Efficient conversion of triacylglycerols and fatty acids to biodiesel in a microwave reactor using metal triflate catalysts†

Aaron M. Socha and Jason K. Sello*

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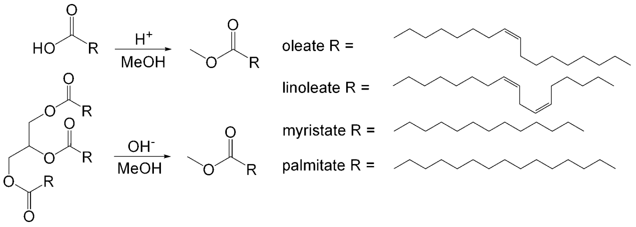
We report that catalytic quantities of the Lewis acidic metal catalysts scandium triflate and bismuth triflate promote conversion of oleic, linoleic, palmitic and myristic acids and their glyceryl triesters to the corresponding methyl esters (biodiesel) in greater than 90% yield upon microwave heating. Additionally, both catalysts could be recovered and reused in esterification reactions at least six times.

Introduction

At the current rate of fossil fuel consumption, it is estimated that global reserves of petroleum will be exhausted by 2050.[1] An established alternative fuel is biodiesel, which is defined as alkyl (*i.e.*, methyl, ethyl, or propyl) esters of fatty acids.[2] The success of biodiesel is based on its large energy return, limited environmental impact, and utility in unmodified, standard diesel engines.[3]

Industrially, both acid-catalyzed esterification of fatty acids and alkali-catalyzed transesterification of triacylglycerols are used to make biodiesel (Scheme 1). The most common biodiesel precursors are triacylglycerols comprising virgin oils directly isolated from plants such as soy, canola, and palm. Typically, the transesterification of triacylglycerols into biodiesel is performed in methanol using catalytic quantities of either potassium hydroxide or sodium hydroxide. A lower cost and more readily abundant source of biodiesel precursors is the waste vegetable oil resulting from food preparation. The cost and positive environmental impact of recycling waste vegetable oil is a significant motivation for its use as a feedstock for biodiesel. In spite of the advantages of waste vegetable oil, its chemical heterogeneity presents challenges for biodiesel production. The major constituents of waste vegetable oil are triacyglycerols, free fatty acids, and water. The free fatty acids, which can be the major constituent of extensively used waste vegetable oil, yield soaps under alkaline reaction conditions that complicate downstream product isolation. Thus, the conversion of waste vegetable oil to biodiesel requires a two-step process: acid-catalyzed esterification of the free fatty acids followed by the hydroxide promoted transesterification of triacylglycerols. Because fatty acid esterification typically uses sulfuric acid, its workup requires additional time, risk, and quickly leads to equipment corrosion.

Reagents commonly used in modern organic chemistry are promising alternatives to current industrial methods for biodiesel production. There are numerous solid acid catalyst alternatives to sulfuric acid,[4] including zeolites,[5] Nafion,[6] Amberlyst,[7] heteropoly acids,[8] and sulfonated sugars.[9] Among the best candidates are the heteropoly acids, which have been shown to convert both free fatty acids and triacylglycerols to methyl esters.[8,18,19] Unfortunately, these solid catalysts are often expensive and rarely outperform H_2SO_4. In spite of their great utility in synthetic organic chemistry, only a few reports of Lewis acids have appeared in the context of biodiesel. For example, $AlCl_3$ was shown to convert canola oil to biodiesel, but the reaction required 18 h at 110 °C and THF as a co-solvent.[20] Similarly, the acetates of Cd, Pb, and Zn were reported to convert both soybean oil and palmitic acid to biodiesel, and this reaction was accelerated significantly in subcritical methanol.[21] However, the toxicity and air-sensitivity of these Lewis acid catalysts precludes their application on an industrial scale. Biodiesel production would greatly benefit from the availability of stable catalysts that can efficiently convert both fatty acids and triacylglycerols into alkyl esters under mild and environmentally benign conditions.



Scheme 1 Industrial processes used to make biodiesel. Acid-catalyzed esterification of free fatty acids (top) and base-catalyzed transesterification of triacylglycerides (bottom).

