Supplementary Materials

Mass production of chemicals from biomass-derived oil by directly atmospheric distillation coupled with co-pyrolysis

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The following is included as the supplementary information for this paper

Supplementary Methods

Quantification of analytes by GC-FID. Quantification of selected components of distillate and distillate fractions was performed on a gas chromatograph (GC-1690, KeXiao Co., Hangzhou, China) equipped with a moderately polar OV-1701 capillary column (30 m × 0.32 mm i.d., film thickness 1.00 µm) and a hydrogen flame ionization detector (FID). The oven temperature was held at 313 K for 12 min, and programmed to ramp at 4 K/min to 453 K and then at 10 K/min to 523 K. The temperature of both injector and FID was set at 523 K. Distillate samples were prepared as ca. 5 wt.% solutions in absolute ethanol and each time 1 µL of the sample was injected. Chromatographic peaks were identified by comparing their retention time with that of authentic compounds. 1-bromobenzene was used as the internal standard (IS) for quantification.

Calculation of the relative response factors (RRF). The response factors of individual compounds relative to the IS, 1-bromobenzene, were determined by preparing and injecting samples containing known amounts of both analytes and bromobenzene. Each sample was analyzed for several times and the relative response factors for each analyte were given as the average values. The relative response factors of 13 selected analytes are listed in Supplementary Table S2. The relative response factors of analyte i is defined as

$$\mathrm{RRF_i} = \frac{A_i/m_i}{A_{IS}/m_{IS}} \tag{1}$$

where A_i and A_{IS} stand for the peak areas of analyte i and IS on the chromatogram, respectively; while m_i and m_{IS} represent the weight of analyte i and IS contained in the

sample.

List of Tables

Table S1 Identified compounds in bio-oils prepared from fast co-pyrolysis of ADR and

rice husk

RT[a] (min)	Compounds	Peak area (%)		
		ADR-0[b]	ADR-20	ADR-35
3.39	formic acid	0.43	0.51	0.67
3.85	hydroxyacetaldehyde	0.51	0.19	0.51
4.23	acetic acid	7.39	6.78	6.08
5.27	acetol	5.64	3.98	3.04
5.80	(1S,2R)-1,2-bis[(2R)-oxiran-2-yl]ethane-1,2-diol	0.46	0.19	0.17
6.04	propanoic acid	0.42	0.75	0.59
8.48	1-hydroxy-2-butanone	0.74	0.55	0.50
9.31	methyl 2-oxopropanoate	1.18	0.91	0.60
9.92	diethoxymethyl acetate	1.00	0.91	0.89
11.09	furfural	2.92	3.05	2.57
12.01	furfuryl alcohol	2.92	2.00	1.53
12.60	1-acetoxy-2-propanone	0.96	0.74	0.68
14.13	2-methyl-2-cyclopenten-1-one	0.76	0.99	n.d.
14.32	2(5*H*)-furanone and/or 2(3*H*)-furanone	1.38	0.86	0.65
14.42	*γ*-butyrolactone	0.79	0.74	0.55
14.71	2-cyclohexen-1-ol	0.36	0.31	0.17
14.98	2-hydroxy-2-cyclopenten-1-one	2.71	1.65	1.34
15.02	5-methyl-2(5*H*)-furanone	0.29	n.d.	n.d.
15.15	1-(3,3-dimethyloxiranyl)ethanone	n.d.	0.23	0.19
16.62	5-methylfurfural	1.13	0.92	0.70
16.70	3-methyl-2-cyclopenten-1-one	0.80	0.77	0.67
17.28	phenol	1.06	1.89	2.27
17.74	2-hydroxy-γ-butyrolactone	0.51	0.45	0.48
18.08	5-methyl-3-hexen-2-one	0.26	0.27	0.22
18.21	1-{2-[2-(methylamino)propyl]phenyl}-1-propanone	0.47	0.42	0.33
19.17	3-methyl-1,2-cyclopentanedione	2.45	2.26	2.35
20.31	*o*-cresol	0.39	0.77	1.18
21.14	*p*-cresol	1.42	2.45	2.34
21.68	guaiacol	1.73	2.26	2.64
22.79	3-ethyl-2-hydroxy-2-cyclopenten-1-one	0.44	0.33	0.39
23.21	1,4-dioxaspiro[2.*4*]heptan-5-one	0.37	0.31	0.31
23.96	2,4-dimethylphenol	n.d.	0.33	0.54
24.31	7-methyl-1,4-dioxaspiro[2.*4*]heptan-5-one	0.22	0.21	0.21

