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Supplementary Data

Hydrothermal Liquefaction of Rice Straw Using Methanol as Co-Solvent

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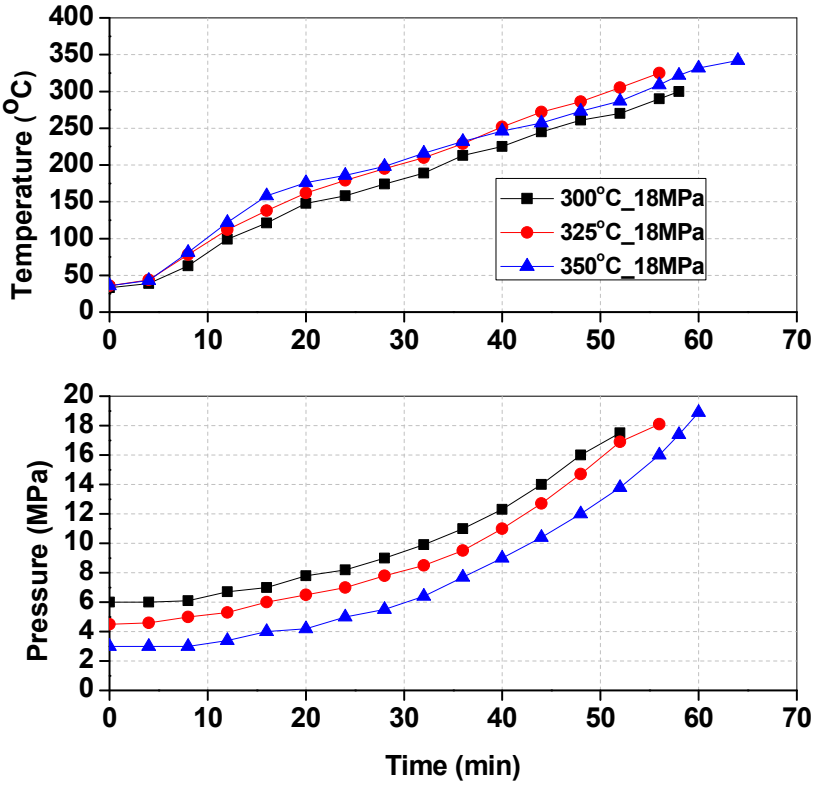

Figure S1. Temperature and pressure profiles from selected experiments performed at rice straw-to-water ratio of 1:10 wt./wt.

Table S1. Composition of bio-crude obtained from experiment R1 (300 °C, 18 MPa, 30 min, Rice straw:water = 1:10). The selectivity of individual compounds is scaled with respect to the yield of bio-crude.

Product	%
Simple oxygenates	**0.46**
2,5-Hexanedione	0.04
3,6-Heptanedione	0.06
5-methyl-3,5-octadien-2-one	0.08
4-methyl-1-indanone	0.05
Ethanone, 1-(3-hydroxy-4-methoxyphenyl)-	0.07
Ethanone, 1-(2,5-dihydroxyphenyl)-	0.05
2-Propanone, 2-(2,4-dimethylphenyl) hydrazone	0.05
Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	0.06
Cyclo-oxygenates	**2.81**
2-Cyclopenten-1-one	0.09
2-Cyclopenten-1-one, 2-methyl-	0.41
2-Cyclopenten-1-one, 3-methyl-	0.46
2-Cyclopenten-1-one, 3,4-dimethyl-	0.24
2-Cyclopenten-1-one, 2,3-dimethyl-	0.59
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	0.03
2-Butyl-2,6-dimethylcyclohexanone	0.06
2-Cyclopenten-1-one, 2,3,4-trimethyl-	0.21
3-Ethylcyclopent-2-en-1-one	0.14
2,3,4,5-Tetramethyl-2-cyclopenten-1-one A	0.04
Cyclohexanone, 3-ethenyl-	0.08
Cyclopentanone, 2-(2-oxopropyl)-	0.31
3-Methyl-3-vinylcyclohexanone	0.07
4-Isopropylcyclohex-2-en-1-one	0.08
Phenolics	**5.80**
Phenol	0.46
Phenol, 2-methyl-	0.17
Phenol, 4-methyl-	0.33
Phenol, 2-methoxy-	1.43
Phenol, 2,4-dimethyl-	0.10
Phenol, 4-ethyl-	0.80
Phenol, 2,3-dimethyl-	0.07
1,2-Benzenediol	0.22
1,2-Benzenediol, 3-methoxy-	0.14
1,2-Benzenediol, 3-methyl-	0.11
Guaiacol, 4-ethyl-	0.82
Phenol, 2-methoxy-3-methyl-	0.05

