Supporting Information

Subcritical Hydrothermal Liquefaction of Microalgae Residues as a Green Route to Alternative Road Binders

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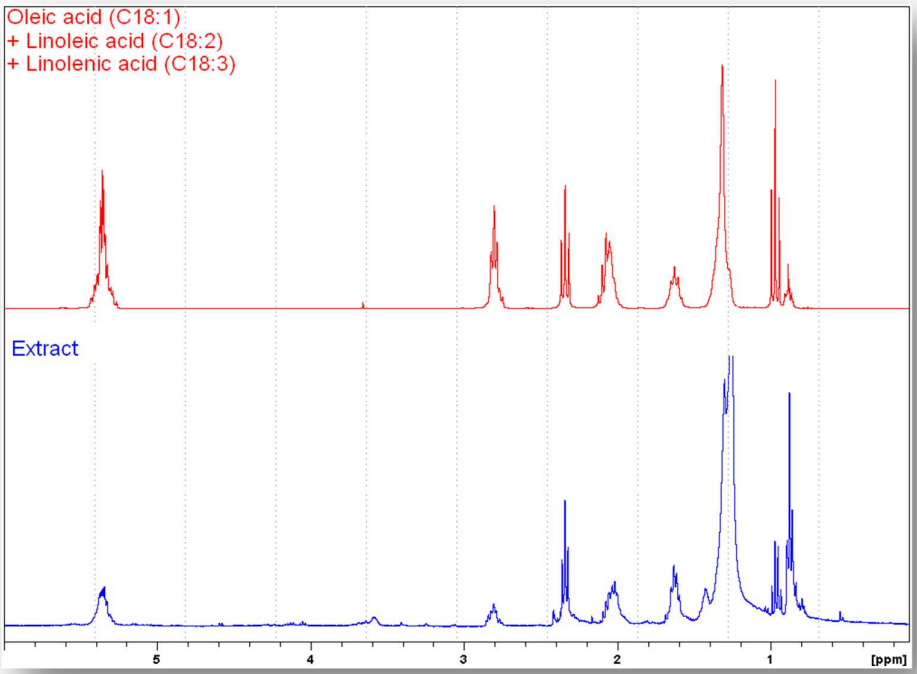


Figure S1: ^{1}H NMR spectra ($CDCl_3$): mixture of commercially free fatty acids (red), chloroform soluble part of the Soxhlet extract of *Scenedesmus sp.* residues (blue).

Table S1: GC-FID or GC-MS identification of fatty acids isolated by Soxhlet extraction from the *Scenedesmus sp.* microalgae residues using a chloroform / methanol mixture (2:1, v/v)[a].

Abbreviation	Name	Abbreviation	Name
C10:0	Capric acid	C16:1	Palmitoleic acid
C15:0	Pentadecylic acid	C18:1	Oleic acid
C16:0	Palmitic acid	C18:2	Linoleic acid
C18:0	Stearic acid	C18:3	Linolenic acid
C19:0	Nonadecylic acid	C20:1	Gadoleic acid
C20:0	Arachidic acid	C20:2	Eicosadienoic acid
C24:0	Lignoceric acid	C20:4	Arachidonic acid
C26:0	Cerotic acid	C20:5	Timnodonic acid
C28:0	Montanic acid	C24:1	Nervonic acid

[a] The relative ratio of the six most abundant fatty acids has been quantified by GC analysis: C16:0 (65%), C18:1 (20%), C18:0 (5.5%), C18:3 (5.5%), C18:2 (4%)

