

SUPPLEMENTARY MATERIAL

EXPERIMENTAL

Materials

CrispaTM gold sunflower oil was obtained from Sime Darby Hudson & Knight (Boksburg, RSA). 98 wt% Acetic acid, 98 wt% formic acid, 99 wt% toluene and 80 wt% potassium hydroxide (KOH) were obtained from Associated Chemical Enterprises (Johannesburg, South Africa). The KOH was dried at 105 °C before use. 37 wt% HCl was obtained from Sigma-Aldrich (Kempton Park, South Africa).

Methods

Crude glycerol preparation was reported previously.¹ In short: Sunflower oil transesterification with ethanol at a molar ratio of 6:1 (ethanol:oil), catalysed by KOH addition (1 wt% of oil), was conducted at 60 °C for 120 min under stirring at 100 rpm.²⁻⁴ After reaction the product mixture was left to separate into biodiesel and glycerol rich layers for 24h.

Organosolv lignin extraction was conducted as previously reported:¹ Milled sugarcane bagasse was firstly dewaxed in toluene/ethanol (2:1, v/v) at 9 mL (g bagasse)⁻¹ for 6 h under reflux at 73 °C. Dried bagasse was extracted in formic acid/acetic acid/water (3:6:1, v/v/v) at 10 mL (g bagasse)⁻¹, 85 °C for 4 h catalysed with HCl (0.1 wt% of bagasse). The filtrate volume was reduced in a rotary evaporator before hemicellulose was precipitated in three volumes 95 v% ethanol. The solvents were evaporated and the lignin precipitated in pH 2 water by centrifugation for 15 min at 4000 rpm.

THF size-exclusion chromatography (SEC)

The SEC-MALLS analysis procedure used was described by Otto et al.⁵ In short: The system consisted of an HPLC (Agilent 1100) with a MALLS detector (Wyatt Corp DAWN DSP photometer, Santa Barbara, CA) using a 5mW He-Ne laser set at 632.8 nm. The concentration was monitored by a RI detector (Agilent 1100 series). The column set consisted of a PLGel mixed bed type C column (7.6 mm x 300 mm, exclusion range 300–2,000,000 g mol⁻¹, particle size of 5 µm) and a Phenogel column (Phenomenex, 7.8 mm x 300 mm, exclusion range > 5000 g mol⁻¹, particle size of 5 µm). The eluent used was THF containing 250 ppm BHT as inhibitor. The flowrate was 1 mL min⁻¹, system temperature was set at 30 °C and the injection volume was 100 µL. The dn/dc value was determined for each sample using the online method described by Lee and Chang.⁶ Polystyrene ($\overline{M}_w = 30000$ g mol⁻¹, dispersity < 1.05) was used as standard.

Product samples were prepared by first derivatizing the material according to the method described by Guerra et al.⁷ About 20 mg of sample was reacted with a mixture (0.25 mL mg⁻¹) of acetic acid/acetyl bromide (92:8, v/v) for 2 h at 50 °C under constant stirring in a closed vial. Afterwards the solvent was removed in a rotary evaporator. THF was immediately added to yield a sample concentration of 2mg mL⁻¹. Samples were stirred for 12 h and then left to stand a further 48h before the filtered samples (0.45 µm PALL Acrodisc GxF/GHP syringe filters) were analysed.

RESULTS AND DISCUSSION

Table S1: Crude glycerol composition.⁸

Constituent	wt%
Fatty acid ethyl esters (FAEE)	27.2±1.3 ^a
MAG	9.6±1.3 ^b
Diacylglycerol	0.8 ^b
Ethanol	14.8±3.7 ^b
Glycerol	25.3±0.5 ^b

^a Determined by GC. 95% Confidence interval based on triplicate analysis.

^b Determined by ³¹P NMR. Based on triplicate analysis.

