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Precision rheological study of the effectiveness of polymer cold flow improvers for corn oil based biodiesel

**Alexander A. Vinogradov, Ilya E. Nifant’ev, Alexey A. Vinogradov,
Roman S. Borisov and Pavel V. Ivchenko**

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S1. Materials and methods

S1.1. Materials

All of the synthetic and polymerization experiments were performed under argon atmosphere. Toluene (Merck, Darmstadt, Germany) was refluxed with Na/benzophenone in the presence of dibenzo-18-crown-6 and distilled prior to use. Methanol (MeOH), maleic anhydride (MA), benzoyl peroxide (BPO), dodec-1-ene, tetradec-1-ene, octadecan-1-ol were used as purchased (Merck, Darmstadt, Germany).

In our studies, we used commercial pour point depressants Keroflux 5686 (BASF, Ludwigshafen, Germany), Dodiflow 8171 (Clariant, Muttenz, Switzerland) that represent grafted ethylene/vinyl acetate copolymers (EVA), and pure EVA copolymer VW353.

$CDCl_3$ (99.8% ^2H, Cambridge Isotope Laboratories, Inc., Cambridge, MS, USA) was distilled over P_2O_5 and stored over 4 Å molecular sieves.

S1.2. Instruments and methods

The ^1H (400 MHz) NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (Bruker, Billerica, MS, USA). The chemical shifts were reported relative to the solvent residual peak ($CDCl_3$, δ: 7.26 ppm).

Gel permeation chromatography (GPC) measurements of the polymers were performed in THF at a flow rate of 1 mL/min at 30 °C using an 1260 Infinity II (Agilent Technologies, Santa

Clara, CA, USA) integrated instrument equipped with PLgel MIXED-C column (2×10^2 – 2×10^6 Da), autosampler and RI-detector. Calibration was achieved using polystyrene standards.

Elemental analysis (C, H, N, O) was performed on a Perkin Elmer Series II CHNS/O Analyzer 2400 (Perkin Elmer, Waltham, MS, USA).

The rheology of the biodiesel samples was examined by the rotational rheometer DHR-3 (TA Instruments, New Castle, DE, USA) using a cone-plane system with smooth surfaces (cone diameter was 25 mm, the angle between ruling of cone and plate was 1°). Viscosity *vs* temperature curves were obtained when cooled with the rate of 1°C min^{-1} and with constant shear rate of 20 s^{-1}.

GC×GC/MS-FID analysis was performed using Leco Pegasus® BT 4D instrument equipped with Agilent 7890A gas chromatograph with an embedded second oven, a two-stage cryomodulator, a flow splitter, a time-of-flight mass analyzer and a flame ionization detector. The gas chromatographic system included two columns (the first one was Restek Rxi-5Sil 30 m × 0.25 mm × 0.25 μm, the second one - Restek Rxi-17Sil 1.7 m × 0.10 mm × 0.10 μm) and was operated in temperature- programmed mode (initial temperature 40 °C for two minutes, heating to 320 °C at a rate of 10 °C/min, holding for 5 min, the temperature of the second oven and the modulator was maintained at a level of 10 and 20 °C higher than the temperature of the first oven, respectively) using helium as a carrier gas. The MS instrument was operated in 70 eV electron ionization mode using 100 Hz recording mode. The flame ionization detector temperature was 340 °C, hydrogen and air flow rates were 40 cm^3/min and 450 cm^3/min, respectively. Analysis results were processed using the CromaTOF software (Leco), the analytes were identified using NIST 20 database, the relative quantities were determined on the basis of FID data presuming equal response factors for all FAMEs.