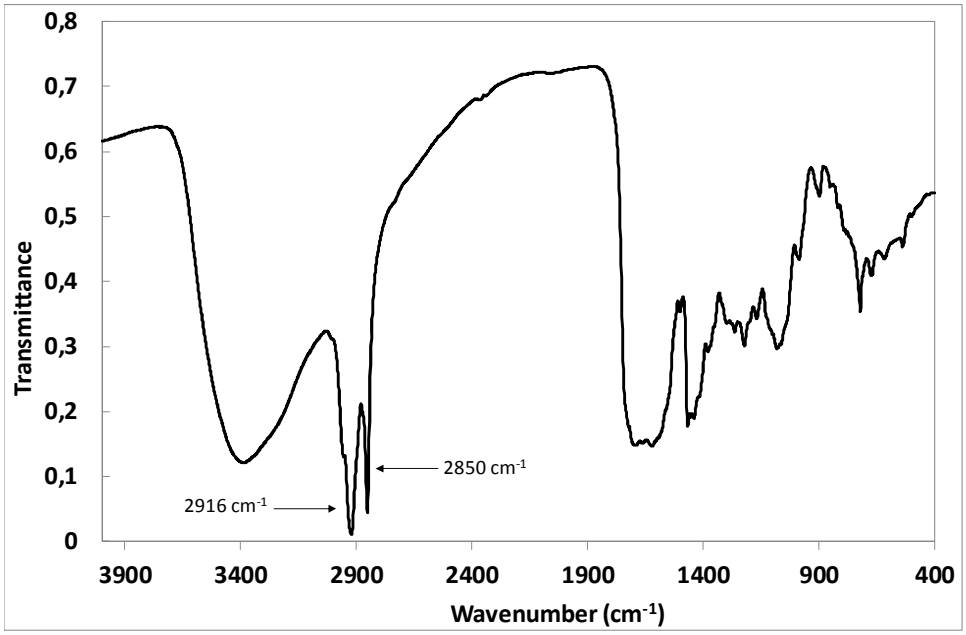


Figure S2: FT-IR spectrum of the chloroform insoluble fraction of the Soxhlet extract of *Scenedesmus sp.* residues.

Table S2: Example of identified fragments after RuO_4-mediated oxidative degradation of the chloroform insoluble fraction of the Soxhlet extract of *Scenedesmus sp.* residues. The fragments have been identified by GC-MS after esterification.

Developed structure	Product	Mw (g/mol)
CH_3-$(CH_3)CH$-$(CH_2)_3$-$(CH_3)CH$-$(CH_2)_3$-$(CH_3)CH$-CO_2Me	methyl 2,6,10-trimethylundecanoate	242
CH_3-$(CH_3)CH$-$(CH_2)_3$-$(CH_3)CH$-$(CH_2)_3$-$(CH_3)CH$-CH_2-CO_2Me	methyl 3,7,11-trimethyldodecanoate	256
CH_3-$(CH_3)CH$-$(CH_2)_{10}$-CO_2Me	methyl 12-methyltridecanoate	242
CH_3-$(CH_3)CH$-$(CH_2)_3$-$(CH_3)CH$-$(CH_2)_3$-$(CH_3)(OCH_3)C$-$(CH_2)_2$-CO_2Me	methyl 4,8,12-trimethyltridecanoate	270
CH_3-$(CH_2)_{13}$-CO_2Me	methyl pentadecanoate	256
CH_3-$(CH_2)_{10}$-$(CH_3)CH$-$(CH_2)_3$-CO_2Me	methyl 5-methylhexadecanoate	284
CH_3-$(CH_2)_{14}$-CO_2Me	methyl hexadecanoate	270
CH_3-$(CH_2)_8$-CH=CH-$(CH_2)_6$-CO_2Me	methyl 8-octadecenoate	296
CH_3-$(CH_2)_2$-$(CH_3)CH$-$(CH_2)_{12}$-CO_2Me	methyl 14-methylheptadecanoate	270
MeO_2C-$(CH_2)_{20}$-CO_2Me	dimethyl docosanedioate	398
MeO_2C-$(CH_2)_{18}$-CO_2Me	dimethyl eicosanedioate	370

