



Catalytic conversions in green aqueous media: Part 4. Selective hydrogenation of polyunsaturated methyl esters of vegetable oils for upgrading biodiesel [☆]

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ABSTRACT

This study deals with the influence of operating parameters on the selective hydrogenation of crude polyunsaturated methyl esters of linseed, sunflower and soybean oils in order to achieve high selectivities up to 79.8 mol% of monounsaturated (C18:1) fatty acid methyl esters (FAME) which is 1st generation biodiesel of increased oxidative stability, energy and environmental performance at a low pour point employing water-soluble Rh/TPPTS catalytic complexes [TPPTS = P(C₆H₄-*m*-SO₃Na)₃] in green aqueous/organic two-phase systems. This study also discloses the great potential of biphasic selective catalytic hydrogenation to produce 2nd generation biodiesel from polyunsaturated FAME of alternative, non-food oil feedstocks which are originally not suitable for biodiesel production or give poor quality biodiesel but combine the advantage that they would not affect food production. Because the mixture of methyl esters of linseed oil mainly consists of C18:3 FAME it constitutes a good model to investigate the effects of parameters on the whole spectrum of the stepwise hydrogenation: C18:3 (linolenates) → C18:2 (linoleates) → C18:1 (oleates) → C18:0 (stearate) and to obtain first information on the selective hydrogenation of alternative, non-food oils with a high C18:3 FAME content to make them suitable for 2nd generation biodiesel formulations.

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1. Introduction

Renewable biomass-based resources are considered to be the new challenge in the development of Green-Sustainable chemistry because they possess a huge potential for energy, chemicals and material production and contribute to an effective management of greenhouse gas emissions [1,2]. In addition, the projected long-term limitations on the exploitation of fossil feedstocks, the domestic production of fuels, the support for local agriculture, the implementations of financial incentives for the use of biomass due to environmental concerns regarding the local air pollution and the global warming problems caused by atmospheric greenhouse gas concentrations, the biodegradability and biocompatibility of many petrochemical based products have also played a role in this respect. According to the EU Directive 2003/30/EC by 2010 biofuels shall be 5.75% of the transportation fuels [3a]. Furthermore, the EU Commission released a plan targeting biofuels for 10% of transportation fuels by 2020 [3b–d]. The US Department of Energy has set such goals that by 2025 biofuels will meet 30% of the fuels, and biomass-based chemicals 25% of the chemicals in the US market [4]. Currently, the production of 1st generation biofuels competes for fertile land with food production. However, about

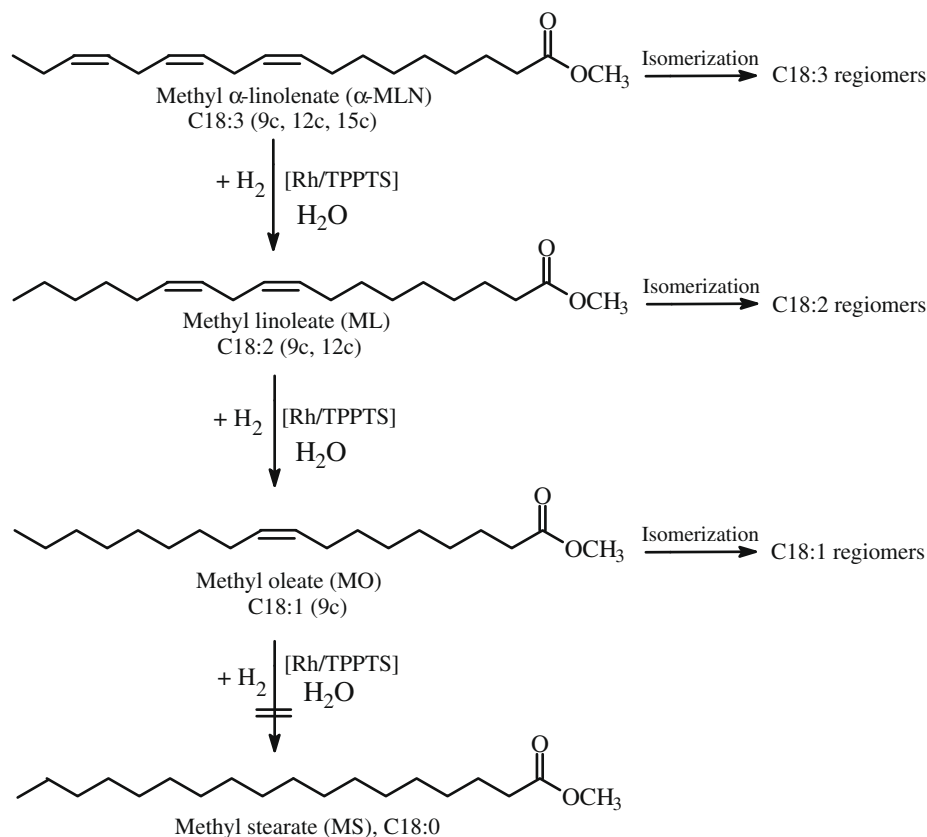
30% of the global fuels demand could be supplied by advanced biofuels, which have to be developed, and their environmentally friendly manufacturing processes would not affect food production [5]. First generation biodiesel is industrially produced by the transesterification route of vegetable oils, animal fats or used frying oils with methanol to give fatty acid methyl esters (FAME) which is commercialized in the EU with rapeseed and sunflower oils, in the USA with soybean oil and in the tropical countries with palm oil [6]. However, problems associated with the use of 1st generation biodiesel remain its oxidative susceptibility to ambient air oxygen, its low-temperature performance and its higher NO_x emissions [7].

Selective hydrogenation processes of alkyl esters of vegetable oils to transform polyunsaturated FAME into monounsaturated (C18:1) esters without increasing the saturated part are of great interest in the fields of production of high quality 1st generation biodiesel [8a–d] and also of biolubricants [8e–g]. The first aim of these processes is to improve oxidative stability because the relative rates of autoxidation are 98 for methyl linolenate (MLN, Scheme 1), 41 for methyl linoleate (ML) and 1 for methyl oleate (MO) [7b–d,8a]. Therefore, selective hydrogenation of polyunsaturated FAME to C18:1 esters substantially increases their oxidation stabilities and greatly improve the ageing/storage properties of biodiesel which makes the addition of synthetic antioxidants superfluous. The second aim of selective hydrogenation to C18:1 esters is to avoid deterioration in low-temperature behavior such

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Scheme 1. Selective hydrogenation of polyunsaturated methyl esters of linseed (MELO), sunflower (MESO) and soybean oils (MESBO) to their monounsaturated (C18:1) counterparts catalyzed by Rh/TPPTS complexes in aqueous/organic two-phase systems. The term "regiomers" refers to all regio-isomers obtained from hydrogenation and/or positional isomerization (along the carbon chain) reactions and all other geometric isomers formed via *cis/trans* isomerization reactions.

as on the pour point because of the higher melting point of the saturated part, i.e. methyl stearate (MS). The third aim is to increase the performance of biofuel. Knothe [7c,i] reported for ethyl linolenate a cetane number of 22.7, for ML: 38.2 and for MO: 59.3. The fourth aim is to combat the NO_x -effect: the increase of NO_x emissions observed in most studies of biodiesel. Pure biodiesel (B 100) increases NO_x emissions by 12% compared with pure petrodiesel and conventional B20 blends (20% biodiesel in petrodiesel) produced a NO_x increase of 3–5% compared to petroleum diesel [7k–n]. It is also showed that NO_x emissions decreased with decreasing unsaturation [7k–n] and when a B20 blend was used where the biodiesel portion contained 76% of MO the biodiesel NO_x -effect was even eliminated [7n].

Moser et al. [8a] partially hydrogenated soybean oil using a heterogeneous Ni catalyst and after transesterification with methanol could improve the oxidative stability of the biodiesel product. Falk et al. [8b] partially hydrogenated polyunsaturated FAME by a heterogeneous Ni catalyst and could increase the oxidation stability at a low pour point of the biodiesel product. Zaccheria et al. [8d] showed that the partial hydrogenation of polyunsaturated methyl esters of alternative, non-food oils afford up to 68% of C18:1 esters using Cu/SiO₂ heterogeneous catalysts and thus improving the oxidative stability, the iodine value and the cetane number at a low pour point of the mixture to render it suitable for biodiesel formulation. Fell and Schäfer [9a,b] homogeneously hydrogenated ML by Ziegler–Sloan–Laporte Ni(acac)₂/Al(C₂H₅)₃ catalytic systems and obtained high selectivities (> 90%) to C18:1 esters. Behr et al. [9c–e] homogeneously hydrogenated fatty acids of sunflower oil by Na₂PdCl₄ in propylene carbonate or DMF and aqueous Na₂CO₃ and achieved selectivities up to 93% to C18:1 acids. After the reaction, addition of *n*-hexane creates a two-phase system allowing the

recovery of the palladium nanoparticle catalyst by a phase separation.

