

Co-Pyrolysis of Torrefied Biomass and Methane over Molybdenum Modified Bimetallic HZSM-5 Catalyst for Hydrocarbons Production

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Table S1. Mineral contents of switchgrass samples before and after ash removal by HNO₃.

Sample ID	Concentration											
	%						ppm					
	P	Ca	K	Mg	Na	S	Fe	Zn	Cu	Mn	B	Ni
Untreated RSG	0.007	0.007	0.004	0.002	<0.001	0.023	24.3	1.5	1.7	1.8	<1.0	<1.0
HNO ₃ treated RSG	0.008	0.007	0.004	0.002	<0.001	0.024	21.9	1.6	1.5	1.7	<1.0	<1.0
Untreated T230SG	0.077	0.223	0.218	0.139	0.005	0.042	262.9	26.4	2.3	84.7	<1.0	1.8
HNO ₃ treated T230SG	0.015	0.058	0.014	0.016	<0.001	0.028	133.9	20.5	37.6	13.4	<1.0	1.4
Untreated T270SG	0.109	0.445	0.269	0.204	0.006	0.053	1970.5	55.5	25.8	155.4	1.2	4.8
HNO ₃ treated T270SG	0.034	0.158	0.061	0.069	0.001	0.033	1012.0	18.8	15.9	52.1	<1.0	2.7

Table S2. Results of two-way ANOVA analysis (p-values < 0.05): Effects of catalyst and reaction environment on the carbon yields of pyrolysis products (At 700 °C reaction temperature using raw switchgrass).

Carbon yield (%)	DOF	Sum of Squares	Variance	F-ratio	P-value	Percent P (%)
<i>(a) BTEX</i>						
Catalyst	4	299.60	74.901	18.49	<<0.05	58.80
Reaction environment	1	70.58	70.576	17.43	<<0.05	13.85
Catalyst*Reaction environment	4	58.35	14.589	3.6	0.023	11.45
Error	20	81.00	4.050			15.90
Total	29	509.53				100
<i>(b) Benzene Derivatives</i>						
Catalyst	4	10.159	2.540	8.06	<<0.05	52.32
Reaction environment	1	0.154	0.154	0.49	0.492	0.79
Catalyst*Reaction environment	4	2.80	0.700	2.22	0.103	14.42
Error	20	6.304	0.315			32.47
Total	29	19.417				100
<i>(c) Polyaromatics</i>						
Catalyst	4	69.596	17.399	24.44	<<0.05	76.42
Reaction environment	1	4.218	4.218	5.92	0.024	4.63
Catalyst*Reaction environment	4	3.014	0.754	1.06	0.403	3.31
Error	20	14.238	0.712			15.64
Total	29	91.066				100
<i>(d) Total HCs</i>						
Catalyst	4	712.2	178.05	16.71	<<0.05	61.41
Reaction environment	1	117.7	117.7	11.04	0.003	10.15
Catalyst*Reaction environment	4	116.7	29.18	2.74	0.058	10.06
Error	20	213.1	10.66			18.38
Total	29	1159.7				100
<i>(e) Oxygenates</i>						
Catalyst	4	1.658	0.415	6.90	0.001	53.28
Reaction environment	1	0.0142	0.0142	0.24	0.631	0.46
Catalyst*Reaction environment	4	0.238	0.059	0.99	0.434	7.67
Error	20	1.201	0.060			38.59
Total	29	3.112				100

Table S3. Results of two-way ANOVA analysis (p-values < 0.05): Effects of reaction temperature and environment on the carbon yields of pyrolysis products (Using MoZn/HZSM-5 catalyst and raw switchgrass).

Carbon yield (%)	DOF	Sum of Squares	Variance	F-ratio	P-value	Percent P (%)
<i>(a) BTEX</i>						
Temperature	4	774.36	193.59	107.92	<<0.05	70.88
Reaction environment	1	204.24	204.24	113.86	<<0.05	18.69
Temperature *Reaction environment	4	83.26	20.82	11.6	<<0.05	7.62
Error	22	33.46	1.79			3.06
Total	31	1092.36				100
<i>(b) Benzene Derivatives</i>						
Temperature	4	19.45	4.87	23.51	<<0.05	63.58
Reaction environment	1	2.23	2.23	10.77	0.003	7.28
Temperature *Reaction environment	4	3.96	0.99	4.77	0.006	12.94
Error	22	4.56	0.21			14.90
Total	31	30.59				100
<i>(c) Polyaromatics</i>						
Temperature	4	93.10	23.27	121.26	<<0.05	85.64
Reaction environment	1	7.21	7.21	37.58	<<0.05	6.63
Temperature *Reaction environment	4	4.74	1.18	6.17	0.002	4.36
Error	22	4.22	0.19			3.88
Total	31	108.70				100
<i>(d) Total HCs</i>						
Temperature	4	1716.97	429.24	101.55	<<0.05	74.63
Reaction environment	1	341.18	341.18	80.72	<<0.05	14.83
Temperature *Reaction environment	4	171.19	42.95	10.16	<<0.05	7.44
Error	22	92.99	4.23			4.04
Total	31	2300.45				100
<i>(e) Oxygenates</i>						
Temperature	4	4.57	1.14	29.45	<<0.05	77.85
Reaction environment	1	0.11	0.11	2.86	0.105	1.87
Temperature *Reaction environment	4	0.36	0.089	2.29	0.092	6.13
Error	22	0.85	0.039			14.48
Total	31	5.87				100