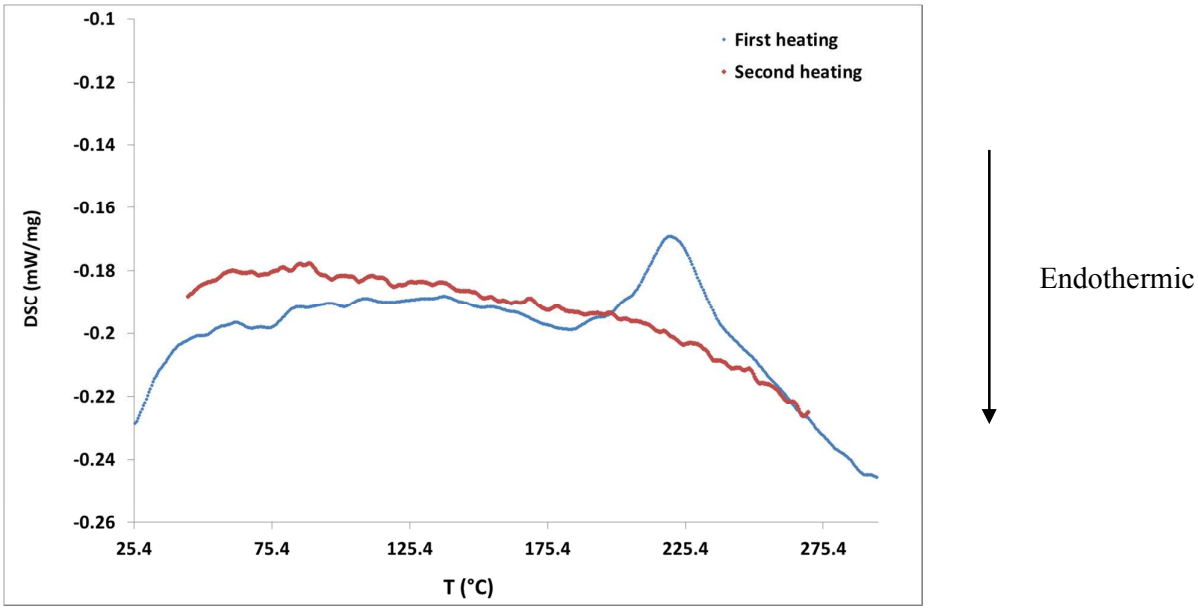


Figure S3: DSC plot of a water/microalgae mixture (4 mL g^{-1}): (red) first scan, (blue) second scan

Table S3: Results from the central composite experimental design used for the HTL of the *Scenedesmus sp.* microalgae residues in a 50 mL autoclave (DSF: dichloromethane soluble fraction, WSF: water soluble fraction, ISR: Insoluble solid residues).

Standard order	Random order	T (°C)	Hold Time	Initial N_2 pressure	Reaction pressure	DSF yield	WSF yield	ISR yield	Total yield

			(min)	(bar)	(bar)	(%)	(%)	(%)	(%)
1	9	260	20	1	47	29	21	25	75
2	14	260	20	30	94	40	21	16	77
3	1	260	40	1	48	28	nd	28	nd
4	19	260	40	30	93	37	20	15	72
5	15	290	20	1	71	39	17	20	76
6	11	290	20	30	127	45	19	9	73
7	8	290	30	1	71	39	17	13	69
8	3	290	30	30	124	45	7	13	65
9	13	250	0	10	54	34	20	20	74
10	20	300	60	10	116	43	13	7	63
11	16	275	0	10	67	37	20	17	74
12	10	275	60	10	78	43	16	9	68
13	2	275	30	0.8	60	36	12	20	68
14	6	275	30	50	168	45	18	9	72
15	4	275	30	10	74	38	16	15	69
16	5	275	30	10	78	42	16	15	73
17	7	275	30	10	72	39	19	15	73
18	12	275	30	10	76	44	18	11	73
19	17	275	30	10	78	41	19	12	72
20	18	275	30	10	74	41	18	11	70

Experimental runs 15-20 correspond to the set of center points (T = 275 °C, initial N_2 pressure = 10 bar, hold time = 30 min - **6 replicates**), which allows to assess the precision of the yield of the water soluble fraction, the dichloromethane soluble fraction, and the insoluble solid residues, with average values of 18±1, 41±1.7 and 13±1.7 %, respectively.

