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ORIGINAL PAPER

Application of metal triflate catalysts for the *trans*-esterification of *Jatropha curcas* L. oil with methanol and higher alcohols

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Abstract This paper describes an experimental study on the application of metal triflate salts for the (*trans*-) esterification of fatty esters (triolein, methyl oleate, methyl linoleate), fatty acid (oleic acid), as well as *Jatropha curcas* L. oil with methanol and higher alcohols (ethanol, *n*-propanol, *iso*-propanol, *iso*-butanol, *tert*-butanol). The effect of the metal type (scandium, bismuth, aluminium, lanthanum, copper, zinc) and process conditions on reaction performance were evaluated. Highest conversions were obtained with $Al(OTf)_3$. Reaction of triolein with methanol gave 99 mol% conversion at 165 °C for 1 h and the main product was the methyl ester. In addition, partial methoxylation of the carbon–carbon double bonds in the fatty acid chains was observed, though their fraction in the mixture was less than 20 mol%. The *trans*-esterification reaction was also successfully performed using higher alcohols, giving >95 % conversions for ethanol, *n*-propanol, *iso*-propanol and *iso*-butanol, whereas *tert*-butanol was not reactive. For the reaction of oleic acid with methanol, quantitative esterification, partial methoxylation of the carbon–carbon double bonds and the formation of small amounts of a lactone was observed. The methodology using $Al(OTf)_3$ was successfully performed on the *trans*-esterification reaction of JO (FFA content of 2.1 wt%) with various alcohols. Key properties (viscosity, pour point and cloud points) of the (branched) Jatropha esters were determined. The best cold-flow properties were obtained for the *iso*-propyl esters of JO, with cloud point and pour point of −3 and −24 °C, respectively.

Keywords (*Trans*-) esterification · Alkoxylation · Isomerisation-γ-lactonisation · Biodiesel · Metal triflates · Cold-flow properties

Introduction

Biodiesel (fatty acid methyl esters) is an important biofuel with an estimated global production volume of nearly 1.1 billion gallons in 2011 [1]. Favorable product properties like high flash point, relatively low viscosity, and only a marginal lower energy content than conventional diesel makes biodiesel a good substitute for fossil diesel in the industry and transportation sectors [2].

A point of concern is the cold-flow properties, expressed in terms of pour point and cloud point, particularly in countries with winter temperatures below 0 °C, leading to plugging and poor combustion performance [2–4]. The pour point of biodiesel is known to be a function of the degree of unsaturation of the fatty acid chains and the average fatty acid chain length and as such is a function of the plant oil source, see Fig. 1 for details. A combination of a high degree of unsaturation and a higher average chain length leads to a lowering of the pour point and, thus, has a positive effect on the cold-flow properties. This relation only holds for oils with average FA chain lengths between 17 and 19, for oils with a much smaller average chain length, for example coconut oil; this relation is not valid.

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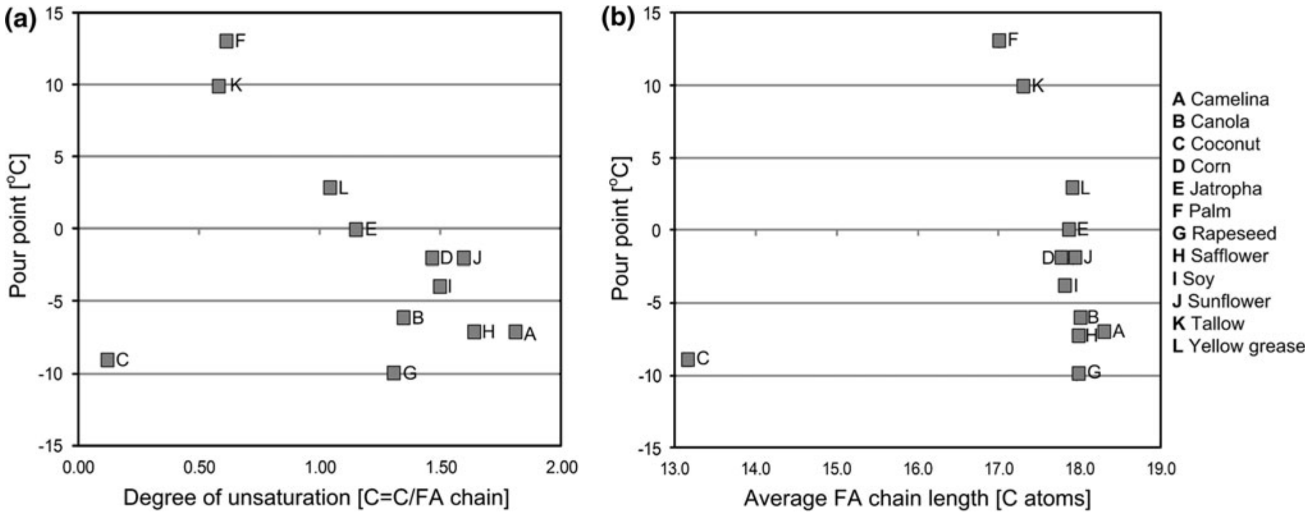


Fig. 1 Effect of **a** degree of unsaturation, and **b** the average chain length of fatty acid methyl esters on pour point (adapted from [5])

Table 1 Cold-flow properties (CP and PP) of fatty acid alkyl esters

Oil source	Ester group							References
	Methyl	Ethyl	*n*-propyl	*Iso*-propyl	*n*-butyl	*Iso*-butyl	2-butyl	
Soybean	1.4/1.0		−1.4/−5.0	−8.2/−10.7	−2.9/−5.3	−7.6/−12.0	−7.9/−12.0	[7]
Canola	1.0/9.0	1.0/6.0		7.0/12.0	6.0/16.0			[8]
Palm	13.0/16.0	8.0/6.0						[8]
Safflower	n.a./6.0	6.0/6.0						[8]
Sunflower	2.0/3.0	1.0/5.0						[8]
Beef tallow	17.0/15.0	15.0/12.0	12.0/9.0	8.0/0.0	9.0/6.0	8.0/3.0		[8]

First value is the CP (°C), second value is the pour point (°C)

In addition to a proper choice of the pure plant oil source, the use of cold-flow improvers or other alcohols than methanol in the *trans*-esterification reaction have been proposed [6]. An overview on the effect of the application of higher alcohols instead of methanol on cold-flow properties for various plant oil sources is given in Table 1. The use of higher alcohols and particularly branched alcohols instead of methanol in general leads to an improvement in the cold-flow properties.

Conventional biodiesel synthesis using acid or base catalysis with higher alcohols is often more cumbersome than for methanol [8, 10]. Full conversion of the oil is more difficult to achieve due to lower reaction rates [9]. Recently, metal triflate catalysts have been introduced for fatty ester synthesis. Scandium and bismuth triflate were shown to catalyse the (*trans*-) esterification of free fatty acids (FFA) and triglycerides very efficiently [11]. For example, the *trans*-esterification of triolein using scandium or bismuth triflate (10 mol%) and MeOH (48 molar excess) at 150 °C for 20–25 min gave a methyl oleate in 92 % ($Sc(OTf)_3$) and 85 % (($Bi(OTf)_3$) yield. For oleic acid, the esterification reaction is much faster at similar conditions and, with 1 mol% of catalyst, essentially quantitative yields were obtained for $Sc(OTf)_3$ in 1 min. Scandium and indium triflate (1–10 mol%) have also been shown to be active catalysts for the *trans*-esterification of lipids in algal biomass with ethanol in a temperature range of 200–235 °C (1–20 molar excess) [12].

We here describe a study on the use of metal triflate catalysts for the synthesis of fatty esters using higher alcohols (C2–C4 alcohols). To the best of our knowledge, the use of C3–C4 alcohols is an absolute novelty of this paper as such catalysts have been explored for methanol and ethanol only. A catalyst screening study on two model reactions, viz., the *trans*-esterification of triolein and the esterification of oleic acid using a range of metal triflates and conventional heating is reported. The effects of the length and type of the alcohol (primary, secondary, tertiary) on catalyst performance were studied. Finally, the best catalysts were also tested for a typical example of a plant oil [*Jatropha curcas* L. oil (JO)] using microwave heating. Relevant product properties (viscosity, pour and cloud point) of the product esters were determined and structure-property relations were derived.