24.38	6-methyl-1,4-dioxaspiro[2.4]heptan-5-one	0.27	0.25	0.16
24.61	4-ethylphenol	1.17	1.79	2.38
25.28	3,5-dihydroxy-2-methyl-4*H*-pyran-4-one	0.29	n.d.	n.d.
25.40	5-(propan-2-yl)dihydrofuran-3(2H)-one	0.50	n.d.	n.d.
25.53	1,2-benzenediol and 4-methylguaiacol	2.34	5.66	7.56
26.29	1,4:3,6-dianhydro-α-d-glucopyranose	0.50	n.d.	n.d.
26.47	2,3-dihydrobenzofuran	3.52	4.29	3.68
26.74	hydroxymethylfurfural (HMF)	1.40	0.90	0.78
26.78	2,3-anhydro-d-galactosan and/or 3,4-anhydro-d-galactosan	1.26	0.54	0.31
26.93	2,3-anhydro-d-mannosan	0.18	0.97	0.80
27.15	2-ethyl-6-methylphenol	n.d.	0.18	0.47
27.78	4-methyl-1,2-benzenediol	n.d.	0.51	1.00
27.86	3-methoxy-1,2-benzenediol and/or 4-methoxy-1,2-benzenediol	n.d.	0.55	0.76
28.10	3-hydroxy-4,4-dimethyldihydrofuran-2(3*H*)-one	0.58	0.49	0.25
28.27	Hydroquinone	n.d.	0.78	0.81
28.54	4-ethylguaiacol	0.83	1.16	1.51
28.81	4-methylcatechol	0.30	1.09	1.66
29.79	4-vinylguaiacol	2.27	1.89	1.89
30.34	1,2,4-cyclopentanetriol	n.d.	0.20	0.24
30.71	4-(2-propenyl)phenol	n.d.	0.59	0.67
30.96	syringol	0.58	0.92	1.15
31.16	6-allylguaiacol	0.15	0.62	0.78
31.50	4-propylguaiacol	n.d.	n.d.	0.55
31.88	6-ethylresorcinol	0.49	0.98	1.51
32.53	vanillin lactoside	0.40	0.23	n.d.
32.70	2,5-dimethylbenzene-1,4-diol	n.d.	0.14	0.16
32.81	3-allyl-6-methoxyphenol	0.15	0.20	0.21
33.94	1,2,3-trimethoxybenzene	0.26	0.35	0.43
34.18	isoeugenol	0.91	1.04	1.17
35.08	4-ethyl-1,2-dimethoxybenzene	0.18	n.d.	n.d.
35.22	1-(4-hydroxy-3-methoxyphenyl)ethanone	n.d.	0.41	0.56
35.80	1,6-anhydro-β-D-glucopyranose (levoglucosan)	18.56	16.52	12.41
36.23	6-hydroxy-3,4-dihydro-2*H*-chromen-2-one	n.d.	0.30	0.29
36.46	1-(4-hydroxy-3-methoxyphenyl)propan-2-one	0.23	0.32	0.40
36.92	3,4-altrosan	1.11	1.46	1.57
37.40	2-(3,4-dimethoxyphenyl)-6-methyl-3,4-chromanediol	0.39	n.d.	n.d.
37.50	4-methyl-2,5-dimethoxybenzaldehyde	n.d.	0.40	0.42

RT^a	Compound	ADR-0^b		
38.25	2,3-anhydro-d-galactosan	0.44	1.04	n.d.
38.36	1,6-anhydro-α-d-galactofuranose	0.35	n.d.	1.00
38.50	3-methoxy-2-methyl-5-(propan-2-yl)cyclohexa-2,5-diene-1,4-dione	n.d.	0.21	0.13
39.85	4-(4-hydroxy-3-methoxyphenyl)butan-2-one	n.d.	0.13	n.d.
41.21	4-allyl-2,6-dimethoxyphenol	0.46	0.39	0.41
41.81	acetosyringone	n.d.	0.24	0.31
42.49	1-(2,4,6-trihydroxyphenyl)pentan-2-one	n.d.	0.15	0.19
45.46	*n*-hexadecanoic acid	3.03	1.48	1.13
47.47	oleic acid	2.24	0.72	0.68

^{a} Retention time. ^{b} ADR-x stands for ADR content in feedstock (x wt.%).

Table S2 The relative response factors of analytes

Analyte	RRF
2,3-Butanedione	0.759
2-Butanone	1.092
Acetic acid	0.390
2,3-Pentanedione	0.808
Acetol	0.597
Propanoic acid	0.391
Furfural	0.845
n-Butyric acid	0.473
Furfuryl alcohol	1.013
Phenol	1.637
Guaiacol	1.166
o-Cresol	1.540
p-Cresol	1.598

Table S3 Ultimate and proximate analyses of rice husk and ADR

	Rice husk	ADR
Ultimate analysis (wt.%, on dry basis)		
C	38.26	66.10
H	5.74	5.81
N	1.14	1.01
O^a	54.86	27.08
Proximate analysis (wt.%, on dry basis)		
Volatile matter	67.91	61.03
Fixed carbon	19.63	38.47
Ash	12.45	0.51

[a] By difference.

Table S4 Yield and separation efficiency of selected compounds in distillate

	Acetic acid	Acetol	Propanoic acid	Furfural	n-Butyric acid	Furfuryl alcohol	Phenol	Guaiacol	o-Cresol	p-Cresol
Formula	$C_2H_4O_2$	$C_3H_6O_2$	$C_3H_6O_2$	$C_5H_4O_2$	$C_4H_8O_2$	$C_5H_6O_2$	C_6H_6O	$C_7H_8O_2$	C_7H_8O	C_7H_8O
Boiling point (K)	391	418	414	435	437	443	455	478	464	475
Yield (wt% of raw bio-oil)										
Fraction 1	1.809	0.717	0.244	0.129	0.021	0.062	0.025	0.042	0.010	0.008
Fraction 2	0.902	0.319	0.110	0.021	0.014	0.020	0.007	0.012	0.003	0.004
Fraction 3	0.465	0.148	0.056	0.009	0.008	0.011	0.004	0.006	0.001	0.003
Fraction 4	0.552	0.189	0.066	0.013	0.009	0.015	0.005	0.008	0.002	0.003
Fraction 5	0.943	0.253	0.128	0.017	0.021	0.032	0.009	0.015	0.004	0.006
Fraction 6	0.402	0.046	0.065	0.002	0.008	0.023	0.009	0.015	0.003	0.005
Whole distillate	5.072	1.672	0.668	0.192	0.082	0.163	0.058	0.097	0.023	0.029
Concentration in Raw bio-oil	5.742	2.711	0.728	0.226	0.135	0.299	0.157	0.239	0.045	0.108
Separation efficiency (%)										
Whole distillate	88.34	61.67	91.80	85.11	60.75	54.39	37.12	40.76	50.68	26.65