1,4-Benzenediol, 2-methyl-	0.07
Phenol, 2,6-dimethoxy-	0.48
1,3-Benzenediol, 2,5-dimethyl-	0.06
Guaiacol, 4-propyl-	0.08
4-Ethylcatechol	0.12
1,4-Benzenediol, mono-tetradecyl ether	0.04
1,3-Benzenediol, 4-ethyl-	0.04
Ethanone, 1-(3-hydroxyphenyl)-	0.13
Ethanone, 1-(4-hydroxyphenyl)-	0.07
Other aromatics	**0.44**
1-Hydroxy-2-methoxy-4-methylbenzene	0.20
3,5-Dimethoxy-4-hydroxytoluene	0.13
Benzene, 1,2,3-trimethoxy-5-methyl-	0.08
Naphthalene, 6-ethyl-1,2,3,4-tetrahydro-	0.04
Indene derivatives	**0.27**
1H-Inden-1-one, 2,3,4,5,6,7-hexahydro-	0.10
1H-Inden-1-one, 2,3-dihydro-	0.08
1H-Inden-5-ol, 2,3-dihydro-	0.06
Indene-1,7(4H)-dione, 3A,7A-dihydro-5-methyl-	0.03
Furan derivatives	**0.25**
Ethanone, 1-(2-furanyl)-	0.07
2-Methyl-5-hydroxybenzofuran	0.10
Furan, 2,3-dihydro-2,5-dimethyl-4-phenyl-	0.07
Esters	**0.20**
2-Butenoic acid, 2-methyl-, hexamethyl ester,	0.10
2-Octynoic acid, methyl ester	0.06
2,4-Hexadienedioic acid, 3-methyl-4-propyl-, dimethyl ester	0.04
Others	**0.57**
2,4-Heptadienal, 2,4-dimethyl-	0.08
Indolizine, 2-methyl-6-ethyl-	0.04
3-Isobutylhexahydropyrrolo[1,2-A]pyrazine-1,4-dione	0.08
n-Tetracosanol-1	0.03
2-Hexenoic acid , 3,4,4-trimethyl-5-oxo-,	0.21
1H-Indole, 2,3-dimethyl-	0.12
Total	**10.80**

Table S2. Composition of bio-crude obtained from experiment R2 (325 °C, 18 MPa, 30 min, Rice straw:water = 1:10). The selectivity of individual compounds is scaled with respect to the yield of bio-crude.

Product	%
Simple oxygenates	**0.32**
3-Hexen-2-one, 3,4-dimethyl-,	0.21
5,8-Decadien-2-one, 5,9-dimethyl-,	0.05
3A,4,5,6-Tetrahydro-2(3H)-pentalenone	0.05
Cyclo-oxygenates	**4.16**
2-Cyclopenten-1-one	0.24
Cyclopentanone, 3-methyl-	0.07
2-Cyclopenten-1-one, 2-methyl-	0.79
2-Cyclopenten-1-one, 2,3-dimethyl-	1.14
2-Cyclopenten-1-one, 3-methyl-	0.60
2-Cyclopenten-1-one, 3,4-dimethyl-	0.20
3,4-Dimethyl-2-cyclopenten-1-one	0.13
2-Cyclopenten-1-one, 2,3,4-trimethyl-	0.09
3-Ethylcyclopent-2-EN-1-one	0.20
2-Cyclopenten-1-one, 4-methyl-5-(1-methylethyl)-, trans-	0.04
Cyclohexanone, 3-ethenyl-	0.20
Cyclopentanone, 2-(2-oxopropyl)-	0.07
Cyclohexanone, 3-vinyl-3-methyl-	0.14
3-Methyl-3-vinylcyclohexanone	0.08
Bicyclo[3.1.1]hept-3-en-2-one, 4,6,6-trimethyl-	0.05
2-Cyclohexen-1-on, 6-methyl-3(1-methylethyl)- (carvenon)	0.14
Aliphatic hydrocarbons	**0.55**
1,2,3,4-Tetramethyl-3-cyclobutene-1,2-diol	0.06
3-Nonyne	0.04
5-Ethylcyclopent-1-enecarboxaldehyde	0.27
2-Pentene, 3-ethyl-4,4-dimethyl-	0.03
1-(2-Propyl)-2,3,5-trimethylcyclopenta-2,4-dien	0.10
2H-1-Benzopyran-2-one, 3,4-dihydro-6-methyl-	0.05
Phenolics	**7.53**
Phenol	0.90
Phenol, 2-methyl-	0.48
Phenol, 4-methyl-	0.44
Phenol, 2-methoxy-	2.35
2,6-DImethylphenol	0.04
Phenol, 2,4-dimethyl-	0.14
Phenol, 4-ethyl-	0.99

Phenol, 2,3-dimethyl-	0.09
Creosol	0.19
Catechol	0.74
Phenol, 3,4,5-trimethyl-	0.03
Phenol, 2-ethyl-4-methyl-	0.07
1,2-Benzenediol, 3-methyl-	0.06
Benzene-1,4-diol	0.03
Guaiacol, 4-ethyl-	0.52
1,2-Benzenediol, 4-methyl-	0.08
Phenol, 2,6-dimethoxy-	0.07
2-Methoxy-4-propyl-phenol	0.05
4-Ethylcatechol	0.12
Ethanone, 1-(3-hydroxyphenyl)-	0.10
Benzaldehyde, 2-hydroxy-3-(2-propenyl)-	0.03
Other aromatics	**0.46**
Benzene, ethyl-	0.06
Benzene, ethenyl-	0.23
1,4-Benzenedicarboxaldehyde, 2-methyl-	0.08
Benzene, (1-methylbutyl)-	0.03
2-Naphthalenol	0.06
Indene derivatives	**0.53**
1H-Inden-1-one, 2,3,4,5,6,7-hexahydro-	0.10
1H-Inden-1-one, 2,3-dihydro-	0.14
1-Indanone, 2-methyl-	0.04
1H-Inden-5-ol, 2,3-dihydro-	0.04
4-Methyl-1-indanone	0.14
7-Methyl-1-indanone	0.04
4-Hydroxy-1-indanone	0.03
Furan derivatives	**0.25**
Ethanone, 1-(2-furanyl)-	0.10
2(3H)-Furanone, dihydro-5-methyl-	0.04
2-Methyl-5-hydroxybenzofuran	0.11
Esters	**0.03**
Nortricyclyl formate	0.03
Others	**1.26**
Butanoic acid	1.16
1H-Indole, 2,3-dimethyl-	0.10
Total	**15.10**

Table S3. Composition of bio-crude obtained from experiment R4 (300 °C, 18 MPa, 60 min, Rice straw:water = 1:10). The selectivity of individual compounds is scaled with respect to the yield of bio-crude.