Experimental Section

Materials

Unrefined JO was obtained from Diligent Energy BV (Eindhoven, The Netherlands). The oil was stored at 6 °C for at least 10 h and the residue was filtered [13]. Refined JO was prepared by degumming, deacidification, bleaching, and deodorisation using a method described in [14]. Metal triflate catalysts (>99.0 %), alcohols (>98.0 %, dried using $MgSO_4$ and stored on molecular sieves before use), sodium methoxide (25 % in methanol), triolein (>97.0 %), tristearine (>99.0 %), oleic acid (>99.0 %), methyl oleate (99.0 %), triacetine, >99.0 %), methyl tert-butyl ether (98.0 %), and chloroform-d (99.8 atom %D) were obtained from Sigma-Aldrich (Steinheim, Germany). $MgSO_4$ (dry) was from Boom BV (Meppel, The Netherlands). All materials were used as received unless otherwise stated.

Methods

Batch experiments with JO and metal triflates as the catalysts were performed in a microwave reactor (Discover and Explorer SP Microwave Synthesizers from CEM's Focused^{TM} Microwave Technology purchased from Beun de Ronde (Abcoude, The Netherlands). Screening reactions were performed in glass ampoules (outside diameter 8 mm, inside diameter 5 mm, length 15 cm) using conventional heating in an oven. This experimental approach was applied to minimise reagent, solvent and catalyst use. The ampoules were filled with the reagents and solvent and sealed with a torch. Maximum pressure in both reactor configurations is about 21 bars and this limits the upper temperature of a reaction. Using vapour pressure curves based on the Antoine equation [15], 165 °C was selected as the maximum reaction temperature for methanol and 180 °C for all higher alcohols. Initial studies (not shown here) showed that the results using conventional heating in glass ampoules and a microwave set-up are comparable.

^{1}H NMR analyses of JO and derivatives were performed on an Oxford AS400 NMR Spectrometer whereas ^{13}C NMR analyses were performed on an Oxford AS200 NMR Spectrometer. $CDCl_3$ was used as the solvent.

GC–MS spectra for structural analysis of the products were recorded on a HP 5890 equipped with a sol–gel capillary column (length 30 m, inside diameter 0.25 mm, and film thickness 0.25 µm) and a mass selective detector. Peak identification was done using the NIST05a mass spectra library. Helium was used as the carrier gas at a flow rate of 0.6 ml/min. The oven temperature was kept at 120 °C for 5 min and heated up to 250 °C at a rate of 3 °C/min, and then held at 250 °C for 15 min. The injector temperature was set at 250 °C.

The cloud and pour point were determined using a Mini Pour/Cloud Point tester model MPC-102A/102L from Tanaka Scientific Limited (Tokyo, Japan), using the L mode with detection intervals of 1 °C. The measurements were performed in triplicate and the average value is given.

The acid value of the starting material and products were determined using a slightly modified procedure reported by the National Cottonseed Products Association (Method number 28.029). The product (0.1 g) was weighed, dissolved in a mixture of diethyl ether and ethanol (50/50 %-v/v) (20 mL), and then titrated with a 0.01 N KOH solution.

The viscosity of JO and modification products was tested using a cone-and-plate rheometer AR1000-N from TA Instrument with a cone of 40 mm in diameter with a 2° angle. The viscosity measurements were conducted at 40 °C for 900 s, with a shear rate of 10 s^{-1}.

Elemental analyses (C and H content) were carried out using an automated Euro EA3000 CHNS analyser with acetanilide as a calibration reference. All samples were analysed at least in duplicate and the average value is given. The theoretical values are based on the chemical composition of the products (GC analyses) and, when relevant, include the fraction of alkoxy groups in the products.

Analytical Data for the JO Used in this Study

Crude JO

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 (m, $–C\boldsymbol{H} = C\boldsymbol{H}–$), 5.26 (m, $OC\boldsymbol{H}$(CH2)2), 4.29 (dd, $J = 11.8$, 4.2 Hz, $OCH(C\boldsymbol{H}_2)_2$), 4.14 (dd, $J = 11.9$, 5.9 Hz, $OCH(C\boldsymbol{H}_2)_2$), 2.76 (t, $J = 6.1$ Hz, $= CH–C\boldsymbol{H}_2–CH =$), 2.30 (t, $J = 7.4$ Hz, $–C\boldsymbol{H}_2COO–$), 2.11–0.99 (m, $–C\boldsymbol{H}_2–$), 0.87 (t, $J = 5.0$ Hz, $–C\boldsymbol{H}_3$, end group). ^{13}C NMR (50 MHz, $CDCl_3$) δ 173.0 ($–\boldsymbol{C}OO–$), 127.9–130.1 ($\boldsymbol{C}H{=}\boldsymbol{C}H$), 69.1 ($–O\boldsymbol{C}H(CH_2)_2$), 62.2 ($–(\boldsymbol{C}H_2)_2CHO–$), 22.8–34.4 ($–\boldsymbol{C}H_2–$), 14.3–14.4 ($–\boldsymbol{C}H_3$, end group).

Elemental analysis, calculated: C 76.7 %, H 11.9 %. Found: C 77.3 %, H 11.3 %.

Acid value: 4.2 mg KOH/g oil.

Catalytic Reactions

Trans-Esterification of JO with Methanol

The *trans*-esterification reaction of JO with methanol was performed using refined JO. The reaction was performed as follows: JO (10 g, 11.5 mmol of triglyceride), 25 wt% sodium methoxide in methanol (0.34 mL, 1.5 mmol of sodium methoxide), and methanol (2.8 mL, 69 mmol) were placed in a three-necked round bottom flask. The mixture was allowed to react under vigorous stirring at 65 °C for 3 h. The resulting emulsion/dispersion was cooled to room temperature. The solids were removed by dropwise addition of water at room temperature without stirring. The liquid was collected and subjected to a centrifugation step to obtain a clear transparent phase. The water addition/centrifugation step was performed three times. The remaining methanol and water were separated from the esters at elevated temperatures under reduced pressure ($T = 50$ °C, 30 mbar) for 4 h. The methyl ester, **1**, was analysed by ^{1}H and ^{13}C NMR and elemental analyses.

Methyl Esters of JO, 1 ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.35 (m, –C***H*** = C***H***–), 3.63 (s, COOC$\boldsymbol{H}_3$, methyl ester), 2.78 (t, $J = 6.2$ Hz, = CH–C$\boldsymbol{H}_2$–CH =), 2.27 (t, $J = 7.5$ Hz, –C$\boldsymbol{H}_2$COO–), 2.12–1.05 (m, –C$\boldsymbol{H}_2$–), 0.83 (t, $J = 7.0$ Hz, –CH_3). ^{13}C NMR (50 MHz, $CDCl_3$) δ 174.2 (–***C***OO–), 130.0–127.9 (***C***H=***C***H), 51.5 (COO***C***H_3, methyl ester), 34.0–22.5 (m, –***C***H_2–), 14.0 (–***C***H_3, end group). Isolated yield: 9.97 g (95 wt% of theoretical yield).

Elemental analysis, calculated: C 77.0 %, H 12.1 %. Found: C 76.9 %, H 12.1 %.

(Trans-) Esterification Reactions of Triolein, Methyl Oleate, and Oleic Acid with Alcohols Using Metal Triflate Catalysts

Catalyst-screening studies were performed using triolein and oleic acid and the appropriate alcohol in glass ampoules using conventional heating. A representative example for methyl oleate and methanol is as follows: the ampoule was loaded with methyl oleate (0.15 g, 0.5 mmol), methanol (1.01 mL, 25 mmol), and catalyst (0.05 mmol). The ampoule was subsequently sealed using a torch and placed in a preheated oven at a pre-determined temperature. After a pre-determined reaction time, the ampoule was taken from the oven and quenched by stepwise submersion in water at 90 °C and water at 20 °C. For safety reasons, particularly for reactions with gas phase formation, the ampoule was subsequently submerged in liquid nitrogen and opened. The liquid product was collected, washed with water, dried over $MgSO_4$, and analysed by ^{1}H and ^{13}C NMR and GC–MS.

