Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Microwave-Assisted Pyrolysis and Analytical Fast Pyrolysis of Macroalgae: Product Analysis and Effect of Heating Mechanism

Ribhu Gautam,[1] S. Shyam,[1] B. Rajasekhar Reddy,[1] Kasivelu Govindaraju[2] and R. Vinu[1,*]

[1]*Department of Chemical Engineering, National Center for Combustion Research and Development, Indian Institute of Technology Madras, Chennai–600036, India*

[2] *Centre for Ocean Research, Sathyabama Institute of Science and Technology, Chennai–600119, India*

[*]Corresponding Author: Dr. R. Vinu, Email: vinu@iitm.ac.in, Phone: +91-44-22574187

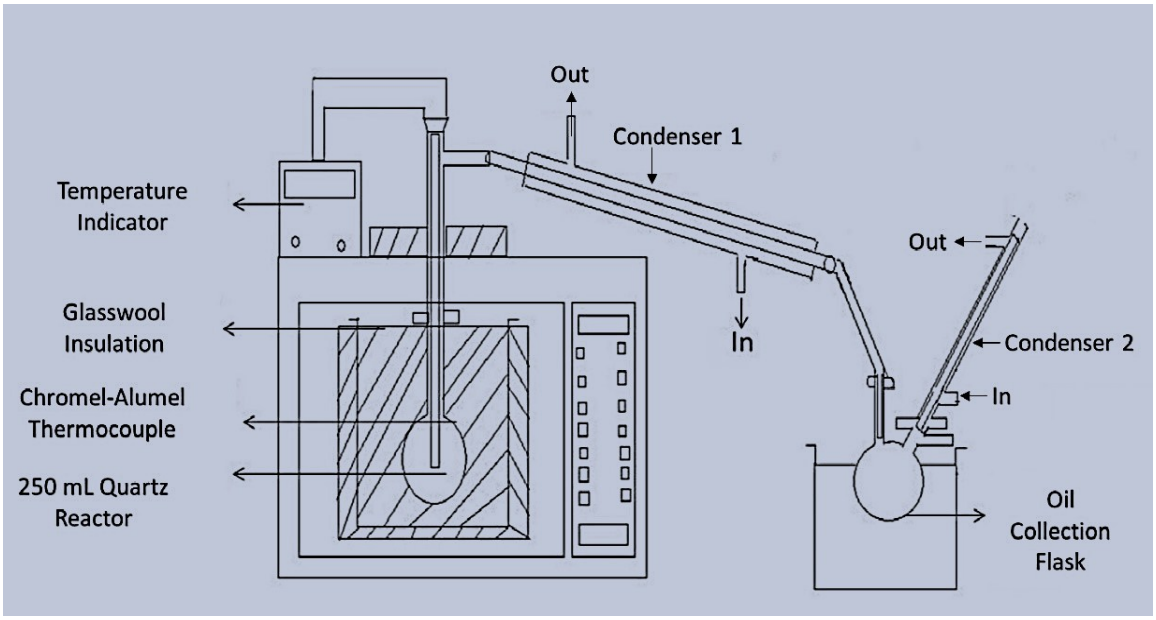

Figure S1. Schematic of the experimental setup used for microwave-assisted pyrolysis.