Table S2: Lignin characterisation⁸

Lignin	C	H	N	Ash (wt%)
KL	51.7 ± 0.7 ^a	3.7 ± 0.2	0.2 ± 0.0	20.2±0
OL	57.7 ± 0.7	5.2 ± 0.0	0.8 ± 0.1	2.6±0.2
LS	42.8 ± 0.1	4.0 ± 0.1	0.2 ± 0.0	16.7±0.4

^a95% Confidence interval based on triplicate analysis.

Table S3: PUF formulation.¹

Reagent	Parts (weight)
Polyol	100
Gelling catalyst	0.86
Blowing catalyst	0.67
Surfactant	2.50
Water	1.25
Isocyanate index (MDI)	1.05

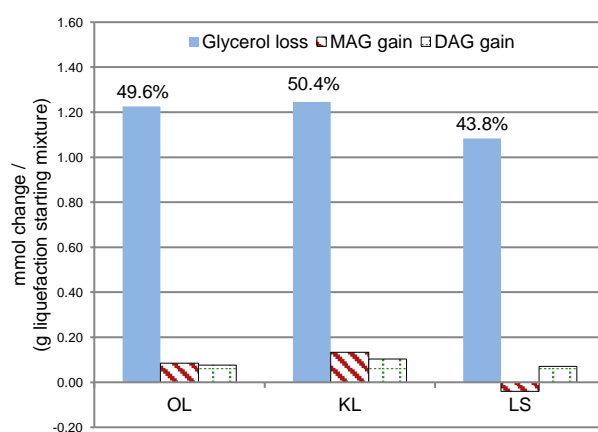


Figure S1: Change in crude glycerol constituent contents during liquefaction of the respective lignins, determined with ³¹P NMR spectroscopy.⁸

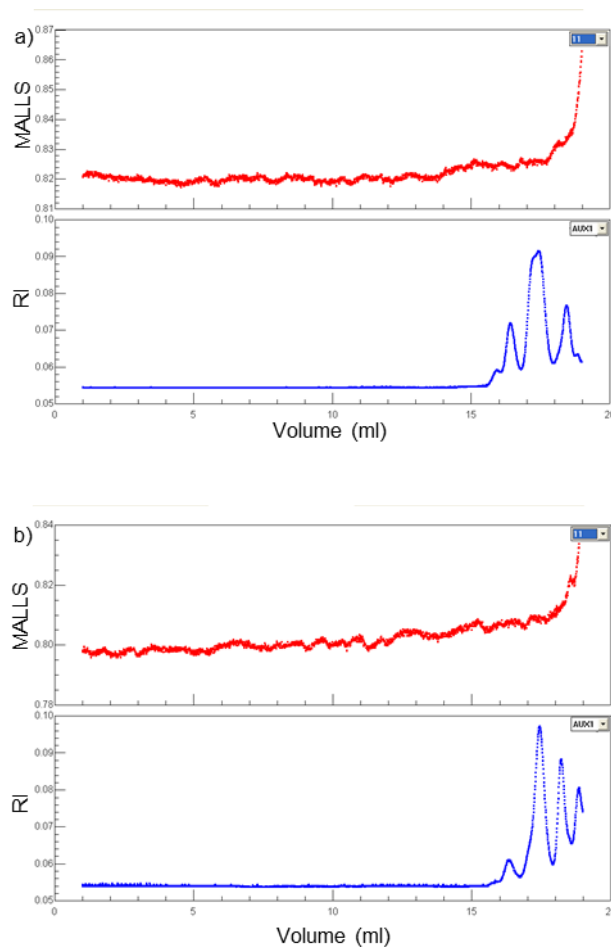


Figure S2: Liquid phase product elution profiles on the THF system: a) KL liquid product, b) LS liquid product (Peaks from 18 mL onwards are due to solvent effects, not attributable to the samples).