For triolein, the ampoule was loaded with triolein (0.31 g, 0.35 mmol), methanol (0.7 mL, 17.5 mmol) and catalyst (0.035 mmol). The reactions were performed in a similar way as for methyl oleate.

The methyl esters fraction in the mixture, η_{methyl}, and the fraction of the methyl esters containing methoxy group in the mixture, η_{methoxy}, are based on integration of ^{1}H NMR spectra using the following equations:

$$\eta_{\mathrm{methyl}}[\mathrm{mol\%}] = \frac{\text{Peak area of CH}_3\text{ methyl esters }(3.69-3.52\,\mathrm{ppm})}{\text{Peak area of CH}_3\text{ end groups }(0.92-0.72\,\mathrm{ppm})} \times 100\%,$$

$$\eta_{\mathrm{methoxy}}[\mathrm{mol\%}] = \frac{\text{Peak area of CH}_3\text{ methoxy group }(3.31-3.22\,\mathrm{ppm})}{\text{Peak area of CH}_3\text{ end groups }(0.92-0.72\,\mathrm{ppm})} \times 100\%.$$

The fraction of other alkyl esters, η_{alkyl}, and alkyl esters with alkoxy groups, η_{alkoxy}, was calculated using a similar method as defined above.

Preparative Trans-Esterification Reactions of JO with Higher Alcohols

The preparative *trans*-esterification reactions of JO with higher alcohols were performed using unrefined JO in a microwave reactor. Typically, a glass vial was loaded with JO (5 g, 20.0 mmol of C=C), alcohol (500 mmol), and catalyst (2 mmol) and placed in the microwave reactor. The mixture was stirred using a double-cross magnetic stirrer (diameter ~1 cm) for 30 s and subsequently heated to the desired temperature in 2 min, and allowed to react for 1 h. The content was cooled to room temperature, washed three times with water and dried over $MgSO_4$. The remaining alcohol distilled of under reduced pressure, at a temperature slightly below the boiling temperature of the alcohol used. The product was analysed by ^{1}H and ^{13}C NMR and GC–MS.

Methoxy Methyl Esters of JO, 2 ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34 (m, –C***H***=C***H***–), 3.65 (s, COOC$\boldsymbol{H}_3$, methyl ester), 3.31 (s, CH–O–C$\boldsymbol{H}_3$, methoxy), 3.10 (m, C***H***–O–CH_3, methoxy), 2.76 (t, $J = 6.1$ Hz, =CH–C$\boldsymbol{H}_2$–CH=), 2.29 (t, $J = 7.5$ Hz, –C$\boldsymbol{H}_2$COO–), 2.10–1.00 (m, –C$\boldsymbol{H}_2$–), 0.87 (t, $J = 7.1$ Hz, –CH_3). ^{13}C NMR (50 MHz, $CDCl_3$) δ 178.1 (***C***=O, lactone), 174.2 (–***C***OO–), 129.9–127.9 (***C***H=***C***H), 81.0 (–***C***H–, lactone), 56.3 (CH–O–***C***H_3, methoxy), 51.4 (COO***C***H_3, methyl ester), 33.9–22.6 (m, –***C***H_2–), 14.0 (–***C***H_3, end group). Isolated yield: 5.01 g (95 wt% of theoretical yield).

Elemental analysis, calculated: C 76.5 %, H 12.1 %. Found: C 76.5 %, H 12.2 %.

Ethoxylated Ethyl Esters of JO, 3 ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 (m, –C***H***=C***H***–), 4.10 (dd, $J = 14.2$, 7.1 Hz, COOC$\boldsymbol{H}_2$$CH_3$, ethyl ester), 3.44 (m, CH–O–C$\boldsymbol{H}_2$$CH_3$, ethoxy), 3.17 (m, $\mathrm{C}\boldsymbol{H}$–O–$\mathrm{CH_2CH_3}$, ethoxy), 2.74 (t, $J = 6.1$ Hz, =CH–$\mathrm{C}\boldsymbol{H}_2$–CH=), 2.26 (t, $J = 7.5$ Hz, –$\mathrm{C}\boldsymbol{H}_2$COO–), 2.09–0.93 (m, –$\boldsymbol{C}\mathrm{H_2}$–), 0.85 (t, $J = 5.2$ Hz, $\mathrm{C}\boldsymbol{H}_3$). ^{13}C NMR (50 MHz, $\mathrm{CDCl_3}$) δ 178.3 ($\boldsymbol{C}$=O, lactone), 173.8 (–$\boldsymbol{C}$OO–), 130.2–127.7 ($\boldsymbol{C}$H=$\boldsymbol{C}$H), 79.3 (–$\boldsymbol{C}$H–, lactone), 64.0 (CH–O–$\boldsymbol{C}\mathrm{H_2CH_3}$, ethoxy), 60.1 (COO$\boldsymbol{C}\mathrm{H_2CH_3}$, ethyl ester), 36.7–19.6 (–$\boldsymbol{C}\mathrm{H_2}$–), 15.6 (CH–O–$\mathrm{CH_2}\boldsymbol{C}\mathrm{H_3}$, ethoxy), 14.4–13.9 ($\mathrm{CH_2}\boldsymbol{C}\mathrm{H_3}$, end group and ethyl ester). Isolated yield: 5.23 g (94 wt% of theoretical yield).

Elemental analysis, calculated: C 77.0 %, H 12.2 %. Found: C 76.7 %, H 12.2 %.

*Propoxylated Propyl Esters of JO, **4*** ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ 5.42–5.17 (m, –$\mathrm{C}\boldsymbol{H}$=$\mathrm{C}\boldsymbol{H}$–), 3.95 (t, $J = 6.7$ Hz, $\mathrm{COOC}\boldsymbol{H}_2\mathrm{CH_2CH_3}$, propyl ester), 3.47–3.27 (m, CH–O–$\mathrm{C}\boldsymbol{H}_2\mathrm{CH_2CH_3}$, propoxy), 3.16 (m, $\mathrm{C}\boldsymbol{H}$–O–$\mathrm{CH_2CH_2CH_3}$, propoxy), 2.74 (t, $J = 6.2$ Hz, =CH–$\mathrm{C}\boldsymbol{H}_2$–CH=), 2.37–2.16 (t, $J = 7.5$ Hz, –$\mathrm{C}\boldsymbol{H}_2$COO–), 2.10–1.03 (m, –$\boldsymbol{C}\mathrm{H_2}$–), 0.91 (t, $J = 7.5$ Hz, $\mathrm{COOCH_2CH_2C}\boldsymbol{H}_3$, propyl ester), 0.86 (m, $\mathrm{C}\boldsymbol{H}_3$, end group and propoxy). ^{13}C NMR (50 MHz, $\mathrm{CDCl_3}$) δ 177.7 ($\boldsymbol{C}$=O, lactone), 173.8 (–$\boldsymbol{C}$OO–), 132.1–126.5 ($\boldsymbol{C}$H=$\boldsymbol{C}$H), 79.4 (–$\boldsymbol{C}$H–, lactone), 70.6 (CH–O–$\boldsymbol{C}\mathrm{H_2CH_2CH_3}$, propoxy), 65.7 ($\mathrm{COO}\boldsymbol{C}\mathrm{H_2CH_2CH_3}$, propyl ester), 35.8–20.5 (–$\boldsymbol{C}\mathrm{H_2}$–), 14.0 ($\boldsymbol{C}\mathrm{H_3}$, end group), 10.7 (CH–O–$\mathrm{CH_2CH_2}\boldsymbol{C}\mathrm{H_3}$, propoxy), 10.3 ($\mathrm{COOCH_2CH_2}\boldsymbol{C}\mathrm{H_3}$, propyl ester). Isolated yield: 5.52 g (95 wt% of theoretical yield).