Table S4. Results of two-way ANOVA analysis (p-values < 0.05): Effects of torrefaction and reaction environment on the carbon yields of pyrolysis products (At reaction temperature of 700 °C using MoZn/HZSM-5).

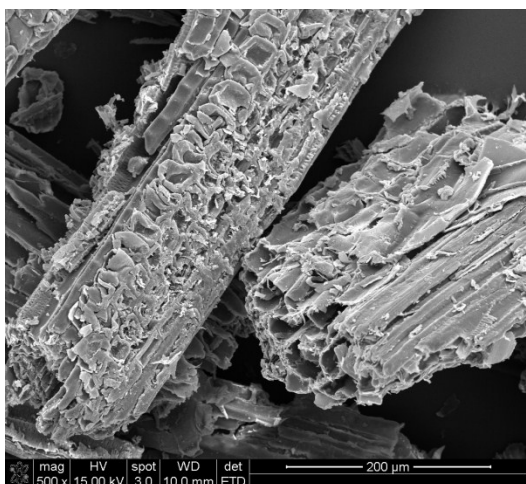
Carbon yield (%)	DOF	Sum of Squares	Variance	F-ratio	P-value	Percent P (%)
<i>(a) BTEX</i>						
Torrefaction	2	463.87	231.935	88.35	<<0.05	77.30
Reaction environment	1	105.79	105.79	40.30	<<0.05	17.63
Torrefaction*Reaction environment	2	15.56	7.778	2.96	0.085	2.59
Error	14	36.75	2.625			6.12
Total	19	600.06				100
<i>(b) Benzene Derivatives</i>						
Torrefaction	2	25.301	12.650	59.05	<<0.05	81.58
Reaction environment	1	2.540	2.540	11.86	<<0.05	8.19
Torrefaction*Reaction environment	2	0.518	0.259	1.21	0.328	1.67
Error	14	2.999	0.214			9.67
Total	19	31.015				100
<i>(c) Polyaromatics</i>						
Torrefaction	2	51.663	25.831	87.68	<<0.05	85.63
Reaction environment	1	6.182	6.182	20.98	<<0.05	10.25
Torrefaction*Reaction environment	2	0.179	0.089	0.30	0.742	0.29
Error	14	4.125	0.295			6.84
Total	19	60.332				100
<i>(d) Total HCs</i>						
Torrefaction	2	1138.61	569.306	93.17	<<0.05	80.66
Reaction environment	1	206.37	206.37	33.77	<<0.05	14.62
Torrefaction*Reaction environment	2	25.82	12.909	2.11	0.158	1.83
Error	14	85.55	6.111			6.06
Total	19	1411.57				100
<i>(e) Oxygenates</i>						
Torrefaction	2	2.915	1.457	31.99	<<0.05	79.73
Reaction environment	1	0.0525	0.0525	1.15	0.301	1.44
Torrefaction*Reaction environment	2	0.0554	0.0277	0.61	0.558	1.52
Error	14	0.637	0.0455			17.42
Total	19	3.656				100

Table S5. Effect of reaction temperature on carbon yields of aromatic hydrocarbons (He=Helium, Me=Methane; Using MoZn/HZSM-5 catalyst and raw switchgrass).