Nowadays, there is increasing interest in catalysis in aqueous/organic two-phase systems employing water-soluble transition metal catalytic complexes because the green aqueous media facilitates recovery and recycling of the catalyst and circumvents the need for toxic organic solvents which provides substantial environmental and economical benefits and water-soluble Rh/TPPTS catalytic complexes [TPPTS = P(C₆H₄-*m*-SO₃Na)₃] have found important applications in aqueous/organic biphasic industrial processes [10]. We reported in a preliminary communication [11b] that the hydrogenation of methyl esters of linseed and sunflower oils proceeds with exceptionally high catalytic activities by water-soluble Rh/TPPTS complexes in aqueous/organic two-phase systems. We now report a detailed investigation of the influence of reaction parameters on the selective hydrogenation of crude polyunsaturated methyl esters of linseed (MELO), sunflower (MESO) and soybean oils (MESBO) in order to achieve high selectivities towards C18:1 FAME which is upgraded 1st generation biodiesel fuel of increased oxidative stability, energy and environmental performance at a low pour point employing water-soluble Rh/TPPTS catalytic complexes in green aqueous/organic two-phase systems. Furthermore, in this full paper we disclose the great potential of the biphasic selective catalytic hydrogenation reaction to produce under mild conditions 2nd generation biodiesel fuel from C18:3 and C18:2 FAME of alternative, non-food oil feedstocks which are originally not suitable for biodiesel production or give poor quality biodiesel fuel but such feedstocks combine the advantage that they would not affect food production. We note, that Antizar-Ladislao and Turrion-Gomez [5e] pointed out that according to the UN definition "2nd generation biofuels are made from lignocellulosic biomass

feedstock using advanced technological processes" some oilseeds substrates coupled with their lignocellulosic feedstocks obtained especially from crops growing in marginal and arid sites may add to 2nd generation biofuels.

2. Experimental

2.1. Materials

Hydrogen (quality 5.0) was purchased from Messer Hellas (Athens) and was used without further purification. Distilled demineralized water was deoxygenated in an ultrasound bath under high vacuum for 2 h. During the deoxygenation the flask was disconnected from the vacuum, and the aqueous solvent was saturated with argon; this procedure was repeated several times. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and dodecyltrimethylammonium chloride (DTAC) were purchased from Acros Organics and used without any further purification. TPPTS was prepared according to literature procedures [12] and isolated with purity higher than 98%. Linseed oil, sunflower seed oil (from *Helianthus annuus*) and soybean oil were purchased from Aldrich, Fluka and MP Biomedicals, respectively, and were used without any further purification.

2.2. Typical transesterification reaction of soybean, linseed and sunflower oils with methanol

Typical transesterification reaction of soybean oil: A 1000-ml, three-necked, round-bottom flask, equipped with a mechanical stirrer, a thermometer and a condenser was charged with 315.0 g of soybean oil and a solution of 185.6 g methanol containing 3.15 g of NaOH. The mixture was stirred at 55 °C for 70 min. The course of the reaction was followed by thin layer chromatography. The reaction mixture was then cooled and further stirred for 5.5 h at room temperature. After phase separation resulted in the isolation of the methyl esters of soybean oil and the glycerol. The glycerol phase (bottom layer) was removed and kept in a separate container. The MESBO phase (top layer) was washed with distilled water several times (pH 7.0), dried over Na_2SO_4 to obtain 250.4 g of crude MESBO mixture which was used as starting material in the hydrogenation reaction without any purification by distillation.

Methyl esters composition of soybean oil was determined by gas chromatography (vide infra) and is given in Table 6. The same procedure was used for the transesterification of linseed and sunflower oils and the composition of methyl esters of linseed oil and sunflower oil were determined by gas chromatography and are given also in Tables 1–5.

2.3. Catalytic hydrogenation experiments

In a typical hydrogenation reaction of MESBO: 1.32 mg (0.005 mmol) $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and 15.39 mg (0.025 mmol) TPPTS, (TPPTS/Rh molar ratio = 5) were dissolved under argon in 15 ml deaerated distilled demineralized water within 1 min of stirring. This aqueous catalyst solution, having a rhodium concentration of 34 ppm, with 1.838 g (10 mmol of C=C units) of MESBO mixture which results a two-phase system with a volume ratio of aqueous/organic phase = 15/2.2, were charged into an Autoclave Engineers autoclave (100 ml) which was previously evacuated and filled with argon. In the reaction mixture the molar ratio of C=C units/Rh was 2000. After a number of pressurising–depressurising cycles with hydrogen to remove last traces of air oxygen, the autoclave was pressured and contents were heated with stirring (stirring rate = 800 rpm). At the reaction temperature of 120 °C the hydrogen partial pressure was 10 bar and the reaction time 10 min. After the reaction the autoclave was cooled to room temperature, vented of hydrogen and the reaction mixture removed. The upper organic layer was easily separated from the lower aqueous layer containing the catalyst and dried over sodium sulfate. The organic layer containing the products was analyzed by gas chromatography (GC) after addition of methyl heptadecanoate as standard.

2.4. Analysis of TPPTS, MELO, MESO, MESBO, FAME and the products of the hydrogenation reaction

The purity of the TPPTS ligand was determined by quantitative $^3\text{P}\{^1\text{H}\}$ NMR analysis in D_2O at 25 °C. δ TPPTS = –5.4 ppm. $^3\text{P}\{^1\text{H}\}$ -NMR spectra (121 MHz, referenced to external 85% H_3PO_4) were recorded on a Varian Unity Plus 300/54 spectrometer. The various *cis*-, *trans*-, polyunsaturated, monounsaturated and saturated FAME isomers contained in the starting materials (MELO, MESO,

Table 1
Effect of reaction time and temperature on micellar biphasic selective hydrogenation of crude MELO catalyzed by Rh/TPPTS complexes.^a

Entry	Starting material	Catalyst precursor	t (min)	T (°C)	C18:3 (total) (mol%)	C18:2 (total) (mol%)	C18:1 (total) (mol%)	<i>cis</i> -C18:1 (total) (mol%)	<i>trans</i> -C18:1 (total) (mol%)	MS (mol%)	TOP ^b (h ⁻¹)
–	MELO ^c	–	–	–	56.8 ^d	16.7 ^e	22.5 ^f	22.5 ^f	–	4.0	–
1/1	MELO	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$	10	50	38.4	20.0	35.9	33.5	2.4	5.7	540
1/2	MELO	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$	60	50	5.3	23.8	58.1	47.6	10.5	12.8	250
1/3	MELO	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$	120	50	5.9	12.6	57.2	25.1	32.1	24.3	140
1/4	MELO	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$	120	22	39.0	19.2	34.4	32.3	2.1	7.4	60
1/5	MELO	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$	120	40	19.3	22.5	49.1	45.7	3.4	9.1	85
1/6	MELO	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$	120	60	0.6	18.9	69.4	48.1	21.3	11.1	150
1/7	MELO	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$	120	70	0.7	8.3	79.1	51.4	27.7	11.9	160
1/8 ^g	MELO	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$	120	80	0.5	8.8	79.8	37.3	42.5	10.9	160
1/9 ^g	MELO	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$	120	90	1.4	8.2	79.3	45.6	33.7	11.1	160
1/10	MELO	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$	120	100	0.5	13.6	77.1	40.1	37.0	8.8	150
1/11	MELO	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$	120	110	13.0	26.3	54.6	42.4	12.2	6.1	110

^a Reaction conditions: P_{H_2} = 10 bar; 2.63 mg (0.01 mmol) $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, 24.63 mg (0.04 mmol) TPPTS (P/Rh molar ratio = 4), 31.66 mg (0.12 mmol) DTAC (DTAC/TPPTS molar ratio = 3); 802.75 mg (5.0 mmol of C=C) of MELO mixture (C=C/Rh molar ratio = 500); 30 ml deaerated distilled demineralized water, [Rh] = 34 ppm, 163.3 mg (1.2 mmol) KH_2PO_4 , pH 7.0 adjusted with 5% aqueous NaOH. Addition of a solution of MELO mixture dissolved in 10 ml of *n*-hexane results a two-phase system with a volume ratio of aqueous/organic phase = 3/1.1; stirring rate = 770 rpm.