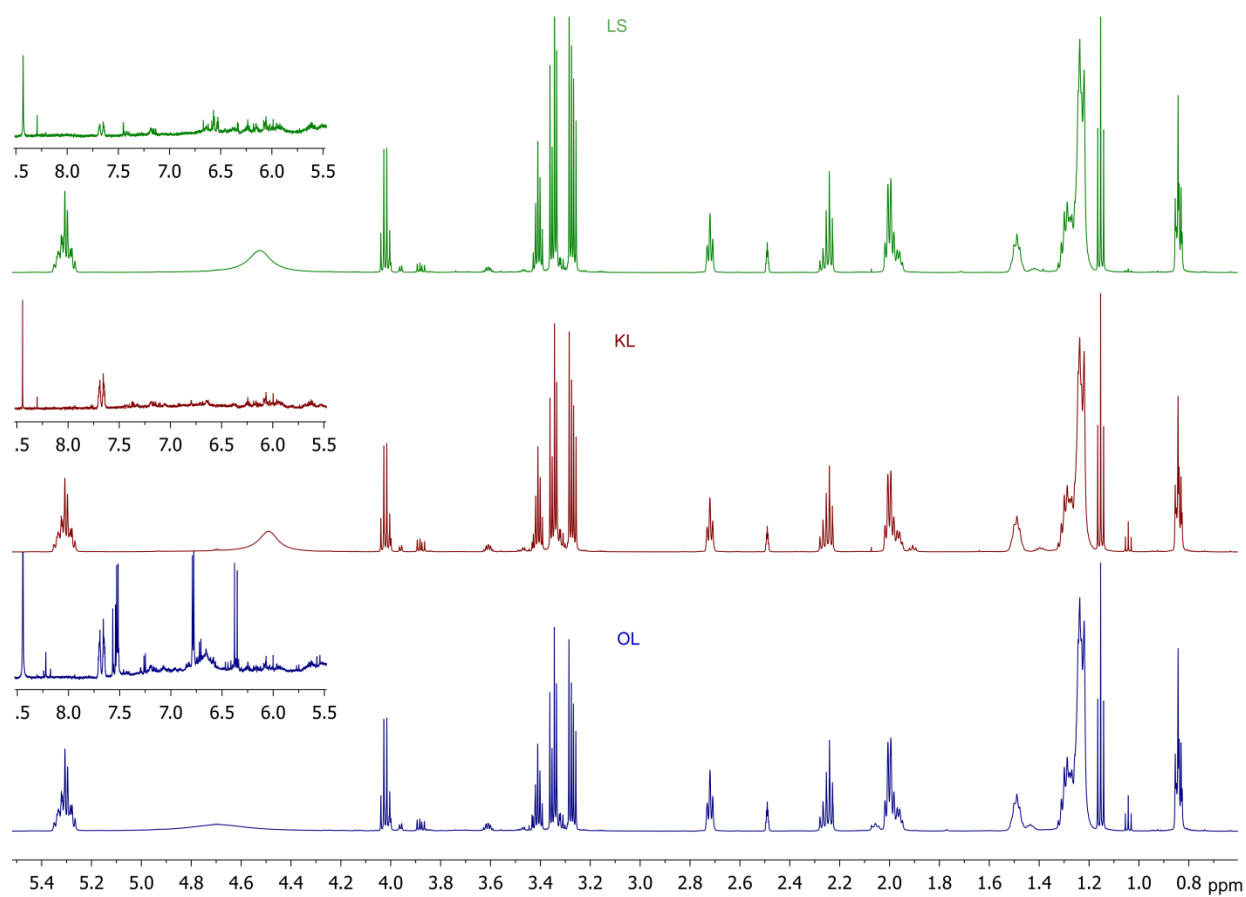


Figure S3: ^1H NMR spectra of liquid phase products.⁸

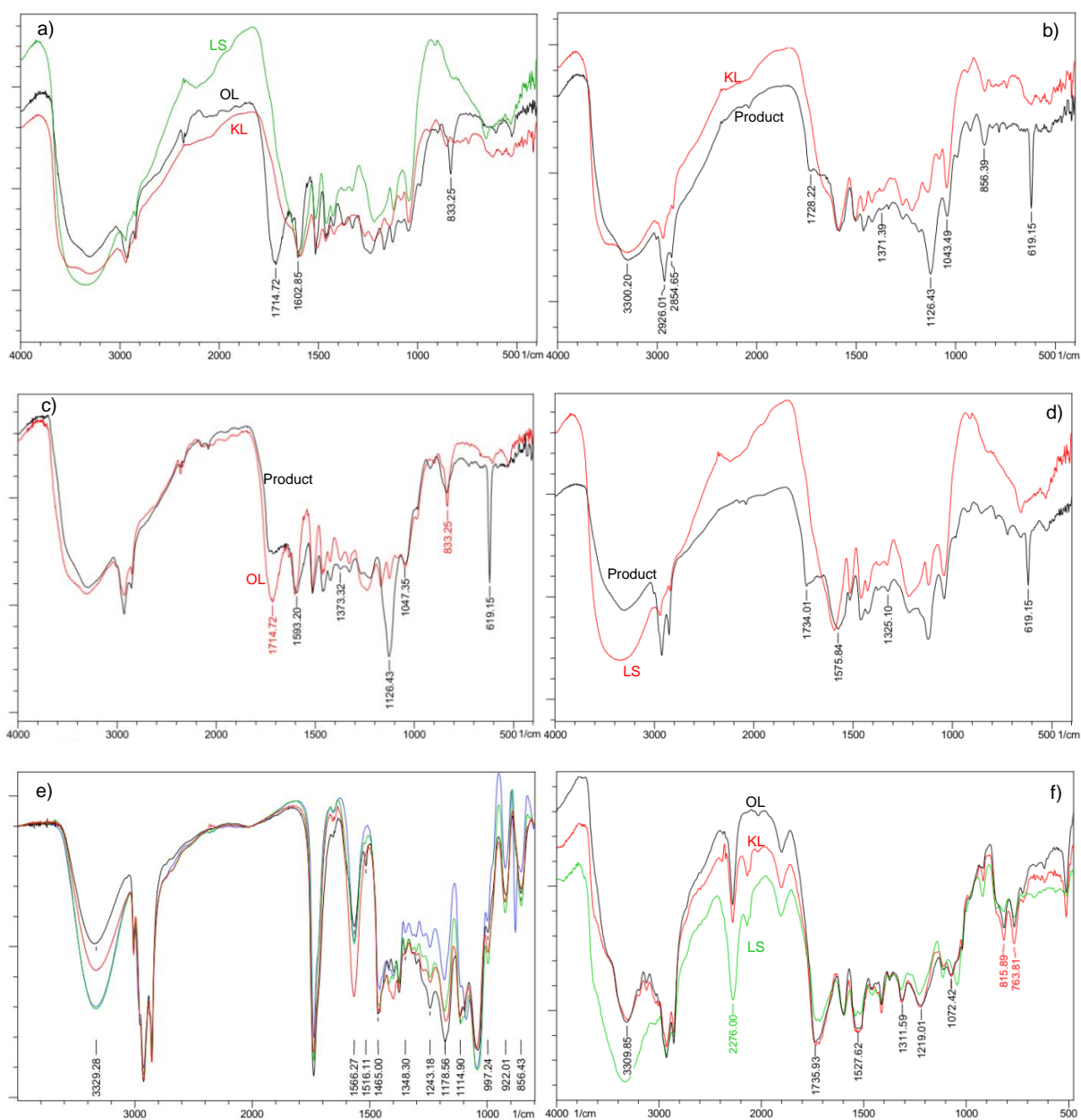


Figure S4: FTIR spectra: a) Lignin, b) KL and solid product, c) OL and solid product, d) LS and solid product, e) Crude glycerol and liquid products (black-OL, red-KL, green-LS, blue-crude glycerol), f) Polyurethanes.

References

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