Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information

TGA analysis of the polar biocrude arising from dichloromethane extraction of the combined aqueous and solid phases, post heptane fraction removal, was performed. These results are shown in Figure SI_1. Due to the presence of low molecular weight oxygenates, the polar biocrude appears to contain a large proportion of lighter boiling fractions, although these fractions cannot be considered to be equivalent to heavy naphtha (90–200 °C) and kerosene (200–270 °C) due to their high hetero atom content. The tendency for polymerisation of the low molecular weight oxygenates under distillation conditions results in the observation of a significant amount of distillation residue (b. p. >540 °C) in this sample as well.

To date this more polar biocrude has not been upgraded further, but may be a useful source of raw materials for the preparation of renewable chemicals as an adjunct to the production of fuels from the non-polar fraction.

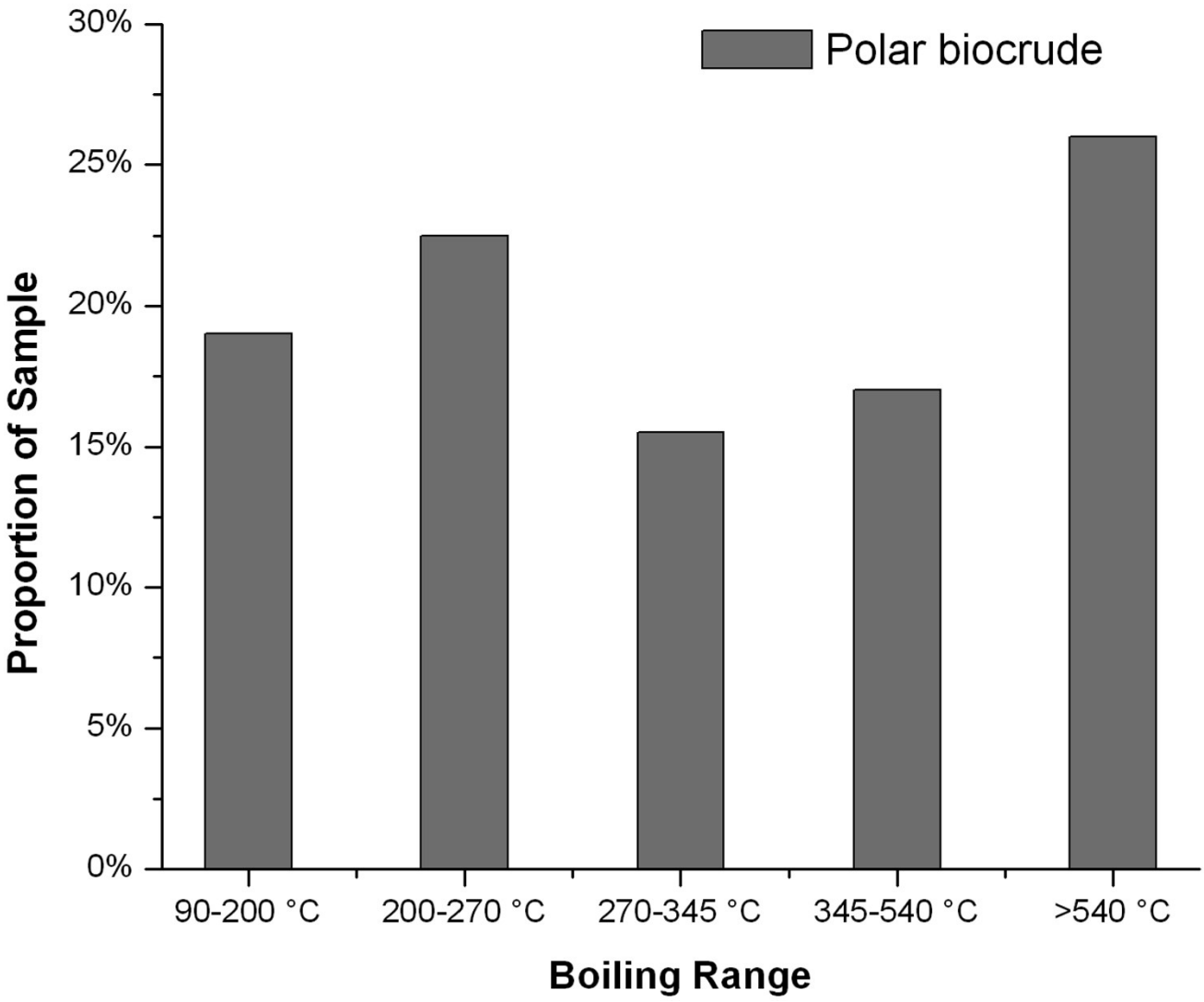

Figure SI_1. TGA boiling range analysis of undistilled polar biocrude samples taken from the aqueous phase and solid material after separation of the *n*-heptane fraction.

^{1}H NMR Analysis

The composition of the non-polar biocrude samples, polar biocrude and residual aqueous phase was assessed by means of quantitative ^{1}H NMR analysis. NMR spectra were collected using a Bruker 300 MHz instrument at about 300 K after 32 scans. ^{1}H NMR was carried out using 90° flip angle with a recycle delay (D1) of 10 seconds. The $CDCl_3$ was used in most of the sample preparations, but CD_2Cl_2 and CD_3CN were also employed in some cases due to the low solubility of certain mixtures in $CDCl_3$. Example spectra are shown in Figure SI_2