^b Defined as mole of hydrogenated C=C units in the C18:3, C18:2, and C18:1 compounds in both the starting material MELO mixture and all other regiomers formed during the course of the reaction per mole of rhodium per hour.

^c Crude MELO 1 except of α -MLN, ML, MO and MS further contained 4.8% of methyl palmitate (MP, C16:0) which was ignored in the experiments.

^d Methyl α -linolenate (α -MLN), C18:3 (9c, 12c, 15c).

^e Methyl linoleate (ML), C18:2 (9c, 12c).

^f Methyl oleate (MO), C18:1 (9c).

^g Both experiments were mentioned in the preliminary communication [11b].

Table 2
Effect of DTAC/TPPTS molar ratio and of the pH on micellar biphasic selective hydrogenation of crude MELO catalyzed by Rh/TPPTS complexes.^a

Entry	Starting material	Catalyst precursor	DTAC/TPPTS molar ratio	pH	C18:3 (total) (mol%)	C18:2 (total) (mol%)	C18:1 (total) (mol%)	cis-C18:1 (total) (mol%)	trans-C18:1 (total) (mol%)	MS (mol%)	TOF ^b (h ⁻¹)
–	MELO ^c	–	–	–	56.8 ^d	16.7 ^e	22.5 ^f	22.5 ^f	–	4.0	–
2/1	MELO	RhCl ₃ ·3H ₂ O/TPPTS	0	7.0 ^g	0.8	10.6	71.4	45.4	26.0	17.2	155
2/2	MELO	RhCl ₃ ·3H ₂ O/TPPTS	1	7.0 ^g	0.4	9.4	67.9	38.7	29.2	22.3	160
2/3	MELO	RhCl ₃ ·3H ₂ O/TPPTS	2	7.0 ^g	0.9	12.8	73.5	42.5	31.0	12.8	150
2/4	MELO	RhCl ₃ ·3H ₂ O/TPPTS	3	7.0 ^g	0.4	9.5	71.7	43.1	28.6	18.4	160
2/5	MELO	RhCl ₃ ·3H ₂ O/TPPTS	4	7.0 ^g	0.6	19.0	69.9	50.0	19.9	10.5	140
2/6	MELO	RhCl ₃ ·3H ₂ O/TPPTS	5	7.0 ^g	0.4	21.2	67.6	46.2	21.4	10.8	140
2/7	MELO	RhCl ₃ ·3H ₂ O/TPPTS	8	7.0 ^g	0.4	22.3	67.5	48.0	19.5	9.8	140
2/8	MELO	RhCl ₃ ·3H ₂ O/TPPTS	2	4.1 ^h	2.5	28.8	57.7	46.6	11.1	11.0	140
2/9	MELO	RhCl ₃ ·3H ₂ O/TPPTS	2	10.5 ⁱ	5.1	34.3	53.4	43.8	9.6	7.2	130

^a Reaction conditions: $T = 70\text{ }^{\circ}\text{C}$; $P_{\text{H}_2} = 10\text{ bar}$; $t = 2\text{ h}$; 2.63 mg (0.01 mmol) RhCl₃·3H₂O; 18.47 mg (0.03 mmol) TPPTS (TPPTS/Rh molar ratio = 3); 802.75 mg (5.0 mmol of C=C) of MELO mixture (C=C/Rh molar ratio = 500); 30 ml deaerated distilled demineralised water, [Rh] = 34 ppm. Addition of a solution of MELO 1 mixture dissolved in 10 ml of *n*-hexane results a two-phase system with a volume ratio of aqueous/organic phase = 3/1.1; stirring rate = 770 rpm.

^b Defined as mole of hydrogenated C=C units in the C18:3, C18:2, and C18:1 compounds in both the starting material MELO mixture and all other regiomers formed during the course of the reaction per mole of rhodium per hour.

^c Crude MELO mixture except of α -MLN, ML, MO and MS further contained 4.8% of methyl palmitate (MP, C16:0) which was ignored in the experiments.

^d Methyl α -linolenate (α -MLN), C18:3 (9c, 12c, 15c).

^e Methyl linoleate (ML), C18:2 (9c, 12c).

^f Methyl oleate (MO), C18:1 (9c).

^g KH₂PO₄ (163.3 mg (1.2 mmol)), pH 7.0 adjusted with 5% aqueous NaOH.

^h No buffer was added.

ⁱ pH adjusted with 5% aqueous NaOH.

Table 3
Micellar selective hydrogenation of crude MELO catalyzed by Rh/TPPTS complexes at different volume ratios of the aqueous to the organic solvent.^a

Entry	Starting material	Catalyst precursor	Water/hexane (volume ratio)	C18:3 (total) (mol%)	C18:2 (total) (mol%)	C18:1 (total) (mol%)	cis-C18:1 (total) (mol%)	trans-C18:1 (total) (mol%)	MS (mol%)	TOF ^b (h ⁻¹)
–	MELO ^c	–	–	56.8 ^d	16.7 ^e	22.5 ^f	22.5 ^f	–	4.0	–
3/1	MELO	RhCl ₃ ·3H ₂ O/TPPTS	10/30	10.6	32.4	50.6	45.0	5.6	6.4	115
3/2	MELO	RhCl ₃ ·3H ₂ O/TPPTS	20/20	0.8	29.5	62.8	49.6	13.2	6.9	140
3/3	MELO	RhCl ₃ ·3H ₂ O/TPPTS	30/10	0.9	12.8	73.5	42.5	31.0	12.8	150
3/4	MELO	RhCl ₃ ·3H ₂ O/TPPTS	35/5	0.6	16.4	70.5	53.1	17.4	12.5	140

^a Reaction conditions: $T = 70\text{ }^{\circ}\text{C}$; $P_{\text{H}_2} = 10\text{ bar}$; $t = 2\text{ h}$; 2.63 mg (0.01 mmol) RhCl₃·3H₂O; 18.47 mg (0.03 mmol) TPPTS (P/Rh molar ratio = 3); DTAC/TPPTS molar ratio = 2; 802.75 mg (5.0 mmol of C=C) of MELO mixture (C=C/Rh molar ratio = 500) dissolved in *n*-hexane added to the deaerated distilled demineralised water containing the catalyst results a two-phase system; H₂O and *n*-hexane = 40 ml total; 163.3 mg (1.2 mmol) KH₂PO₄, pH 7.0 adjusted with 5% aqueous NaOH; stirring rate = 770 rpm.

^b Defined as mole of hydrogenated C=C units in the C18:3, C18:2 and C18:1 compounds in the starting materials MELO mixture and in all other regiomers formed during the course of the reaction per mole of rhodium per hour.

^c Crude MELO mixture except of α -MLN, ML, MO and MS further contained 4.8% of methyl palmitate (MP, C16:0) which was ignored in the experiments.

^d Methyl α -linolenate (α -MLN), C18:3 (9c, 12c, 15c).

^e Methyl linoleate (ML), C18:2 (9c, 12c).

^f Methyl oleate (MO), C18:1 (9c).

Table 4
Micellar biphasic selective hydrogenation of crude MELO catalyzed by Rh/TPPTS complexes under different partial H₂ pressures and C=C/Rh molar ratios in the presence of ether and DTAC at [Rh] = 34 ppm in the aqueous catalyst phase.^a

Entry	Starting material	Catalyst precursor	C=C/Rh molar ratio	P_{H_2} (bar)	C18:3 (total) (mol%)	C18:2 (total) (mol%)	C18:1 (total) (mol%)	cis-C18:1 (total) (mol%)	trans-C18:1 (total) (mol%)	MS (mol%)	TOF ^b (h ⁻¹)
–	MELO ^c	–	–	–	56.8 ^d	16.7 ^e	22.5 ^f	22.5 ^f	–	4.0	–
4/1	MELO	RhCl ₃ ·3H ₂ O/TPPTS	1000	10	1.2	22.0	67.2	54.2	13.0	9.6	3300
4/2	MELO	RhCl ₃ ·3H ₂ O/TPPTS	1000	50	0.5	6.8	65.2	43.1	22.1	27.5	4000
4/3	MELO	RhCl ₃ ·3H ₂ O/TPPTS	1000	70	0.3	5.0	58.9	39.3	19.6	35.8	4100
4/4	MELO	RhCl ₃ ·3H ₂ O/TPPTS	2000	70	0.6	5.9	65.0	42.9	22.1	28.5	8000
4/5	MELO	RhCl ₃ ·3H ₂ O/TPPTS	3000	70	1.9	9.9	65.3	47.8	17.5	22.9	11 100

^a Reaction conditions: $T = 70\text{ }^{\circ}\text{C}$; $t = 10\text{ min}$; 2.63 mg (0.01 mmol) RhCl₃·3H₂O; 24.63 mg (0.04 mmol) TPPTS (TPPTS/Rh molar ratio = 4); 21.11 mg (0.08 mmol) DTAC (DTAC/TPPTS molar ratio = 2), 30 ml deaerated distilled demineralised water, [Rh] = 34 ppm; 163.3 mg (1.2 mmol) KH₂PO₄, pH 7.0 adjusted with 5% aqueous NaOH. Addition of a solution of MELO 1–2 mixtures dissolved in 10 ml diethyl ether results a two-phase system with a volume ratio of aqueous/organic phase = 3/1.1–3/2.6; except entry 4/13, a two-phase system consisting of 30 ml of aqueous solvent with a solution of 15.03 g (100.0 mmol of C=C) of MELO 2 mixture dissolved in 18.8 ml of diethyl ether (aqueous/organic phase = 3/3.5); stirring rate = 850 rpm.

