation in Corn and Soybean Oils^a

Entry	Precatalyst	Reductant (equiv.)		Degree of hydrogenation	Lactate yield (equiv.) ^b
		MeOH	Glycerol		
1		0	0	5% ^{100%}	0.15
2		25	0	100% (65%) ^g	1.00 ^h
3 ^c		0	25	99%	11.6
4 ^d		0	25	90%	19.0
5 ^e		25	0	98%	0.70
6 ^f		25	0	91%	0.72
7		25	0	82%	0.58
8		25	0	98%	0.57
9		25	0	71%	0.49
10		25	0	54%	0.16

^a Reaction condition: 0.5 mL corn oil, 0.3 mol % Ir complex, 5 eq. NaOH, 120 °C, 1 day. Degree of hydrogenation refers only to linolenic acids and excludes oleic acid.

^b Determined by ¹H-NMR.

^cReaction time was 3 days with 10 eq. NaOH.

^dReaction time was 7 days with 25 eq. NaOH.^e Soybean oil was used in place of corn oil.

f Catalyst loading was 30 ppm, total TON > 230k.

^g Isolated yield of FAMEs after esterification with methanol.

$\eta < 99\%$ NMR conversion of glyceride to lactate.

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Table 3Full Hydrogenation of Corn Oil Fatty Acids^a

Entry	Ir precursor	Fe precursor	full hydrogenation
1 ^b	1 (6 mol%)	NA	95%
2 ^c	NA	6 (0.3 mol%)	7%
3	1 (0.3 mol%)	6 (0.3 mol%)	21%
4	1 (0.3 mol%)	6 (0.6 mol%)	34%
5	1 (0.3 mol%)	6 (3.0 mol%)	90%

^a Reaction condition: 0.5 mL corn oil, 5 eq. NaOH, 120 °C, 1 day, 25 eq. MeOH. Fatty acid hydrogenation was evaluated by ¹H-NMR.

^b 15 eq. NaOH, 150 °C, 3 days, 30 eq. glycerol.

^c No conversion of glycerol was observed.