Product	%
Simple oxygenates	**0.05**
3,6-Heptanedione	0.05
Cyclo-oxygenates	**2.20**
2-Cyclopenten-1-one, 2-methyl-	0.16
2-Cyclopenten-1-one, 3-methyl-	0.38
2-Cyclopenten-1-one, 3,4-dimethyl-	0.21
2-Cyclopenten-1-one, 2,3-dimethyl-	0.50
Cyclohexanone, 2-isopropyl-2,5-dimethyl-	0.04
2-Cyclopenten-1-one, 2,3,4-trimethyl-	0.19
3-Ethylcyclopent-2-en-1-one	0.15
Cyclohexanone, 3-ethenyl-	0.09
3-Methyl-3-vinylcyclohexanone	0.07
5-Hydroxy-2,3,3-trimethyl-2-(3-methyl-buta-1,3-dienyl)-cyclohexanone	0.05
Cyclopentanone, 2-(2-oxopropyl)-	0.16
3-Methyl-3-vinylcyclohexanone	0.09
4-Isopropylcyclohex-2-en-1-one	0.07
2(3H)-Naphthalenone, 4,4A,5,6,7,8-hexahydro-	0.04
Aliphatic hydrocarbons	**0.36**
Cyclopentane, 1-acetyl-1,2-epoxy-	0.11
Tricyclo[3.3.1.1(3,7)] decane	0.11
Bicyclo[2.2.2]octa-2,5-diene, 1,2,3,6-tetramethyl-	0.07
Cyclohexane, 1-methyl-2,4-bis(1-methylethenyl)-	0.03
9-Hexacosene	0.04
Phenolics	**6.20**
Phenol	0.55
Phenol, 2-methyl-	0.19
Phenol, 4-methyl-	0.43
Phenol, 2-methoxy-	1.34
Phenol, 2,4-dimethyl-	0.15
Phenol, 4-ethyl-	0.84
Phenol, 3-ethyl-	0.05
Phenol, 2,3-dimethyl-	0.06
1,2-Benzenediol	0.25
Phenol, 3-(1-methylethyl)-	0.12
Phenol, 2-(1-methylethyl)-	0.04
1,2-Benzenediol, 3-methoxy-	0.21
1,2-Benzenediol, 3-methyl-	0.06

Guaiacol, 4-ethyl-	0.78
1,2-Benzenediol, 4-methyl-	0.09
Phenol, 2,6-dimethoxy-	0.42
1,3-Benzenediol, 2,5-dimethyl-	0.06
Guaiacol, 4-propyl-	0.07
4-Ethylcatechol	0.16
Ethanone, 1-(3-hydroxyphenyl)-	0.10
Ethanone, 1-(4-hydroxyphenyl)-	0.08
2-Propanone, (4-hydroxy-3-methoxyphenyl)-	0.03
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	0.06
Ethanone, 1-(2,5-dihydroxyphenyl)-	0.05
Other aromatics	**2.53**
Benzene, ethyl-	1.82
Benzene, ethenyl-	0.15
1-Hydroxy-2-methoxy-4-methylbenzene	0.20
3,5-Dimethoxy-4-hydroxytoluene	0.14
Benzene, 1,2,3-trimethoxy-5-methyl-	0.08
2-Naphthalenol, 3-methoxy-	0.06
Ethanone, 1-phenyl-	0.04
	2.47
Indene derivatives	**0.14**
1H-Inden-1-one, 2,3-dihydro-	0.09
7H-Indeno[5,6-b] furan-7-one, 4,4a,5,6,7a,8-hexahydro-	0.05
Furan derivatives	**0.10**
2-methyl-5-hydroxybenzofuran	0.10
Esters	**0.12**
Fumaric acid, ethyl 3-ethylphenyl ester	0.04
2,4-Hexadienedioic acid, 3-methyl-4-propyl-, dimethyl ester	0.04
2-Isopropyl-5-methylcyclohexyl 3-methyl-4-Methylenecyclopentanecarboxylate	0.04
Others	**0.61**
Urea, N-(2-methoxyphenyl)-N'-phenyl-	0.03
2-Hexenoic acid, 3,4,4-trimethyl-5-oxo-,	0.15
2H-Pyrazolo[3,4-c]pyridin-3-amine, 4,5,6,7-tetrahydro-	0.09
1H-Indole, 2,3-dimethyl-	0.10
1H-Indole, 5,6,7-trimethyl-	0.06
2,4-Heptadienal, 2,4-dimethyl-	0.09
3-Isobutylexahydropyrrolo[1,2-A]pyrazine-1,4-dione	0.06
Ethanone, 1-(1H-pyrrol-2-yl)-	0.04
Total	**12.30**

Table S4. Composition of bio-crude obtained from experiment R5 (325 °C, 18 MPa, 60 min, Rice straw:water = 1:10). The selectivity of individual compounds is scaled with respect to the yield of bio-crude.