Our objective was to identify catalysts that could be useful in an industrial context for the conversion of fatty acids and triacylglycerols into biodiesel. An ideal catalyst would be low cost, limited in toxicity, and insensitive to air and moisture. In light of these considerations, we turned our attention to stable Lewis acidic metal catalysts that have been extensively used in synthetic organic chemistry, especially in the context of green chemistry. An obvious choice was scandium triflate, a well-characterized Lewis acidic metal catalyst that is insensitive to air and moisture.[10] The applicability of this metal catalyst in the context of biodiesel chemistry was given credibility by a report describing its catalytic utility for transesterification of low molecular weight esters.[11]

Results and discussion

Initially, we investigated the utility of scandium triflate for the catalytic conversion of triacylglycerols commonly found in

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Department of Chemistry, Brown University, 324 Brook Street, Box H, Providence, Rhode Island, 02912, USA. E-mail: jason_sello@brown.edu; Fax: +1 401 863 9046; Tel: +1 401 863 1194

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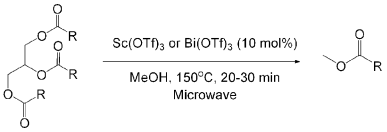
Table 1 Scandium and bismuth triflate-catalyzed transesterification



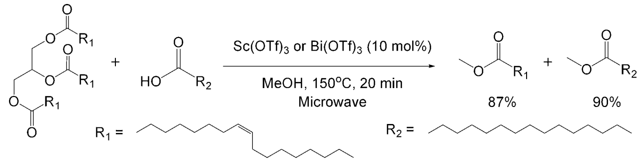
TAG	Catalyst[a]	MeOH eq.	T (°C)	Time (min)	Percent yield[b]
Oleate	$Sc(OTf)_3$	6	20	150	18
Oleate	$Sc(OTf)_3$	12	20	150	31
Oleate	$Sc(OTf)_3$	48	20	150	92
Oleate	$Bi(OTf)_3$	48	25	150	85
Linoleate	$Sc(OTf)_3$	48	20	150	90
Linoleate	$Bi(OTf)_3$	48	25	150	84
Myristate	$Sc(OTf)_3$	48	30	150	82
Myristate	$Bi(OTf)_3$	48	25	150	99
Palmitate	$Sc(OTf)_3$	48	20	150	99
Palmitate	$Bi(OTf)_3$	48	25	150	92

[a] 10 mol % catalyst loading [b] Yields calculated by GC-MS[15,16]

virgin plant oils (glyceryl trioleate, glyceryl trilinoleate, glyceryl trimyristate, and glyceryl tripalmitate) into fatty acid methyl esters in refluxing methanol at 60° C. Interestingly, we found that under these conditions neither catalytic nor stoichiometric quantities of scandium triflate appreciably catalyzed the desired reaction. In turn, we investigated the possibility that microwave heating could promote the desired transformation. Although microwave heating is mostly known for its utility in synthetic organic chemistry,[12] it has also proven to be useful in the context of biodiesel production. Potassium hydroxide promoted transesterification of triacylglycerols into biodiesel is reportedly more efficient in a microwave reactor.[13,14] We were gratified to find that catalytic quantities of scandium triflate promoted efficient methanolysis of the triacylglycerols in a microwave reactor. Optimization of catalyst loading, reaction time, and the methanol stoichiometry revealed the best conditions for transesterification: 10 mol% scandium triflate, 20 min at 150 °C, and a 48 : 1 ratio of methanol to ester of the triacylglycerol. The reaction yields were determined by gas chromatography-mass spectrometry (GC-MS) according to standard procedures.[15,16] Across all substrates, the most significant parameter in the transesterification reaction conditions was the molar ratio of methanol (Table 1). Methanolysis of glyceryl trioleate using catalytic scandium triflate occurred in 18%, 31%, and 92% yield with methanol : ester ratios of 6 : 1, 12 : 1, and 48 : 1, respectively (Table 1). Based on the utility of scandium triflate in these reactions, we assessed the utility of bismuth triflate as a transesterification catalyst. Bismuth triflate is a low-toxicity catalyst that has been extensively used in synthetic organic chemistry.[17] Under similar conditions, we found that it was nearly as effective as scandium triflate in these reactions; however, the reaction time had to be extended to 25 min for the highest yields.

