Supplementary Information: Controlling Viscosity in Methyl Oleate Derivatives Through Functional Group Manipulation

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Viscometry methods

All measurements of kinematic viscosity were performed using Cannon-Manning Semi-Micro calibrated glass capillary viscometers (sizes 100 and 200). Measurements at 40 °C were performed in a water bath with bath temperature controlled by a Thermoline heating element and circulation unit equipped with a Brainchild model BTC-9090 Fuzzy Logic micro-processor-based temperature controller. The viscometer holder from the supplier was mounted in a custom built device allowing fine control over the viscometer angle, which was set using an Empire 581-9 spirit level prior to readings. Measurements at 100 °C were performed in a 90 %v/v glycerol bath in a 2 L conical flask, vigorously stirred and heated on a standard hot plate, with the temperature monitored using an ETS-D5 temperature controller from IKA®. The temperature controller was calibrated prior to use in an ice bath and in boiling water, and the temperature reading near the middle of the viscometer maintained at 100.0 ±0.1 °C. The viscometer holder from the supplier was mounted directly in the opening of the conical flask, and the correct angle also maintained using an Empire 981-9 spirit level. In all cases viscometers were cleaned and loaded in accordance with ASTM standard D445 − 09.[139] The sample was raised above the top measurement line by application of nitrogen pressure for each reading. Errors were calculated as two standard errors of the mean for a minimum of five replicates plus the standard error of the viscometer.

Viscosity calculations

Five readings were taken for each measurement, each being the time taken from when the meniscus crossed the upper mark to when the meniscus crossed the lower mark on the viscometer (see Figure A1). The average of the five time measurements was taken and the viscosity (η) was then calculated using:

$$\eta = t_{av} * c$$

Where t_{av} is the average time and c is the calibration constant of the viscometer. The error was calculated as two standard errors of the mean.

Example calculation:

For compound **5b**, times recorded at 40 °C were: 231.78 s, 232.22 s, 231.81 s, 231.47 s, 231.10 s.

Standard deviation = 0.418, average = 231.68, standard error = 0.187.

$$\eta = t_{av} * c$$

$$= 231.68 * 0.1048$$

$$= 24.28$$

Two standard errors of viscosity measurement based on standard error of time

$$= 2 * \sigma * c$$

$$= 2 * 0.187 * 0.1048$$

$$= 0.039$$

Error based on expanded error of viscometer (0.222%):

$$= \eta * 0.00222$$

$$= 0.054$$

Total error as expanded error + 2σ $= 0.054 + 0.039 = 0.093$

i.e. η=24.28±0.09

Viscosity Index Calculations

The VI is calculated based on the viscosity at 40 °C and 100 °C using ASTM Standard D2270 – 04. The standard contains a table of values for viscosity at 100 °C from 2–70 cSt and corresponding values of L and H. L is the kinematic viscosity at 40 °C of an oil of 0 viscosity index having the same kinematic viscosity at 100 °C as the oil whose index is to be calculated. H is the kinematic viscosity at 40 °C of an oil of 100 viscosity index with the same kinematic viscosity at 100 °C of the oil to be calculated. Values of L and H are either taken directly from the table or calculated

by linear interpolation where the viscosity of the oil to be calculated falls between two values in the table. VI is then calculated using the formula:

$$VI = \left[\frac{L - U}{L - H}\right] * 100$$

Where U is the kinematic viscosity at 40 °C of the oil whose viscosity index is to be calculated.

Example calculation:

For compound (**5b**), U = 24.38±0.09. η_{100} = 4.46±0.016. Relevant values quoted in ASTM D2270 are:

Viscosity at 100 °C	L	H
4.4	30.48	22.92
4.5	31.96	23.81

Linear interpolation between these for η_{100}=4.46 gives L=31.30 and H=23.42, and:

$$VI = \left[\frac{31.30 - 24.38}{31.30 - 23.42}\right] * 100$$

$$= 87.75$$

Upper and lower limits for errors in VI were calculated individually and then the larger used in the quoted error. For the upper limit, the calculated error for η_{40} was subtracted from the viscosity value, and used as U. The calculated error for η_{100} was then added to the η_{100} and this value used to derive L and H from the table. For the lower limit, the reverse procedure was followed.

For example, for compound **5b**, the upper limit was calculated as follows:

$$\eta_{40\,+} = 24.28 - 0.09$$

$$= 24.19 = U$$

$$\eta_{100-} = 4.46 + 0.02$$

$$= 4.48$$

using η_{100}=4.48, L = 31.83, H = 23.73 and:

$$VI = \left[\frac{31.83 - 24.19}{31.83 - 23.73}\right]$$

$$= 90.81$$

The lower limit was calculated by the inverse procedure as 85, and so VI is quoted as 88±3.