Product	%
Simple oxygenates	**0.05**
3A,4,5,6-Tetrahydro-2(3H)-pentalenone	0.05
Cyclo-oxygenates	**1.89**
2-Cyclopenten-1-one	0.05
2-Cyclopenten-1-one, 2-methyl-	0.28
2-Cyclopenten-1-one, 3-methyl-	0.30
3,4-Dimethyl-2-cyclopenten-1-one	0.17
2-Cyclopenten-1-one, 2,3-dimethyl-	0.58
2-Cyclopenten-1-one, 2,3,4-trimethyl-	0.20
3-Ethylcyclopent-2-en-1-one	0.13
Cyclohexanone, 3-ethenyl-	0.13
3-Methyl-3-vinylcyclohexanone	0.06
Aliphatic hydrocarbons	**0.24**
1,5,6,7-Tetramethylbicyclo[3.2.0]hepta-2,6-diene	0.18
2H-1-Benzopyran-2-one, 3,4-dihydro-6-methyl-	0.06
Phenolics	**4.52**
Phenol	0.37
Phenol, 2-methyl-	0.28
Phenol, 4-methyl-	0.28
Phenol, 2-methoxy-	0.96
Phenol, 2,4-dimethyl-	0.12
Phenol, 4-ethyl-	0.84
Phenol, 2,3-dimethyl-	0.06
Catechol	0.28
Phenol, 3-(1-methylethyl)-	0.08
1,2-Benzenediol, 3-methyl-	0.04
Guaiacol, 4-ethyl-	0.44
1,2-Benzenediol, 3-methyl-	0.10
Phenol, 2-methyl-5-(1-methylethyl)-	0.06
Phenol, 2,6-dimethoxy-	0.06
Phenol, 2-methoxy-4-propyl-	0.05
4-Ethylcatechol	0.23
Ethanone, 1-(3-hydroxyphenyl)-	0.08
Ethanone, 1-(4-hydroxyphenyl)-	0.05
Phenol, 2-(2-penten-4-yl)-4-methyl-	0.08
4-Methyl-2-[(2E)-1-methyl-2-butenyl]phenol	0.04
Other aromatics	**0.83**

1-Hydroxy-2-methoxy-4-methylbenzene	0.13
Benzene, 1-ethyl-4-methoxy-	0.06
Naphthalene, 1,2,3,4-tetrahydro-6,7-dimethyl-	0.06
3,5-Dimethoxy-4-hydroxytoluene	0.06
Benzene, 1,2-diethyl-3,4-dimethyl-	0.05
2-Naphthalenol	0.07
Naphthalene, 2,3,4,4a,5,6,7,8-octahydro-2-hydroxy-[.alpha./.beta.]-2,4a-dimethyl-	0.05
Benzaldehyde, 2-hydroxy-3-(2-propenyl)-	0.10
1-Naphthol, 5,7-dimethyl-	0.07
Benzene, ethenyl-	0.19
Indene derivatives	**0.90**
1H-Inden-1-one, 2,3,4,5,6,7-hexahydro-	0.18
1H-Inden-1-one, 2,3-dihydro-	0.14
1-Methylindan-2-one	0.14
1H-Inden-5-ol, 2,3-dihydro-	0.09
7-Methylindan-1-one	0.12
4-Methyl-1-indanone	0.19
4-Hydroxy-1-indanone	0.05
Furan derivatives	**0.05**
10-Methyldodec-2-en-4-olide	0.05
Esters	**0.09**
2-Butenoic acid, 2-methyl-, hexyl ester, (2E)-	0.09
Others	**0.62**
Butanoic acid	0.09
3,4,5,6,7,8-Hexahydro-2H-chromene	0.10
2-(1-Adamantyl)-N-(6-methoxy-3-pyridinyl) acetamide	0.06
5-Formyl-2,4-dimethyl-1H-pyrrole-3-carbonitrile	0.12
1H-Indole, 2,3-dimethyl-	0.15
Indolizine, 2-methyl-6-ethyl-	0.06
2H-1-Benzopyran-2-one, 3,4-dihydro-6-methyl-	0.05
Total	**9.20**

Table S5. Composition of bio-crude obtained from experiment R10 (300 °C, 18 MPa, 60 min, Rice straw:(75:25 water:methanol) = 1:10). The selectivity of individual compounds is scaled with respect to the yield of bio-crude.

Product	**%**
Simple oxygenates	**0.06**
6,6,7-Trimethyl-octane-2,5-dione	0.06
Cyclo-oxygenates	**0.41**

2-Cyclopenten-1-one, 2-methyl-	0.18
2-Cyclopenten-1-one, 3-methyl-	0.04
2-Cyclopenten-1-one, 3,4-dimethyl-	0.04
2-Cyclopenten-1-one, 2,3-dimethyl-	0.15
Aliphatic hydrocarbons	**0.37**
6-methyl-1-octene	0.07
Tetradecane	0.24
Pentane, 3-methoxy-	0.06
Phenolics	**1.28**
Phenol	0.04
Phenol, 2-methyl-	0.04
Phenol, 4-methyl-	0.06
Phenol, 2-methoxy-	0.30
Phenol, 4-(1-methylethyl)-	0.06
Phenol, 4-ethyl-	0.22
Creosol	0.10
Guaiacol, 4-ethyl-	0.41
Phenol, 2-methoxy-4-propyl-	0.05
Other aromatics	**3.34**
Benzene, ethyl-	1.46
Benzene, ethenyl-	1.59
Benzene, (1-methylethenyl)-	0.13
Benzene, 1,4-dimethoxy-	0.16
Furan derivatives	**0.20**
2-Furanmethanol, tetrahydro-	0.20
Esters	**8.53**
Pentanoic acid, 4-oxo-, methyl ester	0.29
Hexanoic acid, 5-oxo-, methyl ester	0.08
Butanoic acid, 2-ethyl-3-oxo-, methyl ester	0.06
Butanedioic acid, dimethyl ester	0.09
Butanedioic acid, methyl-, dimethyl ester	0.13
Pentanedioic acid, dimethyl ester	0.05
Pentanedioic acid, 3-methyl-, dimethyl ester	0.06
Pentanedioic acid, 2-methyl-, dimethyl ester	0.04
Nonanedioic acid, dimethyl ester	0.10
1,2-Benzenedicarboxylic acid, diundecyl ester	0.05
Tetradecanoic acid, methyl ester	0.51
Pentadecanoic acid, methyl ester	0.05
Hexadecanoic acid, methyl ester	2.15
9,12-Octadecadienoic acid (z, z)-, methyl ester	0.33
9-Octadecenoic acid (z)-, methyl ester	3.01
6-Octadecenoic acid, methyl ester	0.72