Elemental analysis, calculated: C 77.5 %, H 12.3 %. Found: C 76.8 %, H 12.3 %.

*Iso-Propyl Esters of JO, **5*** ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ 5.43–5.23 (m, –$\mathrm{C}\boldsymbol{H}$=$\mathrm{C}\boldsymbol{H}$–), 4.99 (m, $\mathrm{C}\boldsymbol{H}\mathrm{(CH_3)_2}$, isopropyl ester), 2.75 (t, $J = 6.1$ Hz, =CH–$\mathrm{C}\boldsymbol{H}_2$–CH=), 2.32 (t, $J = 7.4$ Hz, –$\mathrm{C}\boldsymbol{H}_2$COO–), 2.24 (t, $J = 7.5$ Hz, –$\mathrm{C}\boldsymbol{H}_2$COO–), 2.09–0.98 (m, –$\mathrm{CH_2}$–), 0.86 (t, $J = 5.4$ Hz, $\mathrm{C}\boldsymbol{H}_3$, end group). ^{13}C NMR (50 MHz, $\mathrm{CDCl_3}$) δ 178.9 ($\boldsymbol{C}$=O, lactone), 173.4 (–$\boldsymbol{C}$OO–), 131.10–125.49 ($\boldsymbol{C}$H=$\boldsymbol{C}$H), 67.26 ($\boldsymbol{C}\mathrm{H(CH_3)_2}$, isopropyl ester), 35.1–22.2 (–$\boldsymbol{C}\mathrm{H_2}$–), 21.8 ($\mathrm{CH(}\boldsymbol{C}\mathrm{H_3)_2}$, isopropyl ester), 14.0 ($\boldsymbol{C}\mathrm{H_3}$, end group). Isolated yield: 5.37 g (93 wt% of theoretical yield).

Elemental analysis, calculated: C 77.7 %, H 12.3 %. Found: C 76.9 %, H 12.3 %.

*Iso-Butoxylated iso-Butyl Esters of JO, **6*** ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ 5.43–5.12 (m, –$\mathrm{C}\boldsymbol{H}$=$\mathrm{C}\boldsymbol{H}$–), 3.75 (d, $J = 6.8$ Hz, COO–$\mathrm{C}\boldsymbol{H}_2\mathrm{CH(CH_3)_2}$, isobutyl ester), 3.25–2.99 (m, $\mathrm{C}\boldsymbol{H}$–O–$\mathrm{C}\boldsymbol{H}_2$–CH–$\mathrm{(CH_3)_2}$, isobutoxy), 2.74 (t, $J = 6.2$ Hz, =CH–$\mathrm{C}\boldsymbol{H}_2$–CH=), 2.28 (t, $J = 7.6$ Hz, –$\mathrm{C}\boldsymbol{H}_2$COO–), 2.00 (m, COO–$\mathrm{CH_2C}\boldsymbol{H}\mathrm{(CH_3)_2}$, isobutyl ester) 1.95–1.03 (m, –$\mathrm{C}\boldsymbol{H}_2$–), 0.92 (s, COO–$\mathrm{CH_2CH(C}\boldsymbol{H}_3)_2$, isobutyl ester), 0.90 (s, COO–$\mathrm{CH_2CH(C}\boldsymbol{H}_3)_2$, isobutyl ester), 0.86 (t, $\boldsymbol{J} = 6.0$ Hz, $\mathrm{C}\boldsymbol{H}_3$, end group). ^{13}C NMR (50 MHz, $\mathrm{CDCl_3}$) δ 178.9 ($\boldsymbol{C}$=O, lactone), 173.82 (–$\boldsymbol{C}$OO–), 132.8–125.2 (–$\boldsymbol{C}$H=$\boldsymbol{C}$H–), 79.5 (–$\boldsymbol{C}$H–, lactone), 75.9 ($\boldsymbol{C}$H–O–$\mathrm{CH_2}$–CH–$\mathrm{(CH_3)_2}$, isobutoxy), 70.3 (COO–$\boldsymbol{C}\mathrm{H_2CH(CH_3)_2}$, isobutyl ester), 36.44–21.90 (–$\boldsymbol{C}\mathrm{H_2}$–), 19.5 (CH–O–$\mathrm{CH_2}$–CH–$(\boldsymbol{C}\mathrm{H_3})_2$, isobutoxy), 19.0 (COO–$\mathrm{CH_2}$ $\mathrm{CH(}\boldsymbol{C}\mathrm{H_3)_2}$, isobutyl ester), 14.0 ($\boldsymbol{C}\mathrm{H_3}$, end group). Isolated yield: 5.64 g (94 wt% of theoretical yield).

Elemental analysis, calculated: C 77.5 %, H 12.4 %. Found: C 77.2 %, H 12.4 %.

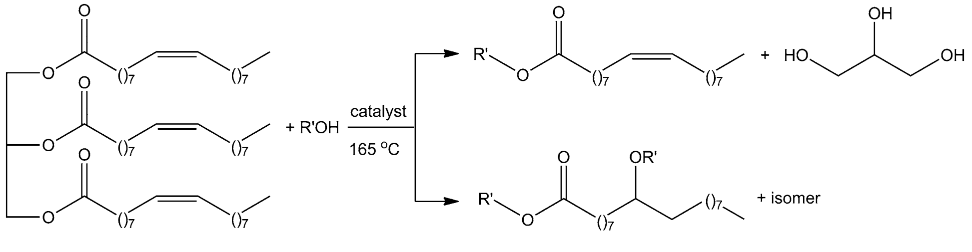
Results and Discussion

Model Studies on the *Trans*-Esterification of Triolein with Methanol using Metal Triflate Catalysts

The potential of metal triflate catalysts for (*trans*)-esterification reactions with higher alcohols was assessed by performing model studies with a system consisting of triolein and methanol (165 °C, 1 h, methanol to triolein molar ratio of 50) using conventional heating, see Scheme 1.

Six metal triflate catalysts were tested, viz., scandium, bismuth, zinc, aluminium, copper, and lanthanum triflate. In addition, aluminium chloride was used as well. The conversion of the triolein to methyloleate was determined using ^{1}H NMR by monitoring the disappearance of characteristic peaks of the glycerol backbone at δ 5.26 and 4.0–4.35 ppm, and the appearance of a characteristic methyl ester peak at δ 3.6 ppm. The results of the catalyst-screening study are presented in Table 2.

$\mathrm{Sc(OTF)_3}$, $\mathrm{Bi(OTf)_3}$, and $\mathrm{Al(OTf)_3}$ were the most active in the series and gave >95 % conversion of the triolein; the other triflates were less active. The conversion using $\mathrm{AlCl_3}$ was considerably lower than with $\mathrm{Al(OTf)_3}$ (7 vs 99 %), indicating that the anion plays a role in the reaction mechanism and affects reaction rates. The major product is



Scheme 1 Reaction products for the *trans*-esterification of triolein with alcohols using metal triflate catalysts

methyl oleate, as confirmed by ^1H and ^{13}C NMR spectra. ^1H NMR spectra of the products also showed a reduction of the intensity of the characteristic peaks of the C=C bonds at δ 5.29 ppm and the appearance of new peaks at δ 3.26 ppm (singlet) and δ 3.08 ppm (multiplet). Apparently, the C=C double bond is reactive under these conditions. A possible side reaction is methanol addition to the C=C bond to form an ether group (alkoxylation, see Scheme 1). Alkoxylation has also been reported by Madrigal [16] for the H_2SO_4-catalysed reaction of soybean oil with alcohols at 100–140 °C. Besides the esters, 18–31 % of the C=C unit was alkoxylated. In a more recent study, Moreau [17] and Pioch [18] described that (partly) methoxy methyl stearate was obtained when methyl oleate or oleic acid was reacted with methanol with dealuminated H-Y faujasites catalyst at 150–190 °C. Related reactivity has also been disclosed for the hydration of 1-phenyl-1-propyne in water using $Sc(OTf)_3$, $In(OTf)_3$, and $Yb(OTf)_3$ at 150–225 °C [19].