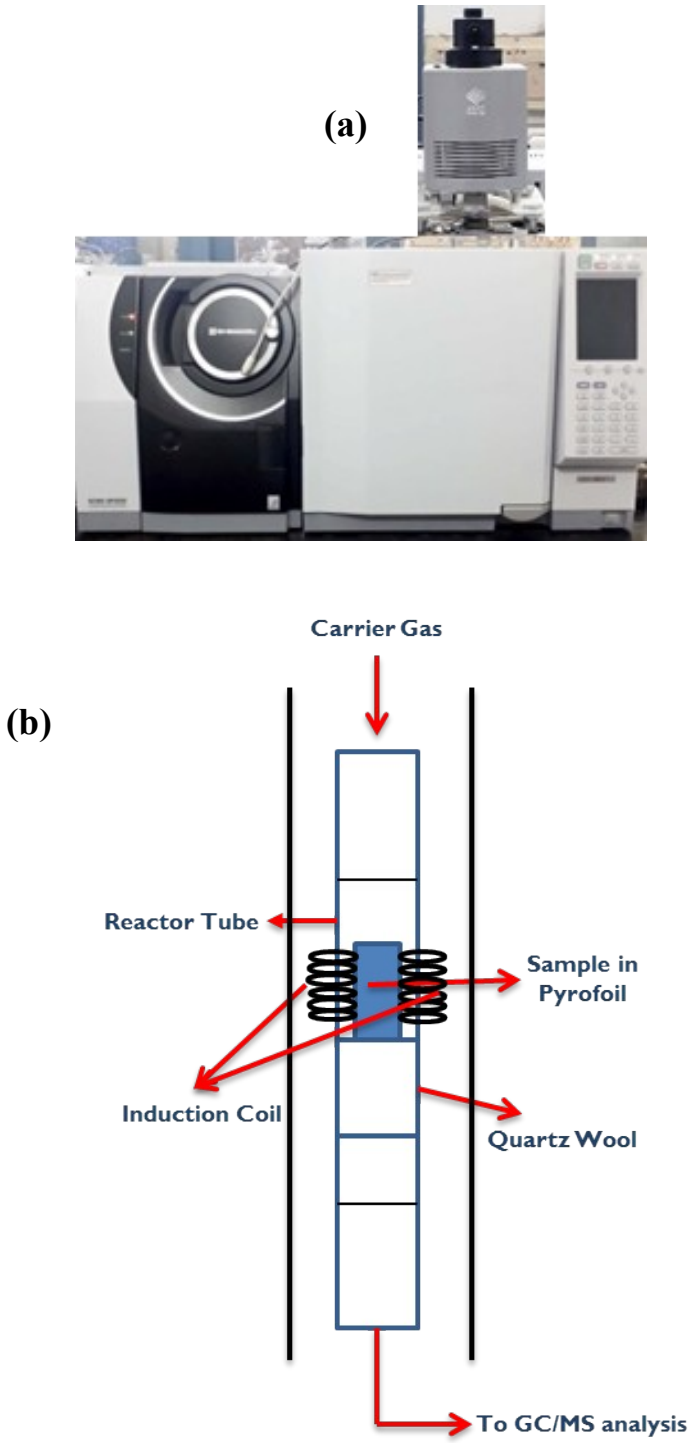

Figure S2. (a) Snapshot, and (b) schematic of JHI-07 Curie point pyrolysis-GC/MS system

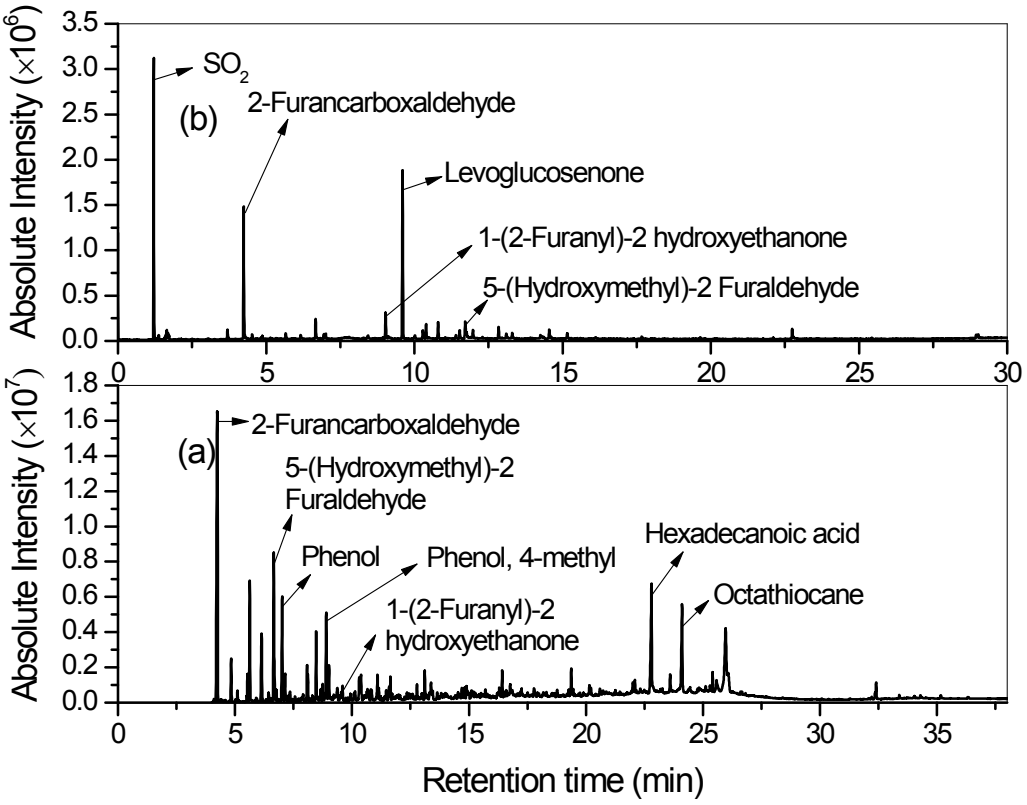

Figure S3. Total ion chromatograms obtained from (a) GC/MS of bio-oil from MAP of *K. alvarezii*, and (b) Py-GC/MS of *K. alvarezii*.