Table S5 Calculation of total quantified carbon in whole distillate

	Formula	Carbon content	Yield in whole distillate wt% of raw bio-oil	Quantified carbon in whole distillate wt% of raw bio-oil
Acetic acid	$C_2H_4O_2$	0.400	5.072	2.029
Acetol	$C_3H_6O_2$	0.486	1.672	0.813
Propanoic acid	$C_3H_6O_2$	0.486	0.668	0.325
Furfural	$C_5H_4O_2$	0.625	0.192	0.120
n-Butyric acid	$C_4H_8O_2$	0.545	0.082	0.045
Furfuryl alcohol	$C_5H_6O_2$	0.612	0.163	0.100
Phenol	C_6H_6O	0.766	0.058	0.045
Guaiacol	$C_7H_8O_2$	0.677	0.097	0.066
o-Cresol	C_7H_8O	0.778	0.023	0.018
p-Cresol	C_7H_8O	0.778	0.029	0.022
2,3-Butanedione	$C_4H_6O_2$	0.558	0.107	0.060
2-Butanone	C_4H_8O	0.667	0.142	0.095
2,3-Pentanedione	$C_5H_8O_2$	0.600	0.039	0.023
Total quantified carbon				3.761

Table S6 Major compounds identified in distillate of bio-oil by GC/MS[a]

Entries	RT (min)[b]	Compounds	Formula	b.p. (K)[c]
1	3.92	2,3-butanedione	$C_4H_6O_2$	361
2	4.00	2-butanone	C_4H_8O	353
3	4.23	acetic acid	$C_2H_4O_2$	391
4	5.27	acetol	$C_3H_6O_2$	418
5	6.07	2,3-pentanedione	$C_5H_8O_2$	383
6	7.37	3-penten-2-one	C_5H_8O	392
7	8.48	1-hydroxy-2-butanone	$C_4H_8O_2$	425
8	9.31	methyl 2-oxopropanoate	$C_4H_6O_3$	409
9	11.09	furfural	$C_5H_4O_2$	435
10	12.01	furfuryl alcohol	$C_5H_6O_2$	443
11	12.60	1-acetoxy-2-propanone	$C_5H_8O_3$	448
12	14.13	2-methyl-2-cyclopenten-1-one	C_6H_8O	430
13	14.50	1-(2-furanyl)-ethanone	$C_6H_6O_2$	456
14	16.62	5-methylfurfural	$C_6H_6O_2$	460
15	16.70	3-methyl-2-cyclopenten-1-one	C_6H_8O	431
16	16.80	1-acetoxy-2-butanone	$C_6H_{10}O_3$	444
17	17.28	phenol	C_6H_6O	455
18	19.17	3-methyl-1,2-cyclopentanedione	$C_6H_8O_2$	518
19	20.31	*o*-cresol	C_7H_8O	464
20	21.14	*p*-cresol	C_7H_8O	475
21	21.68	guaiacol	$C_7H_8O_2$	478
22	24.61	4-ethylphenol	$C_8H_{10}O$	492
23	25.53	4-methylguaiacol	$C_8H_{10}O_2$	521
24	28.54	4-ethylguaiacol	$C_9H_{12}O_2$	520

[a] Only peaks whose peak area percentage above 1% were listed, propanoic acid and *n*-butyric acid were also detected but not listed for their little response on non-polar columns. [b] Retention time. [c] Boiling point (at 760 mm Hg).

Table S7 Elemental analysis of raw bio-oil and its distillation products

	Yield	Elemental analysis (wt.%)			
	(%)	C^a	H	O^b	N
Raw bio-oil	100	39.80	7.73	51.55	0.92
Whole distillate	51.86	13.32	9.80	75.98	0.90
ADR^c	48.14	66.10	5.81	27.08	1.01

[a] Mass balance closure of C atom was 97%. [b] By difference. [c] On dry basis.