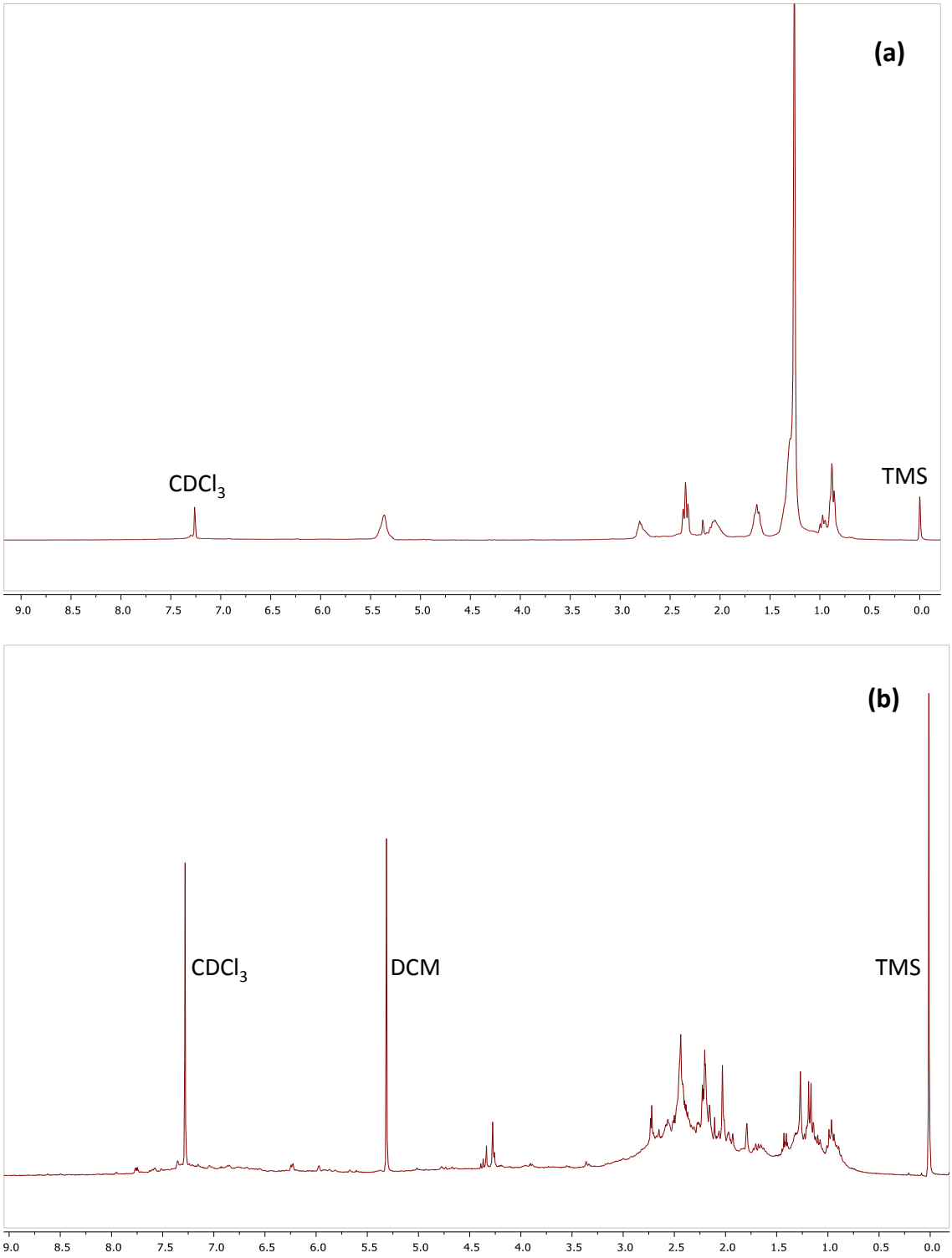

Figure SI_2. ^{1}HNMR spectra of distilled non-polar biocrude (a), polar biocrude (b)

Table SI_1 illustrates the quantitative group analyses of the spectra shown in Figure SI_2. The non-polar biocrude has > 90% of aliphatic protons that include saturated hydrocarbons and methylene and methyl-protons *alpha* to a carbonyl group. The non-polar biocrude generally contain very small amount of O–R protons (<0.1%) and some olefinic and aromatic protons. The only significant difference between the distilled and undistilled samples is the slight reduction in the already low proportion of aromatic compounds present.

Conversely, there are a greater proportion of aromatic compounds in the polar fraction. Corresponding to phenolics and heterocyclic compounds. Additionally the polar fraction also contains a greater proportion of O–R protons but fewer olefinic protons. The residual aqueous fraction contains predominantly low molecular-weight oxygenates and some polar aromatic compounds. Actual species able to be identified in the aqueous phase by ^{1}H NMR include: lactic acid, acetic acid, hydroxyacetone, acetone, methanol, glycerol, ethylene glycol, glycolic acid, hydroquinone, catechol, and formic acid.