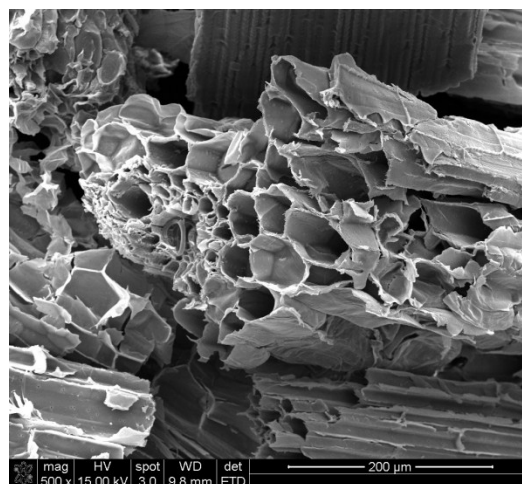
Atmosphere	Temp. (°C)	Carbon yields (C %)			
		BTEX	Polyaromatics	Benzene derivatives	Total HCs
He	400	7.57±0.12	0.99±0.10	2.15±0.21	10.70±0.09
	500	12.75±1.68	2.92±0.26	2.59±0.57	18.26±2.35
	600	13.88±1.77	3.76±0.76	2.46±0.55	20.11±3.05
	700	20.06±1.13	5.76±0.11	3.71±0.30	29.53±1.31
	800	13.98±0.49	3.59±0.21	2.34±0.26	19.91±0.95
Me	400	9.35±1.16	1.30±0.25	2.13±0.28	12.79±1.65
	500	15.65±1.09	3.49±0.69	2.91±0.61	22.05±2.31
	600	24.47±2.02	5.98±0.75	3.99±0.70	34.44±3.44
	700	27.27±1.85	7.16±0.65	4.88±0.65	39.31±2.87
	800	17.06±1.05	3.69±0.35	2.05±0.23	22.79±1.10

Table S6. Effect of reaction temperature on carbon selectivities of aromatic hydrocarbons (He=Helium, Me=Methane, Using MoZn/HZSM-5 and raw switchgrass).

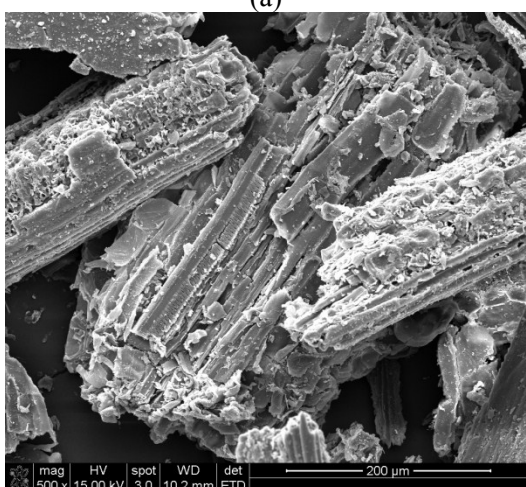
Atmosphere	Temp. (°C)	Carbon selectivity (%)					
		Benzene	Toluene	Ethylbenzene	Xylene	Benzene derivatives	Polyaromatics
He	400	9.26±0.79	27.02±0.96	4.37±0.31	30.06±0.40	20.08±1.92	9.21±0.89
	500	13.30±0.90	28.45±1.24	3.46±0.37	24.62±0.77	14.10±2.03	16.06±0.70
	600	16.88±0.89	29.07±1.42	2.41±0.24	20.87±0.24	12.16±1.08	18.61±1.17
	700	18.40±0.36	27.52±0.26	2.43±0.22	19.57±0.71	12.56±0.48	19.53±1.23
	800	20.59±0.60	28.49±0.48	2.20±0.08	18.83±0.96	11.88±0.67	18.01±0.24
Me	400	9.22±0.29	28.07±0.58	3.74±0.10	32.14±0.77	16.67±0.09	10.16±1.01
	500	12.80±0.58	28.49±1.04	3.01±0.29	26.10±0.50	12.99±1.68	16.62±0.11
	600	17.18±0.91	29.11±0.77	2.69±0.13	22.17±0.90	11.52±0.93	17.34±0.42
	700	18.79±1.00	28.11±1.15	2.67±0.29	19.83±0.78	12.38±0.77	18.22±1.11
	800	28.93±1.99	27.05±1.90	1.76±0.18	17.08±0.59	8.99±0.87	16.20±1.68



(a)



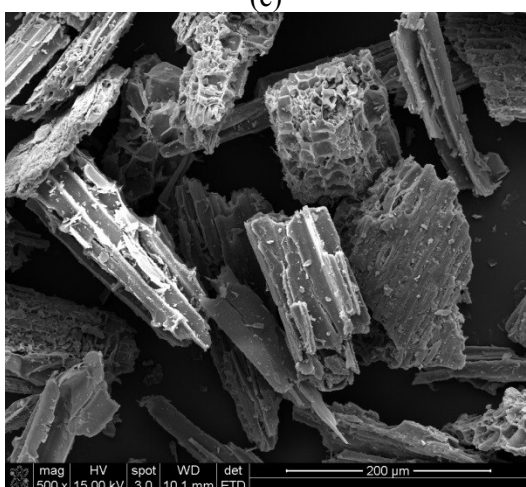
(b)



(c)



(d)



(e)



(f)

Figure S1. SEM images of untreated switchgrass samples and switchgrass after leaching with 0.1 N HNO₃. (a) untreated RSG, (b) RSG treated by HNO₃, (c) untreated T230, (d) T230 treated by HNO₃, (e) untreated T270, (f) T270 treated by HNO₃.