S2. The synthesis and analysis of the sample of biodiesel

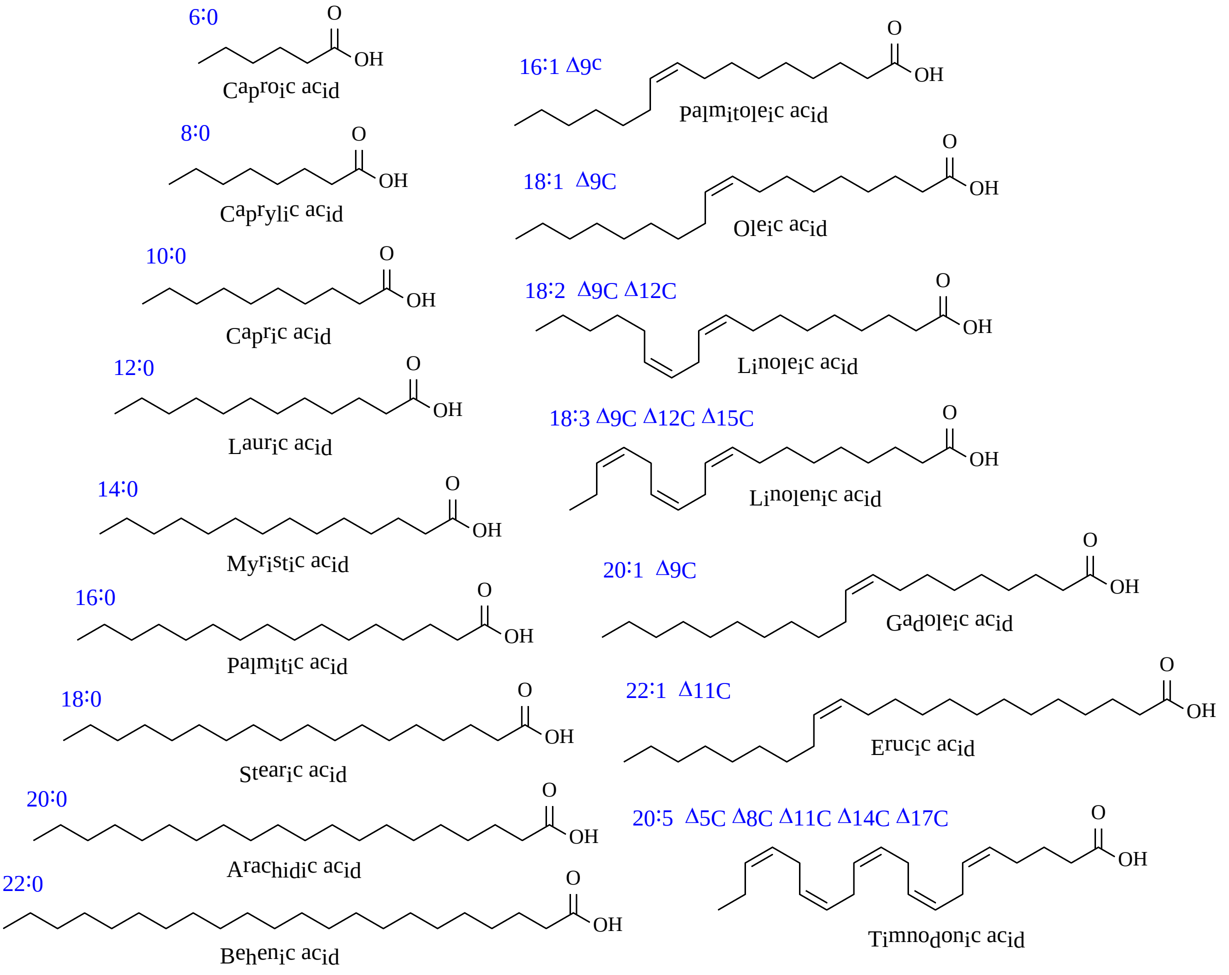


Figure S1. Molecular formula and lipid codes of the main fatty acids in oils and fats, used in the synthesis of biodiesels