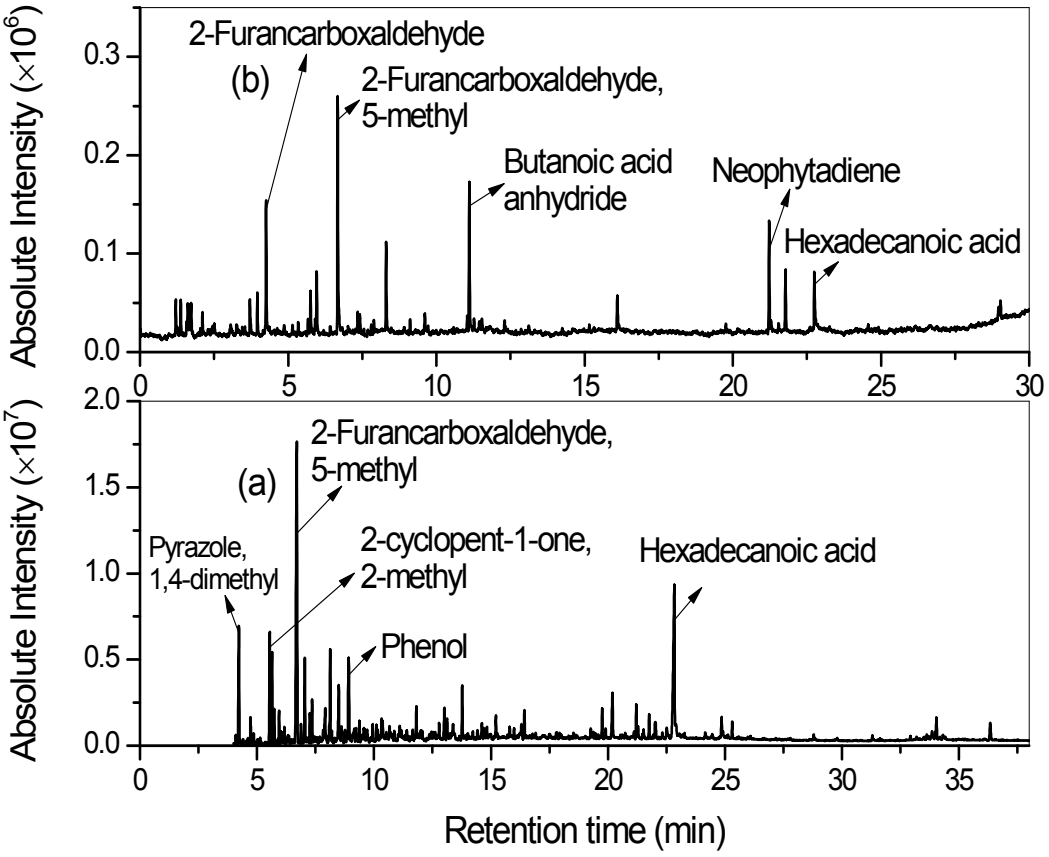

Figure S4. Total ion chromatograms obtained from (a) GC/MS of bio-oil from MAP of *S. wightii*, and (b) Py-GC/MS of *S. wightii*.