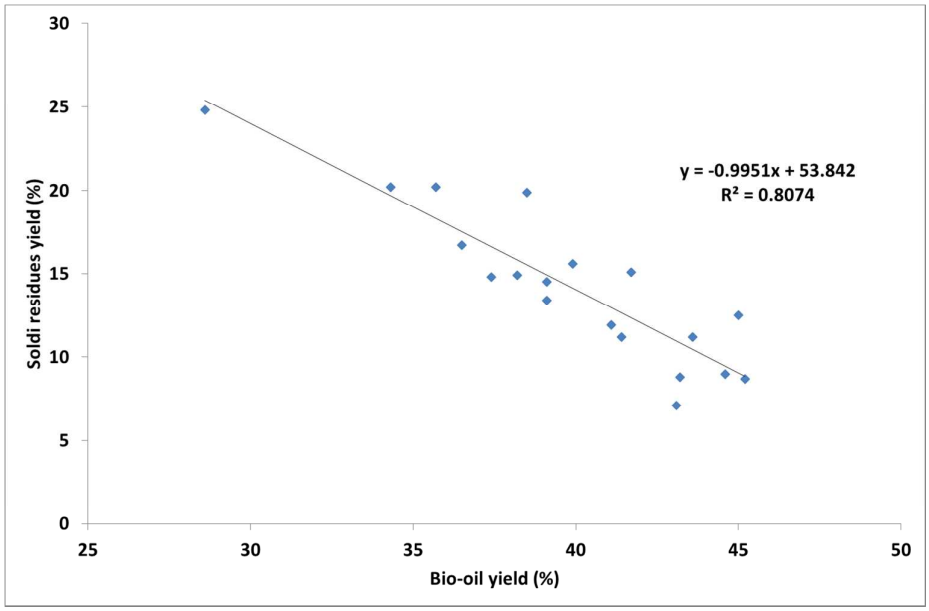


Figure S4: Plotting of the solid residues yield *versus* the dichloromethane soluble fraction yield, from the central composite experimental design used for the HTL of the *Scenedesmus sp.* microalgae residues in a 50 mL autoclave.

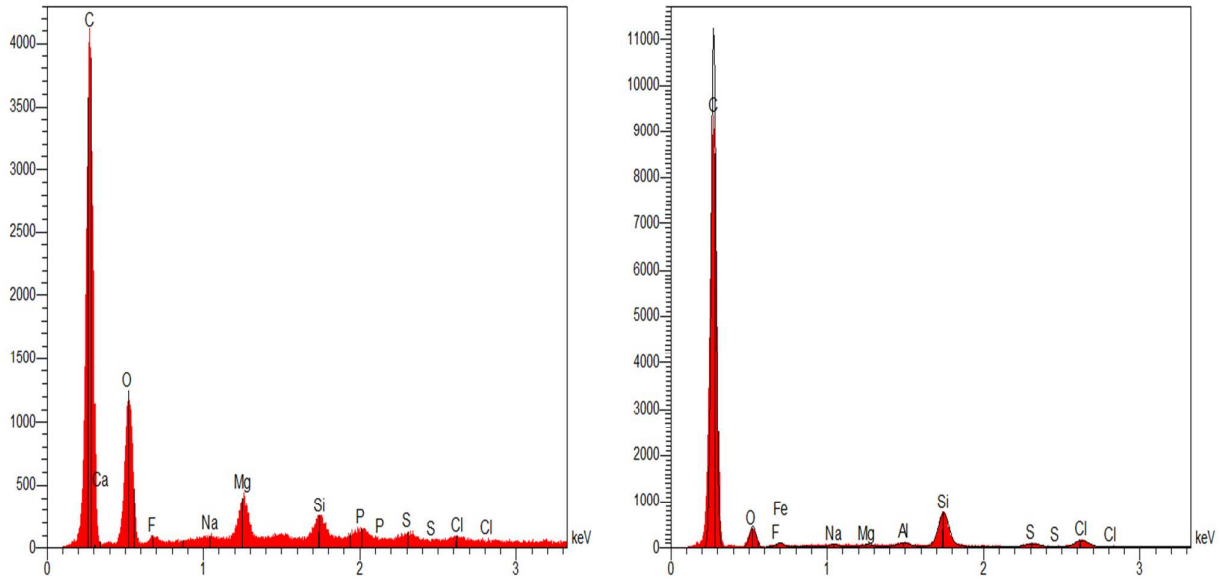


Figure S5: Left: Energy Dispersive X-ray analysis of the *Scenedesmus sp.* HTL fraction (260 °C) insoluble in both water and dichloromethane; Right: Energy Dispersive X-ray analysis of the *Scenedesmus sp.* HTL fraction (260 °C) insoluble in both water and dichloromethane, after HCl treatment. Measurements were performed using a JEOL JSM 5800 LV scanning electron microscope equipped with a SDD energy dispersive spectrometer SAMx.