List of Figures

Figure S1 The integrated process combining co-pyrolysis and atmospheric distillation for conversion of lignocellulosic biomass into chemicals.
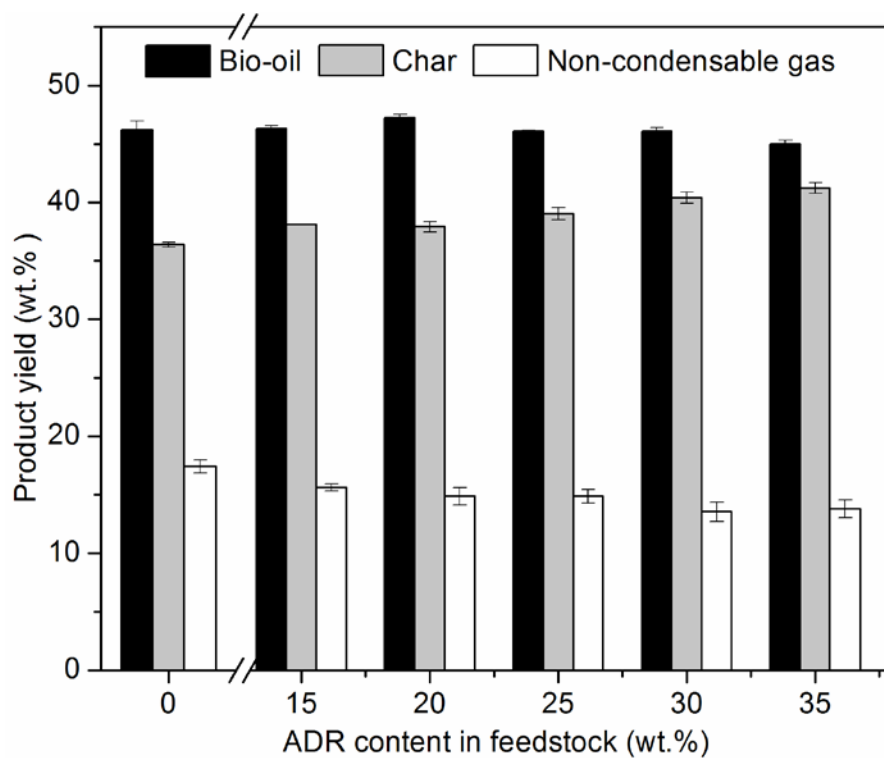
Figure S2 Product yields versus content of atmospheric distillation residue (ADR) in feedstock in fast co-pyrolysis of rice husk and ADR. Mixture of rice husk and ADR at different blending ratios was pyrolyzed at 723 K.
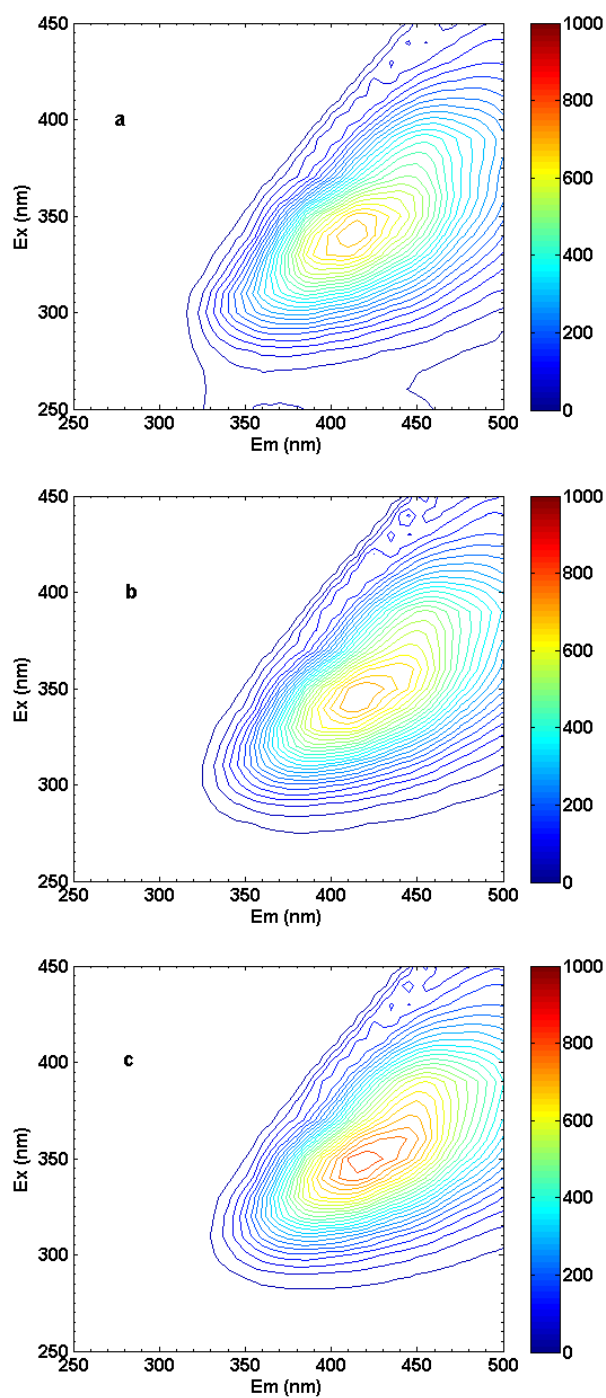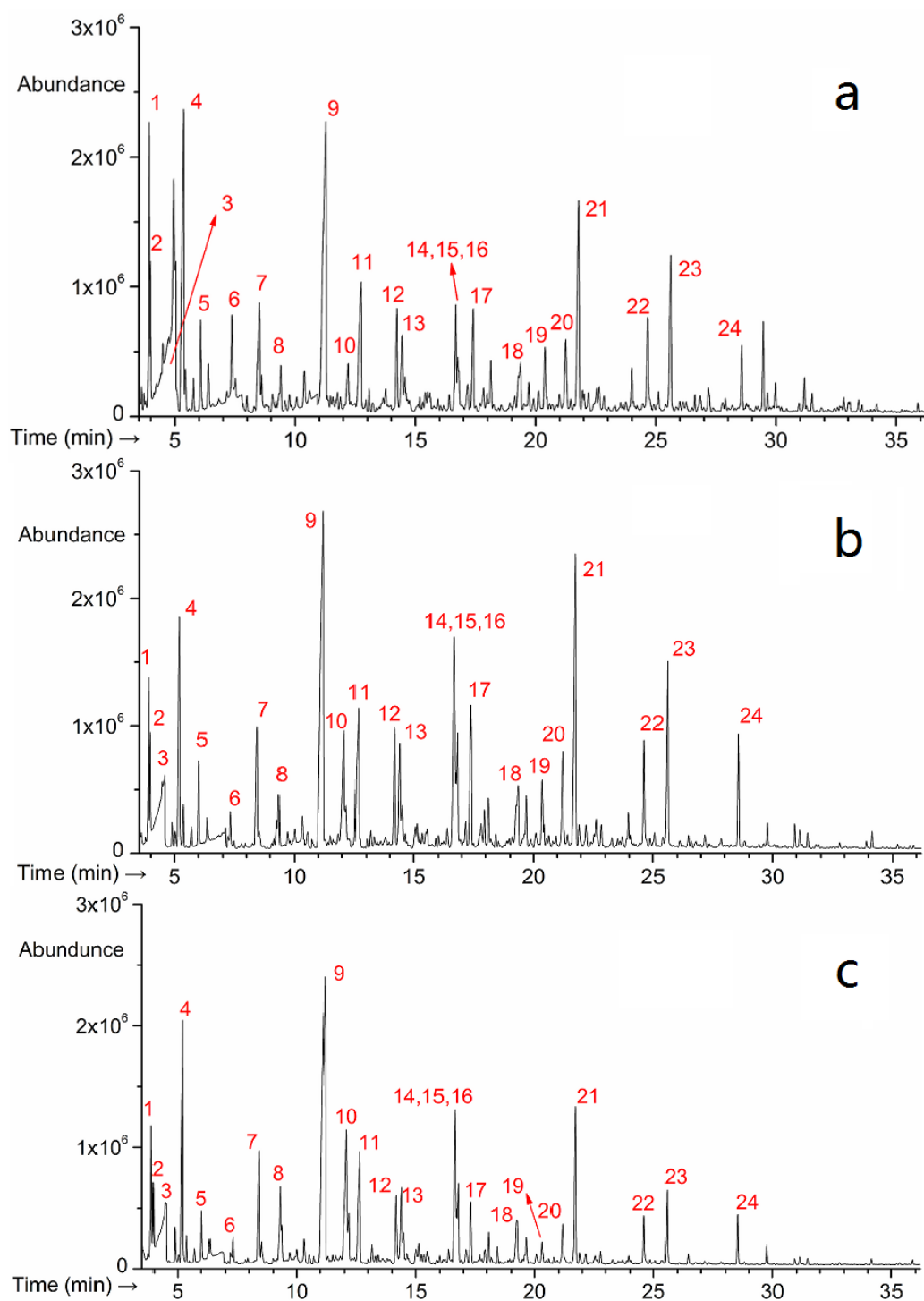
Figure S3 Exitation-emission matrix (EEM) fluorescence spectra of the bio-oils prepared from fast co-pyrolysis of ADR and rice husk at 723 K. (a) ADR content in feedstock: 0; (b) ADR content: 20 wt.%; and (c) ADR content: 35 wt.%.
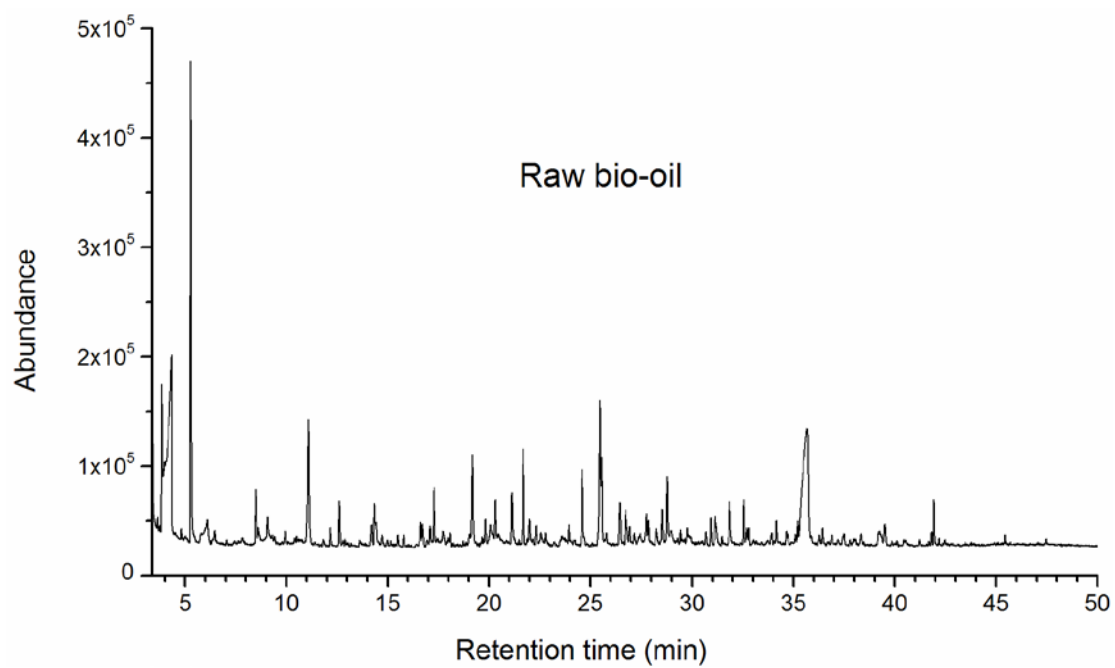
**Figure S4 GC/MS chromatogram of raw bio-oil.**