^b Defined as mole of hydrogenated C=C units in the C18:3, C18:2, and C18:1 compounds in the starting materials MELO 1–2 mixtures and in all other regiomers formed during the course of the reaction per mole of rhodium per hour.

^c Crude MELO 1–2 mixtures except of α -MLN, ML, MO and MS further contained 3.4–4.8% of methyl palmitate (MP, C16:0) which was ignored in the experiments.

^d Methyl α -linolenate (α -MLN), C18:3 (9c, 12c, 15c).

^e Methyl linoleate (ML), C18:2 (9c, 12c).

^f Methyl oleate (MO), C18:1 (9c).

Table 5Biphasic selective hydrogenation of crude MESO catalyzed by water-soluble Rh/TPPTS complexes in aqueous/organic two-phase systems.^a

Entry	Starting material	Catalyst precursor	C=C/Rh molar ratio	T (°C)	t (min)	C18:2 (total) (mol%)	C18:1 (total) (mol%)	cis-C18:1 (total) (mol%)	trans-C18:1 (total) (mol%)	MS (mol%)	TOF ^b (h ⁻¹)
–	MESO 1 ^c	–	–	–	–	69.2 ^d	27.8 ^e	27.8 ^e	–	3.0	–
5/1 ^f	MESO 1	RhCl ₃ ·3H ₂ O/TPPTS	20 000	120	10	46.6	44.9	34.0	10.9	8.5	13 500
5/2	MESO 1	RhCl ₃ ·3H ₂ O/TPPTS	20 000	120	10	44.0	49.3	37.1	12.2	6.7	30 200
5/3	MESO 1	RhCl ₃ ·3H ₂ O/TPPTS	20 000	130	10	59.4	36.2	30.0	6.2	4.4	11 700
5/4	MESO 1	RhCl ₃ ·3H ₂ O/TPPTS	15 000	120	10	16.3	64.5	35.8	28.7	19.2	47 600
5/5	MESO 1	RhCl ₃ ·3H ₂ O/TPPTS	20 000	120	10	25.2	61.9	34.8	27.1	12.9	52 800
–	MESO 2 ^c	–	–	–	–	68.8 ^d	28.4 ^e	28.4 ^e	–	2.8	–
5/6	MESO 2	RhCl ₃ ·3H ₂ O/TPPTS	5000	120	5	0.2	34.1	15.4	18.7	65.7	42 500
5/7	MESO 2	RhCl ₃ ·3H ₂ O/TPPTS	12 000	120	5	3.1	58.0	26.1	31.9	38.9	98 000
5/8 ^g	MESO 2	RhCl ₃ ·3H ₂ O/TPPTS	12 000	120	5	14.7	62.7	35.2	27.5	22.6	81 200
5/9 ^h	MESO 2	RhCl ₃ ·3H ₂ O/TPPTS	12 000	120	5	23.6	58.4	34.2	24.2	18.0	68 400
5/10	MESO 2	RhCl ₃ ·3H ₂ O/TPPTS	12 000	110	5	15.3	62.3	31.5	30.8	22.4	80 500
5/11	MESO 2	RhCl ₃ ·3H ₂ O/TPPTS	12 000	130	5	11.0	60.2	26.3	33.9	28.8	86 500
5/12 ⁱ	MESO 2	RhCl ₃ ·3H ₂ O/TPPTS	15 000	120	5	6.0	68.3	35.8	32.5	25.7	117 000

^a Reaction conditions: P_{H₂} = 50 bar; 1.32 mg (0.005 mmol) RhCl₃·3H₂O; except entry 5/5, 2.63 mg (0.01 mmol) RhCl₃·3H₂O; 9.24 mg (0.015 mmol) TPPTS (TPPTS/Rh molar ratio = 3); 15 ml deaerated distilled demineralized water, pH 4.3; except entries 5/4, 5/5, 30 ml water, pH 4.5; [Rh] = 34 ppm; except entry 5/4, [Rh] = 17 ppm. Addition of MESO 1, 2 mixtures results a two-phase system with a volume ratio of aqueous/organic phase = 15/22–15/2.2. For example in entry 5/8: 15 ml aqueous solvent containing the catalyst and 19.947 g = 22.0 ml (100.0 mmol of C=C) of MESO 1 mixture results a two-phase system with a volume ratio of aqueous/organic phase = 15/22. Stirring rate = 850 rpm.

^b Defined as mole of hydrogenated C=C units of C18:2 and C18:1 compounds in the starting materials MESO 1–3 mixtures and in all other regiomers formed during the course of the reaction per mole of rhodium per hour.

^c Crude MESO 1, 2 mixtures except of ML, MO and MS further contained 4.6–5.5% of methyl palmitate (MP, C16:0) and 0.4–0.6% of methyl behenate (C22:0) which were ignored in the experiments.

^d Methyl linoleate (ML), C18:2 (9c, 12c).

^e Methyl oleate (MO), C18:1 (9c).

^f Addition of 6.2 ml diethyl ether.

^g KH₂PO₄ (81.7 mg (0.60 mmol)), pH 7.0 adjusted with 5% aqueous NaOH.

^h pH 10.4 adjusted with a solution of 5% aqueous NaOH.

ⁱ This experiment was mentioned in the preliminary communication [11b].

MESBO, refined C18:3/C18:2 FAME) and products were identified by comparison of GC and gas chromatography/mass spectrometry (GC/MS) analytic data with data for authentic samples. GC/MS was measured on a Varian Star 3400CX GC coupled with a Varian Saturn 2000 ion trap MS. The GC was equipped with a flame ionization detector (FID) and a SP-2560 capillary column (100 m × 0.25 mm i.d. × 0.2 μm film thickness) which was purchased from Supelco (Athens, Greece). The SP-2560 capillary column is one of the two columns applied in the approved American Oil Chemists' Society (AOCS) official method Ce 1 h–05 for the determination of *cis*-, *trans*-, saturated, monounsaturated and polyunsaturated fatty acids in vegetable or non-ruminant animal oils and fats by capillary GLC method [13]. Carrier gas was He at 230 kPa. The oven temperature was initially at 170 °C for 0 min and then increased to 220 °C at 1 °C/min. The injector and detector temperatures were set at 220 and 230 °C, respectively. GC analyses were run on a Shimadzu GC-14B equipped with a FID detector and a SP-2560 capillary column with conditions as described above in GC/MS analyses.

3. Results and discussion

3.1. Preparation of the Rh/TPPTS catalyst

The Rh/TPPTS catalyst used in this work was prepared in situ after complexation under argon of RhCl₃·3H₂O with TPPTS in H₂O and subjection of the mixture to a hydrogen atmosphere under the chosen hydrogenation reaction conditions. Although the catalyst is added as a rhodium(III) salt the actual catalyst is a rhodium (I) TPPTS complex, i.e. RhCl(TPPTS)₃, formed in situ from RhCl₃·3H₂O with TPPTS under hydrogenation conditions in aqueous media [10c,14]. Dynamic light scattering studies of the Rh/TPPTS catalytic system in aqueous media have proven its homogeneous nature [10c]. An alternative explanation regarding the nature of the catalytic active species namely the formation of catalytic active Rh(0) nanoparticles by reducing RhCl₃·H₂O with

hydrogen and stabilizing in the organic phase with surfactant FAME starting materials which possess a lower *Hydrophilic–Lipophilic Balance* (HLB) could be excluded because recycling experiments of the aqueous phase containing the Rh/TPPTS catalyst showed that the catalytic activity remained high in three consecutive runs in the hydrogenation of MESBO (Table 6, entries 6/16 and 6/17). If catalytic Rh(0) nanoparticles with FAME as protective dispersants were formed in the organic phase than such catalytic species would be separated off during decantation and no catalytic activity would be observed by re-using the aqueous phase in the biphasic hydrogenation of new portions of MESBO as described in entry 6/17. No black rhodium metal aggregates were observed in all biphasic hydrogenation reactions presented here which indicates that the Rh/TPPTS catalyst remains intact without decomposition after the reaction in the aqueous layer which is a clear solution.