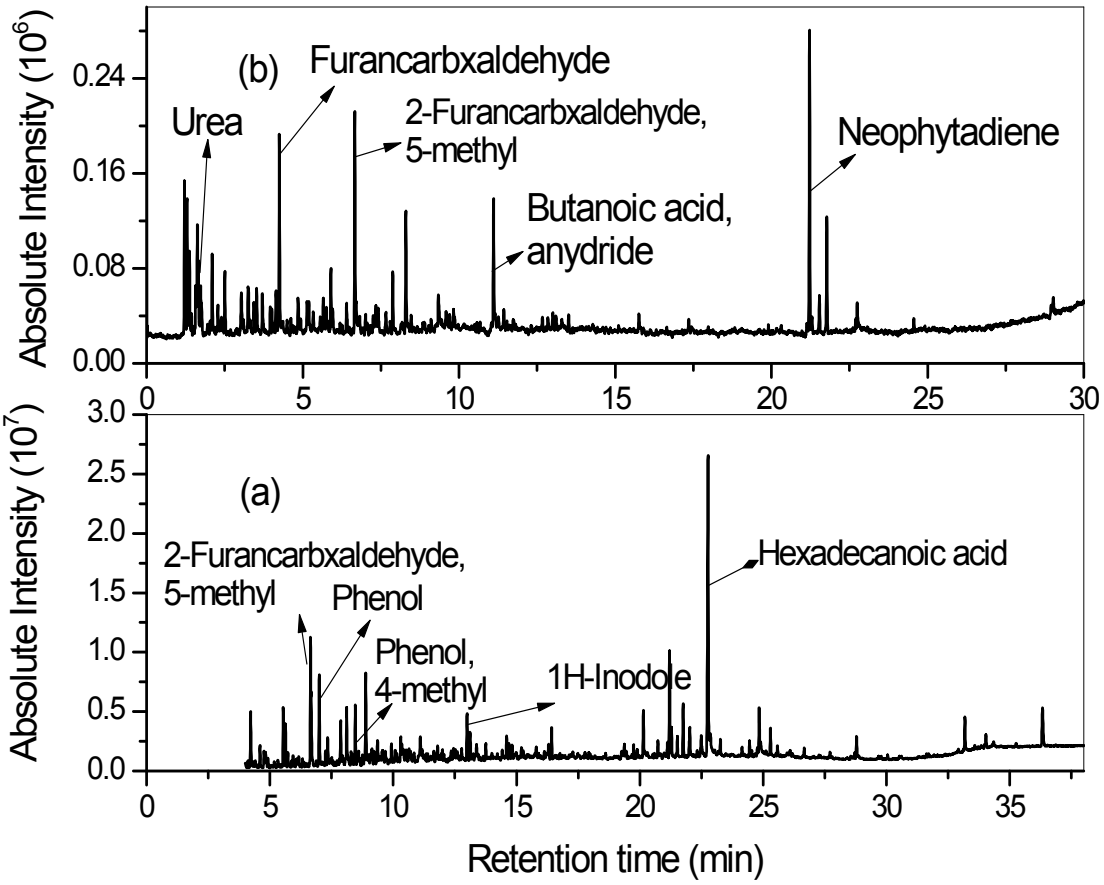

Figure S5. Total ion chromatograms obtained from (a) GC/MS of bio-oil from MAP of *T. ornata*, and (b) Py-GC/MS of *T. ornata*.

Table S1. Composition of pyrolysates obtained from microwave-assisted pyrolysis of the macroalgae. The data are presented as the mean ± S.D, n = 3.

	Selectivity %		
Compounds	***K. alvarezii***	***T. ornata***	***S. wightii***
Alcohols			
Octadecanol	0.64±0.03		
1-Dodecanol, 3,7,11-trimethyl-		0.43±0.02	0.9±0.08
2-Hexadecen-1-ol, 3,7,11,15-tetramethyl-, [r-[r*r*-(e)]]-		1.84±0.10	
1-Hexadecanol, 3,7,11,15-tetramethyl-			0.16±0
Aldehydes/ketones			
4-Cyclopentene-1,3-dione #	0.33±0		
2-Cyclopenten-1-one, 2-methyl-	1.05±0.13	1.83±0.14	3.50±0.45
2-Cyclohexen-1-one			0.56±0.08
2-Cyclopenten-1-one, 3,4-dimethyl-		0.56±0.06	0.80±0.30
3,4-Dimethyl-2-cyclopenten-1-one	0.24±0.04		0.86±0.07
Cyclohexanone, 4-methylene-	0.2±0		
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-			1.68±0.12
2-Cyclopenten-1-one, 2,3-dimethyl-	0.76±0.10	2.90±0.33	4.63±0.42
2-Cyclopenten-1-one, 2,3,4-trimethyl-		1.47±0.14	1.14±0.10
Ethylcyclopentenolone		0.38±0.02	
1-Cyclohexene-4-carboxaldehyde, 1-methyl-		0.57±0.08	
2-Pentadecanone, 6,10,14-trimethyl-			0.98±0.12
Ethanone, 1-(2-hydroxyphenyl)-	0.20±0.02		
Ethanone, 1-(3-methylphenyl)-	0.34±0.04		
Cyclopentadecanone, 2-hydroxy-			0.60±0.05