Octadecanoic acid, methyl ester	0.48
6,9-Octadecadienoic acid, methyl ester	0.05
Eicosanoic acid, methyl ester	0.12
Docosanoic acid, methyl ester	0.11
Tetracosanoic acid, methyl ester	0.07
Others	**0.11**
1-Nonanol, 4,8-dimethyl-	0.06
Methyl 10-oxohexadecanoate	0.05
Total	**14.3**

Table S6. Composition of bio-crude obtained from experiment R11 (300 °C, 18 MPa, 60 min, Rice straw:(50:50 water:methanol) = 1:10). The selectivity of individual compounds is scaled with respect to the yield of bio-crude.

Product	%
Simple oxygenates	**0.64**
2,5-Hexanedione	0.30
3,6-Heptanedione	0.34
Cyclo-oxygenates	**4.24**
2-Cyclopenten-1-one, 2-methyl-	0.95
2-Cyclopenten-1-one, 3-methyl-	0.69
2-Cyclopenten-1-one, 3,4-dimethyl-	0.59
2-Cyclopenten-1-one, 2,3-dimethyl-	1.19
2-Cyclopenten-1-one, 2,3,4-trimethyl-	0.29
Cyclohexanone, 3-vinyl-3-methyl-	0.28
2-Cyclohexen-1-one, 6-methyl-3-(1-methylethyl)-	0.26
Aliphatic hydrocarbons	**0.24**
Cyclohexene 1-methyl-3-(1-methylethenyl)-, (.+-.)-	0.24
Phenolics	**6.80**
Phenol	0.47
Phenol, 2-methyl-	0.22
Phenol, 4-methyl-	0.47
Phenol, 2-methoxy-	1.17
Phenol, 2,3-dimethyl-	0.25
Phenol, 4-ethyl-	1.66
Creosol	0.44
1,2-Benzenediol	0.35
Guaiacol, 4-ethyl-	1.40
4-Ethylcatechol	0.37
Other aromatics	**2.24**
Benzene, 1-methyl-3-(1-methylethyl)-	0.30
Benzenemethanol, .alpha.-methyl-	0.89

Ethanone, 1-phenyl-	0.78
Benzene, 1,1'-(1,2-dimethyl-1,2-ethanediyl)bis-	0.26
Furan derivatives	**0.22**
Benzofuran, 4,7-dimethyl-	0.22
Esters	**16.07**
Propanoic acid, 2-methoxy-, methyl ester	1.01
Pentanoic acid, 4-oxo-, methyl ester	0.64
Hexanoic acid, 5-oxo-, methyl ester	0.22
12-Tridecynoic acid, methyl ester	0.23
Nonanedioic acid, dimethyl ester	0.26
Tetradecanoic acid, methyl ester	1.17
Hexadecanoic acid, methyl ester	3.87
8,11-Octadecadienoic acid, methyl ester	0.35
9-Octadecenoic acid (Z)-, methyl ester	6.92
Methyl 10-oxooctadecanoate	0.23
Eicosanoic acid, methyl ester	0.44
Docosanoic acid, methyl ester	0.40
Tetracosanoic acid, methyl ester	0.32
Others	**0.56**
Phenol, 3-(ethylamino)-4-methyl-	0.28
1H-Indole, 1,2,3-trimethyl-	0.28
Total	**31.00**

Table S7. Composition of bio-crude obtained from experiment R12 (300 °C, 18 MPa, 60 min, Rice straw:(25:75 water:methanol) = 1:10). The selectivity of individual compounds is scaled with respect to the yield of bio-crude.

Product	%
Simple oxygenates	**0.12**
2,5-Hexanedione	0.08
3,6-Heptanedione	0.05
Cyclo-oxygenates	**0.54**
2-Cyclopenten-1-one, 2-methyl-	0.24
2-Cyclopenten-1-one, 3-methyl-	0.09
2-Cyclopenten-1-one, 3,4-dimethyl-	0.07
2-Cyclopenten-1-one, 2,3-dimethyl-	0.09
2-Cyclopenten-1-one, 2,3,4-trimethyl-	0.06
Aliphatic hydrocarbons	**0.25**
Pentane, 3-methoxy-	0.14
Tridecane, 5-propyl-	0.07
9-methylnonadecane	0.04