The efficacy of scandium triflate and bismuth triflate in transesterifications of triacylglycerols motivated a series of experiments to assess their capacity to catalyze esterifications of free fatty acids. As was the case for the transesterification reactions, the metal catalysts did not catalyze the desired reaction in refluxing methanol. However, in a microwave reactor, both scandium triflate and bismuth triflate were remarkably effective as catalysts for the conversion of fatty acids to methyl esters. By optimizing the reaction conditions, we found that the esterification was complete within 1 min using 1 mol% of either metal catalyst at 150 °C with a 48-fold molar excess of methanol (Table 2). In these reaction optimizations, we found that the reaction temperature, reaction time, and the methanol stoichiometry were all critical parameters. As an example of the temperature-dependence, glyceryl trilinoleate was esterified (1 mol% $Sc(OTf)_3$, 48 eq. of MeOH, 1 min reaction time) in 24% yield at 50° C, 81% yield at 100° C, and 97% yield at 150° C. Extension of the reaction time from one minute to five minutes did not enable high yielding esterifications at either 50° C or 100° C. The methanol stoichiometry of the reactions also proved important as the yield dropped from 97% to 55% when the amount of the methanol was reduced from 48 eq. to 12 eq., respectively.

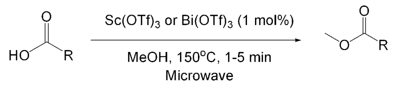
Because the metal catalysts effected conversion of both triacylglycerols and free fatty acids into methyl esters, we hypothesized that they would catalyze simultaneous esterification and transesterification in one reaction vessel. Indeed, we found that 10 mol% of either scandium triflate or bismuth triflate catalyzed the conversion of a 1 : 1 mixture of palmitic acid and glyceryl trioleate to methyl oleate and methyl palmitate in 20 min at 150° C (Scheme 2).



Scheme 2 One pot reaction to convert both triglycerides and FFAs to methyl esters.

Aside from its insensitivity to air and moisture, an asset of scandium triflate is that it can be recovered from reactions and reused. We carried out a series of experiments to assess the recyclability of scandium triflate and bismuth triflate in esterifications and transesterifications. Our attempts to recycle scandium triflate from transesterifications were thwarted by difficulties in separating the recovered catalyst from the glycerol by-product. However, both

Table 2 Scandium and bismuth triflate catalyzed conversion of free fatty acids (FFA) to methyl esters



FFA	Catalyst[a]	MeOH eq.	Time (min)	T (°C)	Percent yield[b]
Linoleic	$Sc(OTf)_3$	48	1	50	24
Linoleic	$Sc(OTf)_3$	48	1	100	55
Linoleic	$Sc(OTf)_3$	48	5	50	30
Linoleic	$Sc(OTf)_3$	48	5	100	81
Linoleic	$Sc(OTf)_3$	48	1	150	97
Linoleic	$Bi(OTf)_3$	48	1	150	98
Linoleic	$Sc(OTf)_3$	12	1	150	55
Linoleic	$Sc(OTf)_3$	24	1	150	75
Oleic	$Sc(OTf)_3$	48	1	150	100
Oleic	$Bi(OTf)_3$	48	1	150	88
Myristic	$Sc(OTf)_3$	48	1	150	98
Myristic	$Bi(OTf)_3$	48	1	150	90
Palmitic	$Sc(OTf)_3$	48	1	150	100
Palmitic	$Bi(OTf)_3$	48	1	150	99

[a] 1 mol % catalyst loading [b] Yields calculated by GC-MS[15,16]

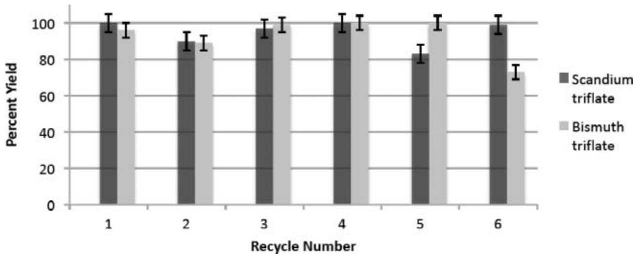


Fig. 1 Yields of palmitic acid esterification from sequential catalyst recycling experiments. Error bars indicate average standard deviation.

metal catalysts could be recycled at least six times for use in the esterification of palmitic acid (Fig. 1). Remarkably, the recovered scandium triflate did not lose any catalytic activity; a reaction using 1 mol% of catalyst that was recycled five times gave a 97% yield in an esterification of palmitic acid.

Conclusions

We found that the Lewis acidic metals scandium triflate and bismuth triflate can efficiently catalyze conversions of the major components of both virgin and waste vegetable oils to methyl esters in a microwave reactor. Our findings highlight the utility of modern synthetic methods and reagents in industrial reactions.