Benzene derivatives			
p-xylene		0.38±0.02	
Benzene, ethenyl-		0.30±0	
Phenol	3.80±0.04	3.12±0.20	3.23±0.12
Phenol, 2-methyl-	2.23±0.28	2.28±0.22	2.65±0.30
Ethanone, 1-phenyl-	0.6±0.05		
2-oxazolin-5-one, 2-phenyl-		0.40±0.04	
Phenol, 4-methyl-	3.80±0.42	4.03±0.34	4.4±0.44
2,6-Dimethylphenol	0.30±0.02		
Phenol, 3-ethyl-		0.44±0.05	
Phenol, 2-ethyl-	0.25±0.02		
Phenol, 2,4-dimethyl-		1.20±0.10	0.53±0.06
Phenol, 3,4-dimethyl-	1.40±0.14	0.60±0.07	0.90±0.08
Phenol, 2,6-dimethyl-	0.60±0.07		0.83±0.05
2-Methylindene		0.40±0.02	
1H-Indene, 1-methyl-		0.38±0.02	
Benzene, (1-methylene-2-propenyl)-		0.50±0.04	
Phenol, 4-ethyl-	0.28±0.02	0.30±0	0.28±0.0
Phenol, 3,5-dimethyl-	0.26±0.02		
Phenol, 3,4,5-trimethyl-		0.42±0.03	
Naphthalene	0.8±0.07	0.93±0.10	0.44±0.02
1,3-benzenediol		0.55±0.06	
Benzene, 1-ethyl-4-methoxy-	0.23±0.12		
1H-Indene, 4,7-dimethyl-		0.45±0.03	
Naphthalene, 1,2-dihydro-6-methyl-		0.58±0.03	
Phenol, 2,4,5-trimethyl-	0.23±0.03		
Phenol, 3,4-dimethyl-,			0.20±0.10

methylcarbamate			
Ethanone, 1-phenyl-			0.48±0.04
Trimethylphenol (2,3,5)			0.23±0
1H-Inden-1-one, 2,3-dihydro-	0.44±0.02	0.3±0.02	
2-Methylnaphthalene	1.09±0.12		
4-Hydroxy-3-methylacetophenone	0.3±0.02		
Naphthalene, 1-methyl-	0.60±0.05	1.68±0.10	1.34±0.12
1,1'-Biphenyl	0.3±0.02		
(Z)-3-Phenyl-2-propenoic acid	0.45±0.02		
Naphthalene, 1,7-dimethyl-	0.33±0.04		
Naphthalene, 2,6-dimethyl-	0.24±0		
1,4-Dimethylnaphthalene		0.42±0.05	
Acenaphthylene	0.30±0.1		
1-Naphthalenol	0.22±0.01		
1-Naphthalenol, 2-methyl-	0.40±0.04		
Anthracene	0.24±0.02		
Carboxylic acids			
Tetradecanoic acid	0.27±0.01	1.63±0.14	2.17±0.24
Myristoleic acid		1.13±0.10	
Hexadecanoic acid	6.02±0.25	14.4±1.30	10.74±0.93
6-Octadecenoic acid, (Z)-		2.00±0.20	
Furan derivatives			
2-Furancarboxaldehyde	18.78±1.10		
2-Furanmethanol			0.22±0.12
Furan, 2-ethyl-			0.38±0.10
Ethanone, 1-(2-furanyl)-	4.30±0.47	1.76±0.10	2.93±0.30
2(3H)-Furanone, 5-methyl-			0.30±0.02

2(5H)-Furanone, 5-methyl-	4.56±0.23		
2(3H)-Furanone, dihydro-5-methyl-	0.4±0.04		
2-Furancarboxaldehyde, 5-methyl-	6.47±0.84	7.00±0.47	19.14±1.30
2(5H)-Furanone, 3-methyl-			0.48±0.08
Ethanone, 1-(5-methyl-2-furanyl)-	1.13±0.20		
Methyl-2(5H)-furanone			0.37±0.05
[(Furan-2-carbonyl)methylamino]acetic acid			0.46±0.10
Ethanone, 1-(2-furanyl)-2-hydroxy-	1.10±0.10		
Benzofuran, 2-methyl-	0.53±0.06		
Benzofuran, 4,7-dimethyl-	1.80±0.14		
2-Tridecylfuran	1.07±0.10		
Hydrocarbons			
2-Pentene, 3-ethyl-4,4-dimethyl-			0.33±0.10
1,3-Hexadiene, 3-ethyl-2-methyl-, (Z)-		1.07±0.14	
Tetradecane	0.5±0.14	0.60±0.08	0.42±0.00
Cyclopentane, nonyl-	0.30±0.02		
2,6,10-Trimethyltridecane		0.26±0.10	0.5±0.08
1-Hexadecene	0.50±0.03	0.37±0.02	0.35±0.04
Pentadecane	0.90±0	1.06±0.13	
Hexadecane		0.54±0.05	0.83±0.10
Cyclopentane, decyl-	0.20±0.10		
1-Octadecene	0.20±0.08		
Heptadecane	0.95±0.10	0.45±0.02	
Nonadecane			0.30±0.07
(2e)-3,7,11,15-Tetramethyl-2-hexadecene #		1.70±0.1	0.87±0.07
Neophytadiene		4.27±0.20	3.05±0.14

