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Article

Unsaturated Renewable Oil Transformation into Novel Biofuel Compositions via an Olefin Metathesis-Transesterification-Hydrogenation Sequence

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O uso sequencial de reações de etenólise, transesterificação e hidrogenação de um óleo renovável modelo para a preparação de potenciais biocombustíveis é reportado. Conversões de até 70% foram obtidas na etenólise de óleo de oliva usando uma pressão relativamente baixa de etileno (2 bar) e tolueno como solvente. O óleo de oliva etenolisado foi transesterificado quantitativamente com metanol e, posteriormente, hidrogenado com hidrogênio molecular sobre Pd/C, resultando em novas composições de biocombustíveis, incluindo diferentes frações de biogasolina, bioquerosene e biodiesel.

The sequential ethenolysis, transesterification and hydrogenation of a model unsaturated renewable oil for the preparation of potential biofuels is reported herein. Ethenolysis conversions of up to 70%, using olive oil, were obtained applying a relatively low 2 bar ethylene pressure and toluene as solvent. The ethenolyzed olive oil was quantitatively transesterified with methanol and, subsequently, hydrogenated with molecular hydrogen over Pd/C, affording access to novel biofuel compositions, including different fractions of biogasoline, biokerosene and biodiesel.

Keywords: organometallic catalysis, catalysis, electrocatalysis and photocatalysis (properties and mechanisms), green chemistry

Introduction

In recent years there has been an increasing interest in the search for new technologies or in the improvement of current ones aiming the development of more sustainable processes. In this context, one of the key areas of interest is the search for new alternatives to fossil fuels, which are non-renewable raw materials and its reserves are dwindling and bound to end in the future. As a consequence, this situation represents a steady threat to our supply chain, including chemicals, energy and materials. Therefore, it is necessary to transform actual refineries into biorefineries in order to achieve a more sustainable economy.[1] Vegetable oils and animal fats represent an attractive renewable feedstock platform.[2-7] Although the use of edible oils is considered polemical due to the competing demand for the food source, non-edible oils, known as the second generation feedstock, are promising substitutes for traditional edible food crops.[8]

Olefin metathesis with oleochemicals is a well-established research field.[6,7,9] It is well known that several metathesis catalysts (Figure 1) are not deactivated by substrates with different functional groups, including those with oxygen, enabling the application of vegetable oils and derivatives as substrates.[10] For instance, the cross-metathesis of fatty acid methyl esters (FAME) has been largely explored with acyclic olefins, resulting either in chain-elongation or -shortening.[11-13] Due to the fact that ethylene can be easily obtained from bioethanol,[14] it makes FAME ethenolysis especially interesting for the production of renewable 1-alkenes (α-olefins) with and without the ω-ester group.[15] In comparison, the direct ethenolysis of vegetable oils has been less explored.[16,17] Both approaches have the potential of providing an interesting platform for the transformation of biomass into renewable chemicals, energy and materials.[13] However, despite the good tolerance to functional groups, olefin metathesis catalysts are poisoned by impurities present in small quantities in vegetable oils, which are intuitively supposed to be increased in its derivatives, more specifically

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In memoriam of Prof Roberto Fernando de Souza

in the monoalkyl esters, due to the alcoholysis step. In this context, the utilization of α-olefin mixtures for the preparation of potential biofuels, obtained from direct vegetable oil ethenolysis, has not yet been explored.

The ethenolysis of unsaturated oils produces α-olefin feedstocks with and without the ω-ester group. α-Olefins without the ω-ester group could be used as high yield catalytic reforming source for the preparation of gasoline/kerosene-type biofuels and direct hydrogenation provides access to the corresponding alkanes (paraffins).[14,18] Furthermore, α-olefins are important feedstocks for detergents, poly(α-olefins), epoxies, alkyl aromatics, esthetic products, flavors and fragrances.[5,19] Biofuels in the range of biogasoline and biokerosene could be obtained by a consecutive transesterification/hydrogenation sequence of the α-olefin mixture.[14,20,21] The chemical similarity with fossil gasoline and kerosene would avoid the necessity to adapt existing motors, which, together with the possibility of mixing these biofuels into fossil fuels, allow its introduction into the market in a non-disturbing way.[4] Besides, these biofuels will not contain aromatic and sulfur impurities. Therefore, addressed in this study is the use of olefin metathesis as key catalytic reaction for the transformation of olive oil (chosen as a model unsaturated oil substrate due to its high oleic acid content) into renewable fuels (Scheme 1). This study does not advocate the use of olive oil as a raw material but aims to investigate the possibility of using this catalytic strategy with highly unsaturated oils.