GC–MS analysis was applied to confirm the presence of methyl ether branches in the fatty acid chain. Two isomers were identified, i.e., methyl 9- and 10-methoxy octadecanoate with mass fragmentation patterns in line with those reported in the literature [17, 20]. The extent of methoxylation was determined using ^1H NMR data and the results are shown in Fig. 2. Clearly, full conversion of the C=C bond was not observed and the maximum fraction of methoxy group was less than 15 % and depending on the metal triflate catalyst. Highest amounts of methoxy groups were observed for the $Bi(OTf)_3$ and $Al(OTf)_3$.

The introduction of branches on the fatty acid chain by an alkoxylation reaction may also have a beneficial effect on the cold-flow properties of the product [16, 21, 22]. Therefore, the effect of process conditions on the $Al(OTf)_3$ catalysed alkoxylation with methanol was investigated with the primary objective to maximise the amount of methoxy branches. For this purpose, the extent of methoxylation was studied by performing reactions using methyl oleate and methanol as model compounds. The reaction time, molar excess of methanol to methyl oleate and catalyst loading were varied. The fraction of the methoxy groups versus time at different molar excesses of methanol is shown at Fig. 3.

The fraction of methoxy groups versus time shows a clear maximum at about 2–3 h reaction time. The maximum fraction was about 18 mol% for the highest methanol to methyl oleate ratio. At prolonged reaction times, the fractions of the methoxy product are lowered to about 5 mol%. This finding is not in agreement with the methoxylation of methyl oleate using solid dealuminated Y faujasites catalysts [17, 18]. Here, the fraction of methoxy products remained constant at a level between 40 and 50 % after prolonged reaction times, indicative for an equilibrium reaction. A possible explanation is the occurrence of other methanol consuming reactions (e.g., etherification, vide infra) catalysed by the metal triflates, driving the equilibrium to the side of the starting material. Further

Table 2 Results of the catalyst-screening study on the *trans*-esterification of triolein with methanol

Entry	Catalyst	Conversion (mol%)
1	$Sc(OTf)_3$	96 ± 1
2	$Bi(OTf)_3$	98 ± 1
3	$La(OTf)_3$	56 ± 2
4	$Cu(OTf)_2$	92 ± 1
5	$Al(OTf)_3$	99 ± 1
6	$Zn(OTf)_2$	65 ± 2
7	$AlCl_3{\cdot}6H_2O$	7 ± 2

The conversion is the average values of at least two experiments. Reaction conditions: 165 °C, conventional heating, 1 h, catalyst intake: 10 mol% to triolein, 50 fold molar excess of MeOH

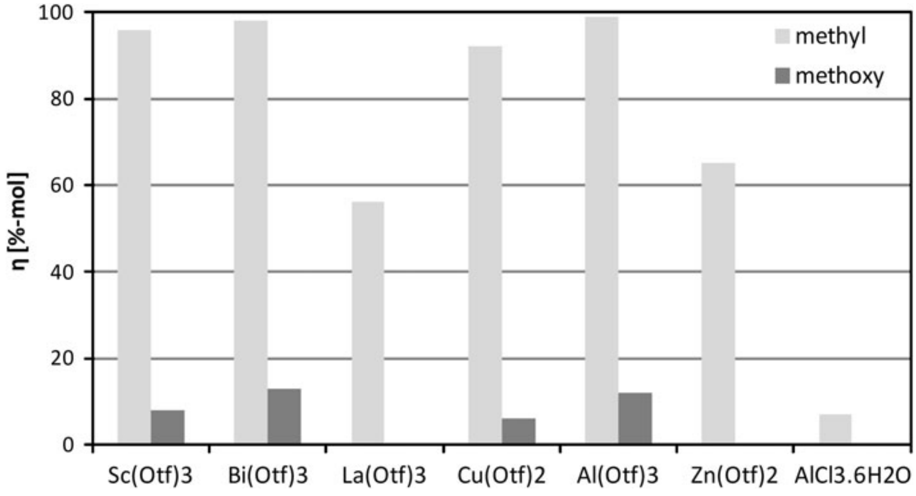


Fig. 2 Catalyst-screening study on the *trans*-esterification and alkoxylation of triolein with methanol (165 °C, conventional heating, 1 h, 10 mol% catalyst intake on triolein, 50 fold molar excess of MeOH)

detailed studies will be required to draw definite conclusions.

Higher catalyst intakes also did not lead to higher fractions of the methoxy products. Using a 50 mol% catalyst loading and a 50 times molar excess MeOH, 16 mol% methoxy product after 1 h reaction time was obtained, which is similar to the value obtained at lower intakes. After 24 h, the amount was reduced to 5 mol%.

The alkoxylation reaction with methanol was also performed with methyl linoleate instead of methyl oleate. With $Al(OTf)_3$ at 165 °C, partial methoxylation of the C=C bonds occurred and an isomeric mixture of mono-methoxy and di-methoxy methyl stearate was obtained (Scheme 2). The presence of these compounds was confirmed by GC–MS analyses. Clear GC peaks with characteristic mass fragmentation patterns in line with literature data [23] were observed for methyl- 9(10),12(13)-dimethoxyoctadecanoate, methyl 9(10)-methoxy-12(13)-octadecenoate, and methyl- 12(13)-methoxy-9(10)-octadecenoate.

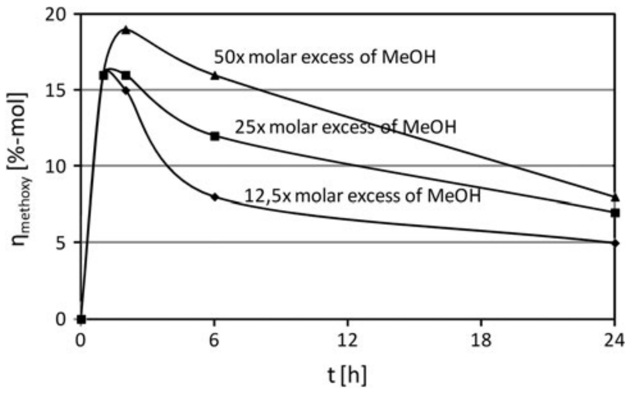


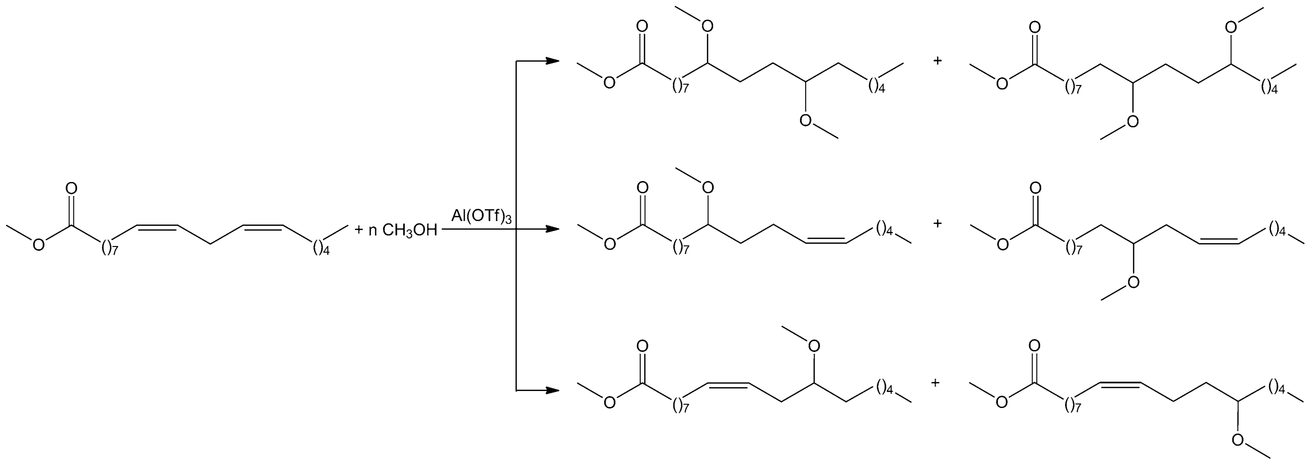
Fig. 3 Methoxylation of C=C bonds versus time at different methanol ratios for the alkoxylation of methyl oleate with methanol using $Al(OTf)_3$ (trendlines are for illustrative purpose only, 165 °C, conventional heating)