Pentadecane, 8-hexyl-		1.40±0.10	
Heneicosane		0.60±0.07	
Docosane		0.35±0.03	
Hexacosane		0.30±0.05	
N-containing compounds			
Pyrazine, methyl-		0.25±0.04	0.27±0.03
Pyrazole, 1,4-dimethyl-			5.24±0.20
Pyridine, 3-methyl-		0.70±0.07	1.08±0.18
L-leucine, ethyl ester		0.63±0.05	
1H-Pyrrole, 2,5-dimethyl-			0.22±0
Pyridine, 2,4-dimethyl-			0.36±0.04
Pyridine, 2,3-dimethyl-			0.22±0.07
2(1H)-Pyrimidinone	0.40±0.02		
1-Acetyl-1H-Imidazole			0.35±0.05
1H-Pyrrole, 2-ethyl-4-methyl-		0.40±0.04	
Ethanone, 1-(1H-pyrrol-2-yl)-			0.28±0.04
2-[(Cyano-methyl-methyl)-amino]-propionitrile		0.40±0.02	
Dihydroxy-5,6-dihydrouracil		0.77±0.03	
Benzeneacetonitrile	0.30±0.04		
Benzene, 1-isocyano-2-methyl-		0.42±0.05	
5,7-Dimethyl-1H-indazole			0.33±0.12
2,5-Dimethyl-3-cis-propenylpyrazine			1.00±0.12
Benzenepropanenitrile		0.30±0.05	
1H-Inden-1-one, 2,3-dihydro-			0.40±0.02
1H-Indole		2.03±0.30	1.23±0.20
2,5,6-Trimethylbenzimidazole	0.97±0.10		

Pyrazine, trimethyl-1-propenyl-, (e)-		0.64±0.08	1.76±0.17
Indole, 3-methyl-		0.83±0.06	0.40±0.05
2-(1H-Indol-3-yl)ethanamine hydrochloride	0.23±0.02		
Pyrrole-3-carbonitrile, 5-formyl-2,4-dimethyl-	0.45±0.07		
[1,2,4]-Triazolo[1,5-a]pyrimidine-2-carboxamide, n-butyl-			0.70±0.06
2-Allyl-3,5-dimethylpyrazine			0.32±0.05
Benzonitrile, 2,4,6-trimethyl-		0.3±0	
Tridecanenitrile		0.62±0.04	0.30±0.02
Hexadecanenitrile	0.55±0.07		
Dodecanamide		0.74±0.05	0.55±0.04
Hexadecanamide	0.2±0	0.92±0.07	0.54±0.03
3-Pyridinol, acetate (ester)	0.36±0.04		
Others			
3-Cyclopentene-1-acetaldehyde, 2-oxo-		2.46±0.23	
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-		1.64±0.14	
Formic acid, butyl ester	0.2±0		
3,7-Dimethyl-6-octen-1-yl phenylacetate	0.2±0		
4H-Pyran-4-one, 3-hydroxy-2-methyl-		0.6±0.04	
2H-Pyran-2-carboxaldehyde, 3,4-dihydro-2,5-dimethyl-	0.9±0.07		
1,4-Cyclohexadien, 6-isopropenyl-1,2,3,4-tetramethyl-	0.28±0		
Octathiocane	4.40±0.03		
Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester		0.82±0.07	

2,2,4-Trimethyl-3-(3,8,12,16-tetramethyl-heptadeca-3,7,11,15-tetraenyl)-cyclohexanol	1.25±0.13

Table S2. Composition of pyrolysates obtained from Curie point analytical pyrolysis-GC/MS of the macroalgae. The data are presented as the mean ± S.D, n = 3.