Phenolics	**1.83**
Phenol	0.10
Phenol, 2-methyl-	0.04
Phenol, 4-methyl-	0.09
Phenol, 2-methoxy-	0.36
Phenol, 2,3-dimethyl-	0.04
Phenol, 4-ethyl-	0.40
1,2-Benzenediol	0.07
Phenol, 3-ethyl-5-methyl-	0.05
Guaiacol, 4-ethyl-	0.55
Phenol, 2,6-dimethoxy-	0.06
2-Methoxy-4-propyl-phenol	0.04
4-Ethylcatechol	0.05
Other aromatics	**0.39**
Benzene, 1-ethyl-4-methoxy-	0.06
1-Hydroxy-2-methoxy-4-methylbenzene	0.25
Benzene 1,4-dimethoxy-	0.08
Furan derivatives	**0.27**
2-Furanmethanol, tetrahydro-	0.27
Esters	**10.44**
Propanoic acid, 2-methoxy-, methyl ester	0.53
Pentanoic acid, 4-oxo-, methyl ester	0.45
Hexanoic acid, 5-oxo-, methyl ester	0.11
Butanoic acid, 2-ethyl-3-oxo-, methyl ester	0.06
Butanedioic acid, dimethyl ester	0.27
Butanedioic acid, methyl-, dimethyl ester	0.13
Hexanoic acid, 4-oxo-, methyl ester	0.05
Benzoic acid, dec-2-yl ester	0.04
10-Undecynoic acid, methyl ester	0.07
Pentanedioic acid, DImethyl ester	0.10
Nonanedioic acid, dimethyl ester	0.12
1,2-Benzenedicarboxylic acid, diethyl ester	0.05
Tetradecanoic acid, methyl ester	0.50
Pentadecanoic acid, methyl ester	0.04
Hexadecanoic acid, methyl ester	1.94
Heptadecanoic acid, methyl ester	0.04
9,12-Octadecadienoic acid (Z,Z)-, methyl ester	0.47
9-Octadecenoic acid (Z)-, methyl ester	3.71
6-Octadecenoic acid, methyl ester	0.69
cis-11-Eicosenoic acid, methyl ester	0.10

Eicosanoic acid, methyl ester	0.16
Fumaric acid, octadecyl 2,2,2-trifluoroethyl ester	0.05
Docosanoic acid, methyl ester	0.28
Tricosanoic acid, methyl ester	0.05
Tetracosanoic acid, methyl ester	0.24
Pentacosanoic acid, methyl ester	0.04
Hexacosanoic acid, methyl ester	0.07
Octacosanoic acid, methyl ester	0.10
Others	**0.45**
Terpineol, dihydro-	0.09
1-Propanol, 3-methoxy-2,2-bis(methoxymethyl)-	0.07
Cyclohexaneethanethiol, thiolacetate	0.04
1,2-DImethylbicyclo[2.2.1] heptan-2-ol	0.04
Phenol, 3-(dimethylamino)-	0.09
4-Methyl-3-(n-ethylamino)-phenol	0.05
1H-Indole, 2,3-dimethyl-	0.04
1-Dodecanol, 3,7,11-trimethyl-	0.05
Total	**14.30**

Table S8. Composition of bio-crude obtained from experiment R13 (300 °C, 18 MPa, 60 min, Rice straw:(50:50 methanol:water) = 1:10, 5 wt.% KOH). The selectivity of individual compounds is scaled with respect to the yield of bio-crude.

Product	%
Cyclo-oxygenates	**7.31**
2-Cyclopenten-1-one	0.31
2-Cyclopenten-1-one, 2-methyl-	2.51
2-Cyclopenten-1-one, 3-methyl-	0.70
2-Cyclopenten-1-one, 3,4-dimethyl-	0.87
2-Cyclopenten-1-one, 2,3-dimethyl-	2.51
3,5-Dimethyl cyclopenten-1-one	0.40
Aliphatic hydrocarbons	**0.59**
Dodecane, 2,2,4,9,11,11-hexamethyl-	0.30
Cyclopropaneoctanal, 2-octyl-	0.29
Phenolics	**15.28**
Phenol	0.98
Phenol, 2-methyl-	0.28
Phenol, 4-methyl-	0.80
Phenol, 2-methoxy-	3.83
Phenol, 3-ethyl-	2.11
Creosol	0.60

1,2-Benzenediol	0.36
Guaiacol, 4-ethyl-	4.10
1,3-Benzenediol, 2-methyl-	0.30
Phenol, 2,6-dimethoxy-	1.34
Phenol, 2-methoxy-4-propyl-	0.26
Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	0.32
Other aromatics	**0.49**
Benzene, ethenyl-	0.49
Furan derivatives	**1.88**
2-Furanmethanol, tetrahydro-	1.48
5-Ethyl-2-furaldehyde	0.39
Esters	**11.85**
Propanoic acid, 2-methoxy-, methyl ester	0.99
Pentanoic acid, 4-oxo-, methyl ester	0.88
Hexanoic acid, 5-oxo-, methyl ester	0.39
Methyl 5-oxononanoate	0.61
Pentanedioic acid, dimethyl ester	0.37
Cyclohexane carboxylic acid, 2-oxo-, methyl ester	0.53
Tetradecanoic acid, methyl ester	1.08
Methyl trans-9-(2-butylcyclopentyl) nonanoate	0.25
9,12-Octadecadienoic acid (Z,Z)-, methyl ester	0.49
9-Octadecenoic acid, methyl ester	4.88
Fumaric acid, 2-heptyl tridecyl ester	0.38
Methyl 18-methylnonadecanoate	0.70
Methyl 20-methyl-heneicosanoate	0.30
Alcohols	**0.70**
3-Dodecanol	0.35
Nepetalactol	0.35
Others	**1.82**
Pyridine, 3-methoxy-	0.26
4-Pyridinol	0.49
1H-Pyrrole, 2,3,4,5-tetramethyl-	0.42
2-Hexenoic acid, 3,4,4-trimethyl-5-oxo-	0.65
Total	**39.90**

Table S9. Composition of bio-crude obtained from experiment R14 (300 °C, 18 MPa, 60 min, Rice straw:(50:50 methanol:water) = 1:10, 5 wt.% NaOH). The selectivity of individual compounds is scaled with respect to the yield of bio-crude.