Figure S5 GC/MS chromatogram of distillate. (a) Distillate from raw bio-oil (start-up of the integrated system); (b) Distillate from bio-oil produced by co-pyrolysis of rice husk and ADR (first run of the integrated system); (c) Distillate from bio-oil produced by co-pyrolysis of rice husk and secondary ADR (second run). Identified peaks are listed in Supplementary Table S6.
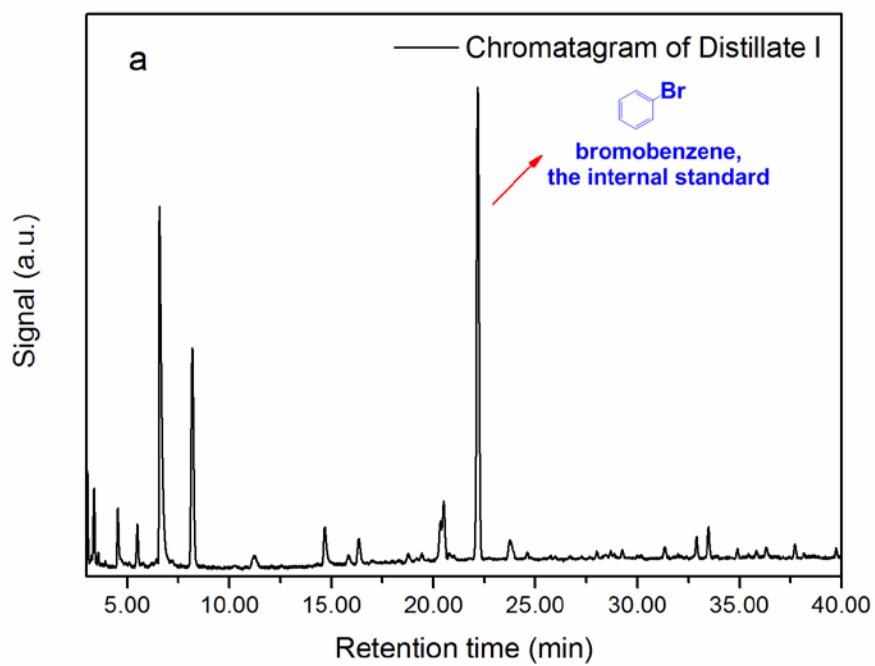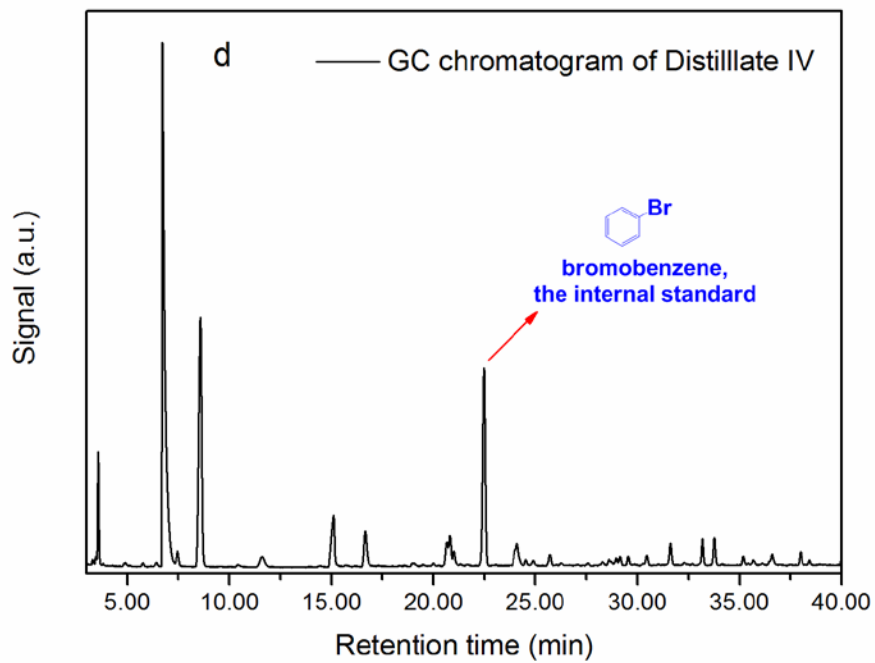
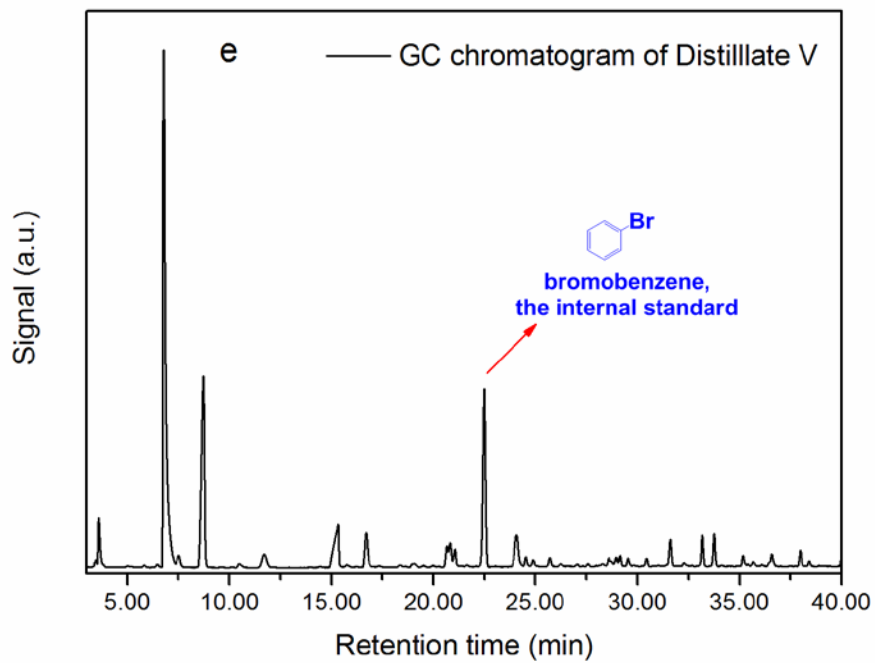**Figure S6 GC chromatograms of distillate Fraction I.**
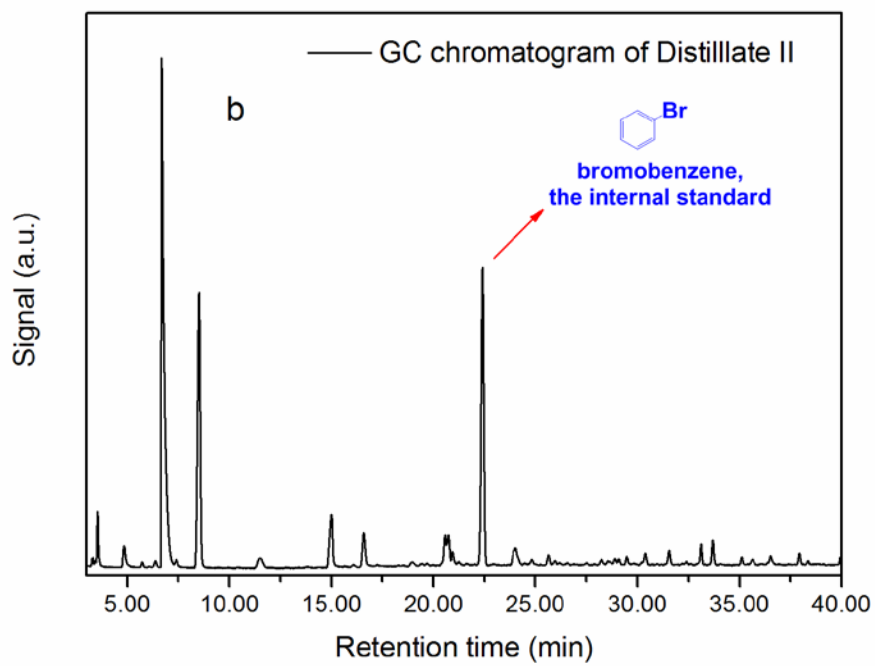
Figure S7 GC chromatograms of distillate Fraction II.
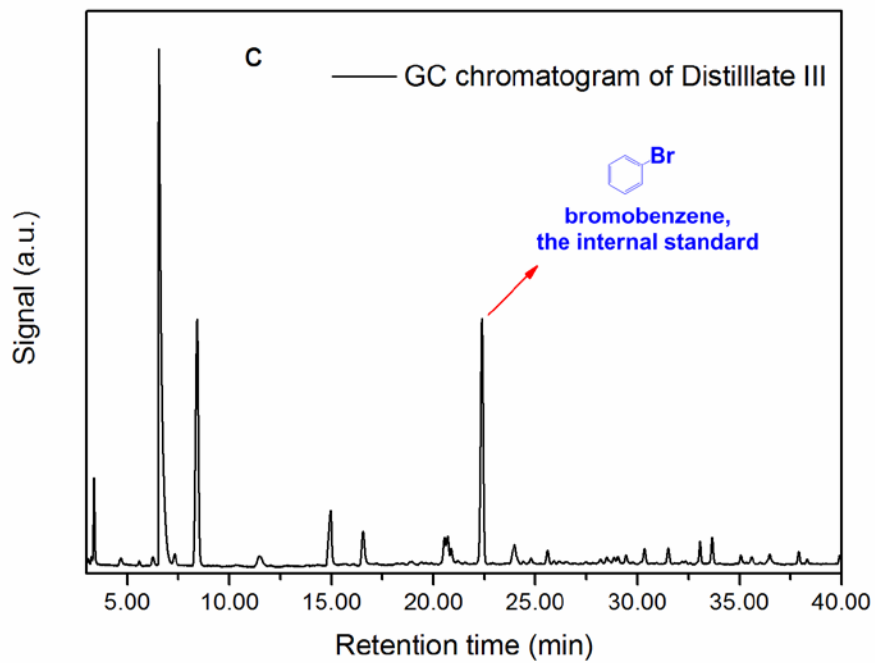
Figure S8 GC chromatograms of distillate Fraction III.