	Selectivity %		
Compounds	***K. alvarezii***	***S. wightii***	***T. ornata***
Alcohols			
1,2-Cyclohexanediol	0.74±0		
2-Butanol, 3-(2,2-dimethylpropoxy)-			2.90±0.35
1-Decanol			0.54±0.02
1,3-Cyclopentanediol, trans-			0.52±0.12
1,2-Benzenediol			0.76±0.14
Carbonyl compounds			
1,2-Cyclopentanedione		0.58±0.10	1.55±0.14
1,2-Cyclopentanedione, 3-methyl-	0.25±0.16		
1,3-cyclopentanedione, 4-hydroxy-2-methyl-			0.62±0.10
1-Phenyl-2-butanone		0.57±0.03	
2,4-Pentanedione, 3-butyl-			0.38±0.07
2-Acetyl-4-hydroxybutricacidlactone		1.26±0.04	0.80±0.20
2-Butanone, 4-(7-methoxy-2-oxepanylidene)-, (e)-			0.83±0.08
2-Butenal		0.20±0.03	
2-Butenal, 3-methyl-			0.38±0.08
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-		0.60±0	2.10±0.27
3-Heptanone, 4-methyl-	0.66±0.23	0.36±0.04	
3-Pentadecanone	1.32±0.20		
3-Pentanone, 2-methyl-			0.50±0.06
4-Cyclopentene-1,3-dione #			0.60±0.05

4-Octanone, 5-hydroxy-2,7-dimethyl-		0.64±0.13	
8-Methoxy-5,5,8-trimethyl-3-nonen-2-one	0.20±0.06		
Butanal	0.58±0		
Cyclobuta[1,2-d:3,4-d']bis[1,3]dioxole-2,5-dione, tetrahydro-		0.95±0.03	
Cyclopent-2-en-1,4-dione		0.57±0.05	0.30±0
Cyclopent-4-ene-1,3-dione	0.12±0	0.36±0.05	
Decanal		0.48±0.02	
Ethanone, 1-(2,5-dihydroxyphenyl)-			0.32±0.03
Ethylcyclopentenolone			0.67±0.16
Methyl vinyl ketone	0.86±0.06		
Pentanal			1.10±0.10
2H-Pyran-2,6(3H)-dione			0.62±0.10
2H-Pyran-2-one	0.20±0.10		
2H-Pyran-2-one, 6-heptyltetrahydro-		0.58±0.07	0.66±0.13
4H-Pyran-4-one, 3-hydroxy-2-methyl-			1.20±0.10
4H-Pyran-4-one, 5-hydroxy-2-methyl-	0.14±0		
Benzeneacetaldehyde	0.17±0		
3-Heptanone, 4-methyl-		0.36±0.04	
Carboxylic Acids			
1,2-Benzenedicarboxylic acid		2.46±0.92	
2,3-Dimethylfumaric acid	0.16±0.06		
Decanoic acid		0.32±0.05	
Hexadecanoic acid	1.08±0.075	4.42±0.85	3.18±0.42
Propanoic acid			0.90±0.10
Anhydrosugars			
Levoglucosenone	18.23±1.77	1.60±0.06	

1,6-Anhydro-.beta.-d-talopyranose	0.53±0.13	0.35±0.06	
1,6-Anhydro-.alpha.-d-galactofuranose	0.23±0.20		
D-Allose	0.34±0.02	1.40±0.13	
Levoglucosan	1.04±0.03	1.17±0.10	
Furan Derivatives			
(5z)-5-(2-Hydroxyethylidene)-2(5H)-furanone #	0.37±0		
1-(2-Furanyl)-2-hydroxyethanone	3.45±0.40		
1-(2-Furyl)-2-butanone			1.80±0.34
1-Propanone, 1-(2-furanyl)-	0.67±0.10		
2(3H)-Furanone, 5-ethenyldihydro-5-methyl-			0.53±0
2(3H)-Furanone, 5-ethyldihydro-			0.85±0.12
2(3H)-Furanone, 5-methyl-	0.74±0.14		
2(5H)-Furanone, 3-methyl-5-methylene-			0.38±0.02
2-Furancarboxaldehyde	14.86±1.15	5.90±0.18	3.97±0.65
2-Furancarboxaldehyde, 5-methyl-	2.74±0.05	16.75±0.30	6.26±0.72
2-Furanmethanol	0.11±0.02		
2-Furanmethanol, tetrahydro-		0.45±0.07	0.72±0.14
2-Methyl-3-(methylthio) furan			3.04±0.20
2-Propylfuran	0.16±0.04		
2-Tridecylfuran	0.13±0.05		
3,4-Furandimethanol	0.14±0.01		
3-Furaldehyde		1.48±0.18	0.64±0.11
5-(Hydroxymethyl)-2-furaldehyde	2.69±0.36		
5-Formyl-2-furfurylmethanoate	1.15±0.04		
5-oxo-Tetrahydro-furan-2-carboxylic acid			0.55±0.02
Ethanone, 1-(2-furanyl)-	0.67±0.03		