Model Studies on the Esterification of Oleic Acid with Methanol Using Metal Triflate Catalysts

A second series of catalytic reactions using metal triflate catalysts were carried out with a free fatty acid (oleic acid) instead of the triolein (Scheme 3). The reactions were performed at two temperatures (135 and 165 °C) using conventional heating. ^{1}H NMR spectra of the reaction product showed quantitative conversion of the free fatty acid to the methyl ester at both temperatures using all catalysts. We selected $Al(OTf)_3$ for further studies as it is the most active catalyst and non-toxic. The triolein conversion for the *trans*-esterification reaction with methanol (vide supra) were not quantitative at 165 °C. Apparently, the esterification reaction is much faster than the *trans*-esterification reaction at these conditions, which is in line with literature data in the (*trans*-) esterification of triolein and oleic acid with $Sc(OTf)_3$ and $Bi(OTf)_3$ [11]. Alkoxylation also occurred, with methoxy fractions in the range as observed for the *trans*-esterification reaction of triolein with methanol.

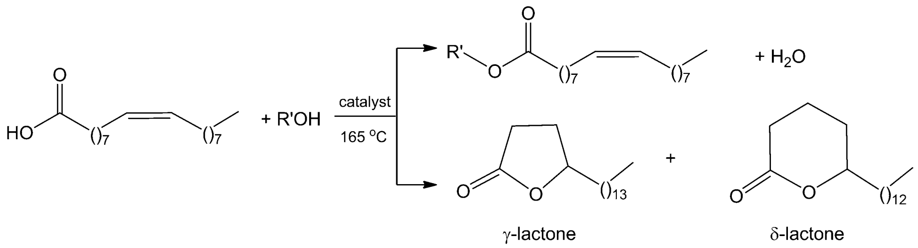
^{13}C NMR spectra of the product show, next to the characteristic peak of the methoxy ester group at δ 56.3 ppm, small peaks at δ 177.2 and δ 80.9 ppm. A possible side reaction is the isomerisation–lactonisation of free fatty acids (Scheme 3). Characteristic peaks of the lactones were not clearly observed in ^{1}H NMR spectra of the products due to overlap with other peaks, and this hampers quantification of the amount of lactones formed. Based on available ^{13}C NMR data [24], the peaks at δ 177.2 and δ 80.9 ppm are indicative for the formation of the γ-lactone instead of the δ-lactone.

The lactonisation of unsaturated fatty acids using metal triflates has been reported in the literature. Gooβen and coworkers [25] reported that AgOTf, $Bi(OTF)_3$, $In(OTf)_2$, and $Cu(OTf)_2$ catalysts are active catalysts for the



Scheme 2 Methoxylation of methyl linoleate using $Al(OTf)_3$ catalyst

Scheme 3 Esterification and lactonisation of oleic acid by metal triflate catalysts



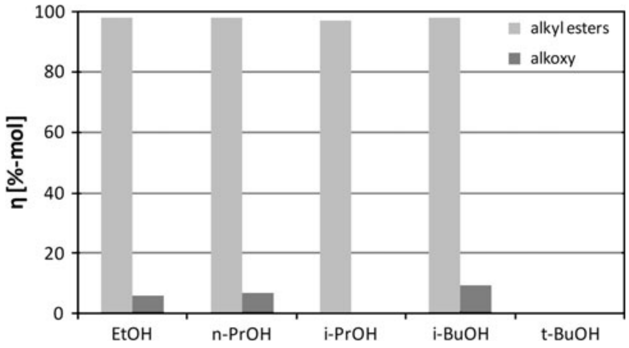


Fig. 4 Fractions of esters and alkoxylated products for the reaction of methyl oleate with higher alcohols using $Al(OTf)_3$ as the catalyst (10 mol% catalyst, 50 fold molar excess of alcohol, 185 °C, conventional heating, 1 h)

isomerisation-lactonisation of 10-undecenoic acid to the corresponding γ-lactone. The highest yield (50 %) was obtained at 160 °C using 5 mol% of the AgOTf catalyst. The isomerisation-lactonisation of internal unsaturated fatty acids with 9, 13, and 18 carbon chains using AgOTf at 130 °C gave γ-lactones in isolated yields between 51 and 72 % (24 h, chlorobenzene) [25]. Cermak and Isbell [24] reviewed methods for the isomerisation–lactonisation of unsaturated fatty acids to give δ- and γ-lactone using sulphuric acid in stoichiometric or super stoichiometric amounts. At low temperatures (<20 °C), the major products were δ-lactones, while γ-lactones were the major products at moderate temperatures (50–150 °C).

Model Studies on the *Trans*-Esterification of Methyl Oleate with Higher Alcohols Using $Al(OTf)_3$

The *trans*-esterification of methyl oleate with higher alcohols (EtOH, *n*-PrOH, *i*-PrOH, i-BuOH, *t*-BuOH) was studied with $Al(OTf)_3$, one of the most active catalysts for the reaction of triolein with methanol using conventional heating (Fig. 2). For all alcohols, except *t*-BuOH, quantitative *trans*-esterification and the formation of the ester of the higher alcohol were observed in 1 h at 165 °C.

Alkoxylation of the C=C bond in the fatty ester also occurred to a significant extent for EtOH, *n*-PrOH, and *i*-BuOH, though the maximum fraction of the alkoxylated ester was again low (<10 %), see Fig. 4 for details.

Alkoxylation was not observed for *i*-PrOH, the only secondary alcohol in the series, presumably for steric/electronic reasons. Similar results were reported for the *trans*-esterification and alkoxylation reaction of soybean oil with *i*-PrOH using H_2SO_4 as the catalyst (140 °C, 19 h) [16].

It is well-known that the rates of *trans*-esterification reactions are highly dependent on the molecular structure of the alcohols. Primary alcohols are the most reactive, followed by secondary alcohol, and the least reactive are tertiary alcohols [26]. As such, it is also not surprising that *t*-BuOH was not reactive under these reaction conditions.

Possible byproducts when using higher alcohols are olefins and ethers by the dehydration/addition reaction (Scheme 4) [27]. To assess the occurrence of these reactions, *i*-PrOH and the $Al(OTf)_3$ catalyst were allowed to react at standard reaction conditions (185 °C, 1 h). The gaseous products were collected and analysed using GC–MS. Both propylene and di-isopropyl ether were detected, proof for the occurrence of dehydration and etherification reaction.

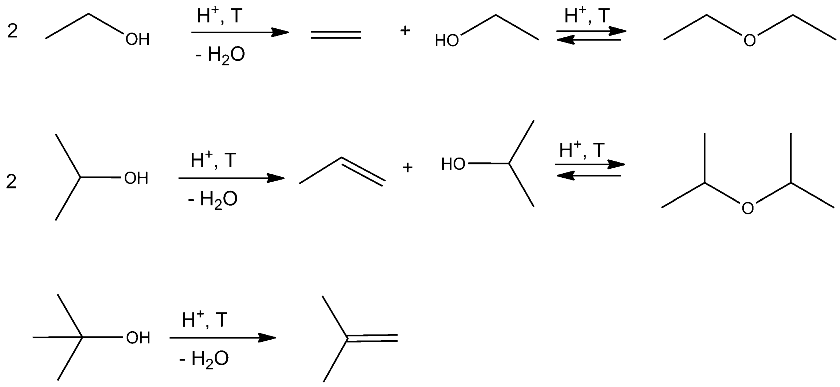
Trans-Esterification Reactions of JO with Alcohols Using $Al(OTf)_3$ as the Catalyst

JO Characterisation

The fatty acid composition of the JO used for this study was determined using GC–MS, and the results are given in Table 3. The composition of JO used in this study is close to that reported in the literature with a very slight difference in the amount of palmitic acid. The total amount of unsaturated fatty acids in the JO used in this study is 82.9 wt%. The acid value was determined by titration and found to be 4.2 mg KOH/g oil, corresponding with a FFA content of 2.1 wt% (as oleic acid), indicating that the oil contains significant amounts of free fatty acids.