For oils where the calculated VI is above 100, a different equation is applied. Here, VI is calculated using :

$$VI = \left[\frac{10^N - 1}{0.00715}\right] + 100$$

where:

$$N = \left[\frac{logH - logU}{logY}\right]$$

and Y is the kinematic viscosity at 100 ° of the oil whose viscosity index is to be calculated (cSt), H is as above, extracted from the table of values provided, and U is also as above, the kinematic viscosity at 40 °C of the oil whose index is to be calculated.

For example, for compound **5a**, η_{100}=4.24=Y and which gives a value of H=21.51, and η_{40}=20.41=U:

$$N = \left[\frac{\log(21.51) - \log_{10}(20.41)}{\log_{10}(4.24)}\right]$$

$$= 0.0364$$

$$VI = \left[\frac{10^{0.0364} - 1}{0.00715}\right] + 100$$

$$= 112$$

Errors are calculated using the same equation, with the upper limit calculated from η_{40} minus its error and η_{100} plus its error, and the lower limit using the reverse.

Activation energy calculations

The Activation Energy of viscous flow was calculated using the viscosity data at 313 K and 373 K using the following method:

Dynamic viscosity (η) is related to the Activation energy (E_A) by the Eyring equation:[1]

$$\eta = Ae^{\frac{E_A}{RT}}$$

Where R is the gas constant and T is the temperature.

Dynamic viscosity is also the product of kinematic viscosity (μ) and density (ρ):

$$\eta = \mu \cdot \rho$$

Taking the natural logarithm of both sides for a given temperature gives:

$$\ln\left(\eta_T\right) = \ln\left(\mu_T\right) + \ln\left(\rho_T\right)$$

Hence at for the viscometry data at 313 K and 373 K we have:

$$\ln\left(\frac{\eta_{373}}{\eta_{313}}\right) = \ln\left(\frac{\mu_{373}}{\mu_{313}}\right) + \ln\left(\frac{\rho_{373}}{\rho_{313}}\right)$$

The small change in density of the compound between 313 and 373 K was estimated using the data for similar molecules reported in from Esteban et al.[2] The density change of biodiesel (BD100) between was judged to be most similar to the molecules in this study. Accordingly this difference was between 313 and 373K was used to evaluate the density term in the equation above.and gives:

$$\ln\left(\frac{\rho_{373}}{\rho_{313}}\right) = \ln\left(\frac{0.8229}{0.8641}\right) = -0.049$$

Using the Eyring equation and adding the constant evaluated above for the density change gives:

$$\frac{E_A}{R}\left(\frac{1}{373} - \frac{1}{313}\right) = \ln\left(\frac{\mu_{373}}{\mu_{313}}\right) - 0.049$$

and hence:

$$E_A = R \cdot \frac{\ln\left(\dfrac{\mu_{373}}{\mu_{313}}\right) - 0.049}{\dfrac{1}{373} - \dfrac{1}{313}}$$

The values of which are given in Table 4. In the article text.

DSC data for pure compounds

Table S1. Glass transition (T_G) and crystallization onset (T_{CO}) temperatures of branched methyl oleate derivatives.

Compound	T_{CO} (°C)	T_G (°C)
(**1c**) α-OH benzyl ether		−71
(**1a**) α-OH cyclohexyl ether		−68
(**1b**) α-OH methylcyclohexyl ether		−73
(**2b**) α-OH benzoic ester		−59
(**2a**) α-OH cyclohexanecarboxylic ester	−26	−68
(**7b**) α-OMe benzoic ester		−72
(**7a**) α-OMe cyclohexanecarboxylic ester		−82
(**6c**) α-OMe benzyloxy ether		−82
(**5b**) deshydroxy benzoic ester	−70	
(**5a**) deshydroxy cyclohexanecarboxylic ester	−72	
(**4**) deshydroxy benzyloxy ether	−77	

Biodiesel additive tests

Table S2. ΔT_{CO} of tallow biodiesel additive mixtures at 15 %w/w additive concentration.

| Additive	ΔT_{CO} (°C)		ΔT_{CO} (°C)
(**1c**) α-OH benzyl ether	−2 ±1	(**7a**) α-OMe cyclohexanecarboxy ester	−2 ±1
(**1a**) α-OH cyclohexyl ether	−2 ±1	(**6c**) α-OMe benzyloxy ether	−2 ±1
(**1b**) α-OH cyclohexanemethoxy ether	−2 ±1	(**5b**) deshydroxy benzoic ester	−2 ±1
(**2b**) α-OH benzoic ester	−2 ±1	(**5a**) deshydroxy cyclohexanecarboxy ester	−2 ±1
(**2a**) α-OH cyclohexanecarboxy ester	−2 ±1	(**4**) deshydroxy benzyloxy ether	−2 ±1
(**7b**) α-OMe benzoic ester	−2 ±1		