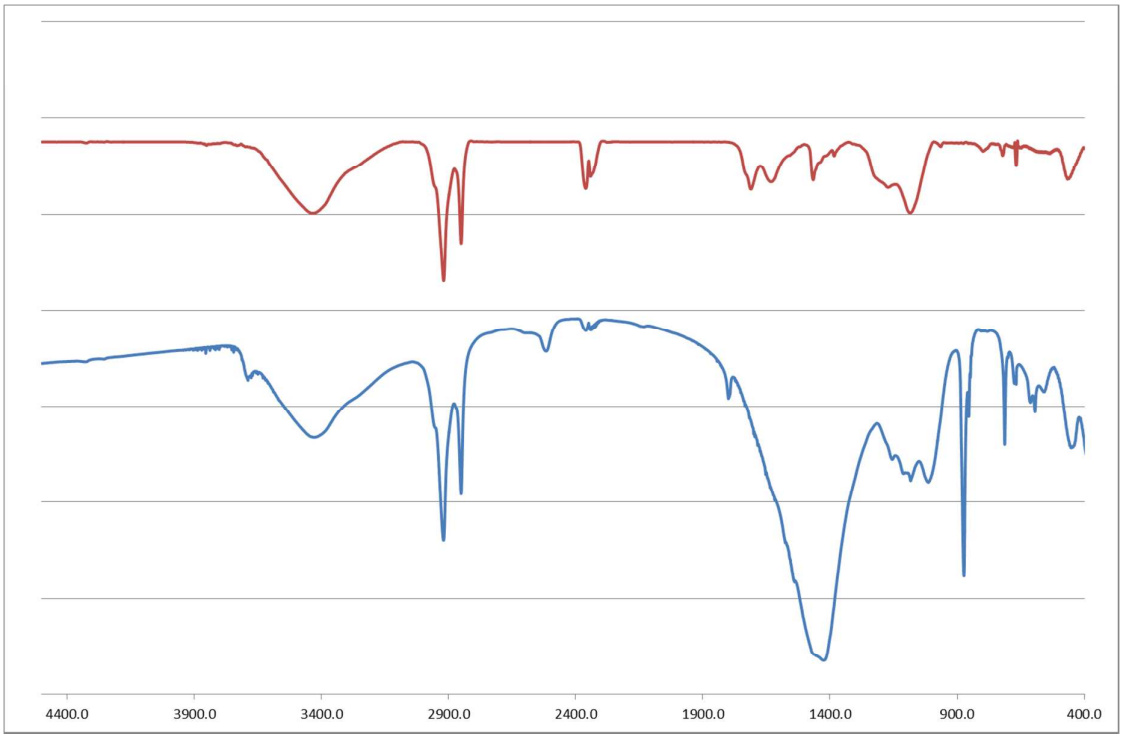


Figure S6: Blue curve: FTIR spectrum of the *Scenedesmus sp.* HTL fraction (280 °C) insoluble in both water and dichloromethane ; Red curve: FTIR spectrum of the *Scenedesmus sp.* HTL fraction (280 °C) insoluble in both water and dichloromethane, after HCl treatment.