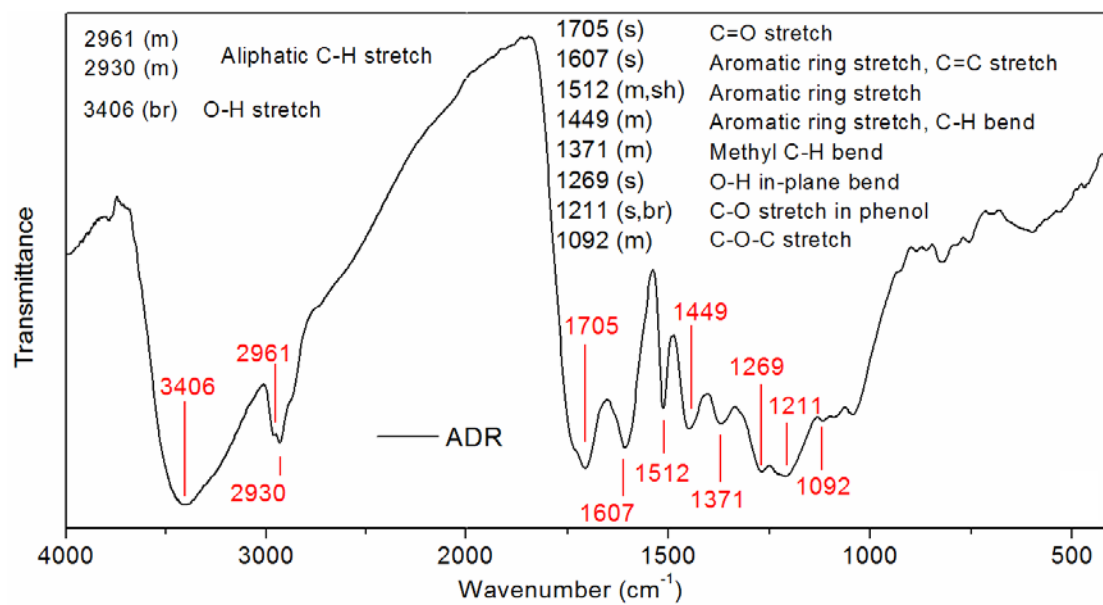**Figure S9 GC chromatograms of distillate Fraction IV.**