Table SI_1. Proton distribution according to chemical shift range of oils resulting from HTU of *Oedogonium* (*N*–) with different co-solvents

Fraction	**Process**	**Aliphatic protons (0–3.5 ppm)**	**O–R protons (3.5–4.5 ppm)**	**Olefinic protons (4.5–6.5 ppm)**	**Aromatic protons (6.5–8.5 ppm)**	**Aldehyde protons (> 9 ppm)**
Heptane	Undistilled	92.4	< 0.1	2.8	4.9	< 0.1
Heptane	Distilled	93.3	< 0.1	4.5	2.2	< 0.1
DCM	Extracted	89.0	2.5	0.7	7.8	< 0.1
Aqueous	Separated	62	31	>0.1	5	2

For the aqueous phase samples, ^{1}H NMR spectra were recorded on a 400 MHz Bruker spectrometer (resonance frequency 400.13 MHz) equipped with a 5 mm inverse ^{1}H-X auto-tuning broadband probe. All experiments were performed at 25 °C. The samples were diluted with D_2O (H_2O:D_2O 1:1), then filtered through a PTFE syringe filter (0.45 µm pore size, 13 mm diameter). The spectra were acquired in 32 scans, under solvent suppression, with a 90° pulse and 2.4 s decay delay. Water-soluble compounds were identified by comparison of sample spectra to the spectra of commercially available compounds, and identification was confirmed by spiking the sample solution with an aliquot of the authentic compound.