Example DSC curves
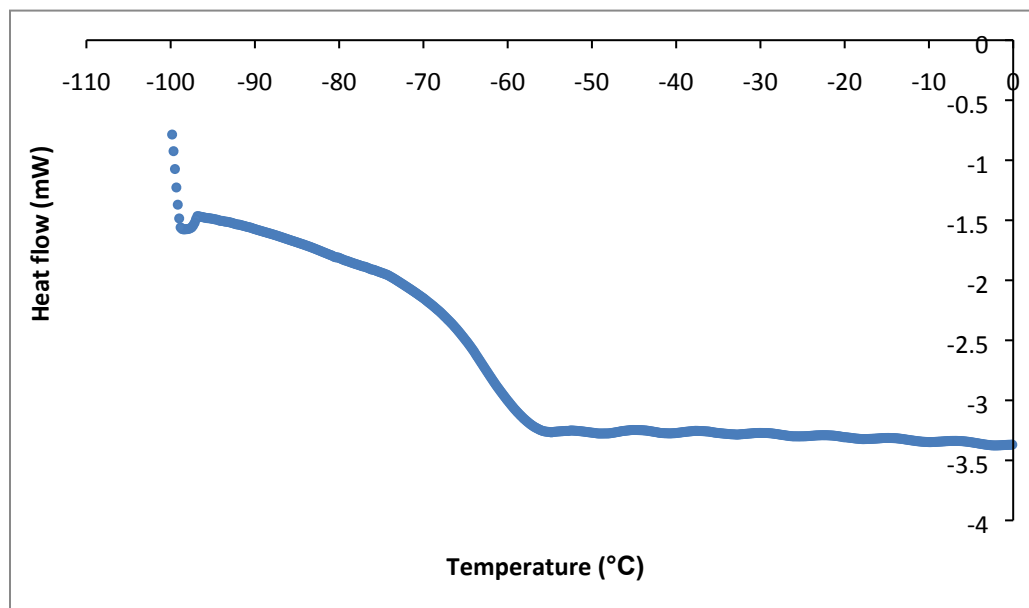
Figure S1. DSC cooling curve for α-hydroxy benzoic ester (2b) showing glass transition with onset at −59 °C.
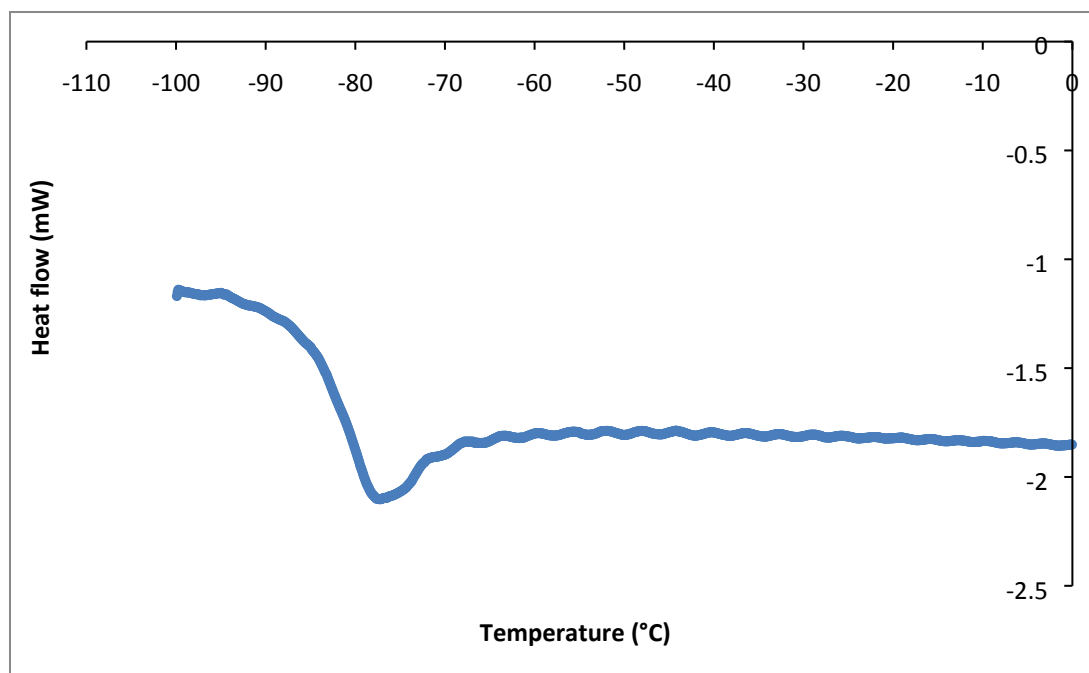