3.2. Selective hydrogenation of methyl esters of vegetable oils to C18:1 FAME catalyzed by Rh/TPPTS complexes in green aqueous/organic two-phase systems

First, we studied the performance of the Rh/TPPTS catalyst in the micellar biphasic selective hydrogenation of crude MELO and subsequently investigated the biphasic partial hydrogenation of crude MESO and MESBO, which are currently the feedstocks in Europe and USA for the industrial production of 1st generation biodiesel with the aim to increase selectively the content of the C18:1 esters (Scheme 1) in order to upgrade biodiesel fuel in terms of increased oxidative stability, higher energy and environmental performance at a low pour point. Furthermore, we recovered the Rh/TPPTS catalyst in active form from organic reaction products by simple phase separation and recycling experiments were carried out in order to prove that the catalytic activity remained high in several consecutive runs.

3.2.1. Selective hydrogenation of crude MELO

MELO was selected as a starting material mixture because it mainly consists of α -MLN, a C18:3 FAME, (Scheme 1, Tables 1–4) and therefore it constitutes a good model for two reasons: (i) to study the effects of reaction parameters on the whole spectrum of the stepwise biphasic hydrogenation reaction of polyunsaturated FAME: C18:3 (linolenates) \rightarrow C18:2 (linoleates) \rightarrow C18:1 (oleates) \rightarrow C18:0 (stearate) and (ii) to obtain first information on the potential of this useful reaction to produce 2nd generation biodiesel fuel from alternative, non-food oil feedstocks with a high C18:3 FAME content which are originally not suitable for biodiesel formulations but have the great advantage that such feedstocks would not compete with food production. The bis-allylic positions in common polyunsaturated FAME such as α -MLN (two bis-allylic positions at C-11 and C-14) and ML (one bis-allylic position at C-11) are even more prone to autoxidation than simple-allylic positions. Therefore, the content of MLN is restricted in the European Biodiesel Standard EN 14214 because of the propensity of α -MLN to autooxidise with a much higher relative rate of 98 compared to ML and MO with autoxidation relative rates of 41 and 1, respectively. It has been also reported [8f,g] that the oxygen absorption rate in linolenic, linoleic and oleic acid is 800/100/1, respectively. However, the EN 14214 allows up to 12 mol% of MLN to be contained in biodiesel fuel in order not to exclude high-oleic rapeseed oil which is the major vegetable oil feedstock in the EU for the production of 1st generation biodiesel fuel [6e]. The European Biodiesel Standards EN 14214 for vehicle use and EN 14213 for heating oil use call for determining oxidative stability of biodiesel at 110 °C with a minimum induction period of 6.0 h for vehicle use and of 4.0 h for heating oil use by the Rancimat method as described in EN 14112 which is nearly identical to the American Oil Chemist's Society, Oil Stability Index (OSI) method Cd12b-92. In EN 14214 and EN 14213 is included another specification for the measurement of total unsaturation of FAME contained in biodiesel fuel which is the iodine value of up to 120 (g I₂/100 g biodiesel) for vehicle use and up to 130 (g I₂/100 g biodiesel) for heating oil use [6e].

One of the aims of selective hydrogenation of alkyl esters of vegetable oils to C18:1 compounds is to avoid deterioration regarding the pour point of biodiesel fuel and also of biolubricants. To preserve fluidity it is mandatory not to increase the melting point of the mixture that depends on both the amount of saturated MS, which has a melting point of +39.1 °C, and the extend of *cis/trans* (geometrical) and of positional (along the carbon chain) isomerization. For example the melting point of MO is –19.9 °C and of methyl elaidate (C18:1, 9t) is +10.0 °C. This aim for selective hydrogenation is especially important for the biodiesel used in northern and mountainous parts of Europe and North America.

Hydrogenation of polyunsaturated FAME selectively to *cis*-C18:1 esters using water-soluble catalytic complexes in aqueous/organic two-phase systems is an interesting approach regarding the field of edible oil hydrogenation. In the past, the so-called hardening processes of edible oil hydrogenation were industrially carried out over commercial Ni-based heterogeneous catalysts which produced up to 30% *trans*-fats [15]. The aims of traditional hardening of edible oils were to increase their melting temperature and thus increasing the consistency for use as margarine and to improve the oxidative stability while an important amount of the C=C units in the fatty acid chain was *cis/trans*-isomerized. In recent years the negative health effects of *trans*-fats received increasing attention and are considered to be even more detrimental than saturated fats. Both *trans*- and saturated fatty acids contained in margarine are strongly correlated with a higher concentration of plasma LDL-cholesterol. The decisions in Europe to limit and in USA to declare the *trans*-isomers contained in fatty foodstuffs caused a demand for hardstocks with lower *trans*-isomers content.

Therefore, there is increasing interest in the development of new industrial hydrogenation processes producing lower amounts of *trans*- and saturated fats [15]. One development involves the use of homogeneous highly selective catalytic transition metal complexes to obtain selectively *cis*-C18:1 fats and such catalysts should be easily and quantitatively recovered and recycled. Ideal homogeneous catalytic systems for such conversions would be water-soluble transition metal catalytic complexes to act in aqueous/organic two-phase systems.

3.2.1.1. Effect of reaction time and temperature. Table 1 presents the activity and selectivity of the Rh/TPPTS catalyst towards C18:1 FAME as a function of reaction time and temperature in the hydrogenation reaction of MELO in aqueous/organic two-phase systems. The hydrogenation of MELO started immediately with hydrogen consumption without an induction period of the reaction. Therefore, no prereluction of the Rh/TPPTS catalyst was carried out and only made sure that the reaction conditions were well chosen in order to obtain reproducible results. All the following experiments were carried out systematically without a prior prereluction of the Rh/TPPTS catalyst. The selectivity to C18:1 ester regiomers increased with the reaction time to give within 60 min a total content of 58.1 mol% of C18:1 esters in the Rh/TPPTS-catalyzed hydrogenation of MELO at a molar ratio of C=C units/Rh = 500 and P/Rh = 4, a reaction temperature of 50 °C, 10 bar H₂ partial pressure and a rhodium concentration of 34 ppm in water at a pH value of 7.0 which was adjusted by a KH₂PO₄/NaOH-buffer in the presence of the cationic surfactant dodecyltrimethylammonium chloride (DTAC) at a molar ratio of DTAC/TPPTS = 3 and addition of the organic solvent *n*-hexane to result a volume ratio of aqueous/organic solvent = 30/10 in micellar biphasic aqueous/organic two-phase systems (Table 1, entry 1/2). At a longer reaction time of 120 min the selectivity to C18:1 ester regiomers decreased to 57.2 mol% and the saturated undesired final product MS was obtained with a higher selectivity of 24.3 mol% (Table 1, entry 1/3).

The catalytic activity and selectivity towards C18:1 esters in the Rh/TPPTS-catalyzed partial hydrogenation of MELO increases with increasing temperature from 22 up to 80 °C to give TOF values from 60 up to 160 h⁻¹ and selectivities to C18:1 ester regiomers from 34.4 up to 79.8 mol% at a molar ratio of C=C units/Rh = 500 and P/Rh = 4 under 10 bar H₂ partial pressure and a rhodium concentration of 34 ppm in water at a pH value of 7.0 in the presence of DTAC (molar ratio of DTAC/TPPTS = 3) and addition of *n*-hexane within 120 min reaction time in micellar aqueous/organic two-phase systems (Table 1, entries 1/4–1/8). Raising the reaction temperature higher has a negative effect on the reaction rate and on the selectivity to C18:1 esters in the micellar biphasic hydrogenation of MELO to give at 110 °C a TOF value of 110 h⁻¹ and a total content of 54.6 mol% of C18:1 esters (Table 1, entry 1/11). The formation of *trans*-C18:1 ester compounds increases with increasing temperature up to 80 °C to give a total content of *trans*-C18:1 esters up to 42.5 mol% within 120 min reaction time (Table 1, entry 1/8). At higher reaction temperatures such as 110 °C the selectivity to *trans*-C18:1 esters decreased to give a total content of 12.2 mol% (Table 1, entry 1/11).