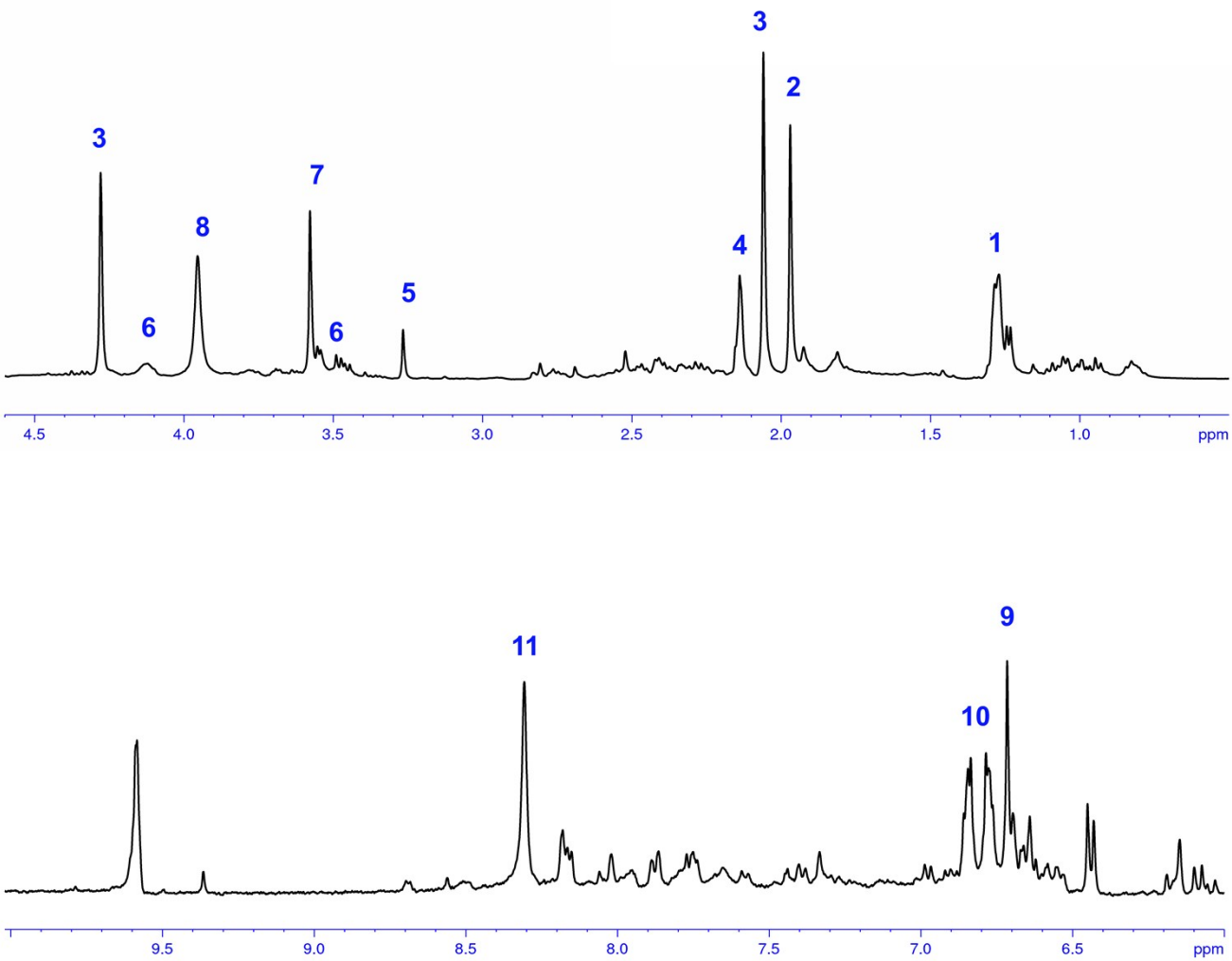

Figure SI_3. Aqueous phase NMR with water suppression: "aliphatic region" (*top*); "aromatic region" (*bottom*). Resonances from the identified species are labelled from 1–11, which are listed in Table SI_2 below.