Ethanone, 1-(3-hydroxy-2-furanyl)-	0.59±0.04		
Furan, 2-methyl-		1.78±0.18	
Furan, 3-methyl-	0.35±0		
Methyl hexofuranoside #	0.35±0.10		
N-containing Compounds			
[4-(Aminomethyl)oxan-4-yl]methanol	0.13±0		
2,4-Imidazolidinedione, 5-methyl-5-(2-methylpropyl)-	1.08±0.27		
2-Methyl-1,2-propanediamine		0.36±0.02	
3-Hexanamine		1.68±0	2.03±0.05
4-Pyridinol			1.50±0
5-Nonylamine			1.40±0.08
5-Pyrimidinecarboxaldehyde, 1,2,3,4-tetrahydro-2,4-dioxo-			0.80±0.16
6-Azacytosine		0.50±0.10	
Diisopropylcyanamide	1.04±0.12		
Ethylamine, N,N-di(pentyl)-		0.68±0.08	
Guanosine		0.67±0.06	
Indolizine			0.60±0.12
Methanamine, n,n-dimethyl-			2.20±0.63
Methanamine, n-methyl-n-nitroso-		0.66±0.16	2.05±0.08
N-tert-Butylethylamine		0.48±0.12	1.28±0.14
Piperidine, 1-nitroso-			0.58±0.04
Urea	0.50±0.10	1.00±0.35	2.80±0.25
1H-Pyrrole, 2-methyl-			0.30±0.03
2-Acetonyl-9-[3-deoxy-.beta.-d-ribouranosyl]hypoxanthine	0.28±0.08		
2H-Pyrazole-3-carboxylic acid, 2-methyl-	0.16±0.03		

Pyrazine, methyl-			0.94±0.14
Butanoic acid, 2,3-dimethyl-4-nitro-, 1,1-dimethylethyl ester	1.36±0.06		
L-Alanine, N-methoxycarbonyl-, isobutyl ester			1.02±0.03
L-leucine, ethyl ester			1.23±0.16
Hydrocarbons			
Cyclohexene, 3,5,5-trimethyl-	0.52±0.03		
Cyclohexane, 1,1'-[1,2-ethenediyl]bis-	0.30±0.12	7.55±1.12	
3-Hexene, (z)-		1.20±0.43	0.38±0.02
Neophytadiene			11.37±0.13
Squalene		0.53±0.04	
Others Oxygen Containing Compounds			
1,2-Ethanediol, diformate		1.92±0.13	0.94±0.10
1,3-Dioxolane, 2,2-dimethyl-4,5-di-1-propenyl-		0.30±0.10	0.48±0
1,4-Dioxadiene	1.14±0.03	0.48±0.10	1.00±0.08
2,4-Pentadienoic acid, 1-cyclopenten-3-on-1-yl ester	0.46±0.02	0.64±0.13	
2-Heptanol, acetate	0.90±0.03		
Benzeneacetic acid, 1,1-dimethylethyl ester		6.97±0.10	1.78±0.16
Butane, 1,2:3,4-diepoxy-, (+/-.)-		0.40±0.10	1.14±0.16
cis-2,3-Epoxyheptane	0.23±0.08	0.56±0.15	
Formic acid, butyl ester	0.90±0.05		
Methyl 4-pentenyl ether	0.72±0.10		
Oxazolidine, 2,2-diethyl-3-methyl-		0.93±0.05	
Pent-2-enoic acid ethyl ester			0.42±0
Proceroside		3.90±0.26	

Vinyl butyrate			1.07±0.28
2H-Pyran-2-carboxaldehyde, 3,4-dihydro-2,5-dimethyl-	1.02±0.06		
Isosorbide	0.40±0		
Octanoic acid, pyrrolidide	0.32±0.13		
2-Propenoic acid, 2-propenyl ester			1.28±0.04
2-Propenoic acid, methyl ester			0.63±0.12
Sulfur dioxide	22.98±2.60	1.57±0.32	2.08±0.16