Preparative Reactions of JO with Higher Alcohols

Preparative reactions of JO with methanol and various higher alcohols (EtOH, *n*-PrOH, *i*-PrOH, *i*-BuOH, *t*-BuOH) using $Al(OTf)_3$ were performed in a microwave reactor ($T = 165$ or 180 °C, catalyst intake of 10 mol%, 25 fold molar excess of alcohol, 1 h). After reactions, the esters



Scheme 4 Possible reaction pathways for the dehydration and etherification of primary, secondary and tertiary alcohols [27–29]

Table 3 Fatty acid composition of the crude JO used in this study

Fatty acid		This study		Literature (wt%) [30]
		(wt%) (GC-FID)	(mol%)	
Palmitoleic acid	C16:1	0.9	1.0	0–1.3
Palmitic acid	C16:0	11.7	12.7	14.1–15.3
Linoleic acid	C18:2	43.8	43.5	29.0–4.2
Oleic acid	C18:1	38.2	37.6	34.3–45.8
Stearic acid	C18:0	5.3	5.2	3.7–9.8
Total unsaturated acids		82.9	82.1	63.4–91.3

were obtained as yellow liquids in >93 wt% isolated yield and analysed by ^{1}H and ^{13}C NMR and elemental analyses. An overview of the results is given in Table 5. *t*-BuOH was not reactive, a result in line with the model component study. The reaction with *i*-PrOH was carried out at 135 °C. At higher temperatures, the pressure exceeded the maximum pressure in the microwave reactor due to the formation of a gas phase component like propylene by the catalytic decomposition of *i*-PrOH (vide supra).

The FFA value of the products ranged between 0.05 and 0.06 (wt%), and this value is considerably lower than the JO feed (2.1 wt%). This indicates that both *trans*-esterification of the triglycerides and esterification of the free fatty acids occurred, in line with the model component studies.

^{1}H NMR spectra of the products (Fig. 5) and ^{13}C NMR show the presence of the ester and alkoxy groups (Table 4). The extent of alkoxylation was in line with the model component studies, and the highest fraction was obtained using *i*-BuOH (Table 5). In addition, small amounts of γ-lactones were detected in ^{13}C NMR spectra, though they could not be quantified.

Properties of the JO Derivatives

Relevant physical properties of the JO ester derivatives with an emphasis on cold-flow properties were determined.

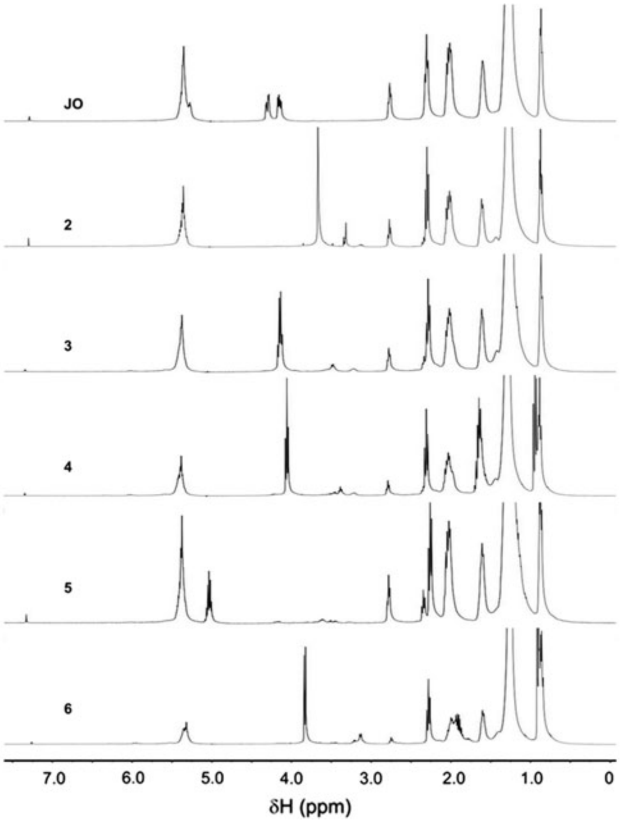


Fig. 5 ^{1}H NMR spectra of JO and derivatives

The viscosity of the JO feed and the higher alcohol esters derived thereof are provided in Table 6. As expected, the viscosity of the esters is considerably lower than that of the original JO. The ester substituent affects the viscosity and the viscosity increases with the number of carbon atoms in the alcohol, viz., 5.76 for MeOH to 8.26 mPa.s for *i*-BuOH. The synthetic methodology described here leads to partial alkoxylation of the C=C of the fatty acids chains. To check whether these branches affect the viscosity of the product, the viscosity of the JO methyl ester (**2**) was compared with a JO methyl ester (**1**) prepared by a standard

Table 4 Summary of characteristic peaks for products of the reaction of JO with higher alcohols

Alcohol	Ester group (ppm)		Alkoxy group (ppm)		Lactone group (ppm)
	^{1}H NMR	^{13}C NMR	^{1}H NMR	^{13}C NMR	^{13}C NMR
MeOH	3.65 ($C\boldsymbol{H}_3$)	51.4 ($\boldsymbol{C}H_3$)	3.31 ($C\boldsymbol{H}_3$), 3.10 ($C\boldsymbol{H}$)	56.3 ($\boldsymbol{C}H_3$)	178.3 (C=O), 81.0 ($\boldsymbol{C}H$)
EtOH	4.10 ($C\boldsymbol{H}_2$)	60.1 ($\boldsymbol{C}H_2$)	3.44 ($C\boldsymbol{H}_2$), 3.17 ($C\boldsymbol{H}$)	64.0 ($\boldsymbol{C}H_2$)	178.3 (C=O), 79.3 ($\boldsymbol{C}H$)
n-PrOH	3.95 ($OC\boldsymbol{H}_2$), 0.91 ($C\boldsymbol{H}_3$)	65.7 ($O\boldsymbol{C}H_2$), 10.3 ($\boldsymbol{C}H_3$)	3.47–3.27 ($OC\boldsymbol{H}_{2-}$), 3.16 ($C\boldsymbol{H}O$), 0.86 ($C\boldsymbol{H}_3$),	70.6 ($O\boldsymbol{C}H_2$), 10.7 ($\boldsymbol{C}H_3$)	177.7 (C=O), 79.4 ($\boldsymbol{C}H$)
i-PrOH	4.99 ($C\boldsymbol{H}$)	67.3 ($\boldsymbol{C}H$), 21.8 $(\boldsymbol{C}H_3)_2$	–	–	178.9 (C=O)
i-BuOH	3.75 ($OC\boldsymbol{H}_2$), 2.00 ($C\boldsymbol{H}$), 0.92 and 0.90 $(C\boldsymbol{H}_3)_2$	70.3 ($O\boldsymbol{C}H_2$), 19.0 $(\boldsymbol{C}H_3)_2$	3.25–2.99 ($C\boldsymbol{H}OC\boldsymbol{H}_2$)	75.9 ($\boldsymbol{C}HOCH_2$), 19.5 ($\boldsymbol{C}H_3$)	176.9 (C=O), 79.5 (CH),

Table 5 Overview of results for the reaction of JO with higher alcohols using $Al(OTf)_3$ as the catalyst

Compound	Alcohol	η_{alkyl} (mol%)	η_{alkoxy} (mol%)	Final acid value (mg KOH/g oil)
Methoxy methyl esters of JO (**2**)	MeOH[a]	98 ± 1	11 ± 2	0.10
Ethoxylated ethyl esters of JO (**3**)	EtOH[b]	98 ± 1	9 ± 2	0.11
Propoxylated propyl esters of JO (**4**)	*n*-PrOH[b]	98 ± 1	8 ± 1	0.11
Iso-propyl esters of JO (**5**)	*i*-PrOH[c]	97 ± 2	0	0.13
Iso-butoxylated *iso*-butyl esters of JO (**6**)	*i*-BuOH[b]	98 ± 1	21 ± 3	0.12
–	*t*-BuOH[d]	0	0	n.d.