Table SI-2. Compounds identified by ^{1}H-NMR in the separated aqueous phase

Label[a]	Compound name
1	lactic acid
2	acetic acid
3	hydroxyacetone
4	acetone
5	methanol
6	glycerol
7	ethylene glycol
8	glycolic acid
9	hydroquinone
10	catechol
11	formic acid

[a] label as displayed in the NMR spectra (Figure SI-3)

GCMS Analysis

GC-MS analysis was carried out on the non-polar biocude, the polar biocrude and the aqueous phases from *N*– *Oedogonium* HTL. The products identified are listed in **Table SI_3** and were categorized by functional group. A box highlighted in green indicates that the retention time and molecular weight of the compound were validated and consistent with an authentic sample. A box highlighted in yellow indicates that the compound is highly likely to be present in the sample, but has not been validated with an authentic sample. An "N" indicates the amount of this compound was negligible. Both the biocrudes contain a number of saturated and unsaturated cyclic ketones such as 3-methyl-1,2-cyclopentenedione and 3-ethyl-2-hydroxy-2-cyclopenten-1-one. Furans like 2-acetyl-5-methylfuran are present in very small amount in these biocrudes. Other aromatic compounds such as phenol are also present in these mixtures. Most of the cyclic ketones found in the non-polar biocrude (e.g. 2,3-dimethyl-2-cyclopenten-1-one) are also present in the polar DCM extract. In addition, less branched cyclic ketones such as cyclopentanone and cyclohexanone are found in the polar biocrude. There are also significant amount of lactones and furans, for example gamma-valerolactone and furfural, which are not present in the non-polar biocrude. The DCM extract also contains a number of other aromatic compounds, most of which are also present in the non-polar fractions.

Table SI_3. List of compounds identified in non-polar & polar biocrudes and aqueous phases from *Oedogonium* (*N*–) by GCMS

		Fraction		
Group	**Compound**	**Non-polar**	**Polar**	**Aqueous**
Acids	Acetic acid			
Ketones	hydroxyacetone			
	1-hydroxy-2-butanone			
	2,5-hexanedione			
	cyclopentanone			
	cyclohexanone			
	1,4-cyclohexanedione			
	2-cyclopenten-1-one			
	2-methyl-2-cyclopenten-1-one			
	2,3-dimethyl-2-cyclopenten-1-one			
	3,4-dimethyl-2-cyclopenten-1-	N		

	one			
	3-methyl-1,2-cyclopentanedione			
	3-ethyl-1,2-cyclopentanedione			
	2,4-dimethyl-1,3-dicyclopentanedione	N		
	3-ethyl-2-hydroxy-2-cyclopenten-1-one			
Lactone	gamma-valerolactone			
	2,3-dimethyl-4-hydroxy-2-butenoic lactone			
Furans	furfural			
	5-methylfurfural			
	5-(hydroxymethyl)furfural			
	2-acetylfuran			
	2-acetyl-5-methylfuran	N	N	
	2-furyl hydroxymethyl ketone			
Other Aromatics	benzaldehyde		N	
	benzyl alcohol	N	N	
	phenol			
	m-cresol	N		
	o-cresol	N	N	
	phenylethyl alcohol		N	
	catechol			
	4-methylcatechol			
	hydroquinone		N	
	2-methylhydroquinone			
	guaiacol	N	N	
	2-methoxy-4-methylphenol	N		
	4-ethyl guaiacol	N		

Due to the complex nature of the samples Table SI_3 must be interpreted with the understanding that the failure to detect a compound in any given sample does not necessarily indicate complete absence of that compound in the sample. It should also be noted that a

particular compound may be a closely related isomer (or isomeric mixture) of the one specified in the table.

Table SI_4 .Elemental analysis of the non-polar biocrude distillation residue

Sample[a]	**%C**	**%H**	**%O**[b]	**%N**	**%S**
1	84.4	5.1	4.4	3.7	< 0.1
2	86.9	3.7	4.3	2.4	<0.1

[a] Contains inorganic material

[b] Measured value