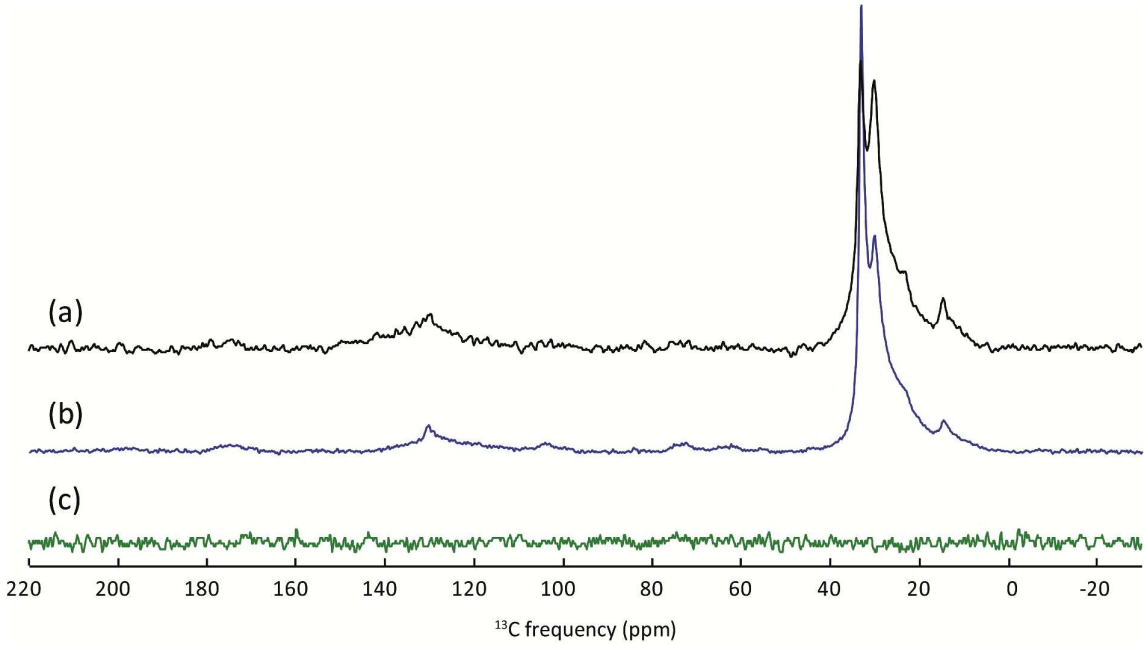


Figure S7: (a) ^{13}C quantitative MAS, (b) ^{13}C-{^{1}H} CP-MAS and (c) ^{13}C-{^{1}H} refocused INEPT MAS NMR spectra of the *Scenedesmus sp.* HTL fraction (260 °C) insoluble in both water and dichloromethane, after HCl treatment.

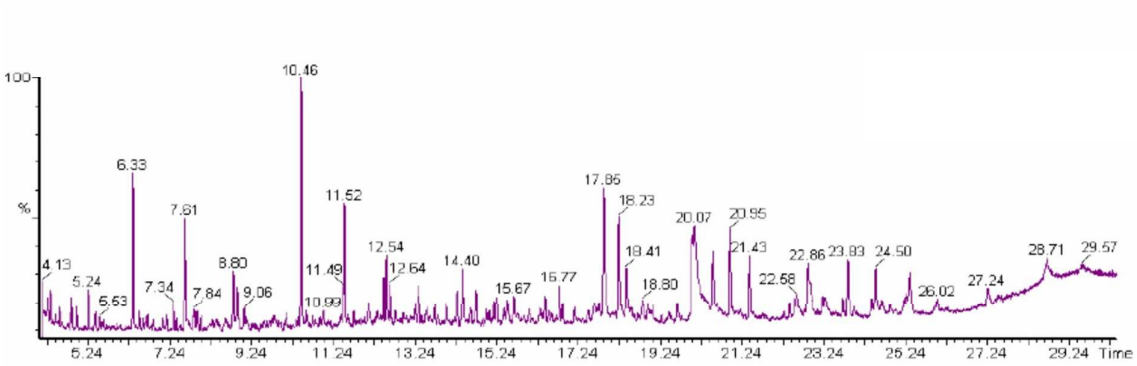
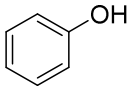
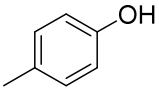
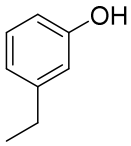
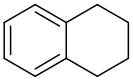
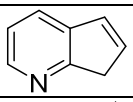
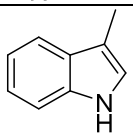
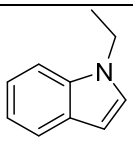
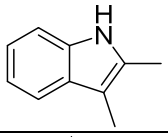
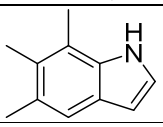
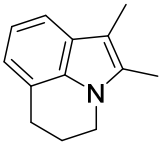
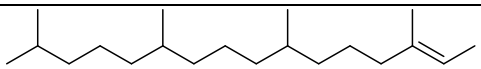
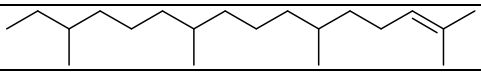
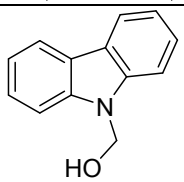
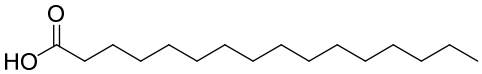
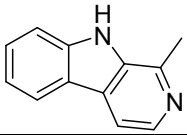
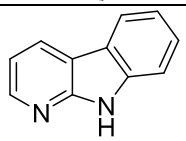
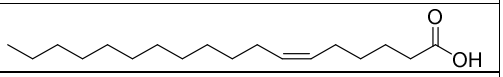
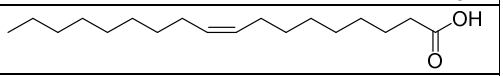
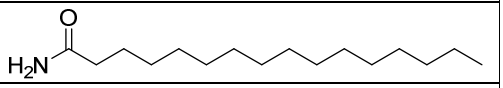
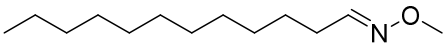
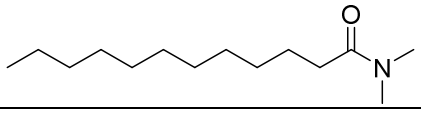
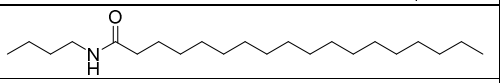


Figure S8: Typical GC-MS chromatogram obtained for the part of the water insoluble HTL fraction solubilized in dichloromethane. Some examples of products identified by MS is given in the table below.