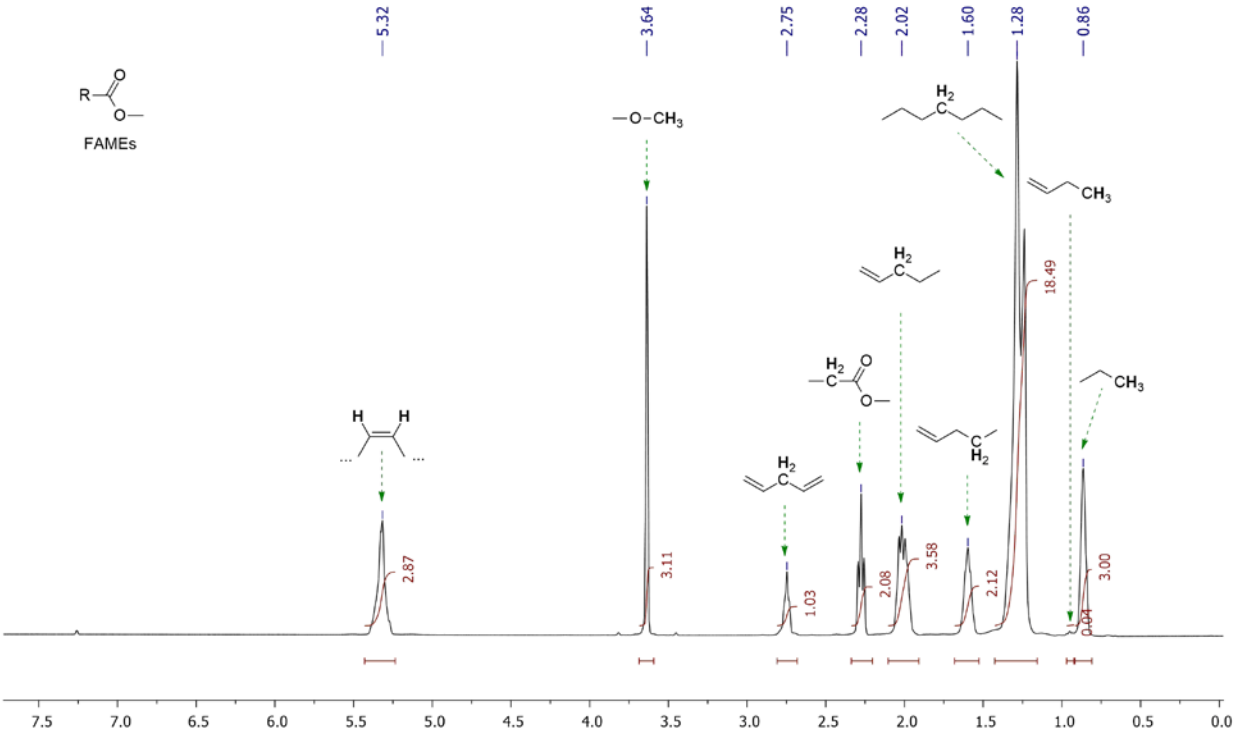
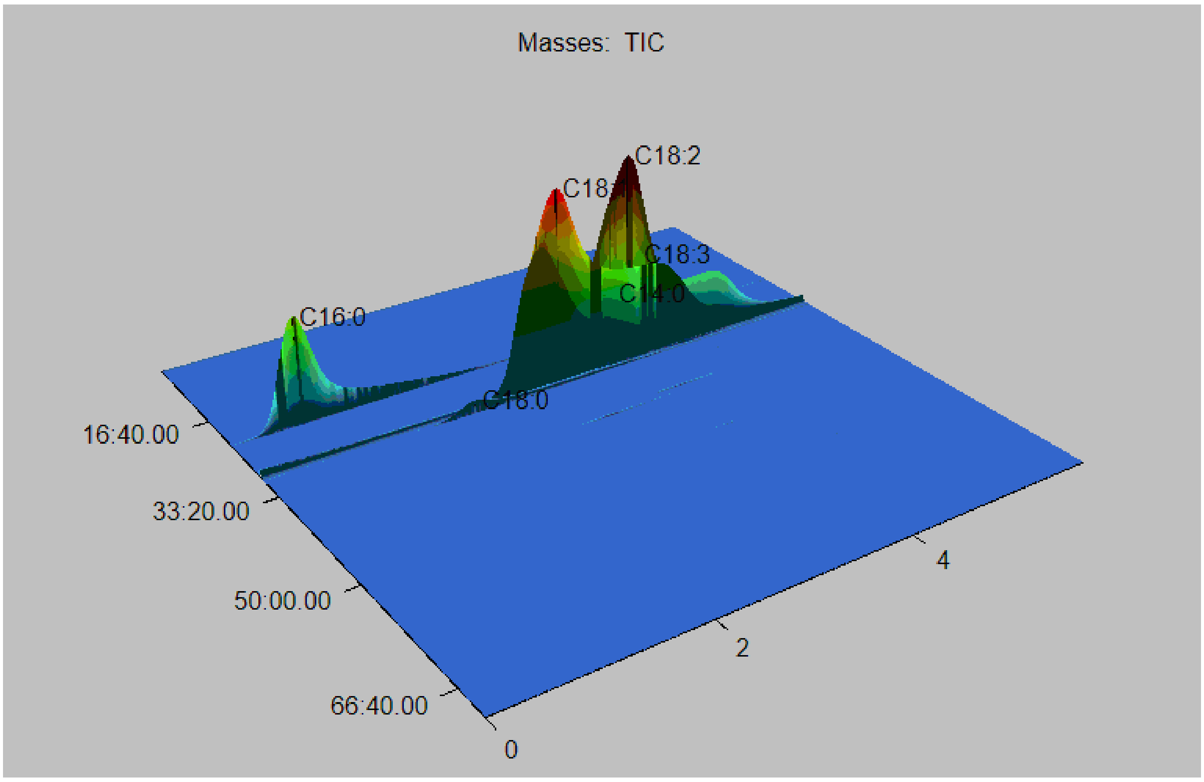