Experimental

General considerations

All the manipulations involving air and/or moisture-sensitive chemicals were performed using standard Schlenk techniques under either argon or nitrogen atmosphere. Toluene (Vetec) was purified by distillation with sodium/benzophenone, and stored over molecular sieves under inert atmosphere. Dichloromethane (Vetec), *n*-butylvinyl ether (Aldrich), methanol (Vetec), KOH (Vetec), anhydrous $MgSO_4$ (Vetec), aqueous H_2SO_4 (Vetec), palladium supported on activated carbon (Pd/C, 5 wt.%, Aldrich), deuterated chloroform (99.8%, Cambridge Isotope Laboratories), ethylene (99.999%, Air Liquide) and hydrogen (99.999%, White Martins) were used as received. The Grubbs first (G1) and second (G2) generation and Hoveyda-Grubbs second-generation (HG2) metathesis catalysts were purchased from Aldrich and used as received. Olive oil (Monde) was purchased from local stores and purified either by passing through an aluminum oxide column or as follows: activated charcoal (5.0 g) was added to a solution of olive oil (30.0 g) in dichloromethane (90 mL) and the resulting mixture was stirred overnight,

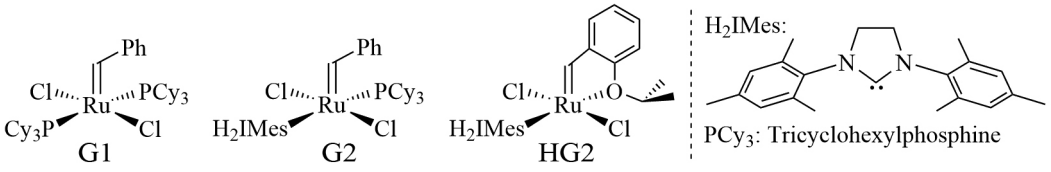
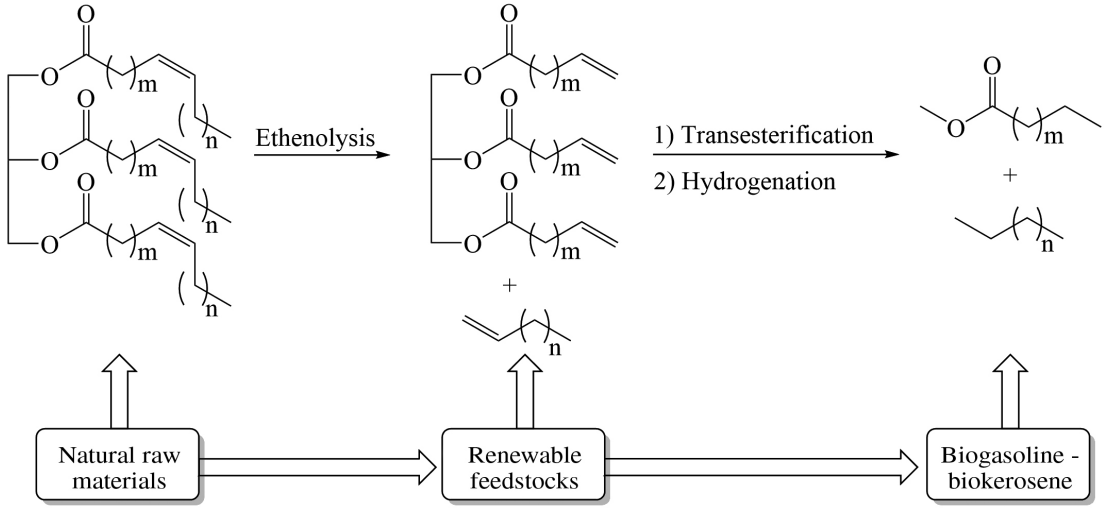


Figure 1. Ruthenium alkylidene metathesis catalysts.



Scheme 1. Strategy applied to the transformation of unsaturated oils into renewable fuels.

followed by filtration through silica and, subsequently, a basic aluminum oxide column. Solvent removal under reduced pressure afforded a slightly yellowish oil. The ethenolysis and hydrogenation reactions were performed in a 300 mL Parr reactor.