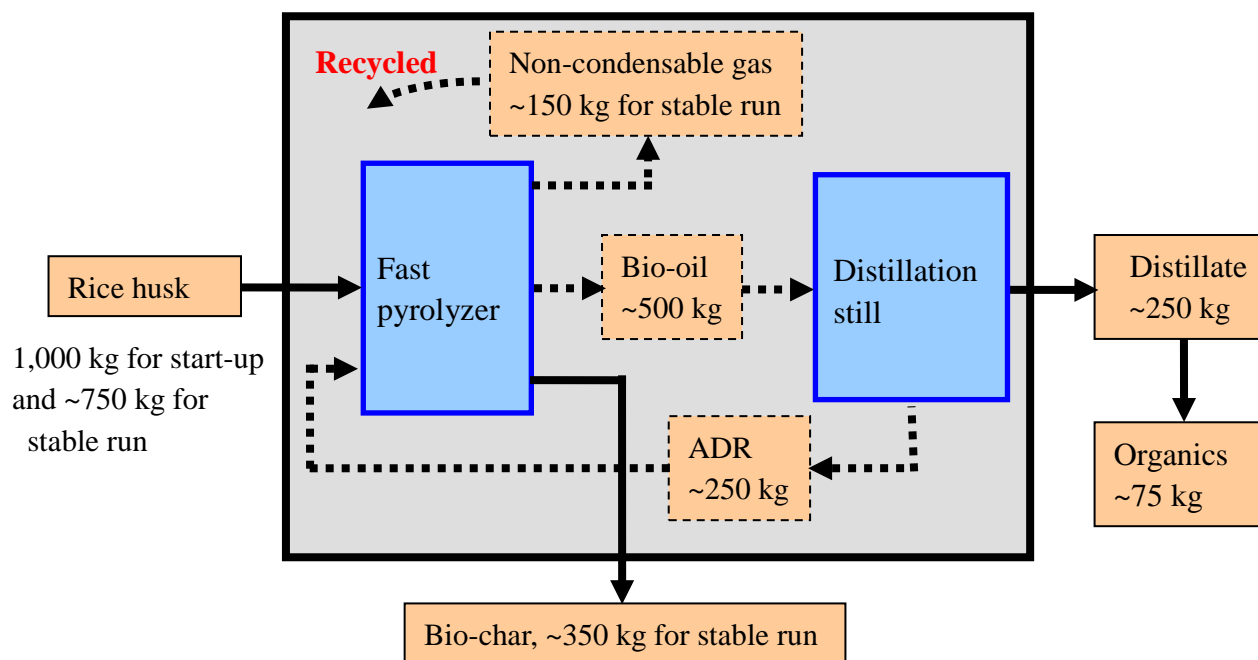**Figure S10 GC chromatograms of distillate Fraction V.**