Figure S2. ^{1}H NMR spectrum ($CDCl_3$, 20 °C) of corn oil based biodiesel



Name	R.T. (min:sec)	Area %
C14:0	15:34.05, 4.434	0.035
C16:0	22:10.09, 0.661	18.628
C18:2	28:46.12, 3.798	34.499
C18:1	28:58.12, 3.001	38.412
C18:3	28:58.12, 4.382	4.218
C18:0	29:58.12, 2.061	3.987
C20:0	37:58.16, 3.094	0.22

Figure S3 GC×GC/MS-FID plot and data for corn oil based FAMEs

S3. The synthesis and analysis of the copolymers of maleic anhydride

Methylidenealkanes were synthesized according to previously described method [P. V. Ivchenko and I. E. Nifant’ev, *Polymer Sci. Ser. A*, 2018, **60**, 577]. Copolymers of maleic anhydride and olefins were synthesized using modified method presented in our recent article [I. E. Nifant’ev, A. A. Vinogradov, G. N. Bondarenko, S. A. Korchagina, A. V. Shlyakhtin, V. A. Roznyatovsky and P. V. Ivchenko, *Polymer Sci. Ser. B*, 2018, **60**, 469].

S3.1. The synthesis of the copolymers of maleic anhydride

Maleic anhydride (0.980 g, 10 mmol), α-olefin or methylidene alkane (10 mmol), and toluene (10 mL) were mixed in a two-necked flask prefilled with argon. The flask was placed into an ethylene glycol bath. Upon keeping for 5 min at an external bath temperature of 105 °C, a solution of benzoyl peroxide in toluene (0.1 mol/L, 0.5 mL, 0.05 mmol) was added to the reaction mixture. After 4 h the mixture was cooled, the solvents were removed under reduced pressure, and the residue was washed with methanol (3×20 mL) and dried in vacuum. The main characteristics of the products are given below.

Poly[(maleic anhydride)-alt-(11-methylenetricosane)]. The yield of the product (the colorless viscous mass) was 3.39 g (78%). ^{1}H NMR ($CDCl_3$, 20°C) δ: 3.5–2.5 (br, 2H), 1.25 (br, 42H), 0.87 (br. t, 6H) ppm. For $C_{28}H_{50}O_3$ anal. calcd. (%): C, 74.29; H, 11.58; O, 14.14.Found: C, 75.01; H, 11.95; O, 13.04. M_n = 9.1 kDa, $Đ_M$ = 1.77.

Poly[(maleic anhydride)-alt-(13-methyleneheptacosane)]. The yield of the product (the colorless viscous mass) was 3.93 g (80%). ^{1}H NMR ($CDCl_3$, 20 °C) δ: 3.5–2.5 (br, 2H), 1.25 (br, 50H), 0.87 (br. t, 6H) ppm. For $C_{32}H_{58}O_3$ anal. calcd. (%): C, 78.31; H, 11.91;O, 9.78. Found: C, 79.14; H, 12.13; O, 8.73. M_n = 11.2 kDa, $Đ_M$ = 2.28.

Poly[(maleic anhydride)-alt-(1-tetradecene)]. The yield of the product (the colorless powder) was 2.12 g (72%). ^{1}H NMR ($CDCl_3$, 20 °C) δ: 3.5–2.5 (br, 2H), 1.25 (br, 25H), 0.87 (br. t, 3H) ppm. For $C_{18}H_{30}O_3$ anal. calcd. (%): C, 73.43; H, 10.27; O, 16.30. Found: C, 73.63; H, 10.33; O, 16.04. M_n = 10.7 kDa, $Đ_M$ = 1.90.

S3.2. Functionalization of the copolymers of maleic anhydride

Maleic anhydride copolymer (10 mmol), octadecan-1-ol (5.68 g, 21 mmol), and toluene (10 mL) were placed in the flask filled with argon and equipped with a Dean–Stark head. The mixture was heated, and H_2SO_4 (20 μL) was added. The mixture was refluxed with stirring for 10 h, cooled, the solvents were removed under reduced pressure. The residue was washed with methanol (3×20 mL) and dried under vacuum.