3.2.1.2. Effect of DTAC/TPPTS molar ratio and of the pH value. The presence of the cationic surfactant DTAC has a minor effect on the catalytic activity and selectivity to C18:1 esters in the Rh/TPPTS-catalyzed hydrogenation of MELO at a molar ratio of C=C units/Rh = 500 and of TPPTS/Rh = 3 in the presence of *n*-hexane in micellar aqueous/organic two-phase systems (Table 2, entries 2/1–2/7). The selectivity to C18:1 esters increases with increasing amount of DTAC to give at the molar ratio of DTAC/TPPTS = 2 a total content of 73.5 mol% of C18:1 esters (Table 2, entry 2/3). Addition of a higher amount of DTAC gives rise to a drop in the selectivity to

C18:1 esters to obtain at the molar ratio of DTAC/TPPTS = 8 a total content of 67.5 mol% of C18:1 esters (Table 2, entry 2/7). However, in the absence of the cationic surfactant DTAC the activity and selectivity to C18:1 esters remained high to give under the same reaction conditions a TOF of 155 h^{-1} and a total content of C18:1 esters of 71.4 mol% (Table 2, entry 2/1).

These results were rationalized by assuming that lecithin (Fig. 1) which is a natural phospholipid inherent in several vegetable oils [16] is probably present in small amounts in our crude MELO starting material mixture and therefore micellar catalysis is also operative without any addition of external cationic surfactants as described in entry 2/1 where DTAC is replaced by lecithin in the selective hydrogenation reaction mixture of MELO catalyzed by Rh/TPPTS in aqueous/organic two-phase systems.

Another explanation for the catalytic activity of Rh/TPPTS complexes in the hydrogenation reaction of the heavy starting material MELO without addition of any surfactants in aqueous/organic two-phase systems could be that the FAME starting material itself act as a surfactant possessing a low HLB value and micellar catalysis is also operative. It should be noted, that the polarity of lower and mid range methyl esters of ω -alkenecarboxylic acids allows their conversion in the Rh/TPPTS-catalyzed hydroformylation reaction in aqueous/organic two-phase systems with acceptable rates only up to 9-decenecarboxylic acid methyl ester [17]. In contrast, higher ω -alkenecarboxylic acid methyl esters such as 10-undecene- and 13-tetradecene-carboxylic acid methyl esters reacted slowly but reaction rates could be increased by adding cationic surfactants. Anionic and non-ionic surfactants were less effective. The effect that the addition of only cationic surfactants to Rh/TPPTS catalytic systems accelerates the rates of catalytic reactions could be explained due to the attraction between the negatively charged Rh/TPPTS complex ions with the positively charged cationic end of the surfactant which increases the concentration of the catalyst in the micelle [17].

The micellar selective hydrogenation of MELO catalyzed by Rh/TPPTS complexes in aqueous/organic two-phase systems is influenced by the pH value of the aqueous phase containing the catalyst and the surfactant DTAC at a molar ratio of DTAC/TPPTS = 2 (Table 2, entries 2/3, 2/8, 2/9). The highest activity (TOF = 150 h^{-1}) and selectivity to C18:1 esters of 73.5 mol% were achieved under neutral conditions at pH 7.0 adjusted by a $\text{KH}_2\text{PO}_4/\text{NaOH}$ -buffer (entry 2/3).

The catalytic activity was slightly lower under acidic conditions with a pH value of 4.1 and basic conditions at pH 10.5 to give TOF's of 140 and 130 h^{-1} , respectively (entries 2/8 and 2/9). The selectivity to C18:1 regiomers was lower at acidic conditions (pH 4.1) to give 57.7 mol% and much lower under basic conditions (pH 10.5) to yield a total content of 53.4 mol% (entries 2/8 and 2/9). The lower catalytic activity and selectivity to C18:1 esters exhibited by Rh/TPPTS catalytic complexes under acidic conditions with a pH value of 4.1 in aqueous media could probably not be explained by protonation of the hydride moiety of intermediate catalytic Rh/TPPTS-species involved in the catalytic cycles because at such acidic media of pH 4.3 exceptionally high catalytic activities (TOF = $117\,000 \text{ h}^{-1}$) and a total content of 68.3 mol% of C18:1 esters were achieved in the biphasic partial hydrogenation of MESO

in aqueous/organic two-phase systems (Table 5, entry 5/12). It is highly probable that the lower catalytic activity and selectivity towards C18:1 esters under acidic and basic conditions is caused by destabilization of the catalytic micelles by lowering the attraction between the negatively charged Rh/TPPTS complex ions and the positively charged cationic heads of DTAC or/and of lecithin.

3.2.1.3. Effect of the ratio of the aqueous/organic solvent. The micellar Rh/TPPTS-catalyzed selective hydrogenation of MELO was carried out at different volume ratios of water/*n*-hexane in the range of 10/30 to 35/5 at a molar ratio of C=C units/Rh = 500, TPPTS/Rh = 3, DTAC/TPPTS = 2 at 70 °C under 10 bar pressure, a pH value of 7.0 adjusted by a $\text{KH}_2\text{PO}_4/\text{NaOH}$ -buffer within 2 h of reaction time in aqueous/organic two-phase systems (Table 3, entries 3/1–3/4). The highest activity (TOF = 150 h^{-1}) and the highest content of 73.5 mol% of C18:1 FAME was obtained at a ratio of water/*n*-hexane = 30/10 (entry 3/3). At higher and lower volume ratios of water/*n*-hexane both the activity and selectivity to C18:1 esters decreased to give at a volume ratio of 35/5 a TOF of 140 and 70.5 mol% of C18:1 ester (entry 3/4) and at a ratio of 10/30 a TOF of 115 h^{-1} and a total content of 50.6 mol% of C18:1 compounds (entry 3/1).

The highest catalytic activity and selectivity to C18:1 regiomers obtained at a volume ratio of water/*n*-hexane of 30/10 could probably be explained by a stabilization of the “normal” micelle rationale whereas at a higher volume ratio of 35/5 such micellar reactors are probably destabilized and at the lower volume ratio of 10/30 “reversed” micelles are probably favored with solubilisation of an aqueous microdroplet of the Rh/TPPTS catalyst in the organic bulk phase unable effectively to catalyze the hydrogenation reaction.

Using crude MELO high contents to the desired C18:1 regiomers up to 73.5 mol% (entry 3/3) were achieved in the selective hydrogenation reaction and therefore all the subsequent biphasic partial hydrogenation reactions were carried out using crude MELO, MESO and MESBO starting materials.

3.2.1.4. Effect of hydrogen partial pressure and of the C=C units/Rh molar ratio. The effects of hydrogen partial pressure and of the molar ratio of C=C units/Rh in the biphasic partial hydrogenation of crude MELO is shown in Table 4. Both, the H_2 pressure and the C=C units/Rh molar ratio have a pronounced effect on the activity of the Rh/TPPTS catalyst. The catalyst activity increased with increasing pressure and increasing molar ratio of the C=C units of MELO to the rhodium catalytic complex. First, the effect of hydrogen pressure on the micellar biphasic partial hydrogenation reaction of crude MELO was examined at a molar ratio of C=C units/Rh = 1000 (entries 4/1–4/3). The catalytic activity increased from TOF = 3300 h^{-1} to TOF = 4100 h^{-1} with increasing H_2 pressure from 10 to 70 bar at a reaction temperature of 70 °C and molar ratios of C=C units/Rh = 1000, TPPTS/Rh = 4, DTAC/TPPTS = 2, a volume ratio of water/diethyl ether = 30/10, a rhodium concentration of 34 ppm in water at a pH value of 7.0 adjusted by $\text{KH}_2\text{PO}_4/\text{NaOH}$ -buffer within 10 min reaction time in micellar aqueous/organic two-phase systems (entries 4/1–4/3). The selectivity to C18:1 esters at a molar ratio of C=C units/Rh = 1000 decreased with

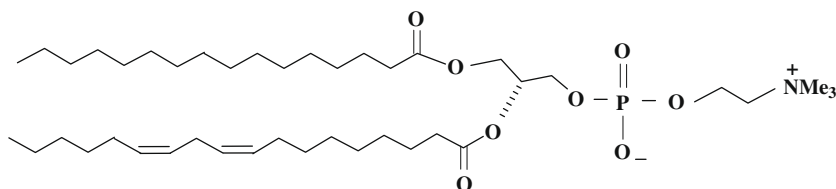


Fig. 1. Structure of the zwitterionic phospholipid surfactant lecithin (phosphatidylcholine).