Figure S11 Optical image of ADR in powder form.

Figure S12 FTIR spectrum of ADR. Recorded at a resolution of 4 cm^{-1} on an Equinox 55 infrared spectrometer (Bruker Optics GmbH, Germany) at room temperature by the KBr pellet method.

Figure S13 Schematic of the integrated co-pyrolysis-atmospheric distillation process with mass balance data.

Supplementary Text

Characteristics of atmospheric distillation residue (ADR). The atmospheric distillation residue (ADR) inherited the irritant odor from bio-oil and was black solid in as-received form at room temperature (Fig. 2). When milled into powder, ADR showed brownish black color (Fig. S11). The FTIR spectrum (Fig. S12) of ADR reflected its oxygenated nature with strong absorption peaks of O-H and C=O moieties. The peaks at 1607, 1512, and 1449 cm^{-1} were indicative of the existence of aromatic rings, while the peak at 1211 cm^{-1} indicated that phenolic hydroxyl groups were contained, and the absorption at 1092 cm^{-1} evidenced the existence of ether and/or ester linkage in ADR. In addition to aromatic rings, aliphatic moieties were also contained in ADR, as shown by the absorption peaks at 2961, 2930, and 1371 cm^{-1}.

Ultimate and proximate analyses (Table S3) show that ADR had little ash content (0.51 wt%) and was carbon-rich (66.10 wt%). But its fixed carbon content was 38.47 wt%, twice that of rice husk, indicating that a larger proportion of carbon atoms in ADR would be left over to form bio-char in the pyrolysis process, compared with rice husk. The volatile matter content (61.03 wt%) of ADR was comparable to that of rice husk (67.91 wt%), suggesting that ADR might also be a suitable feedstock for fast pyrolysis as rice husk was.