2a: the yield 78%, M_n = 18.8 kDa, $Đ_M$ = 1.26.

2b: the yield 72%, M_n = 27.0 kDa, $Đ_M$ = 2.71.

2c: the yield 82%, M_n = 17.3 kDa, $Đ_M$ = 1.54.

S4. DSC data

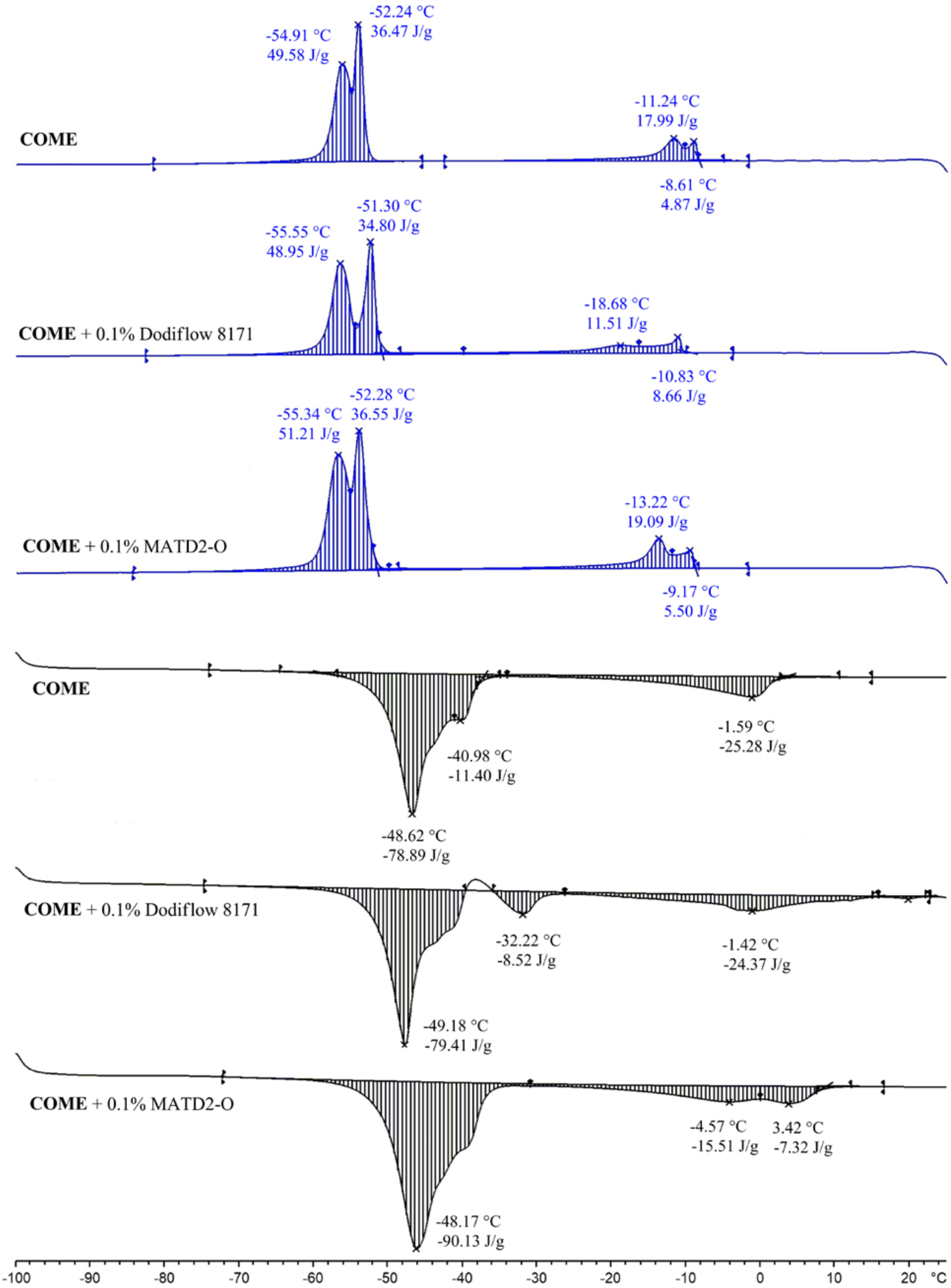


Figure S4. Cooling (top, blue) and heating (bottom, black) DSC curves for the mixture of corn oil methyl esters (COME, corn biodiesel) and COME with addition of 0.1 wt % Dodiflow 8171 and **2c** (MATD2-O)