Table 6
Biphasic selective hydrogenation of crude MESBO catalyzed by Rh/TPPTS complexes in aqueous/organic two-phase systems.^a

Entry	Starting material	Catalyst precursor	C=C/Rh molar ratio	P/Rh molar ratio	T (°C)	P _{H₂} (bar)	t (min)	C18:3 (total) (mol%)	C18:2 (total) (mol%)	C18:1 (total) (mol%)	cis-C18:1 (total) (mol%)	trans-C18:1 (total) (mol%)	MS (mol%)	TOF ^b (h ⁻¹)
–	MESBO ^c	–	–	–	–	–	–	9.5 ^d	59.6 ^e	26.6 ^f	26.6 ^f	–	4.3	–
6/1	MESBO	RhCl ₃ ·3H ₂ O/TPPTS	2000	5	70	10	10	0.8	26.8	60.1	20.3	39.8	12.3	5000
6/2	MESBO	RhCl ₃ ·3H ₂ O/TPPTS	2000	5	80	10	10	0.7	21.0	64.5	32.8	31.7	13.8	5700
6/3	MESBO	RhCl ₃ ·3H ₂ O/TPPTS	2000	5	90	10	10	0.2	17.0	68.4	32.2	36.2	14.4	6200
6/4	MESBO	RhCl ₃ ·3H ₂ O/TPPTS	2000	5	100	10	10	0.2	11.2	70.5	38.2	32.3	18.1	6900
6/5	MESBO	RhCl ₃ ·3H ₂ O/TPPTS	2000	5	110	10	10	0.1	10.3	72.5	45.5	27.0	17.1	7050
6/6	MESBO	RhCl ₃ ·3H ₂ O/TPPTS	2000	5	120	10	10	0.1	6.7	73.9	44.1	29.8	19.3	7500
6/7	MESBO	RhCl ₃ ·3H ₂ O/TPPTS	2000	3	120	10	10	0.2	2.3	71.1	46.6	24.5	26.4	8000
6/8	MESBO	RhCl ₃ ·3H ₂ O/TPPTS	2000	4	120	10	10	0.1	2.9	70.9	44.6	26.3	26.1	7900
6/9	MESBO	RhCl ₃ ·3H ₂ O/TPPTS	6000	3	120	10	5	2.5	32.5	57.0	16.3	40.7	8.0	24 600
6/10	MESBO	RhCl ₃ ·3H ₂ O/TPPTS	6000	3	120	40	5	0.8	21.4	63.9	27.2	36.7	13.9	33 700
6/11	MESBO	RhCl ₃ ·3H ₂ O/TPPTS	6000	3	120	70	5	0.2	4.7	56.2	30.8	25.4	38.9	46 200
6/12	MESBO	RhCl ₃ ·3H ₂ O/TPPTS	6000	3	120	100	5	0.1	0.6	44.0	25.5	18.5	55.3	49 300
6/13	MESBO	RhCl ₃ ·3H ₂ O/TPPTS	9000	3	120	100	5	0.0	9.0	58.0	26.0	32.0	33.0	64 800
6/14	MESBO	RhCl ₃ ·3H ₂ O/TPPTS	12 000	3	120	100	5	1.2	23.5	56.0	14.2	41.8	19.3	63 900
6/15	MESBO	RhCl ₃ ·3H ₂ O/TPPTS	11 000	3	130	100	5	2.8	28.2	56.5	15.6	40.9	12.5	50 200
6/16	MESBO	RhCl ₃ ·3H ₂ O/TPPTS	2500	5	120	10	10	0.4	20.0	68.6	22.3	46.3	11.0	7300
6/17 ^g	MESBO	3rd recycle catalyst	2500	–	120	10	10	2.1 ^h	27.5 ^h	63.4 ^h	20.1 ^h	43.3 ^h	9.0 ^h	5900 ^h

^a Reaction conditions: 1.32 mg (0.005 mmol) RhCl₃·3H₂O, 15 ml deaerated distilled demineralized water, pH 4.3; [Rh] = 34 ppm. Addition of MESBO results a two-phase system with a volume ratio of aqueous/organic phase = 15/13.2–15/2.2. For example in entry 6/14: 15 ml aqueous solvent containing the catalyst and 11.02 g = 13.2 ml (60.0 mmol of C=C units) of MESBO mixture results a two-phase system with a volume ratio of aqueous/organic phase = 15/13.2. Stirring rate = 750–850 rpm.

^b Defined as mole of hydrogenated C=C units of C18:3, C18:2, and C18:1 compounds in the starting materials MESBO mixture and in all other regiomers formed during the course of the reaction per mole of rhodium per hour.

^c Crude MESBO except of α-MLN, ML, MO and MS further contained 8.6% of methyl palmitate which was ignored in the experiments.

^d Methyl α-linolenate (α-MLN), C18:3 (9c, 12c, 15c).

^e Methyl linoleate (ML), C18:2 (9c, 12c).

^f Methyl oleate (MO), C18:1 (9c).

^g The aqueous catalyst layer (15 ml) of entry 6/16 after separation was re-used 3 times after addition, each time, of 2.29 g (12.5 mmol) MEBSO.

^h Results of the 3rd recycling experiment.

increasing H₂ pressure to give under 10 bar a total content of 67.2 mol% and under 70 bar pressure 58.9 mol% of C18:1 compounds (entries 4/1–4/3). As expected, the selectivity towards the undesired saturated product MS increased from 9.6 to 35.8 mol% with increasing pressure from 10 to 70 bar (entries 4/1–4/3).

The catalytic activity considerably increased from TOF = 4100 h⁻¹ to TOF = 11 100 h⁻¹ and the selectivity to C18:1 esters also increased from 58.9 to 65.3 mol% with increasing molar ratios of C=C units/Rh from 1000 to 3000 at a reaction temperature of 70 °C in the micellar partial hydrogenation of MELO in aqueous/organic two-phase systems (entry 4/3–4/5). The selectivity to MS decreased with increasing C=C units/Rh molar ratios to give 35.8 mol% MS at C=C units/Rh = 1000 and 22.9 mol% MS with C=C units/Rh = 3000 (entries 4/3–4/5).

3.2.2. Partial hydrogenation of crude MESO

In the selective hydrogenation reaction of MESO at a molar ratio of C=C units/Rh = 20 000 the absence of diethyl ether (entry 5/5) caused a major positive effect on both the catalytic activity (TOF = 52 800 h⁻¹) and selectivity to C18:1 esters (61.9 mol%) compared to the catalytic activity of TOF = 13 500 h⁻¹ and selectivity of 44.9 mol% to C18:1 esters obtained in the presence of diethyl ether (entry 5/1) under the same conditions, i.e. 120 °C, 50 bar pressure, a molar ratio of TPPTS/Rh = 3, a rhodium concentration of 34 ppm in water, a pH value of 4.3 within 10 min of reaction time. A further biphasic hydrogenation reaction of MESO at a molar ratio of C=C units/Rh = 20 000 under the same conditions except with a rhodium concentration of 17 ppm in water showed that the catalytic activity remained high (TOF = 30 200 h⁻¹) in the absence of diethyl ether (entry 5/2). The effect that the presence of diethyl ether at a high molar ratio of C=C units/Rh = 20 000 give rise to a drop in the catalytic activity could probably be explained by mass transfer limitations resulting from the lower solubility of the diethyl ether/MESO mixture in water containing the Rh/TPPTS catalyst.

At a higher reaction temperature of 130 °C both the catalytic activity and selectivity to C18:1 esters decreased to give TOF = 11 700 h⁻¹ and 36.2 mol%, respectively, (entry 5/3) compared to the activity of TOF = 52 800 h⁻¹ and a total content of 61.9 mol% to C18:1 esters (entry 5/5) obtained at 120 °C and a molar ratio of C=C units/Rh = 20 000 under the same conditions in aqueous/organic two-phase systems. At a lower molar ratio of C=C units/Rh = 15 000 at 120 °C and 50 bar within 10 min reaction time the TOF was 47 600 h⁻¹ to yield a total content of 64.5 mol% of C18:1 compounds (entry 5/4).