Ethenolysis

Typical procedure: prior to use, the purified olive oil (2.00 g) was degassed by five freeze-pump-thaw cycles and then dissolved in 15 mL of toluene. The oil solution was transferred to the reactor vessel under an argon atmosphere. An ethylene pressure of approximately 2.0 bar was applied and the temperature increased to 50 °C. After temperature stabilization, the ethylene pressure was released and the metathesis catalyst added (in 5 mL of toluene). The reactor was pressurized with the desired ethylene pressure and the pressure valve closed. At the end of the reaction, the ethylene pressure was released and 80 μL of *n*-butylvinyl ether (dissolved in 1.0 mL of toluene) was added. The reaction mixture was stirred for 10 min and then passed through a small silica column. The products were analyzed by ^{1}H nuclear magnetic resonance (NMR) spectroscopy.

Transesterification

Transesterification was performed according to a two consecutive steps acid-base literature procedure.[22] The products were analyzed by ^{1}H NMR.

Hydrogenation

Hydrogenation reactions were performed using a modified literature procedure.[21] Ethenolyzed/transesterified product (10.0 g, dissolved in 10 mL of toluene) and 0.5 g of Pd/C were added to the Parr reactor. The temperature was raised to 100 ºC and a 5 bar hydrogen pressure was applied. After stirring the reaction mixture at 200 rpm for 100 min, the solids were filtered off and toluene was removed by fractional distillation. The products were analyzed by ^{1}H NMR and gas chromatography-mass spectrometry (GC-MS).

^{1}H NMR analysis

The ^{1}H NMR spectra were recorded on a Varian Inova 300 equipment at 300 MHz at ambient temperature, using deuterated chloroform as solvent. The chemical shifts are given in parts *per* million (ppm) and referenced to the tetramethylsilane (TMS) signal (0.0 ppm). The spectra were recorded on a pulse angle of 45º, with 64 scans and 1.0 s relaxation time. Experiments varying the relaxation time from 0.3 to 2.0 s resulted in conversion variations of less than 3% (for experimental details about the calculation of conversions see Supplementary Information).

GC-MS analyses

GC-MS analyses were performed on a Shimadzu QP2010-GCMS equipped with a flame ionization detector (FID) detector. A 30-m RTX-5MS column containing 5% phenylmethylpolysiloxane was used as stationary phase. Starting temperature: 70 °C; time at starting temperature: 1 min; ramp: 10 °C min^{-1}; ending temperature: 250 ºC; flow rate: 3.0 mL min^{-1} (Ar); split ratio: 50.0; inlet temperature: 250 ºC; detector temperature: 250 ºC; column oven temperature: 70 º C.

Results and Discussion

In general, reports on the cross metathesis of natural oil derivatives are focused on the use of methyl oleate as substrate.[6,7,11] Therefore, we have chosen olive oil to perform our studies due to its high oleic acid content.[2,7,11,23] However, it is worth mentioning that other possibilities of either edible or non-edible oils containing basically the same or even higher amounts of unsaturated chains could be employed as well (Table 1).

The tests for olive oil ethenolysis optimization were performed using commercially available ruthenium alkylidene complexes as catalysts (Table 2). In a first attempt, alumina-purified oil, G1 and 45 bar of ethylene pressure were reacted for 120 min. A considerably low conversion of 14% was obtained (Table 2, entry 1). Increasing the toluene to oil molar ratio from 1:4 to 1:15 resulted in a slight improvement of the ethenolysis conversion (Table 2, entry 2). This effect, most likely due to enhanced ethylene solubilization, has previously been demonstrated to improve FAME ethenolysis.[24] Further improvement in the conversion was obtained after decreasing the oil to catalyst ratio from 2000:1 to 100:1 (Table 2, entry 3). These results suggest that small amounts of impurities in the oil deactivate the catalytic species and, therefore, are responsible for lowering the conversion when smaller amounts of catalysts were applied. Previous reports have shown that substrate purification is crucial for the improvement of metathesis conversions.[25] For instance, researchers from Materia Inc. recently reported an impressive improvement in the propenolysis conversion of soybean oil FAME upon treatment with Magnesol®, which allowed the use of very low catalyst loadings.[17] In this project, we rather used activated carbon as purifying

Table 1. Unsaturated fatty acid compositions in edible and non-edible oils[8]