Values are average values of two duplicate experiments. Reaction conditions: 25× molar excess of alcohol, catalyst loading: 10 mol% to C=C

n.d. not determined

[a] At 165 °C

[b] At 180 °C

[c] Reaction temperature 145 °C due to pressure safety limit of reactor (21 bars)

[d] 135 °C due to pressure safety limit of reactor (21 bars)

Table 6 Dynamic viscosity of JO and derivatives at 40 °C

Compound	Alcohol	Viscosity ($\times 10^{-3}$ Pa s)
JO	–	34.06
Methyl esters of JO (**1**)	MeOH[a]	4.47
Methoxy methyl esters of JO (**2**)	MeOH[b]	5.76
Ethoxylated ethyl esters of JO (**3**)	EtOH	6.93
Propoxylated propyl esters of JO (**4**)	*n*-PrOH	7.66
Iso-propyl esters of JO (**5**)	*i*-PrOH	8.20
Iso-butoxylated *iso*-butyl esters of JO (**6**)	*i*-BuOH	8.26

[a] Prepared using a standard base catalysed *trans*-esterification of JO with methanol

[b] Prepared using the synthetic methodology described in this paper; product contains -OMe groups in fatty acid chain

base catalysed *trans*-esterification of JO with methanol. The viscosity of **2** is a factor 1.3 higher than that of **1**, an indication that the presence of methoxy branches slightly increases the viscosity.

The cold-flow properties of the JO and higher alcohol derivatives were determined and the results are given in Fig. 6. The CP and PP of JO were −2 and −3 °C, respectively, and these values are in line with literature data (CP of 2 °C [31] and PP of −3 °C [31, 32]). The PP is in the expected range for plant oils, see Fig. 1, with higher levels of unsaturation leading to lower PP values.

The CP and PP of the methyl esters of JO, **1**, were 0 and 1 °C, respectively. These values are slightly higher than for JO. Apparently, the *trans*-esterification reaction with methanol does not have a significant effect on cold-flow properties, though it considerably lowers the viscosity (vide supra). PP and CP values for several plant oils and methyl esters derived thereof are given in Table 7. It shows that in general the CP is increased upon *trans*-esterification while an opposite effect is observed for the PP.

For comparison, the PP and CP of pure triolein (**7**) and methyl oleate (**8**) were determined. The CP/PP of triolein and methyl oleate are in the same range, −23/−26 and −24/−30 °C, respectively. The values for methyl oleate

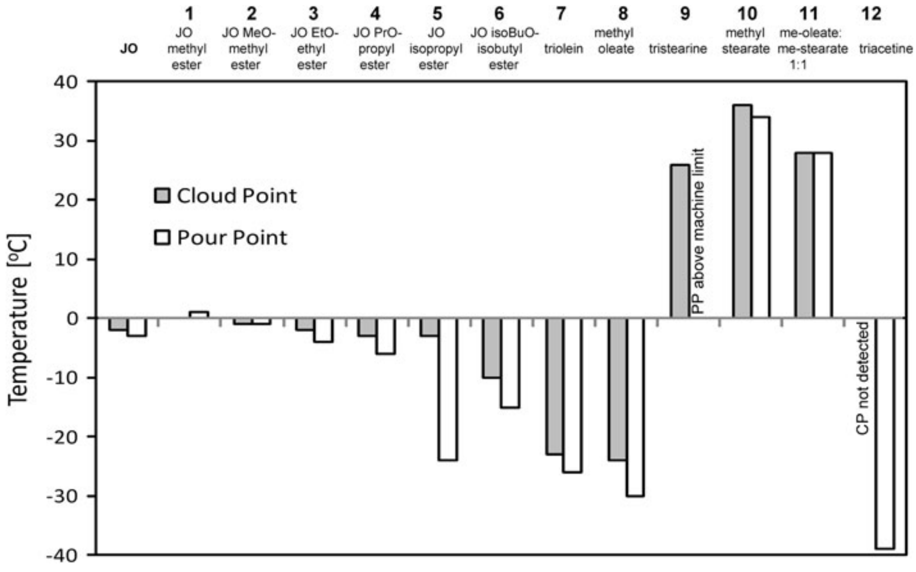


Fig. 6 Cold-flow properties of JO and derivatives

Table 7 Cold-flow properties of PPO and their alkyl esters

	Plant	CP/PP values		Mol ratio unsaturated/ saturated chains	Average chain length	References
		Oil	Methyl ester			
1	Castor	4.0/−15.0	7.0/−25.0	97.0/3.0	18.0	[33]
2	Pumpkin	3.0/−8.0	5.0/−12.0	79.3/20.7	17.8	
3	Groundnut	8.0/−3.0	10.0/−6.0	69.4/30.5	18.2	
4	Rapeseed	−3.9/−31.7	−2.0/−9.0	94.0/6.0	17.9	[34]
5	Soybean	−3.9/−12.2	2.0/−1.0	89.5/10.5	17.9	
6	Sunflower	7.2/−15.0	0.0/−4.0	92.0/8.0	17.9	

are much lower than for the JO methoxy methyl esters (**2**), likely caused by the saturated fatty ester fraction in the JO methoxy methyl esters, which is known to most prone to crystallisation. Support for this statement was obtained by measuring the PP and CP of methyl stearate (**10**) and mixtures of methyl stearate and methyl oleate (1–1 wt ratio, **11**). Methyl oleate has a CP and PP of −24 and −30 °C, while the values for methyl stearate are much higher and are 36 and 34 °C, respectively (see Fig. 6). The mixture **11** gave a CP and PP of 28 °C, close to those of methyl stearate. Thus, the cold-flow properties of fatty acid methyl esters are affected heavily by the amount of saturated fatty acid chains.

The synthetic methodology reported in this paper for the synthesis of the methyl ester of JO results, besides the introduction of ester groups, also applies to the introduction of methoxy groups (-OMe) on the fatty acid chain by methoxylation of the C=C bonds. The effect of these additional branches on the PP and CP was probed by comparing the values with that of the JO methyl esters (**1**) prepared using standard base catalysed methodology. The PP and CP of the methyl ester with -OMe ether groups (**2**) are 1–2 °C lower than the methyl ester without these additional branches. Thus, the effect of OMe branches on cold-flow properties is limited, which could be due to the relatively low amounts of the methoxy groups (vide supra).

A number of JO esters with different alcohols were prepared and this allows an assessment of the effect of the size of the JO ester group on cold-flow properties. When considering the primary alcohols in the series (MeOH, EtOH, *n*-PrOH, *i*-BuOH), the C4 alcohol in the series (**6**) give the lowest PP and CP, viz −10, and −15 °C versus −1 and −1 °C for the methyl ester **2**. Thus, the cold-flow properties are considerably improved by using higher alcohols for the esterification reaction. The lowest values for the CP and PP were obtained for the secondary alcohol in the series (*i*-PrOH, **5**), −3 and −24 °C, respectively. Thus, not only the number of carbon atoms in the alcohol but also the position of the substituents on the ester group plays a role.

Conclusions

Metal triflates were shown to be active catalysts for the simultaneous *trans*-esterification of the triglycerides and the esterification of the FFA in JO with various alcohols. Besides (*trans*)-esterification, partial alkoxylation of the carbon–carbon double bonds in the fatty acid chain, and to a lesser extent, isomerisation-γ-lactonisation of the free unsaturated fatty acids in the oil occurred. Aluminium triflate was found to be the most active catalyst, next to bismuth triflate and scandium triflate. Quantitative yields were obtained for the *trans*-esterification reaction when using primary and secondary alcohols, whereas a tertiary alcohol like *t*-BuOH was not reactive. Alkoxylation of the carbon–carbon double bonds was accomplished exclusively for primary alcohols, with higher alcohols being more reactive. Cold-flow properties of the Jatropha oil derivatives were determined and best results were obtained for the *iso*-propyl esters of JO, with CP and PP values of −3 and −24 °C, respectively.

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