Product	**%**
Cyclo-oxygenates	**2.81**

2-Cyclopenten-1-one	0.09
2-Cyclopenten-1-one, 2-methyl-	0.70
2-Cyclopenten-1-one, 3,4-dimethyl-	0.46
2-Cyclopenten-1-one, 2,3-dimethyl-	0.82
2-Cyclopenten-1-one, 3-methyl-	0.31
2-Cyclopenten-1-one, 2,3,4-trimethyl-	0.17
2-Cyclohexen-1-one, 4,4-dimethyl-	0.10
2,3,4,5-Tetramethyl-2-cyclopenten-1-one	0.15
Aliphatic hydrocarbons	**3.20**
Octane, 1-ethoxy-	0.11
3-Hexadecene, (Z)-	0.14
Hexacosane	0.20
Tetracosane	0.38
Hexatriacontane	0.85
Eicosane	0.27
Dotriacontane	0.26
Squalene	0.65
Eicosane	0.17
Docosane	0.18
Phenolics	**2.92**
Phenol	0.26
Phenol, 4-methyl-	0.19
Phenol, 4-methoxy-	1.04
Phenol, 3-ethyl-	0.49
Phenol, 2-methoxy-3-methyl-	0.10
1,2-Benzenediol	0.12
Guaiacol, 4-ethyl-	0.62
Phenol, 2,6-dimethoxy-	0.11
Other aromatics	**0.33**
Benzene, 1,4-dimethoxy-	0.15
1,1'-Biphenyl, 2,2',5,5'-tetramethyl-	0.18
Furan derivatives	0.23
2-Furanmethanol, tetrahydro-	0.23
Esters	**11.92**
Pentanoic acid, 4-oxo-, methyl ester	0.10
Diethyl phthalate	2.02
Tetradecanoic acid, methyl ester	0.17
1,2-Benzenedicarboxylic acid, bis (2-methylpropyl) ester	0.73
Hexadecanoic acid, methyl ester	0.65
1,2-Benzenedicarboxylic acid, dibutyl ester	0.18

7,10-Octadecadienoic acid, methyl ester	0.09
9-Octadecenoic acid, methyl ester	0.89
6-Octadecenoic acid, methyl ester, (Z)-	0.10
Octadecanoic acid, methyl ester	0.12
Hexadecanoic acid, 2-methylpropyl ester	0.12
9-Octadecenoic acid (Z)-, tetradecyl ester	0.37
Bis(2-ethylhexyl) phthalate	3.03
1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester	2.86
1,2-Benzenedicarboxylic acid, dinonyl ester	0.40
Pentanedioic acid, dimethyl ester	0.09
Alcohols	**9.58**
3-Pentanol	0.34
1-Dodecanol	5.38
1-Tetradecanol	2.25
5,9-Dimethyl-1-decanol	0.11
n-Nonadecanol-1	1.50
Others	**3.51**
2-Methyl-n-phenylacrylamide	0.14
Hexadecanamide	0.10
9-Octadecenamide	0.78
Octadecanamide	0.09
13-Docosenamide, (Z)-	2.39
Total	**34.50**

Table S10. Composition of bio-crude obtained from experiment R15 (300 °C, 18 MPa, 60 min, Rice straw:(50:50 methanol:water) = 1:10, 5 wt.% K_2CO_3). The selectivity of individual compounds is scaled with respect to the yield of bio-crude.

Product	%
Cyclo-oxygenates	**9.58**
Cyclopentanone, 2-methyl-	0.41
2-Cyclopenten-1-one, 2-methyl-	2.40
9-Oxabicyclo[3.3.1]nonan-2-one	0.25
2-Cyclopenten-1-one, 3-methyl-	1.12
2-Cyclopenten-1-one, 3,4-dimethyl-	1.11
2-Cyclopenten-1-one, 2,3-dimethyl-	2.93
2-Cyclopenten-1-one, 2,3,4-trimethyl-	1.06
Carvenone	0.31
Aliphatic hydrocarbons	**0.75**
1-Cyclohexene, 1-ethynyl-	0.28
Cyclooctene, 1,2-dimethyl-	0.24