Oil	Unsaturated fatty acid / %				
	Palmitoleic (16:1)	Oleic (18:1)	Linoleic (18:2)	Linolenic (18:3)	Total
Olive[a]	0.92	75.5	7.02	0.66	84.10
Canola[a]	0.21	62.41	20.12	8.37	91.11
Peanut[a]	0.06	48.71	31.06	0.23	80.06
Soybean[a]	0.08	21.35	56.02	7.15	84.60
Tobbaco seed[b]	0.2	14.54	69.49	0.69	84.92
Milkweed seed[b]	6.8	34.8	48.7	1.2	91.5
Caper spurge[b]	0.5	81.46	3.71	2.78	88.45
Jatropha[b]	0.7	39.1	41.6	0.2	81.6
Rice bran[b]	0	47.5	35.4	1.1	84.0
Chinese tallow seed[b]	3.7	16.7	31.5	41.5	93.4
Croton[b]	0.11	9.95	74.31	3.62	87.99

[a]Edible oil; [b]non-edible oil.

agent. After treating the olive oil with activated carbon, instead of alumina, significant conversion improvements were obtained, a clear indicative that activated carbon better removes catalyst-poisoning impurities present in the oil than alumina does. For instance, when the alumina-purified oil was used, a 52% conversion was only possible to be reached after 2 h with an oil to catalyst ratio of 100:1. Treatment of the oil with activated carbon allowed obtaining basically the same conversion after only 30 min with a lower catalyst loading (Table 2, entries 3 and 4).

With the positive influence of both oil purification and substrate solubilization, the catalyst screening was the following parameter to be studied. Both Grubbs first (G1) and second (G2) generation metathesis catalysts show similar performance in the ethenolysis of olive oil under the same experimental conditions (Table 2, entries 5 and 6). However, the Hoveyda Grubbs second-generation metathesis catalyst (HG2) was much less efficient, resulting in a conversion of only 19% (Table 2, entry 7). Similar results for the ethenolysis of methyl oleate were reported by Grubbs and co-workers.[26] The olive oil conversion remained constant when the reaction time was varied from 30 to 60 min with catalyst G1 (Table 2, entry 5 and 8), indicating that the ethenolysis reached its equilibrium at or before 30 min. Increasing the ethylene pressure from 1 to 2 bar resulted in the highest conversion of 70% (Table 2, entries 8 and 9), which is attributed to olive oil self-metathesis suppression. A further ethylene pressure increase resulted in slightly reduced conversions (Table 2, entry 10 and 11), which was most likely the result of enhanced ethylene self-metathesis and/or catalyst decomposition, decreasing the conversion of the desired cross-metathesis products.[26]

The importance of the appropriate purification of the substrate can be highlighted comparing the ethenolysis conversion of an olive oil FAME (synthesized in our lab) and the same reaction using commercial methyl oleate, using the same purification procedure (passing through an alumina column) and similar reaction conditions (Table 2, entries 12 and 13). When the synthesized olive oil FAME was used as substrate a much lower conversion was obtained as compared to the conversion obtained when commercial methyl oleate was used. The same is true when comparing the conversions obtained in the ethenolysis of olive oil and olive oil FAME (Table 2, entries 4 and 12). This observation is attributed to residual impurities remaining in the FAME after the methanolysis step.

Figure 2 shows the ^{1}H NMR spectra of the substrates and products of each catalytic reaction applied in the current biofuel strategy. The olive oil ethenolysis (Table 2, entry 4) resulted in the appearance of the typical terminal olefinic hydrogen signals between 4.8 and 6.0 ppm (Figures 2a and 2b).

The α-olefins obtained in the ethenolysis were used as feedstock for biofuel preparation, using sequential transesterification and hydrogenation reactions. The respective methyl esters were obtained after transesterification with methanol following a double step process, as confirmed by ^{1}H NMR (Figure 2c).[22] Further hydrogenation with 5 wt.% Pd/C and 5 bar of hydrogen afforded biofuels with different compositions (Table 3).[21] Complete olefin hydrogenation was obtained, as confirmed either by ^{1}H NMR (Figure 2d) of the product mixture or gas chromatography analysis (Supplementary Information). The biofuels were obtained as mixtures of biogasoline, biokerosene and biodiesel components (Table 3). As expected, higher biogasoline/biokerosene contents were obtained when feedstocks with higher ethenolysis conversions were used. If desired, the biogasoline, biokerosene and biodiesel fractions might be easily separated by fractional distillation.