Figure S2. DSC cooling curve for deshydroxy benzoic ester (2b) showing crystallization peak with onset at −70 °C.
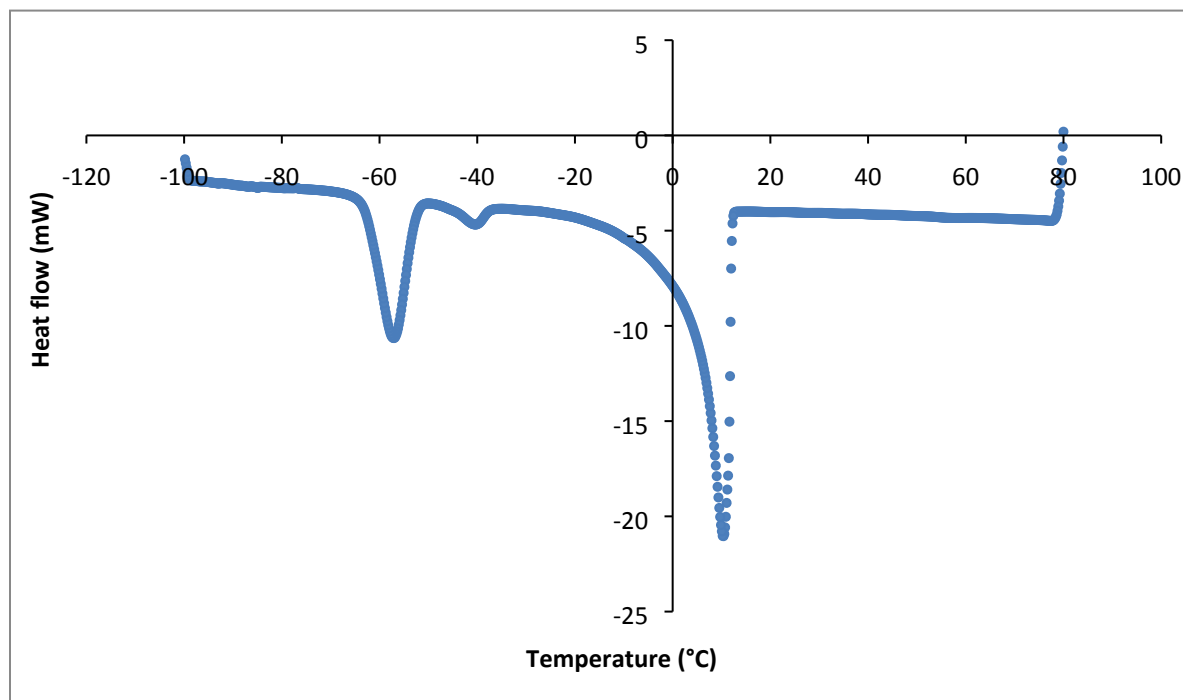
Figure S3. DSC cooling curve for 15% α-hydroxy benzoic ester (2b) showing the first crystallization peak with onset around −14 °C, and further low temperature crystallization events likely to correspond with freezing of unsaturated FAMEs.

Characterisation data for byproducts

BENZYL 9(10)-BENZYLOXY-10(9)-HYDROXYSTEARATE 1D

^{1}H NMR (300 MHz, CDCl3) δ 7.44–7.12 (m, 10H, Ar–**H**), 5.11 (s, 2H, CO$_2$C**H$_2$**Ph), 4.64 (d, J = 11.4 Hz, 1H, C**H**H'Ph), 4.49 (d, J = 11.4 Hz, 1H, CH**H'**Ph), 3.52 (app. bs, 1H, C**H**OH), 3.25 (app. q, J = 5.5 Hz, 1H, C**H**OBn), 2.41–2.20 (m, 3H, CO$_2$C**H$_2$**, CHO**H**), 1.72 − 1.12 (m, 26H), 0.88 (t, J = 6.5 Hz, 3H, CH$_2$C**H$_3$**).

METHYL 9(10)-BENZYLOXY-10(9)-METHOXYSTEARATE ESTOLIDE 6D

HRMS ESI+ (m/z) 845.62658 calculated for C$_{52}$H$_{86}$O$_7$Na$^+$, found 845.62684. ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.07–4.97 (m, 1H, CO$_2$C**H**), 4.65–4.49 (m, 4H, C**H$_2$**Ph), 3.66 (s, 3H, CO$_2$C**H$_3$**), 3.45–3.34

(m, 5H, CHOC**H₃, C**HOBn), 3.22–3.12 (m, 1H, C**H**OCH₃), 2.29 (t, *J* = 7.5 Hz, 4H, C**H₂**CO₂), 1.70–1.12 (m, 58H), 0.95–0.80 (m, 6H, CH₂C**H₃**).

References

1. D. R. Rohindra, R. A. Lata, R. K. Coll, Eur. J. Phys. 2012, 33, 1457–1464
2. B. Esteban, J.-R. Riba, G. Baquero, A. Rius, R. Puig, Biomass and Bioenergy 2012, 42, 164–171.