Retention time (min)	Name	Structure
6.33	phenol	
7.61	4-methylphenol	
8.81	3-ethylphenol	
8.89	1,2,3,4-tetrahydronaphtalene	
10.46	5H-cyclopenta[b]pyridine	
11.52	3-methyl-1H-indole	
12.54	N-ethyl-1H-indole	
12.64	2,3-dimethyl-1H-indole	
13.33	5,6,7-trimethyl-1H-indole	
14.39	2,3-dimethylindole-1,7-trimethylene	
16.27	3,7,11,15-tetramethyl-2-hexadecene	
16.42	2,6,10,14-tetramethyl-2-hexadecene	
16.77	9H-carbazole-9-methanol	
17.85	palmitic acid	

18.23	1-methyl-9H-pyrido[3,4-B]indole	
18.41	9H-pyrido[2,3,b]indole	
20.00	6-octadecenoic acid	
20.05	Oleic acid	
20.51	hexadecanamide	
20.95	dodecanal O-methyl oxime	
21.39	N,N-dimethyldodecanamide	
22.86	N-butyloctadecanamide	
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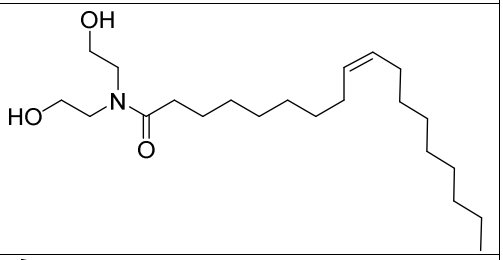
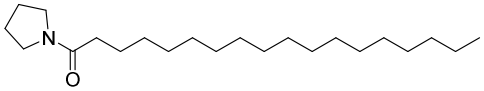
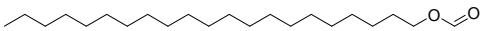
23.74	Oleic diethanolamide	
24.41	1-(1-oxooctadecyl)pyrrolidine	
25.20	1-heneicosylformate	

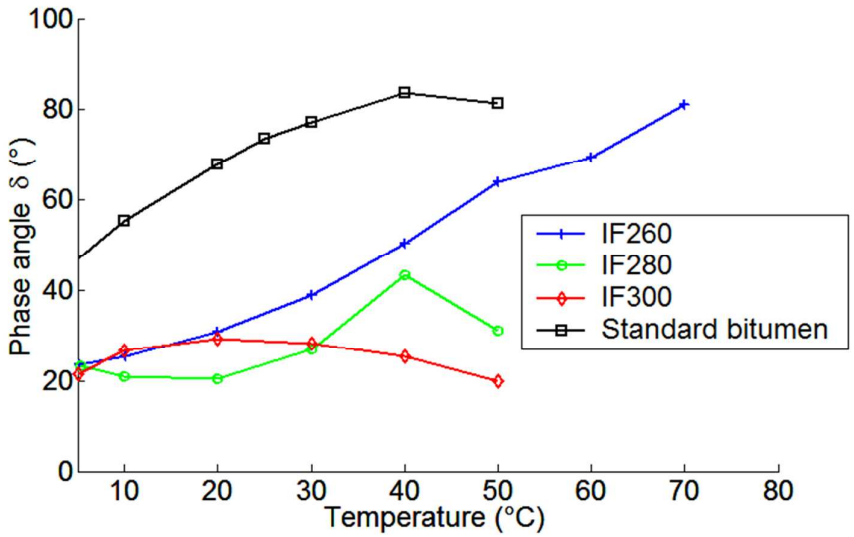


Figure S9: Phase angle versus temperature at 1 Hz, for the water insoluble HTL fractions (IF260, IF280, IF300) compared to a standard bitumen.