Table 2. Optimization of the olive oil ethenolysis conditions at 50 °C[a]

entry	Oil / g	Toluene:oil ratio[b]	Catalyst	Oil:catalyst ratio[b]	Pressure / bar[c]	time / min	Conversion / %[d]
1	10	1:4	G1	2000:1	45	120	14
2	10	15:1	G1	2000:1	45	120	23
3	10	13:1	G1	100:1	45	120	52
4	10[e]	1:4	G1	2000:1	45	120	37
5	2[e]	63:1	G1	333:1	1	30	50
6	2[e]	63:1	G2	333:1	1	30	48
7	2[e]	63:1	HG2	333:1	1	30	19
8	2[e]	63:1	G1	333:1	1	60	49
9	2[e]	63:1	G1	333:1	2	60	70
10	2[e]	63:1	G1	333:1	3	60	64
11	2[e]	63:1	G1	333:1	4	60	63
12	10[f]	1:12	G1	2000:1	45	120	8
13	5[g]	1:6	G1	2000:1	45	240	48

[a]G1: Grubbs 1st generation catalyst; G2: Grubbs 2nd generation catalyst; HG2: Hoveyda-Grubbs 2nd generation catalyst; [b]molar ratio; [c]ethylene pressure; [d]determined by ^{1}H NMR (see Supplementary Information); [e]olive oil treated with activated carbon; [f]transesterified olive oil; [g]commercial methyl oleate.

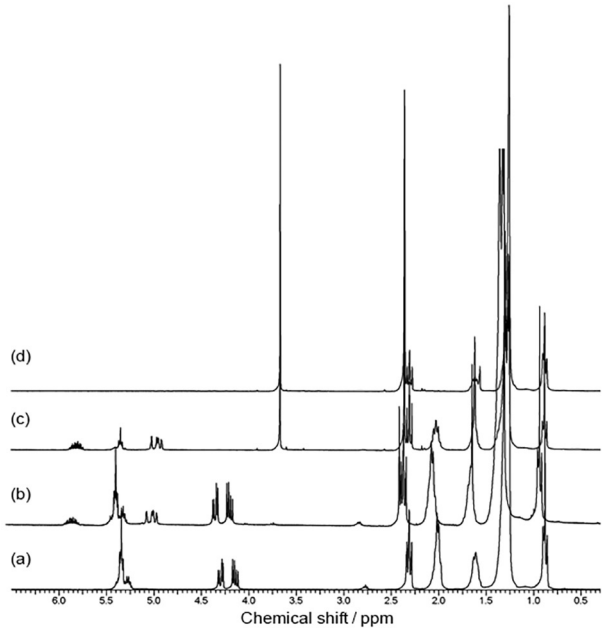


Figure 2. ^{1}H NMR spectra of (a) olive oil; (b) ethenolysis products; (c) transesterification products and (d) hydrogenation products.

Conclusions

The olefin metathesis, transesterification and hydrogenation sequence proved to be a promising strategy to transform renewable unsaturated oils into novel biofuel compositions. Optimization of the olive oil ethenolysis conditions resulted in a 70% conversion when using the first generation Grubbs metathesis catalyst (G1). The ethylene concentration proved to be a fundamental parameter for promoting the formation of the desired cross-metathesis products. Subsequent methanolysis and hydrogenation of the α-olefin ethenolysis products afforded potentially renewable fuels of different biogasoline/biokerosene and biodiesel compositions. These initial studies provide a strategic starting point for the development of this catalytic process with non-edible highly unsaturated oils.

Table 3. Composition of olive oil-based potential biofuels produced after sequential ethenolysis, transesterification and hydrogenation

Component C_{10}-C_{18}	Potential biofuel[a,b]		
	1 (10)[c]	2 (42)[c]	3 (52)
Decane	7.9	15.8	19.1
Methyl decanoate	10.4	25.9	27.0
Methyl hexadecanoate	11.9	11.0	13.2
Methyl octadecanoate	68.8	45.0	36.5
Biogasoline/biokerosene (C_{10}) in biofuel / %	18.3	41.7	46.0
Biodiesel (C_{16}-C_{18}) in biofuel / %	80.7	56.0	49.6

[a]Compositions determined by GC-MS; [b]numbers between parentheses show the ethenolysis conversion (%) determined by ^{1}H NMR; [c]not reported in Table 1.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

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