The biphasic partial hydrogenation reaction of MESO is strongly influenced by the pH value of the aqueous solution containing the Rh/TPPTS catalyst at a C=C units/Rh molar ratio of 12 000 and of TPPTS/Rh = 3 at 120 °C, 50 bar, a rhodium concentration of 34 ppm in water within 5 min of reaction time (entries 5/7–5/9). The highest catalytic activity of TOF = 98 000 h⁻¹ was obtained at a pH of 4.3 in the absence of a buffer (entry 5/7). At a pH value of 7.0 adjusted by a KH₂PO₄/NaOH-buffer the reaction rates were lower to give a TOF of 81 200 (entry 5/8) and under basic conditions with a pH of 10.4 adjusted by NaOH the catalytic activity further decreased to obtain a TOF of 68 400 h⁻¹ (entry 5/9). The effect that at increasing pH values the TOF decreases (entries 5/7–5/9) suggests a homogeneous nature for the Rh/TPPTS catalyst in aqueous media at acidic conditions. This pH effect is used as an evaluation method to decide for the presence of a homogeneous catalyst or for nanoparticles. Daguinet and Dyson [18] developed this pH evaluation method as a screen to help to assess for the homogeneous nature of transition metal catalytic complexes vs. heterogeneous nanoparticles.

The catalytic activity and selectivity to C18:1 esters in the selective hydrogenation of crude MESO increases with increasing molar

ratio of C=C units/Rh from 5000 to 12 000 and 15 000 to give TOF values from 42 500 to 98 000 and up to the exceptionally high catalytic activity of TOF = 117 000 h⁻¹ and obtain total contents to C18:1 esters from 34.1 to 58.0 and up to 68.3 mol% at 120 °C, 50 bar, a pH of 4.3 and a rhodium concentration of 34 ppm in water within 5 min in aqueous/organic two-phase systems (entries 5/6, 5/7, 5/12). The unusual high catalytic activity of TOF = 117 000 h⁻¹ is even more remarkable when one considers that the starting material crude MESO is a mixture of higher molecular weight functionalized internal olefins/dienes and furthermore it contrasts with the general perception that industrially applied Rh/TPPTS catalytic complexes normally exhibit very low rates in the conversions of higher molecular weight substrates in aqueous/organic biphasic systems [10]. This exceptionally high catalytic activity could probably be rationalized by assuming that interactions take place between the aqueous solvent and catalytic intermediate species involved in the hydrogenation catalytic cycles. Interactions of Rh/TPPTS catalytic intermediate species with the aqueous solvent have been recalled to explain the relative high catalytic activities of 1700 TOF's obtained in hydroformylation reactions of acrylic esters in aqueous/organic biphasic systems [19].

Increasing the temperature from 110 to 120 °C at a molar ratio of C=C units/Rh = 12 000 the catalytic activity increased from TOF = 80 500 to 98 000 h⁻¹ (entries 5/10 and 5/7) and raising further the temperature to 130 °C has a negative effect on the reaction rate to give a TOF value of 86 500 (entry 5/11) in the hydrogenation reaction of crude MESO in aqueous/organic two-phase systems.

3.2.3. Selective hydrogenation of crude MESBO

Typical results obtained in the Rh/TPPTS-catalyzed biphasic selective hydrogenation reaction of crude MESBO to obtain mainly C18:1 regiomers at 70–130 °C, 10–100 bar hydrogen partial pressure, molar ratios of TPPTS/Rh = 3–5 and of C=C units/Rh = 2000–12 000 at a pH value of 4.3 and low rhodium concentrations in the aqueous solution ([Rh] = 34 ppm) in the absence of added external surfactants, buffers and organic solvents with recycling experiments of the Rh/TPPTS catalyst in three consecutive runs are given in Table 6.

In the selective hydrogenation of crude MESBO catalyzed by Rh/TPPTS complexes in aqueous/organic two-phase systems both the catalytic activity and selectivity towards C18:1 esters increased with increasing reaction temperature from 70 to 120 °C to give at 120 °C a TOF of 7500 and 9 mol% of C18:1 regiomers under 10 bar hydrogen partial pressure, a molar ratio of C=C units/Rh = 2000 and of TPPTS/Rh = 5 at a pH value of 4.3 and a rhodium concentration of 34 ppm in water within 10 min of reaction time (entries 6/1–6/6). The catalytic activity increased with decreasing molar ratio of TPPTS/Rh from 5 to 3 under the same conditions (entries 6/6, 6/8 and 6/7) to give at the molar ratio of TPPTS/Rh = 3 a TOF value of 8000 (entry 6/7).

The catalytic activity was found to vary linearly with respect to hydrogen partial pressure. The TOF's increased from 24 600 to 49 300 with increasing pressure from 10 to 100 bar at a reaction temperature of 120 °C and molar ratios of C=C units/Rh = 6000 and of TPPTS/Rh = 3 within 5 min of reaction time (entries 6/9–6/12).

The reaction rates and the selectivity to C18:1 compounds in the selective hydrogenation of crude MESBO increased to TOF = 64 800 h⁻¹ and 58.0 mol% of C18:1 esters at a higher molar ratio of C=C units/Rh = 9000 (entry 6/13) and a further increase in the C=C units/Rh molar ratio to 12 000 give rise to a drop in the catalytic activity to obtain a TOF of 63 900 (entry 6/14) at 120 °C under 100 bar pressure within 5 min in aqueous/organic two-phase systems. At a higher reaction temperature of 130 °C and a molar ratio of C=C units/Rh = 11 000 the catalytic activity further decreased to give a TOF value of 50 200 with a total con-

tent of 56.5 mol% of C18:1 esters and 12.5 mol% of MS under 100 bar hydrogen pressure within 5 min reaction time (entry 6/15). Joo et al. [20] hydrogenated fatty acids of soybean phosphatidyl choline using water-soluble Rh/TPPMS catalysts [TPPMS = $\text{PPh}_2(\text{C}_6\text{H}_4\text{-}m\text{-SO}_3\text{Na})$] and obtained under mild reaction conditions, i.e. atmospheric pressure and room temperature up to 10.0 wt.% of stearate.

In order to obtain more information regarding the stability of Rh/TPPTS catalysts in the biphasic hydrogenation of methyl esters of vegetable oils recycling experiments with three consecutive runs were performed in the partial hydrogenation reaction of crude MESBO in aqueous/organic two-phase systems (entries 6/16, 6/17). The Rh/TPPTS-catalyzed biphasic partial hydrogenation of crude MESBO was carried out using a molar ratio of C=C units/Rh = 2500 and of TPPTS/Rh = 5 at 120 °C under 10 bar pressure within 10 min to give a TOF of 7300 and a total content of 68.6 mol% of C18:1 esters (entry 6/16). The aqueous catalyst phase of the reaction as described in entry 6/16 was recycled three times after addition of a fresh portion of crude MESBO starting material each time and performing the biphasic reactions under the same conditions, i.e. at a molar ratio of C=C units/Rh = 2500, 120 °C under 10 bar pressure within 10 min reaction time. After the third recycling experiment both the reaction rates and the selectivity to C18:1 compounds remained high where the TOF was 5900 with a total content of 63.4 mol% to C18:1 esters (entry 6/17).

4. Conclusions

The work presented in this paper demonstrated again the high potential of green aqueous-phase organometallic catalysis through a new application using renewable resources. In this detailed and comprehensive investigation of the influence of several operating parameters such as the reaction time, temperature, hydrogen partial pressure, C=C units/Rh and surfactant/TPPTS molar ratios, the pH value and the ratio of aqueous/organic phase was demonstrated that the selective hydrogenation of renewable crude polyunsaturated methyl esters of linseed, sunflower and soybean oils to their C18:1 counterparts proceeds with high selectivities up to 79.8 mol% of C18:1 esters which is upgraded 1st generation biodiesel fuel of improved oxidative stability, higher energy and environmental performance at a low pour point employing water-soluble Rh/TPPTS catalytic complexes under mild reaction conditions in green aqueous/organic two-phase systems. Moreover, it was disclosed that this useful biphasic selective catalytic hydrogenation reaction in green aqueous media possesses a great potential to produce under mild conditions 2nd generation biodiesel fuel when applying alternative, non-food oils feedstocks with a high C18:3 and C18:2 FAME content which are originally not suitable for biodiesel production or give poor quality biodiesel fuel but have the advantage that such feedstocks would not compete with food production. The industrially applied Rh/TPPTS catalysts were easily recovered in active form from organic reaction products by a simple phase separation and recycling experiments showed that both the catalytic activity and selectivity to C18:1 compounds remained high in three consecutive runs. Because this useful biphasic selective catalytic hydrogenation reaction may yield new process for the production of 1st and especially of 2nd generation biodiesel fuel, heating oil and biolubricants from many renewable oil feedstocks we are currently investigating the scope of this biphasic catalytic reaction regarding the nature of renewable starting material, the application of inexpensive transition metals modified with TPPTS and other water-soluble ligands and the comparison with classic heterogeneous catalyst.

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