Cholesta-3,5-diene	0.23
Phenolics	**11.13**
Phenol	0.76
Phenol, 2-methyl-	0.33
Phenol, 4-methoxy-	3.33
Phenol, 3-ethyl-	2.10
Creosol	0.67
1,2-Benzenediol	0.38
1,4-Benzenediol, 2-methoxy-	0.35
Guaiacol, 4-ethyl-	2.40
4-Methoxy-2,3-dimethylphenol	0.27
Phenol, 2,6-dimethoxy-	0.23
Phenol, 2-methoxy-4-propyl-	0.30
Other aromatics	**1.23**
Benzene, ethenyl-	0.31
1-hydroxy-2-methoxy-4-methylbenzene	0.54
Benzene, 1,4-dimethoxy-	0.39
Indene derivatives	**0.34**
1H-Indene, octahydro-	0.34
Furan derivatives	**1.17**
2-Furanmethanol, tetrahydro-	1.17
Esters	**7.01**
Propanoic acid, 2-methoxy-, methyl ester	0.37
Methyl 2-methoxypropanoate	0.33
6-Nonenoic acid, methyl ester	0.32
Pentanoic acid, 4-oxo-, methyl ester	0.57
Hexadecanoic acid, 1-methylethyl ester	0.22
2-Propenoic acid, 3-phenyl-, 1-ethenyl-1,5-dimethyl-4-hexenyl ester	0.34
Hexadecanoic acid, methyl ester	2.02
9-Octadecenoic acid, methyl ester	2.16
6-Octadecenoic acid, methyl ester, (Z)-	0.67
Others	**2.59**
1H-Pyrrole, 2,3,5-trimethyl-	0.50
4(H)-Pyridine, n-acetyl-	0.23
Dimethyl 2-methylsuccinate	0.32
1H-Pyrrole, 2,3,4,5-tetramethyl-	0.41
Cyclohexane, (methylthio)-	0.41
1H-Pyrrole, 2-ethyl-3,4,5-trimethyl-	0.24
3-Methylbenzothiophene	0.47
Total	**33.80**

S11. Sample calculations to determine the energy recovery (%) and ECR from various experiments.

Energy required for heating of rice straw:

$$Energy\ of\ rice\ straw, E_F = m_{RS} \times HHV_{RS}$$

$$E_F = 30\ g \times 12.1 \frac{kJ}{g} = 363 kJ$$

Heat of rice straw:

$C_{p,RS} = \sum_i^n x_i \times C_{pi}$

Rice straw:

	Mole fraction (x)	C_p (J/g K)
C	0.371	0.709
H	0.052	14.304
O	0.443	0.918
N	0.005	1.04
S	0.001	0.71

$C_{p,RS}$ = 0.84 J/g-K

$$Q_{RS} = m_{RS} \times C_{p,RS} \times \Delta T$$

$$Q_{solids} = 30\ (g) \times 0.84 \left(\frac{J}{gK}\right) \times (573.15 - 298.15)(K) = 6930\ J = 6.93\ kJ$$

Heat of water:

$$Q_w = m_w \times C_{p\,w} \times \Delta T$$

$$Q_w = 300\ mL \times 1 \left(\frac{g}{mL}\right) \times 1208.75 \left(\frac{J}{g}\right) = 362625\ J = 362.62\ kJ$$

$$Q_w = 150\ mL \times 1 \left(\frac{g}{mL}\right) \times 1208.75 \left(\frac{J}{g}\right) = 181312\ J = 181.31\ kJ$$

Heat of Methanol:

$$Q_m = m_m \times C_{p\,m} \times \Delta T$$

$$Q_m = 150\ mL \times 0.79 \left(\frac{g}{mL}\right) \times 275.54 \left(\frac{J}{g}\right) = 32651\ J = 32.65\ kJ$$

Heat required for HTL process (E_{HTL}):

Water:

$$E_{HTL} = \frac{(Q_S + Q_{RS}) \times (1 - \eta_h)}{\eta_c}$$

$$E_{HTL} = \frac{((m_w \times C_{p\,w} \times \Delta T) + (m_{RS} \times C_{p,RS} \times \Delta T)) \times (1 - \eta_h)}{\eta_c}$$

$$E_{HTL} = \frac{(362.62 + 6.93) \times (1 - 0.5)}{0.7} = 263.96\ kJ$$

Water + Methanol:

$$E_{HTL} = \frac{((m_w \times C_{p\,w} \times \Delta T) + (m_m \times C_{p\,m} \times \Delta T) + (m_{RS} \times C_{p,RS} \times \Delta T)) \times (1 - \eta_h)}{\eta_c}$$

$$E_{HTL} = \frac{(181.31 + 32.65 + 6.93) \times (1 - 0.5)}{0.7} = 157.79\ kJ$$

Energy of products (E_P):

Water:

$$E_p = (M_{BC} \times HHV_{BC}) + (M_{BCh} \times HHV_{BCh}) + (M_G \times HHV_G)$$

$$E_p = (3.69 \times 35300) + (7.44 \times 18500) + (4.5 \times 12160) = 322617\ J = 322.62\ kJ$$

Water + Methanol (50:50 vol.%/vol.%):

$$E_p = (9.3 \times 32800) + (5.52 \times 11730) + (4.5 \times 12160) = 424509\ J = 424.51\ kJ$$

Water + Methanol (50:50 vol.%/vol.%) + KOH:

$$E_p = (11.97 \times 32400) + (4.95 \times 7230) + (4.5 \times 12160) = 478336\ J = 478.34\ kJ$$

Energy recovery (%):

$$Energy\ recovery = \frac{E_P}{E_F + Q_S} \times 100$$

Water:

$$Energy\ recovery = \frac{322.62}{725.62} \times 100 = 44.5\ \%$$

Water + Methanol (50:50 vol.%/vol.%):

$$Energy\ recovery = \frac{424.51}{576.96} \times 100 = 73.6\ \%$$

Water + Methanol (50:50 vol.%/vol.%) + KOH:

$$Energy\ recovery = \frac{478.34}{576.96} \times 100 = 82.9\ \%$$

Energy consumption ratio (ECR):

$$ECR = \frac{E_{HTL}}{E_{BC}}$$

Water:

$$ECR = \frac{263.96}{130.26} = 2.03$$

Water + Methanol (50:50 vol.%/vol.%):

$$ECR = \frac{157.79}{305.04} = 0.52$$

Water + Methanol (50:50 vol.%/vol.%) + KOH:

$$ECR = \frac{157.79}{387.83} = 0.41$$