Although the rare earth metal triflates were effective catalysts in transesterifications in a microwave reactor, the reactant stoichiometry and the temperature in these reactions were significantly higher than those reported for the microwave-enhanced conversion of triacylglycerols into biodiesel using potassium hydroxide.[13] In spite of this limitation, the metal triflates are of interest because they can catalyze the simultaneous conversion of triacylglycerols and fatty acids into the corresponding methyl esters. The esterification reaction is particularly noteworthy because it is complete in one minute and requires only 1 mol% of the metal catalysts with microwave heating. Further, these catalysts can be recovered and reused in subsequent esterifications. To the best of our knowledge, this is the first time that scandium and bismuth triflates have been shown to catalyze the esterification of fatty acids. The scandium triflate catalyzed conversion of carboxylic acids into esters is novel; reports of esterification with this reagent have been limited to mixed anhydrides.[22] In any case, our findings suggest that both scandium and bismuth triflates have utility in the industrial production of biodiesel from components of plant and animal derived oils and fats.

Experimental section

General methods

All transesterification and esterification reactions were performed with analytical grade reagents (Sigma Aldrich) and were used without further purification. Microwave reactions were performed in a Biotage Initiator microwave reactor using 0.2–0.5 mL and 0.5–2.0 mL microwave reaction vials equipped with magnetic stirring bars and Reseal™ septa. GC-MS analysis was performed on a Hewlett Packard 5971A GC-MS system using an HP5-MS column. Splitless injections of 1 µL were made using an initial temperature of 60 °C, holding for 2 min, then 20 °C min^{-1} ramp to 280 °C, and holding for 2 min. Helium was used as the carrier gas. To determine yield, reaction mixtures were diluted to the midpoint of the calibration curve with a known solution of methyl stearate (assuming quantitative conversion to product). The TIC area ratios (TIC sample/TIC internal standard) were compared to the respective TIC area ratios of the standard curves.[15,16] Five-point linear calibration curves were prepared in triplicate for each methyl ester analyte using methyl stearate as an internal standard. The R^2 values of the curves were between 0.98 and 0.99 for each methyl ester and used to calculate the percent error in the midpoint (see ESI†). The error for methyl oleate, methyl linoleate, methyl myristate, and methyl palmitate midpoints (509 µM) were 3.9%, 3.6%, 8.7%, 5.3%, respectively.

All reactions were performed in duplicate and analyzed in triplicate, and the tabulated percent yields represent an average of the six data points obtained from each reaction.

Selected non-quantitative transesterifications were analyzed by thin-layer chromatography (TLC) on EMD silica gel 60 F254 plates using a 1 : 1 hexanes : dichloromethane solvent system to assess the presence of acylglycerol starting materials.

Chemistry

All transesterifications used 35 μmol of the triacylglycerol and 10 mol% of either $Sc(OTf)_3$ or $Bi(OTf)_3$. The reactions were carried out in the microwave reactor with either 6, 12, or 48 equivalents of methanol per ester of the triacylglycerol for the indicated period of time. Upon completion, the reactions were analyzed as described in the general methods section. Analytical TLC of non-quantitative reactions revealed only the presence of triacylglycerol starting materials; no mono- or di-acylglycerols were detected.

All esterifications used 100 μmol of the fatty acid and 1 mol% of either $Sc(OTf)_3$ or $Bi(OTf)_3$. The reactions were carried out in the microwave reactor with either 12, 24, or 48 equivalents of methanol per fatty acid for the indicated period of time. Upon completion, the reactions were analyzed as described in the general methods section.

In the case where the esterification and transesterification were carried out in "one-pot", 35 μmol of triolein and 85 μmol of palmitic acid were dissolved in 205 μL of MeOH with 10 mol% (3.5 μmol) of either $Sc(OTf)_3$ or $Bi(OTf)_3$. The reactions were heated to 150 °C for 20 min in the microwave reactor. Upon completion, the reactions were analyzed as described in the general methods section.

The catalyst recycling experiments for esterification reactions of palmitic acid were executed based on observations that catalyst recovery at each recycling step was approximately 80%. Thus, the initial esterification was carried out in the microwave reactor (1 min, 150 °C) with 100 mg (0.39 mmol) of palmitic acid in 800 μL of MeOH with 10 mol% of catalyst. Upon completion, the reaction was analyzed as described in the general methods section. The dichloromethane-diluted reaction mixture was subjected to aqueous workup to separate the catalyst from the methyl ester product. The aqueous phase was lyopholized to recover the catalyst as a white powder. Five subsequent reactions were performed as described using 10 mol% of recovered catalyst. In the sixth and final recycled reaction, only 1 mol% of the recovered catalyst was used to ensure that it was fully active.

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